# 39. *The Course of Autoxidation Reactions in Polyisoprenes and Allied Compounds. Part VI. The Peroxidation of Rubber.*

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The course of reaction in the autoxidation of rubber has been studied, principally under photochemical conditions. In ultra-violet light high yields of peroxide are formed in the very early stages of oxygen absorption, but soon decay reactions set in so that the ratio of the peroxidic oxygen content to the oxygen intake decreases rapidly. The secondary products are hydroxylated compounds.

Examination of the changes in unsaturation, in hydroxylic oxygen content, and in peroxidic oxygen content, as oxidation proceeds, leads to the conclusion that the oxygen enters mainly or wholly at α-methylenic carbon atoms to produce hydroperoxide groups and not by addition at double bonds. Chain scission accompanies oxidation, even from the outset of reaction, causing striking reductions in the molecular weight. The consumption of oxygen in relation to the degree of degradation produced is discussed.

Peroxides have repeatedly been shown to appear during the slow oxidation (perishing) of rubber in air, and also during both its milling in air and the passage of air or oxygen through its solutions : yet in none of the recorded experiments has the production of any very substantial proportion of peroxide been demonstrated. This arises largely because under many conditions of autoxidation no very considerable proportion of peroxide is in fact present in the oxidation product at any stage, but in part because no convenient and reasonably accurate method of determining the peroxide content in so insoluble a substance as rubber has been available. It must inevitably happen in a long-chain molecule of polymer-homologous type containing on the average about 5,000 autoxidisable olefinic units that the progressive entrance of a heterogeneous element will yield a large variety of closely similar products if attack is fairly evenly distributed over the chain, but when, as in the case of oxygen, the heterogeneous element enters the hydrocarbon as a diatomic molecule the atoms in which can ultimately separate and become attached to the carbon chain in a variety of ways, and causes, as the result of its progressive incorporation, scission of the chain at an ever-increasing number of the olefinic units, then the potential range of diversity of the products becomes enormously increased.

*General Course of Autoxidation Reactions.*—In consequence of the above-mentioned diversity it is perhaps not surprising that examination of the character of many scores of (catalysed) thermal oxidation products obtained by one of us with Dr. E. S. Narracott over a fairly wide range of oxygen input has given little detailed information respecting the course of autoxidation (details are omitted from the present communication). These products were, in general, neutral (*i.e.*, insoluble in aqueous alkali) up to the oxidative stage at which *ca.* 0·9 atom of oxygen per isoprene unit had been supplied to the hydrocarbon, and after this stage increasingly acidic until, at the highest stage of oxidation attained (*i.e.*, at 30% of oxygen input and temperature above 70°) only acidic materials were obtained. The average molecular weight of the oxidation products decreased rapidly as oxidation proceeded, that of the neutral products becoming reduced ultimately to a few thousand units * and that of the acidic products, as judged by their equivalent weights,† ultimately to *ca.* 700—800 units. It thus appears likely that the oxidative scission reactions which are responsible for the reductions in molecular weight produce in the first place fragments with neutral end groups (presumably $-CHO$ and $-CO{\cdot}CH_3$, through severance of the polyisoprene chains at the double bonds), and these end groups in the main escape further oxidative attack (to give carboxyl groups) until a fairly definite overall stage of oxygenation is reached. Oxidative degradation of the rubber, however, was not confined to the production of shortened and somewhat oxygenated chains : there were always formed, even from the outset of reaction, small, but not negligible, proportions of water and carbon dioxide—and possibly also traces of other volatile compounds such as the carbon monoxide and hydrogen observed by Dupont (*Bull. Soc. chim. Belg.*, 1936, **45**, 57; 1936, **46**, 21) to accompany water and carbon dioxide in the autoxidation of *cyclo*hexene and methyl*cyclo*hexene—and these volatile materials must, from the constancy of their formation from purified as well as from impure rubbers, be regarded as secondary decomposition products of the rubber itself, and not merely of the non-hydrocarbon constituents in the rubber.

Recent experiments have shown that the primary autoxidation products of rubber and of other olefins (*i.e.*, the peroxido-derivatives) survive in better yield under photochemical conditions of formation than under thermal conditions, provided exposure to light is not too prolonged, and hence the photochemical products lend

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* The (viscosity) molecular weights given in this paper are calculated by use of Gee's constant for rubber. The average molecular weight for unoxidised rubber on this basis is 350,000 or about 2½ times that which would be obtained by use of the formerly-accepted Staudinger constant.

† The acids being assumed to be monobasic.

themselves more readily to investigation of the first stage of autoxidative reaction than do the corresponding thermal products. Preliminary runs under photochemical conditions, a petroleum-soluble fraction of rubber dissolved in benzene being used, have given liquid or resinous products generally comparable as regards their neutral or acidic character and their degraded condition with the above-mentioned products of thermal oxidation, but showing considerably higher peroxide yields in the earlier stages of reaction. The details in Table I refer to representative products obtained at *ca.* 35° over a range of oxygen intake from 2% to 25%, the intake being determined approximately from the change in gas volume, and the oxygen content of the product more exactly by careful ultimate analysis.

TABLE I.

*Photo-oxidation of petroleum-soluble rubber* (*in benzene*) *at* ca. 35°.

| Approx. $O_2$ input (%).* | Character of product. | Oxygen content (%). | Atoms per $C_5H_8$. | Peroxidic oxygen (%). | Iod. value. | | *M.* |
|---|---|---|---|---|---|---|---|
| | | | | | Found. | Calc.¶ | |
| 2 | Neutral, ether-sol. | 2·0 | 0·09 | 1·3 | 356 | 348·6 | 60,000 |
| 7 | ,, ,, | 6·95 | 0·32 | 2·7 | 312 | 290 | — |
| 8 (a) | ,, ,, (94%) | 7·9 | 0·37 | 1·2 | 308 | 280 | — |
| 8 (b) | ,, ether-insol. (6%) † | 9·4 | 0·44 | — | — | — | — |
| 13 | ,, ether-sol. | 11·6 | 0·56 | 4·0 | 265 | 238 | — |
| 22 (a) | ,, ,, (94%) | 18·1 | 0·94 | 5·4 | 220 | 162 | 2,100 |
| 22 (b) | Acidic, ,, (3%) | 20·55 | 1·10 | 0·0 | — | — | — |
| 22 (c) | ,, ether-insol. (3%) | 27·15 | 1·58 | 0·0 | — | — | — |
| 32 (a) | ,, ether-sol. (33%) ‡ | 18·7 | 0·98 | 0·1 | 214 | 155 | — |
| 32 (b) | ,, ,, (15%) | 30·2 | 1·84 | — | — | — | — |
| 32 (c) | ,, ether-insol. (52%) § | 28·5 | 1·69 | 0·0 | 115 | 40·7 | 1,300 |

* Based on weight of rubber taken.
† Insoluble in all the ordinary solvents for rubber.
‡ This portion separated out in the form of its sodium salt on shaking the ethereal solution of the oxidation product with alkali.
§ Soluble in alcohol.
¶ Calculated on the ring-peroxide hypothesis (see J., 1942, 122).

In all these preliminary runs the iodine values of both neutral and acidic products were higher than would have obtained if the ingoing oxygen had added at, and had so saturated, an equivalent proportion of the olefinic double bonds in the rubber molecule. Both the neutral and the acidic products contained a high proportion of hydroxylic oxygen, as determined by the Zerewitinoff method, which amounted in the early stages of oxidation to rather more than half the total oxygen content,* but fell off somewhat later. Products of neutral character survived down to a molecular weight of *ca.* 2000. In all cases the acidic products contained more oxygen than the corresponding neutral products, but none of the acidic materials contained more than a trace of peroxidic oxygen, although it is to be borne in mind that the use of solutions of caustic alkali in separating acidic from neutral products inevitably causes some peroxidic decomposition with concomitant oxidative attack elsewhere in the system (cf. Part I, J., 1942, 115).

*The Early Stages of Autoxidation.*—The net result of the foregoing photo-oxidations was to produce a series of oxygenated rubbers in which at best only about 65% of the ingoing oxygen survived at the end of the operation in peroxidic form. Since, under the most favourable conditions of oxidation discovered, the ratio of peroxidic oxygen surviving in the product to ingoing oxygen declined rapidly with increasing oxygen intake (pointing to the inevitable onset of secondary decay reactions), it was necessary in order to investigate the structural character of the undeteriorated peroxido-derivatives to work with lightly oxidised rubbers. Even so, success in arriving at definite conclusions was wholly governed by ability to measure with reasonable accuracy (1) the oxygen intake of the rubber, and (2) the peroxidic oxygen content of the products together with their active hydrogen value and unsaturation. The most troublesome of these measurements was that of the oxygen intake, which had to be made under fluctuating temperature conditions in the presence of a volatile hydrocarbon solvent, some water vapour, and traces of carbon dioxide; the principal error, due to the solvent vapour, could be eliminated by use of a compensating device, but the residual error was still ±5% as a maximum. For the determination of active hydrogen values (and hence of the corresponding hydroxylic oxygen values) the method of Bolland, devised for the purpose, has given very satisfactory and consistent results. With respect to the determination of unsaturation in rubbers, no method hitherto described approaches in accuracy and consistency that of the iodine value method † under conditions of operation essentially as described by Kemp (*Ind. Eng. Chem.*, 1927, **19**, 531; *ibid.*, *Anal. Ed.*, 1934, **6**, 52), and it has proved easily possible by careful attention to experimental procedure to duplicate results consistently within 1 unit, *i.e.*, to reduce the error of observation in the present experiments to within ±0·3%.

In tracing the changes in oxygen content, peroxide content, active hydrogen value, unsaturation, and molecular weight from stage to stage during the earlier course of oxidation, it proved impracticable either to

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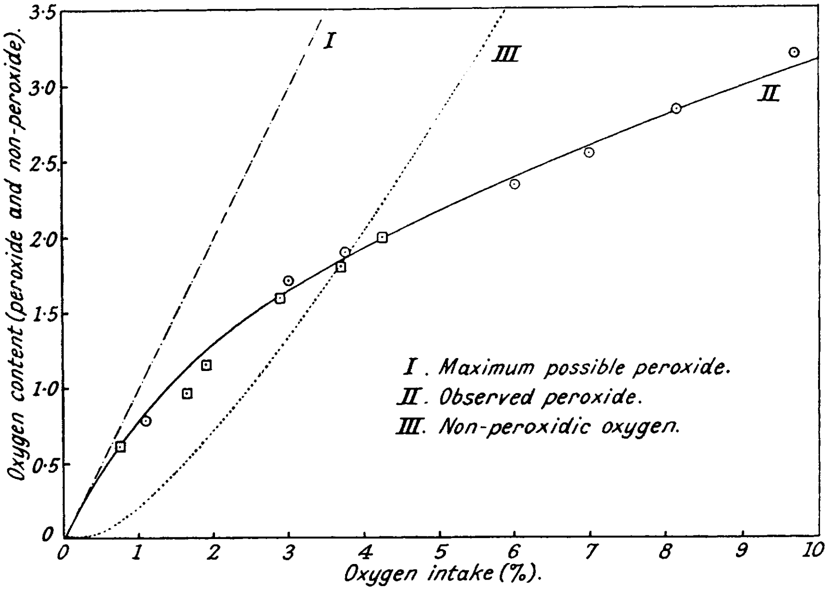
* For the accurate measurement of small concentration of hydroxyl in high-molecular compounds the Zerewitinoff method is unsuitable, and has been superseded in our later determinations. Under the most painstaking conditions of operation it gave results too high by 10—15%, but under less careful conditions was entirely misleading.

† The tendency for polyisoprenes to undergo substitution rather than addition under the action of halogens has been the subject of a separate investigation. No significant degree of substitutive reaction has been found to occur with iodine chloride under the conditions laid down by Kemp for iodine value determinations.

carry out carefully controlled oxidation on a large enough scale to supply representative samples for all of the numerous observations required at each of the oxidative stages, or even to secure sufficiently accurate measurement of the oxygen intake when absorption was interrupted at the end of each stage for the removal of test samples. It was found best to carry out a separate oxidation (from the same batch of rubber solution) for each oxidative stage, whilst keeping the intensity of illumination and the temperature as constant as possible through all stages. This procedure had the disadvantage that the curves representing variation of the individual functional values over the whole course of oxidation covered were somewhat less smooth than would otherwise have been the case (since small differences in illumination, reaction temperature, etc., from experiment to experiment were impossible to avoid), yet in all essential respects it proved satisfactory.

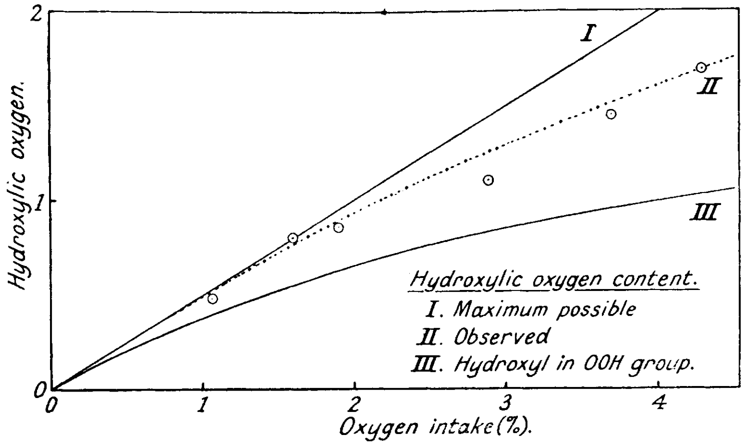
*The Peroxide Yield.*—Determination of the variation of peroxidic oxygen content from stage to stage over the earlier course of photo-oxidation of rubber has, because of its importance, been carried out both in a series of separate single-stage experiments spread over the range of oxygenation to be covered, and in a single multi-stage experiment with interruptions at different oxidative stages. Curve II (Fig. 1) shows the respective results in relation to the oxygen intake, the circles representing the results of the single-stage experiments and the squares those of the multi-stage experiment. The yield of peroxide falls off steadily from 80% at just less than 0·05 atom to 38% at 0·41 atom of oxygen per $C_5H_8$ unit. The highest peroxide yields yet measured by us in these early stages fall around 90% of the oxygen intake, and if our methods of experimental determination were sufficiently exact to be applicable in the still earlier stages, they would probably show a value approaching 100%. It may well be, although it is not proved, that at *all* stages in the photo-oxidation of rubber the whole of the ingoing oxygen is incorporated in the first place in peroxidic form.

FIG. 1.



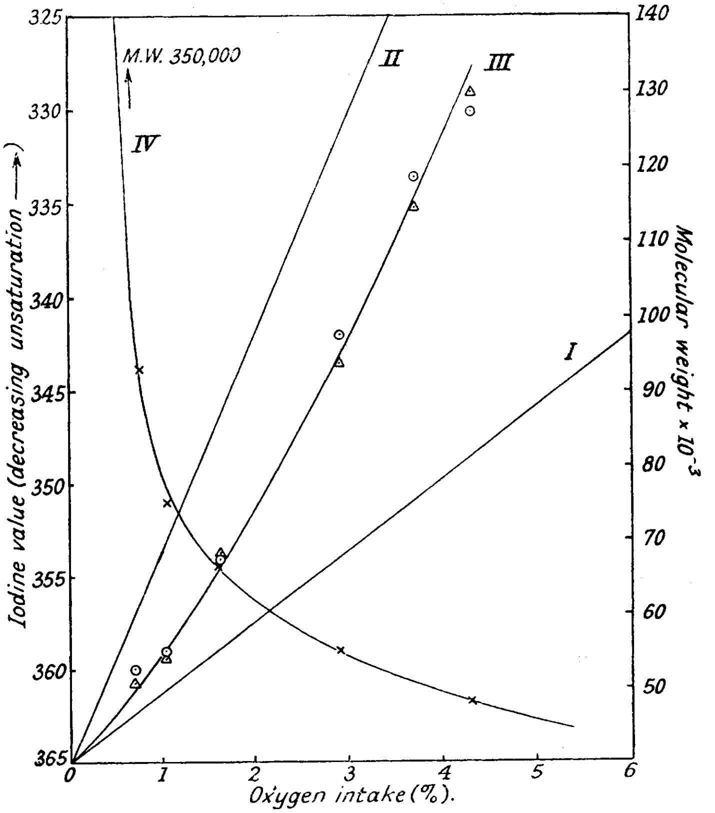
*The Character of the Peroxide Groups.*—It has been noted above that increase in the oxygen content of oxidised rubbers is consistently accompanied by increase in the active hydrogen content. Since existing evidence (cf. Parts I and II) indicates that the normal decomposition product of a hydroperoxide formed in the absence of special decomposition catalysts is the corresponding alcohol (the active oxygen atom of each hydroperoxide group being expended in oxidative attack at a near or remote double bond), it is to be expected that each molecule of oxygen absorbed will inevitably produce one hydroxyl group (this either forming part of an original OOH group or appearing as a secondarily formed OH group), and this expectation will hold provided that all the peroxide groups formed in rubber are hydroperoxide groups and that no secondary condensation or dehydration reactions occur in the oxidised rubber. Therefore, in the absence of the latter types of secondary reaction, and complete initial incorporation of the oxygen in the form of ·OOH groups being assumed, the observed hydroxylic oxygen content of any oxidation product is likely to be half the value of the corresponding oxygen intake. The hydroxylic oxygen content can be determined with reasonable precision *via* the active hydrogen content, and the degree of departure of the experimental from the calculated hydroxylic oxygen values is shown in Fig. 2 (curves I and II). It is seen that in the very early stages of oxidation, where nearly all of the oxygen present occurs in peroxide groups, there is little deviation of the observed from the calculated values and hence the peroxide groups themselves cannot be other than hydroxylic (*i.e.*, hydroperoxidic). Later, however, when peroxide decay is rapid and the proportion of secondarily-formed hydroxyl groups should, in terms of the hypothesis, have become important and be increasing steadily, the observed hydroxylic oxygen values are seen to fall short of the calculated ones (*e.g.*, by 15% at 4·25% oxygen intake). The falling off must be attributed either to disappearance or to non-formation of the *simple* hydroxyl groups.

FIG. 2.



The steady overall increase in the proportion of *simple* hydroxyl groups as oxidation proceeds is to be seen in Fig. 2 by subtracting the ordinates of the curve III (expressing the change in the hydroxylic oxygen content of the hydroperoxide groups, *i.e.*, in the half-values of the observed peroxidic oxygen contents shown in curve II, Fig. 1) from the ordinates of the curve II, Fig. 2 (expressing the change in the observed total hydroxylic oxygen). There is nothing to indicate that the progressive falling away from the expected hydroxylic values is due to the formation of something less than one hydroxyl group per peroxide group (*e.g.*, as the result of some degree of ketone formation in place of alcohol formation *). On the other hand, there is abundant evidence that oxidised rubbers lose water readily and unavoidably on keeping, and more readily still on heating; and indeed, the tendency represents an ever-present complication in the compilation of accurate quantitative data concerning the oxidation of rubber, owing to the impossibility of drying specimens to constant weight at temperatures above room temperature. In the present experiments consistent results have been obtained by drying the samples in a high vacuum at room temperature and making determinations on them as far as possible within two days of their isolation from the solvent : the result of mere keeping of the specimens for a week in a high vacuum at room temperature is seen in the rather low hydroxylic oxygen values at two points on curve I, Fig. 2. The gradual loss of water promoted by warming the oxidation products at reduced pressures leads to increased viscosity of solutions of the products and to increased molecular weight, and on this account it seems likely, although it is not formally established, that the elimination of water results in ether formation (largely intermolecular) rather than in the production of double bonds by dehydration. The existence of this secondary tendency to the spontaneous loss of water † being taken into account, the production of hydroxyl groups is in fairly satisfactory agreement with expectation on the basis of the hydroperoxidation hypothesis.

FIG. 3.



*The Effect of Peroxidation on the Unsaturation.*—Peroxide groups formed by the action of oxygen on olefins can only be hydroperoxidic if they are formed by introduction of the reagent at one or other of the methylene groups of the chain, so leaving the olefinic unsaturation intact. Hence in the very early stages of the oxidation of rubber the original unsaturation of the rubber should be undiminished, although as peroxide decay gets under way saturation of the double bonds will take place increasingly, as it does in the olefinic systems already considered. In order to demonstrate the uniform occurrence of hydroperoxidation

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* Assay of well-oxidised rubbers shows only very small ketone contents, which are simply accounted for by scission reactions.

† The loss as shown in curve I, Fig. 2, is of the correct order for loss due to spontaneous dehydration.

throughout the process of oxygen absorption, it must be shown that the degree of unsaturation surviving at any stage in the reaction is quantitatively related to the fraction of the absorbed oxygen which remains at that stage in peroxidic form. Such a demonstration, however, can only be successful in the comparatively early stages of reaction where to no serious extent is peroxidising power being consumed in post-saturation processes, *i.e.*, in chain-scission reactions requiring the expenditure of active oxygen beyond the stage at which one such active atom (from one ·OOH group) has been used in saturating one double bond.

The experimental results obtained for lightly oxidised rubber are shown in Fig. 3, where : (*a*) curve I represents the small change in overall unsaturation (expressed by decrease in the iodine value) which would obtain if all the oxygen entered in hydroperoxidic form and no peroxide-decay occurred, (*b*) curve II represents the rapid diminution of unsaturation which would occur if the ingoing oxygen molecule added at, and saturated the double bonds, and (*c*) curve III connects a series of pairs of points (circles and triangles), each pair referring to one of a series of separate experiments spaced over the early stages of oxidation (*i.e.*, up to a 5% oxygen intake), and one point in each pair representing the experimentally observed diminution of unsaturation and the other the corresponding calculated value derived as indicated above * from the proportions of peroxidic and non-peroxidic oxygen found in the rubber at the different points of observation. The agreement between observed and calculated values is very good in view of the known error in the methods of determination. The disappearance of unsaturation as oxidation progresses is seen to be substantial, amounting even as early as 2·6% of oxygen intake to nearly 50% of that possible on the double-bond-addition hypothesis; the rate of disappearance of unsaturation, however, appears to settle down to a roughly steady rate (> half the maximum calculated on this hypothesis), although since each pair of points on curve III represents a separate oxidation, with unavoidable slight differences in conditions from experiment to experiment, the true slope of the curve may differ slightly from that shown.

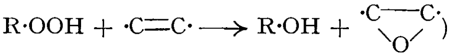
*Chain-scission Reactions.*—The distribution of the active oxygen which is rendered available for oxidative purposes during peroxide decay between (1) mere double-bond-saturation reactions (*e.g.*, saturation according to the scheme  $R{\cdot}OOH + {\cdot}C{=}C{\cdot} \longrightarrow R{\cdot}OH + \underset{\diagdown O \diagup}{{\cdot}C{-}C{\cdot}}$) and (2) chain-scission reactions has not yet been closely studied. Certain observations of interest, however, have been made. In Fig. 3, curve IV, is shown the progressive diminution in molecular weight of the rubber samples used above over a course of oxidation ranging from 0% to 4·3% of oxygen intake. The most spectacular diminution comes, of course, in the very early stages of oxidation, where, apparently, minute proportions of oxygen can have a profound effect : *e.g.*, an intake of about 1% of oxygen is sufficient to reduce the molecular weight from 350,000 to *ca.* 75,000. The stoicheiometric features of this degradation, however, deserve some scrutiny. From the decrease in molecular weight the number of double bonds broken can be determined, and from this number together with the corresponding oxygen intake value the average number of oxygen atoms which are absorbed by the rubber in severing one C–C bond can be calculated. This number is seen from Table II to be considerable, and to rise as oxidation progresses. It would seem, therefore, that no very simple scheme for the utilisation of oxygen for scission purposes (*e.g.*, such a scheme as Staudinger's, expressed by ${\cdot}C{=}C{\cdot} + O_2 \longrightarrow {\cdot}CO + {\cdot}CO$) is likely to be correct unless there exists a special capacity on the part of some few of the incorporated oxygen molecules (*e.g.*, in R·OO–) for effecting scission.

TABLE II.

*Degradation of rubber during oxidation* (*in* cyclo*hexane*).

| Oxygen intake, %. | Mol. wt. of product (in benzene). | Oxygen atoms per mol. introduced. | Number of bonds broken. | Oxygen atoms absorbed per bond broken. |
|---|---|---|---|---|
| 0·00 | 324,000 | — | — | — |
| 0·75 | 93,000 | 152 | 2·50 | 60·8 |
| 1·04 | 75,000 | 210 | 3·32 | 63·5 |
| 1·62 | 67,000 | 343 | 3·83 | 87·6 |
| 2·9 | 55,000 | 587 | 4·90 | 120·0 |
| 4·3 | 48,000 * | 871 | 5·75 | 151·1 |

* In benzene + methyl alcohol.

Two points, however, with regard to this number of oxygen atoms absorbed per double bond broken, are to be borne in mind. First, it represents only a very rough estimate since, in order to take reasonably accurate account of the oxygen which is consumed in producing (concomitantly with the scission) the small amounts of water and carbon dioxide which are known to be formed, it would be necessary to determine the oxygen intake correctly within ±0·01%—a requirement quite unattainable with solutions of rubber. Secondly, the number comprises not only those of the original oxygen molecules which expend their oxidising power (more or less directly) in effecting the scission of a C–C bond, but all those other oxygen molecules which are concurrently incorporated in the rubber chain (as ·OOH groups or their decay products) without actually causing scission. No close estimate, therefore, can be made of the average oxygen expenditure in purely scission reactions.

Bound up with the question of oxygen utilisation in chain-scission processes is the problem of scission mechanism. It is conceivable that peroxidic radicals R·OO– play some small part in the attack on double bonds,

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* On the assumption that no chain-scission (with an accompanying consumption of oxygen in excess of 1 mol. to (I) has occurred.

but for the most part the scission mechanism seems to depend on the oxidative action of completely-formed hydroperoxide molecules, R·OOH. Whether epoxy-compounds represent *usual intermediates* in the scission process remains to be determined, but the subject of chain-scission mechanism can be studied more suitably with comparatively small olefinic molecules than with rubber, and is left for future investigation.

*Conclusions.*—(1) High yields of peroxides (80—90%) are to be observed in the early stages of the photo-oxidation of rubber, but later on, decay reactions occur to a serious degree. Both the primary and the secondary products of oxidation are hydroxylated.

(2) The observed unsaturation and active-hydrogen values of the peroxidised rubber formed in the early stages of oxygen absorption are incompatible with the view that oxygen adds at the double bonds of the rubber; on the contrary, they are quite compatible with the view that incorporation of the oxygen results in the formation of hydroperoxide groups.

(3) Oxidative scission of the chain-molecules begins at the outset of oxidation and rapidly reduces the molecular weight. The quantity of oxygen absorbed by the rubber at any point in the oxidation appears to be more than adequate, stoicheiometrically, to bring about scission of the chains by *multi-stage* mechanisms at the required number of unsaturated centres to correspond with the observed reduction in molecular weight. The precise mechanisms involved, however, are obscure, and may involve in some small measure the reaction of radical intermediates such as R·OO–.

(4) Water and carbon dioxide are formed in small proportions from the earliest stages of autoxidation, and elimination of water continues after the oxidation products have been isolated.

## EXPERIMENTAL.

*Materials.*—(a) *Rubber.* For convenience, a " sol " fraction of rubber, obtained by partial dissolution of crepe rubber in light petroleum (b. p. 40—60°), was employed. The crepe rubber was cut up and thoroughly extracted with acetone in the usual manner, and the residue then extracted with light petroleum in the all-glass modification of Pummerer, Andriessen, and Gündel's apparatus described by Bloomfield and Farmer (*Trans. Inst. Rubber Ind.*, 1940, **16**, 69). In the latter operation the extracts obtained in the first 48 hours were rejected as containing oxygenated rubber, and the later extracts were well mixed and their rubber content precipitated by addition of excess of 95% alcohol. For the earlier experiments the solvent and alcohol adhering to the rubber were removed by evaporation at 15 mm. pressure, and the rubber finally dried at 0·5 mm. and 56° in a pistol drier. The dried rubber was stored in purified nitrogen in a desiccator, the nitrogen being removed by evacuation and replaced every 48 hours. For the later experiments the precipitated rubber was freed from solvent and alcohol by evaporation first at 15 mm. and 30°, and then at 0·5 mm. and room temperature, and finally it was dried for 48 hours at $10^{-5}$ mm. and room temperature. The rubber so obtained was rapidly cut up into small pieces (2 mm. thick), placed in glass tubes in 2-g. or 5-g. batches, and the tubes evacuated on a high-vacuum line for 4—6 hours and then sealed carefully whilst still attached to this line. The tubes were covered with black paper and kept in the dark until required. Samples of " sol " rubber so stored retained over long periods their physical and chemical properties without any detectable deterioration. The following values are typical of samples prepared in this way: N, 0·09; ash, 0·065; C, 87·65; H, 11·85; P.O.C., <0·02%; *M*, 324,000.

(b) *Nitrogen.* In all operations with rubber, its solutions and derivatives in which desired oxidation was not in progress, or vacuum conditions obtaining, the containing vessel was filled with purified nitrogen, commercial " purified nitrogen," which had been freed from residual oxygen by Fieser's process, being used.

(c) *Chloroform.* The " AnalaR " reagent gave consistent results when used as solvent for iodine-value determination.

(d) *Carbon disulphide.* The *colourless* " AnalaR " reagent was quite satisfactory for iodine-value determinations, but when through long storage after it had been exposed to air the reagent became yellow, it was distilled over and stored over sticks of sodium hydroxide.

(e) cyclo*Hexane.* The commercial hydrocarbon was shaken for 24 hours with 20% oleum (changed after 12 hours), very thoroughly washed with alkali and with water, and finally rectified under a jacketed Widmer column.

### *Preliminary Experiments.*

*Method of Oxidation.*—A 2% solution of rubber in purified benzene was placed in a 500-c.c. quartz flask fitted with a mechanical stirrer (mercury seal) and with a side arm. The side arm was connected through a calcium chloride tube to an oxygen reservoir, and the air in the flask was displaced by oxygen. The flask was illuminated and somewhat warmed (*ca.* 35°) by a Hanovia mercury-vapour lamp, S. 500, placed 6—8 inches away. After a short induction period (<1 hour) the stirred solution began to absorb oxygen, and absorption proceeded fairly rapidly. The gas volume absorbed was read off directly, and corrected only for temperature and pressure. For the lower stages of oxidation 250-c.c. portions of 2% rubber solution were taken, and for the higher stages 500—1000-c.c. portions. The duration of oxidation varied from 2 to 80 hours.

*The Oxidation Products.*—The reaction mixture was freed from solvent by distillation under reduced pressure, and, in the case of those products containing less than 10% of oxygen, the residue was divided into ether-soluble and -insoluble fractions by agitation with peroxide-free ether. At the more advanced stages of oxidation it was necessary to redivide the ether-soluble fraction into neutral and acidic portions by shaking the ethereal solution with dilute aqueous sodium hydroxide (or sodium bicarbonate). The separation of the aqueous alkaline layer from the ether layer was usually very slow owing to emulsification, and hence there was some unavoidable diminution in the (already small) peroxide content of the separated materials due to the action of alkali, and doubtless in consequence a corresponding small increase in the degradation of the oxidised rubber. On each of the products determinations for carbon, hydrogen, oxygen (diff.), P.O.C., and iodine value were made, and in the case of certain of the products determinations for hydroxylic oxygen (Zerewitinoff) and molecular weight (viscosity). The essential data are listed in Table I.

### *Later Experiments.*

*General Procedure.*—Owing to practical difficulties in uniform cooling and effective irradiation of a large vessel during shaking, and to serious inaccuracies arising from (*a*) frequent interruptions of the oxidation process, (*b*) the difficulty in withdrawing at each stage numerous carefully measured portions of the viscous solution without incurring any loss, and (*c*) severe depletion of the stock (tending to make the samples unrepresentative) towards the end of the process, the multi-stage procedure was used only for checking the trend of variation in the proportions of single functional groups, and particularly for observing the relation of peroxide formation to oxygen absorption, since this required the withdrawal of only 2—3 c.c. of solution at each oxidative stage. For the purpose of following the structural changes occurring in the early stages of oxidation, a series of separate oxidations spaced over the range of oxidation to be studied was found advantageous. The adoption of this procedure made it necessary to maintain the temperature and illumination as constant as possible during all stages of the oxidation, and to employ a standard method of withdrawal of samples and isolation of the oxidised rubbers. All oxidations were conducted in carefully purified *cyclo*hexane at 12° with fairly rapid shaking, the ultra-violet lamp being placed 4 inches from the oxidation vessel.

*The Oxidation Vessel* (Fig. 4).—This consisted of a 300-c.c. Pyrex flask, *A*, connected with a manometer and compensator, *B*. The compensator, which was connected to one side of the manometer with a cone and socket joint (B 10 size) secured with spring clips, contained 1—2 c.c. of the pure solvent, and served to compensate (when tap *C* was closed) for the partial pressure of the solvent in the reaction vessel. The compensator was easily detachable for cleaning purposes. The volume of the vessel was 343 c.c.

The free space in the vessel was the difference between the volume of the apparatus and the volume of the rubber solution ordinarily taken, *i.e.*, 343 – 100 c.c. To this had to be added the volume of gas dissolved in the solvent, *viz.*, 0·15 c.c. per c.c. of *cyclo*hexane. Hence the total effective gas space was [243 + (100 × 0·15)] c.c. = 258 c.c.

At the start of each experiment the mercury stood at the same height in the two arms of the manometer. When tap *C* was closed and the oxidation began, the pressure in flask *A* diminished owing to consumption of oxygen, and this caused a shift of the mercury level towards *A*. The gas space in *B* thus became greater and that in *A* slightly smaller, but whereas the change in volume in *A* was negligible compared with the total gas volume (258 c.c.), that in *B* was significant, and could not be neglected in determining the true change in oxygen pressure. In order to permit measurement of the latter, the manometer had already been calibrated against a standard manometer before introduction of solution and solvent into *A* and *B* respectively. The true change of pressure in *A* was found to approximate closely to the observed change in pressure ×1·075, for the range of change of pressure observed.

FIG. 4.

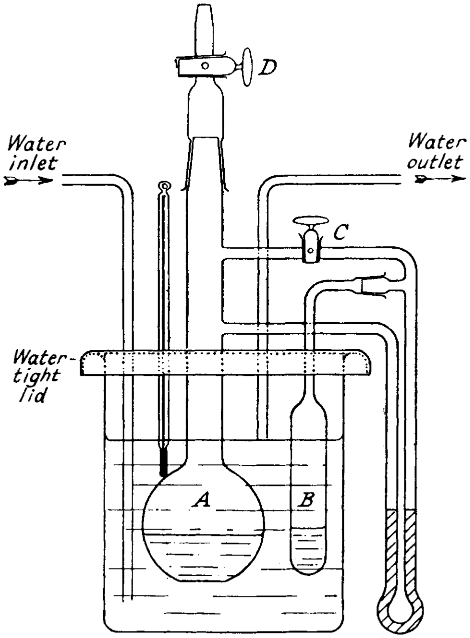
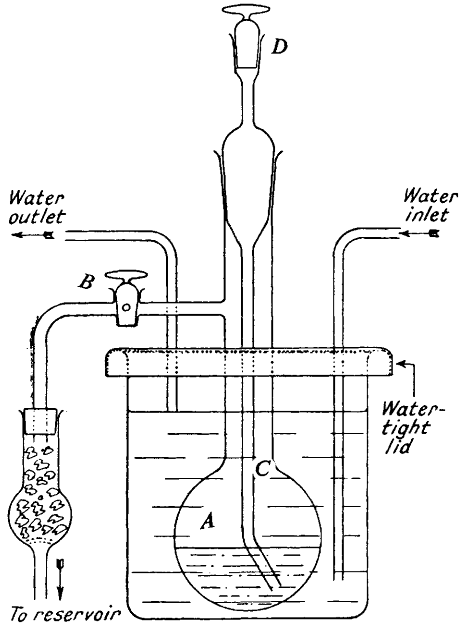


FIG. 5.



For measurements where the oxygen intake to be employed was in the range 0·5—2·0%, a charge in the flask of 2 g. of rubber in 150 c.c. of *cyclo*hexane was advisable; where the intake was to exceed 2% a charge of 1 g. of rubber in 100 c.c. of solvent was sufficient. With these quantities the accuracy of measurement of the oxygen intake fell within ±5% of the true value. The charge was prepared by shaking mechanically (12 hours) a weighed sample of " sol " rubber (see above) together with the requisite amount of *cyclo*hexane in a 150-c.c. bottle from which all air had been removed by evacuation and its place taken by purified nitrogen. The rubber solution was transferred to the oxidation apparatus by means of a funnel having a long stem, and the funnel and bottle were well washed with a further 50 c.c. of solvent. Then the compensator was charged with 1—2 c.c. of pure solvent and re-attached to the manometer arm.

The whole reaction vessel was cooled in ice water until the *cyclo*hexane had completely frozen; then it was evacuated with an oil pump (using an interposed liquid-air trap) with taps *C* and *D* open; finally, oxygen was admitted, up to 400 mm. pressure. Tap *D* was then closed, and the vessel enclosed in a beaker provided with close-fitting lid, water inlet and exit tubes for water-cooling, and a thermometer. The apparatus was mounted on a shaker near to a Hanovia mercury vapour lamp, S 500. The apparatus was shaken, water at 12° was circulated through the beaker for 30—60 mins. (tap *C* open) to permit equilibrium to be established throughout the system; then tap *C* was closed and the lamp switched on. After the desired stage of oxidation had been reached, the lamp was switched off and the apparatus shaken for a period to allow equilibrium to be established again. The difference in height of the mercury columns in the two arms of the manometer was read. The temperature of the cooling water was maintained constant throughout. The percentage weight of oxygen absorbed was given by $32(p/760)(V/22{,}400)(100/W)(273/T)$, where $p$ is the corrected change in pressure, $V$ the total gas space, $W$ the weight of rubber in solution, and $T$ the absolute temperature.

*Measurement of Oxygen Intake.*—In the early stages of reaction the method described above is employed; in the later stages the observed intake (%) can be checked by calculating the oxygen absorbed (%) from the oxygen contents of the product and of the original rubber, each of these being determined (by difference) from careful carbon and hydrogen determinations. No generally effective way of compensating for the small amounts of water, carbon dioxide, or other highly volatile materials formed during the oxidation has been found, and hence the error due to this cause is left uncorrected.

*Determination of Peroxidic Oxygen.*—The method already described by Bolland *et al.* (*Trans. Inst. Rubber Ind.*, 1941, **17**, 29) was used. For lightly oxidised rubbers there is great danger of partial precipitation and consequently incomplete reaction when the reagent is added to their solutions; hence, when the *total* oxygen content is below 15% the recommended mixture (73 : 27, by vol.) of benzene and methanol for dissolving the ferrous thiocyanate reagent must be strictly employed. When, however, the oxygen content of the oxidation product exceeds 15% the admixture of benzene with the methanol can be dispensed with.

*Determination of Active Hydrogen.*—This proceeded satisfactorily by the method of Bolland (*ibid.*, 1941, **16**, 267) when the solvent employed for the oxidised rubbers was dry toluene and the Grignard reagent was made up first in dry ether and the uncombined ether subsequently removed completely in a high vacuum and replaced by dry xylene.

*Determination of Unsaturation.*—As with other polyisoprenes studied, the most consistent and precise values for the unsaturation of rubber have been obtained by the iodine-value method. Halogens possess considerable powers of substitution when reacting with olefinic substances, including rubber. The conditions under which iodine chloride reacts quantitatively and conveniently with rubber have been closely investigated by Kemp (*loc. cit.*) and Kemp and Müller (*loc. cit.*); we have found the latter's method to be very satisfactory over a wide range of conditions, but we had slightly to modify the procedure developed for rubber to render it applicable to oxidised rubbers.

Kemp and Müller used carbon disulphide as solvent for rubber but for oxidised rubbers chloroform is a more satisfactory solvent (Kemp, Bishop, and Lasselle, *Ind. Eng. Chem.*, 1931, **23**, 1444). We found 50 c.c. of chloroform to suffice to dissolve *and retain in solution* oxidised rubbers containing $>5\%$ of oxygen, but 75 c.c. are required for products containing $<5\%$ of oxygen. Great care is necessary in the addition of Wijs's solution in order to avoid precipitation of any of the rubber; it should be slowly and cautiously released from a pipette, with calcium chloride tube attached,* *on to the sides* of the bottle, and if a wide-mouthed bottle is used for the determination there is no difficulty in doing this while at the same time imparting a rotatory motion to the rubber solution. In this way an undue concentration of the added reagent at one point is avoided. If precipitation of the rubber accidentally occurs during addition of the reagent the determination is abandoned; later, when the reagent has fully reacted with the rubber, precipitation does not matter.

The operation is then conducted in the way described by Kemp and Müller, except as regards one detail. Previous work on the autoxidation of *cyclo*hexene (cf. Part I) showed that even the slightly peroxidised hydrocarbon gives too low iodine values owing to reaction of the peroxide with excess of the potassium iodide used in the determination. In the case of oxidised rubbers the effect of peroxide groups is much less but is not negligible. It is found that the undesired reaction can be greatly suppressed by using 100—150 c.c. of water for dilution purposes instead of the 75 c.c. recommended by Kemp. This serves substantially to eliminate error due to peroxidic action.

The end-point with most samples can be obtained within half a drop of thiosulphate, if the latter is well washed down and thoroughly incorporated in the test solution by vigorous shaking. The accuracy of determination is thus within ±0·3%.

*Multi-stage Oxidations.*—The rate of formation of peroxidic groups with increasing oxygen intake was conveniently followed in a multi-stage experiment using the apparatus illustrated in Fig. 5. This consisted of a litre flask *A* as receptacle for the rubber solution, to which was attached a side arm (carrying a tap *B* and calcium chloride tube) for making connexion with the oxygen reservoir. The neck of the flask was closed by a ground-in hollow stopper, the lower end of which was sealed to a glass tube *C*, bent as shown, reaching nearly to the bottom of the flask, and the upper end to a short tube fitted with a ground-in stopper *D*. The tube *C* was required for the withdrawal of samples.

10 G. of sol rubber of low peroxide content were dissolved in 400 c.c. of pure *cyclo*hexane contained in a stoppered bottle (nitrogen atmosphere), a mechanical shaker being used. The solution was transferred to the flask *A*, the bottle being rinsed out with a further 100 c.c. of *cyclo*hexane. The tube *C* and stopper *D* were placed in position, and the flask evacuated by means of an oil-pump (tap *B* open). In this operation the flask was tilted so that the lower end of *C* cleared the surface of the liquid in the flask. Tap *B* was then closed, the flask was enclosed in a covered beaker, acting as cooling jacket, through which cold water at constant temperature (14°) circulated, and the whole was mounted on a mechanical shaker. The flask was connected to the oxygen reservoir, and filled with oxygen; then, after a short period of gentle shaking, the gas in both was brought to atmospheric pressure. The volume of gas in the reservoir and its temperature were noted. Then a mercury vapour lamp placed 4 inches from the flask was turned on, and the flask shaken rapidly.

At the end of each oxidative stage the lamp was turned off, the flask was shaken slowly for 30—45 mins. to ensure that equilibrium had been reached, and the volume of gas remaining in the oxygen reservoir (after adjustment of the pressure to atmospheric pressure) and the temperature were observed. The stopper *D* was then removed, the level of solution in the tube *B* was raised by increasing the pressure in the oxygen reservoir, and a sample (exactly 3 c.c.) of the reaction product removed for peroxide determination by means of a long-stemmed graduated pipette. Since any unmeasured loss of solution would entail inaccuracy in the later stages of oxidation, it was necessary to avoid undue wetting of the walls of the pipette. The results of a typical multi-stage oxidation are shown graphically in curve II, Fig. 1 (dots in circles).

*Single-stage Oxidations.*—These were conducted at *ca.* 12° in the apparatus described above (Fig. 4). Immediately the oxidation of a sample was complete, the oxidised solution was pipetted into a cylindrical evaporation vessel, 55 mm. wide, fitted with interchangeable, flange-jointed lids suitable for attachment to a vacuum line or for use in distillation of the solvent. 10—15-C.c. portions of the solution were immediately taken for determination of the peroxidic oxygen content and the active hydrogen content of the oxidised rubber; an aliquot portion was also taken for determination of the concentration of oxidised rubber therein. Since *all* the necessary determinations could not be made at once (the determination of active hydrogen alone took 6—8 hours) the remainder of the solution was treated as follows. The solution was freed from solvent by evaporation at 15 mm. pressure and 30°, and the residue then dried completely in the flange-jointed vessel *at room temperature*—first at 0·5 mm. for 2—4 hours, and finally at $10^{-5}$ mm. for 24—30 hours. The oxidised rubber at the end of this drying process was entirely free from solvent. The dry, oxidised material was kept attached to the vacuum line at room temperature until *all* the analytical determinations (iodine, peroxide, and active hydrogen values, and molecular weight) had been satisfactorily completed; when, however, samples were to be withdrawn the flange-jointed vessel was filled with dry nitrogen before being removed from the vacuum line. When the required sample had been quickly removed, the flange-jointed vessel was returned to the vacuum line and re-evacuated. All samples withdrawn for analytical measurements were protected against bright sunlight and were weighed and used promptly. Peroxidic oxygen determinations were usually made with measured volumes of the solution immediately after the oxidation was completed and again with a dried sample : the difference between the values so obtained was small. All samples of oxidised rubber very slowly lost water in a high vacuum even at room temperature, and this loss increased

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* Since moisture hinders the addition of iodine chloride to the olefinic centres it is desirable to prevent its entrance from the air both in filling and in emptying the pipette.

considerably as the temperature rose. For this reason, samples which had been kept at room temperature for 7 days gave unduly low values for the active hydrogen content—a contingency which was not at first realised.

All molecular-weight determinations were made by the viscosity method. The following details apply to a typical run : 1·5 g. of " sol " rubber (iod. val., 365·0) in 150 c.c. of *cyclo*hexane were oxidised at 11° for 90 mins. The change in pressure corresponding to a free space in the vessel of 208·0 c.c. was 29·0 mm. The oxidised material gave the values : oxygen intake, 0·75 ; P.O.C., (in solution) 0·62, (dry) 0·60% ; iod. val., 360·0, 359·4, 360·0 [Calc. : (i) on basis of saturation effected by the non-peroxidic oxygen, 360·8 ; (ii) on basis of ring peroxide hypothesis, 356·0] ; *M*, 93,000. The progressive change in the respective values from stage to stage in the oxidation is shown graphically in Figs. 1—3.

We thank Dr. G. Gee for carrying out the molecular-weight determinations.

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