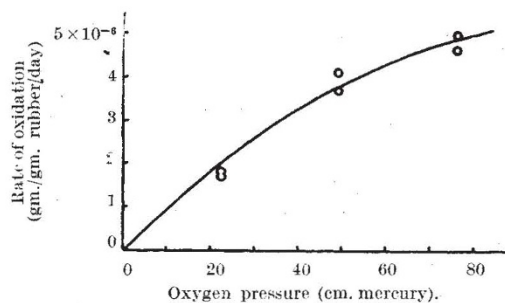


Reaction between Oxygen and Rubber

SEVERAL investigations^{1,2,3,4} on the effect of pressure on the reaction between natural rubber and gaseous oxygen in its initial stages have been made by following the rate of disappearance of the oxygen in a closed system. In the experiments, the oxygen pressure decreased spontaneously as oxygen combined. Under these conditions, the results may be vitiated if time effects occur such as might arise from the rate of combination of oxygen dissolved in the rubber outpacing the rate of dissolution of fresh gas, or from the formation of unstable oxidation catalyses.

We have carried out oxygen absorption experiments under conditions of constant pressure, with rubber specimens for which we have evidence that their state of subdivision is such as to prevent any complication from diffusion effects, and have come to the following conclusions.

1. At constant pressure the rate of oxidation reaches a constant and reproducible value. (Our experiments have been confined to combined oxygen proportions not exceeding 1 per cent by weight.)
2. Contrary to earlier suggestions⁴, the oxidation-rate is greater the greater the oxygen pressure (Fig. 1).



OXIDATION OF UNVULCANIZED SMOKED SHEET RUBBER AT 40° C.

3. The rate of oxidation using dry air free from carbon dioxide is greater than that using undiluted oxygen at the same partial pressure.

The following further conclusions are based on experiments involving alteration in oxygen pressure.

4. After storage in a vacuum, the rate of oxidation of rubber in oxygen under constant pressure slowly increases, for several hours, from zero to the 'equilibrium rate' for that oxygen pressure. This period is considerably greater than that required for solubility equilibrium.

5. If, after the rate of oxidation under constant pressure has become constant, the oxygen pressure is reduced to a new constant value, the rate of oxidation falls slowly for several hours from a high initial value to the new constant rate corresponding with the lower pressure. This high initial rate is sometimes greater than the constant rate at the higher pressure. These statements may also be true in strict converse for an increase in oxygen pressure.

6. The persistence of an oxidation-rate greater than the 'equilibrium rate' immediately succeeding a reduction in pressure (see 5) can invalidate conclusions from experiments involving a changing pressure, and may explain the lack of agreement between results of earlier workers.

A detailed account of this work will be published later.

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¹ Williams and Neal, *Ind. Eng. Chem.*, **22**, 874 (1930).

² Dufraisse, *Rubber Chem. and Tech.*, **11**, 268 (1938).

³ Milligan and Shaw, *Proc. Rubber Tech. Conf.* (London), 537 (1938).

⁴ Morgan and Naunton, *Proc. Rubber Tech. Conf.* (London), 599 (1938).

Ethereal Sulphate Content of Agar Specimens

IN 1942, through the kindness of Dr. A. P. Orr of the Marine Station, Millport, specimens of agars of known history were examined to see if evidence could be secured for the formulation of Jones and Peat¹, which demands a relatively high sulphur content (S, 1.8 per cent; that is, SO₄, 5.4 per cent).

The specimens had been extracted from the algae with boiling water without any chemical treatment, and the agars purified by freezing and thawing; the results are tabulated below:

Plant	Source	Ash	SO ₄ (in ash)	SO ₄ (total)
<i>Gracilaria confervoides</i>	Plymouth	2.2%	0.9%	1.3%
<i>Gelidium crinale</i>	Dunure (Ayrshire)	3.6	0.7	1.4

These figures may be compared with those reported by Barry and Dillon² for an agar extracted from *Gelidium latifolium*, which gave ash, 2.6 per cent; S, 0.36 per cent. It is clear that none of the above specimens contain sufficient sulphate to account for the proportion of 2:4-dimethyl-3:6-anhydro-β-methyl-*l*-galactoside (9 per cent¹; 11.5 per cent³) isolated from methylated agar, on the former of which the 'sulphate formula' proposed by Jones and Peat is based.

From their experiments with periodic acid, Barry and Dillon² concluded "that the 3:6-anhydro-*l*-galactose isolated from agar in the form of its 2:4-dimethyl derivative is not an artefact produced during the methylation process¹, but a constituent of the agar molecule". That this appears to be true for commercial samples of agar has been pointed out previously^{3,4,5,6}, but it is difficult to believe that there is no connexion between the 3:6-anhydro-*l*-galactose units and the sulphate groups, since the alkaline hydrolysis of methylhexoside sulphates gives rings of this type⁶. If, as Jones and Peat¹ suggest, all the galactose residues which ultimately become 3:6-anhydro-*l*-galactose residues carry sulphuric ester groups at the same time, the present evidence points to the conclusion that most of these sulphate residues are removed at some stage prior to the actual extraction of the polysaccharide from the plant. An alternative view would be a gradual removal of sulphate groups during the life of the plant with 3:6-anhydride formation, followed by the formation of ethereal sulphates on other galactose residues, the sulphur content remaining approximately constant throughout.

Finally, it should be stated that there is as yet no direct evidence that the sulphate groups remaining in the agar after isolation are located on C₆ of the