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The Oxidation of Rubber Vulcanisates

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The slow, spontaneous deterioration in the tensile strength and elongation of rubber vulcanisates at room temperature, known as natural ageing is due principally to a reaction between the rubber and oxygen [1]. Although ageing is not identical with oxidation [2] the relation between these two phenomena provides a convenient mean of comparison.

It is generally accepted that an absorption of approximately one per cent by weight of oxygen corresponds to the complete destruction of a vulcanisate with regard to its mechanical properties [1].

The Arrhenius curve of the reaction can be determined by measurements in the range 50—150° C. Here the rate of oxidation will have a proper value allowing the completion of a run in a convenient amount of time. Using the obtained graph the rate of oxidation may be determined by extrapolation.

Index of ageing is here defined as the time required for the reaction of approximately 20 millimols of oxygen per mol C_5H_8 *i. e.* roughly one percent on the weight of the rubber. If a relationship can be derived between this index of ageing and the rate of ageing determined by mechanical means such data would be useful in calculating the resistance to ageing of a given vulcanisate.

Dufraisse [3] used a manometric technique in his fundamental study of the function of inhibitors in various autoxidation reactions. The conception of "inverse catalysis" as cited by Moureu and Dufraisse in theire exposition of the theory of antagonistic peroxides arose out of these investigation. Christiansen [4] showed that the reaction mechanism proposed was inadequate and proposed a chain reaction.

Dufraisse has constructed an apparatus which permits the simultaneous measurement of the rate of oxidation in 10—20 absorbers, and has shown the principal influence of a series of factors such as combined sulphur, time and temperature of vulcanisation, concentration of filler and inhibitor etc. Ordinarily the measurements are performed in comparison with a standard sample and the absolute values of the rates are not calculated [5,6].

According to a similar manometric method Williams and Neal [7] investigated acetone extracted vulcanisates, and stated a constant dp/dt corresponding to zero order reaction, which in turn was explained by the conception of a chain mechanism without attempting a quantitative formulation. Similar measurements were carried out by Morgan and Naunton [8], who confirmed the zero orden reaction for acetone extracted vulcanisates and concluded with the statement that the rates were in agreement with the Arrhenius equation. A chain reaction was described according to Bäckström [9], which gave quantitative expression of the kinetics.

The value of these manometric measurements has been somewhat reduced through an investigation by Carpenter [10]. Carpenter determined the rates in a constant pressure device and found that the rate of oxidation varied with the pressure of the oxygen in contradiction to the manometric findings, and further that the sample continued to oxidise at the same rate after reduction of the pressure of oxygen for a considerable time. This persistency of rate of oxidation is assumed as the possible explanation of the zero order reaction found by the manometric method.

Shelton and Winn [2] stated an autocatalytic reaction on vulcanisates of GR—S (the American buna rubber). The initial phase of the reaction could be described by the superposition of a first order reaction at active centres in the butadiene-styrene-structure and a zero order reaction with normal structures. The same kinetics were stated by Stafford [11] for irradiated rubber vulcanisates measured at constant pressure. On raw rubber le Bras [12] found more complicated variations of the rate of oxidation at constant pressure. Le Bras used a very interesting apparatus in which the oxygen was prepared by electrolysis, a method which is not free from danger as a trace of ozone might be expected in the electrolytic oxygen.

Unfortunately the determination and isolation of the peroxides in rubber is still an unsolved problem and in consequence the fundamental base for the kinetic treatment of the problems is lacking. The theory proposed by Bolland and Gee [13] for the autoxidation of esters of linoleic acid, however, seems to be a very attractive explanation which might be extended to the oxidation of rubber as mentioned by Mesrobian and Tobolsky [15]. According to Bolland and Gee the initiation is performed by free radicals formed by thermal decomposition of the peroxide and the termination by reactions between the radicals.

In a somewhat similar manner Cole and Field [14] explain the oxidation of GR—S where the free radical is formed through reaction of the diene complex with active oxygen. Termination by an inhibitor of the phenylnaphthylamine type is effected by reaction between the primary peroxide and the imino-hydrogen atom in the inhibitor, whereby a new free radical with insufficient energy for chain propagation is formed.

In spite of the foregoing criticism of the manometric method it shows some indisputable merits, namely its simplicity and the ease with which multiple determinations are performed. In the following experimental part therefore, we will try to elucidate the possibilities of the method in respect of reproducibility of the results and for the empirical determination of the effects of antioxygens and of copper and manganese soaps.

PREPARATION OF THE SAMPLES

All compounds were mixed on an ordinary laboratory mill with all precautions. The raw rubber was cut from the interior of a selected bale of smoked sheets. Slabs were moulded in a cavity in iron moulds 200 × 100 × 2 mm^3 between two hard, polished aluminum plates and immediately cooled in water after the removal from the press. The slabs were cut into about 10 × 20 mm^2 pieces and crumbed by 4—5 passages through tight rollers on the mill. The crumbs were further disintegrated in a small mill furnished with helical blades and the resulting powder sieved to pass 100 % through 30 mesh and 0 % through 60 mesh. The surface of the samples was approximately 200—300 cm^2/cm^3 and the value was roughly determined by counting all grains in 1—10 mg powder weighed on a microbalance and evenly spread on a piece of millimeter paper.

THE ABSORBERS

Preliminary experiments were carried out in a modified Dufraisse absorber made of glass. The absorber was filled with oxygen by flushing from a tank 10 min. This method brought about some difficulties in avoiding streaks in the grease used for the sealing of the ground glass joints, which was turned 180° to close the connection with the atmosphere through corresponding channels in the glass stopper and the absorber joint. Those difficulties are quite avoided in the absorber described below (Fig. 1).

The absorber is fitted with a very carefully ground joint 1 sealed with a proper amount of Cellogrease (Fisher Scientific Co.) on the upper third of the stopper. The reaction vessel *R* has a volume of 10 ml and the capillary is 500 mm with a bore of 0.8—1 mm and a volume of 0.3—0.4 ml. The capillary extends 15 mm into *R* and is covered by the perforated micro beaker *5*. In the mercury reservoir the capillary is fixed in a rubber stopper with a smooth bore, moistened with very little glycerol. The position of of the end of the

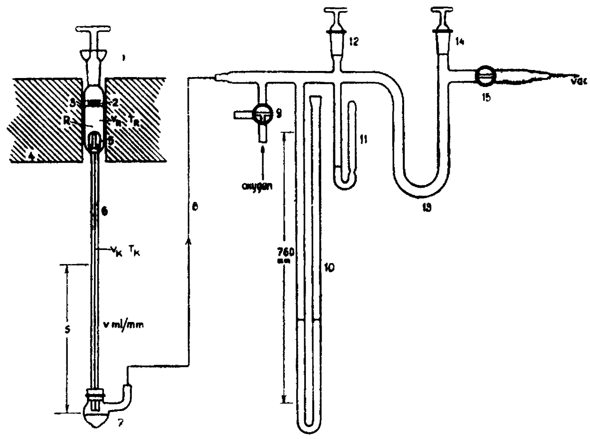

Fig. 1. Oxygen absorber.

capillary is adjusted to a few millimeters over the mercury surface. 2 g of rubber of the mentioned fineness are introduced into the absorber and 0.3—0.4 g ascarite is placed over the sample in a micro glass *2* to absorb water and carbon dioxide. The absorber is evacuated and filled by oxygen from the tank by means of the manometer *10—11* and the cocks *9—15.* This process is repeated 4—5 times, each time reaching a moderate vacuum about 2—5 mm Hg. Finally the absorber is lowered in the mercury, applying a slight pressure on the stopper *1.* At the last filling with oxygen one may stop at a pressure 40—70 mm below the barometric pressure, which forces the mercury to mount in the capillary, and the readings can take place immedeately after heat equilibrium is reached. Heating of the absorbers is performed in holes drilled in an electrically heated and automatically temperature controlled aluminiumblock *4* in which 10—20 parallel manometer can be placed. The temperature differential in the rubber sample is about 0.1—0.5° C using a closely controlled heating current.

Measurements at temperatures below 50° C are made in the absorber shown in Fig. 2. The capillary is 350 mm with a lumen of 2 mm. The filling with oxygen is performed by using the same method described above, with the auxiliary system placed in the ground glass joint g. The sealing liquid, ethyleneglycol, is stored in the funnel *h*, and the cock *i* is opened after the final addition of oxygen and the glycol flows in *e*, sealing the absorber. The funnel is then removed and the absorber placed in a water thermostat and is finally closed by means of the stopper with the cock *i*. By opening *i* and applying

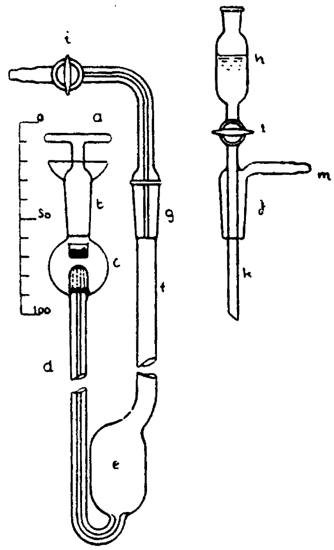

Fig. 2. Closed absorber.

gentle suction by mouth the glycol meniscus may be adjusted to any desired position in the capillary *d*. The rate is here measured with close temperature control and without influence of fluctuations of the barometric pressure. The vapor pressure of glycol is 2 mm at 35° C.

Most of the measurements were not conducted in absolute darkness but in very weak diffuse daylight.

CALCULATION OF THE RATE OF OXIDATION

With the symbols used in Fig. 1 and volume of the capillary w ml/mm the amount of oxygen in the absorber is given by:

$$O_2 = \text{p. f. } (V_R \cdot \perp_R + V_K^* \perp_K) \text{ mols}$$
$$f = 273.2/760 \cdot 22392 = 1.605.10^{-5}$$
$$V_K^* = V_K - s.w$$
$$\perp = 1000/T$$

and the pressure in the absorber

$$p = B - s$$

where s is the height of the mercury column in the capillary, B the barometric pressure, V_K the total and V_K^* the volume corresponding to s of the capillary. By differentiation in respect to time h (hours) the rate is

$$v = \frac{dO_2}{dt} = -f \cdot \frac{dp}{dt}\left[V_R \perp_R + \perp_K(V_K + w\ (2p - B))\right] \qquad (I)$$

v is expressed in moles O_2 pro hour and g C_5H_8 omitting the constant 10^{-8} in all quotations of rates of oxidation.

The condition for zero order reaction is determined by integration of (I) keeping v constant:

$$\frac{K}{t \cdot f} = -Ap - Dp^2 + C \qquad (II)$$

where K denotes the constant value of v at temperature T and the constants of integration are

$$A = V_R \perp_R + \perp_K(V_K - wB)$$
$$B = w \cdot \perp_K$$
$$C = AB + DB^2$$

Consequently a straight line s—t relation corresponds to a slight decrease in v and opposite the s—t curve concording to a zero order reaction must be concave to the s-axis as the following calculation will show. Chosing $V_R = 9$ ml, $\perp_R = 3.7$, $\perp_K = 3.4$, $V_K = 0.4$ ml, $B = 760$ mm Hg, $w = 0.000\,8$ ml/mm og dp/dt = const. = 10 mm Hg/h one have:

Table 1.

s mm Hg	v^s	t hours
0	591.6	0
100	583	9.89
200	574	19.63
300	565	29.22
400	556	38.67
500	547.9	47.97

v^s: rate of oxidation corresponding to s mm Hg

The column v^s is calculated from equation (I) and it is seen that the rate decreases 7 % calculated on v^0, which is insignificant compared with the normal accuracy of the method. The column t is calculated at $v = 591.6 = \text{const.}$ from equation (II):

$$368.6 \cdot t = -32.59 \cdot p + 0.0027\ p^2 + 26339$$

and the curvature of the s—t line becomes very little.

For the absorber Fig. 2 kept at constant temperature T the rate is calculated from:

$$v = f \cdot \perp \frac{dp}{dt}\left[V_0 + \frac{w}{b}\,(2\ p - B)\right] \qquad \text{(Approx.! III)}$$

where V_0 denotes the combined volume of absorber and capillary corresponding to $s = 0$ and b the ratio of the density of glycol at $T°$ and mercury at 273° ($b = 7.91 \cdot 10^{-2}$ at 35° C.)

The readings of t, s, B and T_K are tabulated and the s—t curve plotted graphically.

RATE OF OXYDATION OF A STANDARD VULCANISATE

I. Without addition af antioxygen

As a typical fast oxidising vulcanisate a DPG-vulcanisate with the following formula was used throughout the investigation:

Smoked sheet	1 000	1 000
Sulphur	15	15
DPG	15	15
Zincoxide	100	100
Whiting	1 060	1 040
Carbon black	30	30
Antioxygen	nil	20

Vulcanisation unless otherwise stated 15 min/152° C
Vulcanisates without antioxygen are termed —
with » » » +

All the rates cited in the following tables are rates corresponding to $s = 0$: *the initial rate* computed from the s—t curve. In the Table 2 are collected some data concerning the purity of the fillers used:

Table 2.

Filler	% Cu	% Mn	% Fe
Danish whiting	0.0004	0.01	0.1
Winnofil (ICI)	0.0003	0.007	0.08
Zincoxide	0.005	nil	nil

Though all measurements on the — vulcanisates were conducted with great care with powders of approximately the same surface it will be seen from Table 3 that it is impossible to reproduce the value of v. The reproducibility in double or multiple runs using the same samples is well established at about $\pm$ 5—10 %, but changing to a new mix using exactly the same ingredient can yield results which will differ widely. This is the case for the three samples 4620C, 47161B and 4823 all with Danish whiting, of which 4620 is slow and 4823 fast oxidising and 47161 gives an Arrhenius line of a different slope. One must content oneself to locate an upper and lower line for the area in which the vulcanisate by chance will locate itself, and the limitiation is almost given by the $\perp$-log v-lines for 4620C and 4823. The purity of the whiting does not seriously affect the rates as shown by 4839 containing the pure precipitated stearic acid coated calcium carbonate from ICI (Winnofil) placed intermediately in the interval. The sample 4852 is made from a washed and vacuum dried smoked sheet from the interior of a bale. This process is expected to remove some of the natural antioxidants in the rubber, but 4852 on the contrary is slow oxidising at the lower limit of the interval.

All graphs of s-t are with great accuracy *strictly linear* up to 200—300 mm Hg at temperatures below 100° C and in some cases graphs with a slight increase in ds/dt occur *i. e.* almost zero order reaction. At higher temperatures (120—140° C) the curves initially start as straight lines but at 100—200 mm Hg the ds/dt value will rapidly decrease. Rates above 150 000 are not realised, not even with samples to which is added a considerable amount of copper stearate. Above 100° C the diffusion is becoming a controlling factor and it is difficult to prepare samples with surfaces exceeding about 300 cm^2/cm^3. Due to the lack of consistency it is impossible to determine the kinetic constants with a reasonable accuracy, but the energy of activation (mean value from Table 3) is round 21 kcal and the constant H about 15.6 (mol/mol.sec). Finally we can calculate a mean Arrhenius line given by

$$\log_{10} v = 8.52_3 - 4.63_0 \cdot \perp$$

Table 3. Initial rates of oxidation for vulcanisates without antioxygens.
mols O_2 per hour and g C_5H_8 ($\times 10^8$).

°C	No. of mix Rubber Filler surface	4620 C SS [1] whiting [2]	47161 B SS [1] whiting [2]	4823 SS [1] whiting [2] 186	4839 SS [1] Winnofil [3] 213	4852 washed SS whiting [2] 198	cm^2/cm^3
25		9.4					
27				22.3			
31.7		18.6					
33.0			27.7				
34.5[4]					20.3	21.1	
40.7		37.0					
45.6			132				
49.3		120					
57.5			477				
59.5				671	603	485	
60.4		340					
69.4			1 680				
74.4				2 860			
79.5			3 800		1 940	1 640	
89.4				9 100			
100.4				18 500	11 400	6 900	
121.3				44 000			
	$\log_{10} v°$ [5]	7.809 − 4.436 · ⊥	9.844 − 5.016 · ⊥	8.371 − 4.504 · ⊥	8.874 − 4.778 · ⊥	7.711 − 4.414 · ⊥	
	H [6] mols/mols · sec	14.00	18.68	15.30	16.45	13.77	
	Q [6] kcol	20.4	23.1	20.7	22.0	20.3	

[1] Standard smoked sheets.
[2] Washed Danish whiting.
[3] Stearic acid coated, precipitated calcite from J. C. J.
[4] Measured in the closed absorber (Fig. 2).
[5] Derived by regression analysis.
[6] Arrhenius equation $\ln v° = H \quad \frac{Q}{R \cdot T}$

which will be used as an average standard in discussing retardation by antioxygens and acceleration by copper and manganese soaps in the following measurements.

Table 4. Tensile properties.
Sample 47 · 161 B.

Addition %	Antioxygen parts	TB [1] kg/cm²	M_3 [2] kg/cm²	EB [3] %
nil	—	152	54	510
0.01 Cu [4]	—	157	57	510
0.05 Cu [4]	—	134	44	540
0.01 Mn [5]	—	132	38	520
0.05 Mn [5]	—	85	14	640
nil	2 [6]	163	55	520

[1] Tensile at break.
[2] Modulus at 300 % elongation.
[3] Elongation at break.
[4] As copper stearate.
[5] As manganese oleate.
[6] 2 part per 100 Smoked Sheets (Antioxygène A, Francolor).

II. Compounds with copper and manganese

To the base formula were added various amounts of copper stearate containing 9.4 per cent copper and manganese oleate with about 1 per cent manganese. The tensile and modulus of the vulcanisates is definitely reduced and the elongation increases as the figures in Table 4 will show.

The addition of 0.01 per cent of copper causes a little increase in tensile and modulus presumably through a cross-linking of oxygen. The chain scission is very clearly shown at the higher copper concentration and further in all cases with manganese. These samples age very fast at room temperature in the dark, and surface tackiness is developed in a few days, while the tackiness of copper containing specimens appears after some weeks. The *s-t graphs* are all very characteristic with *pronounced increase* in ds/dt in many cases after a straight line initial curve, recalling the well known autocatalytic process with a period of induction.

A set of samples with pale crepe instead of smoked sheets was typical in this respect as would be anticipated from the lower content of natural antioxygens in the crepe. The *s-t* graphs are shown in Fig. 3 and the rates tabulated in Table 5 which in addition shows the reproduction of duplicate determinations. The base — vulcanisat is very closely coinciding with 4823 (Table 3). The graph for 4620 H with 0.01 % copper proceeds as a straight line for

Table 5. Initial and final rates of oxidation Pale Crepe vulcanisates with Cu and no addition of antioxygen [1].

mols O_2 per hour and g C_5H_8 · (× 10^8).

Sample	% Cu [2]	°C	initial rate ∼ $s = 0$ [3]	final rate ∼ $s = 500$
4620 G	nil	31.0	36.4 ± 1.6	
		49.4	253 ± 23	
		59.6	699 ± 21	
4620 H	0.01	31.0	88.7 ± 1.2	696 ± 1
		49.4	545 ± 15	
		59.6	1 270 ± 46	14 800 ± 5 500
4620 I	0.05	49.4	980 ± 24	
		59.6	3 900 ± 285	19 280 ± 125
4620 J	0.1	49.4	1 520 ± 90	
		59.6	5 000 ± 45	33 750 ± 1 650

[1] 2 mm slabs vulcanised 60 min at 142°C, surface of powder 280 cm^2/cm^3. All figures mean value of duplicate runs.

[2] As copper stearate.

[3] s in mm Hg.

the first 80 hours, then the slope is increasing at an even rate to 120 hours after which the increase becomes rapid. The figures in Table 5 show that the *final rates may exceed the initial rates by 5—6 units.*

The corresponding rates for smoked sheets are given in Table 6 and some typical s-t graphs shown in Fig. 4. The autocatalytic course is still evident

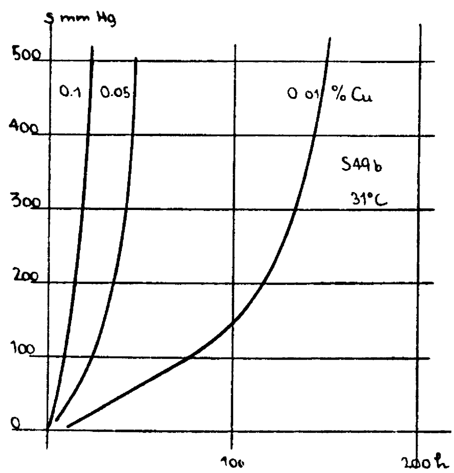

Fig. 3. s-t for Crepe (without antioxygen. + Cu).

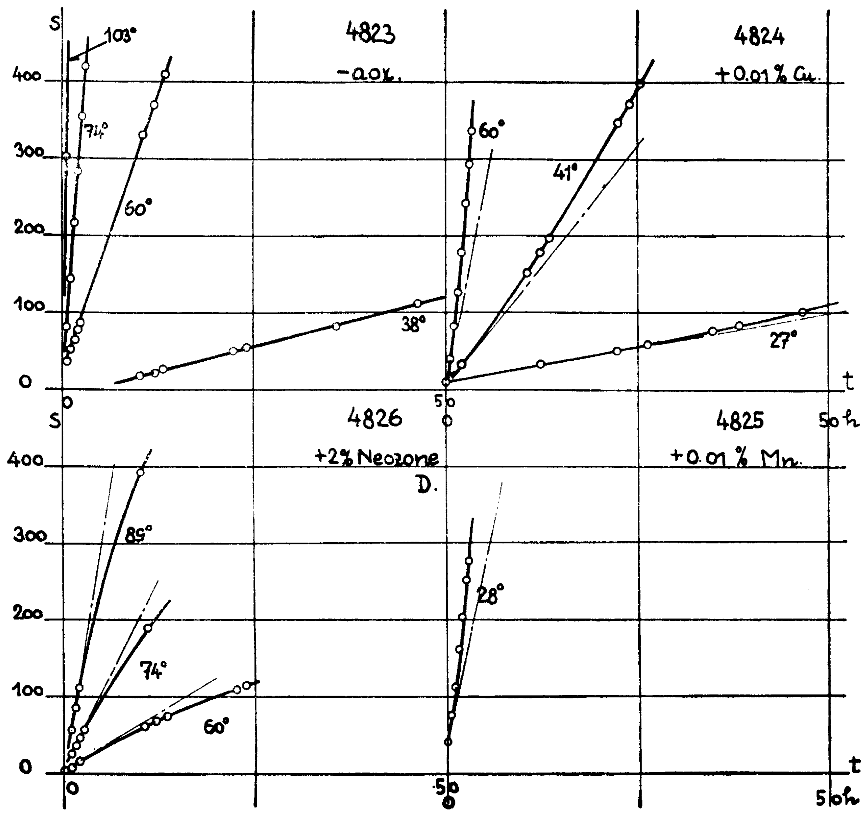

Fig. 4. s-t for smoked sheets ± with antioxygen, Mn and Cu as indicated. ± Mn and Cu.

but much less pronounced as in the case of the crepe. At the higher temperature the *s-t* graphs her have a point of inflexion, the reason for which is obscure as an inefficiency of diffusion might not be expected (Fig. 5).

The freshly prepared sample 4824 has constants very alike the base compound in accordance with the analogy in tensiles. If the sample is subject to ageing at room temperature the rate of oxidation increases very much as the sample of 48 178, aged 2 months, shows. The Arrhenius line in addition has much less slope.

(The sample 47 178 finally was measured at the time where the transition from a dry powder, to a very tacky sponge took place and during this transformation which lasted six days, the initial rate was increased from *2300 to 5300*, (at 28° C). Finally the sample formed a hard mass with an aromatic and sharp smell. The measurements show the possibility of an increase in rate

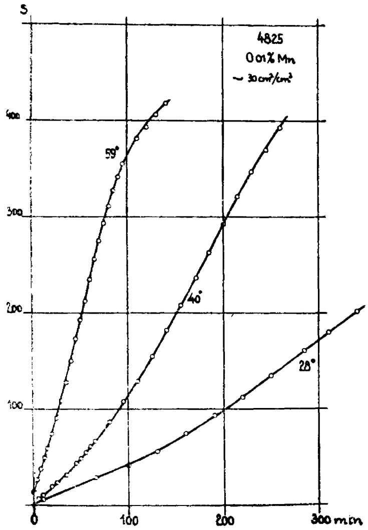

Fig. 5. s-t for smoked sheets + 0.01 Mn, 2 × 1 mm² slabs.

under conditions where a servere reduction of surface and diffusion must be assumed.)

Resuming we may stress that the *s-t curves show increasing values of ds/dt* and the magnitude of the rates are undefined depending upon the natural ageing of the sample. The acceleration may be judged as follows: with 0.01 % copper about 5 units for the fresh vulcanisate, about 200 units for aged vulcanisates and ranging towards 500 units for samples with 0.01 % manganese.

III. The effect of antioxygens

The graphs of the *s-t* values are all showing a *very pronounced decrease in ds/dt,* the shape of the curves resembles those cited of Carpenter [10] and Milligan and Shaw [17]. The order of reaction is in many cases approximately unity. Though the determination of the initial rate is not very well defined due to the geometry of the *s-t* curve the reproduction is very satisfying and all measurements of vulcanisates containing common antioxygens — as phenyl-β-naphthylamine (PBN) *e. g.* — are *concentrated at the same Arrhenius line* with good accuracy (A—A in Fig. 6).

The retardation is rather modest *e. g.* at 25° C about 2.6 units and at 70° C 3.4 units for phenyl-naphtylamines and aldolamines. For the more effective antioxygens of the phenylene-diamine aryl-substituted types the retardation may be judged to about 7 units at lower and intermediate temperatures.

Table 7 gives the date for various + vulcanisates.

Table 6. Initial rates of oxidation for vulcanisates with addition of copper and manganese without antioxygen.
mols O_2 per hour and g smoked sheets ($\times 10^8$).

No. of mix % addition condition of sample surface cm^2/cm^3	47 178 0.01 Cu [1] aged 2 mths 280	48 24 0.01 Cu [1] fresh 260	4825 0.01 Mn [2] fresh 30 [3]	4825 0.01 Mn [2] fresh 70 [4]
°C				
27.0		48.8		
28.0	2 300		2 060	
38.0		188		
38.9	5 400		3 000	
41.0				18 000
57.5	17 100	2 070		69 200
58.8			9 400	
69.4	39 400			
74.4		8 200		
$\log_{10} v^{\circ}$ [5]	$5.51 - 3.06 \cdot \perp$	$10.33 - 5.00 \cdot \perp$	$2.52 - 2.18 \cdot \perp$	
Q kcal	14.1	23.0	10.0	
H	8.71			

[1] As copper stearate.
[2] As manganese oleate.
[3] Cut with razor in 2×1 mm^2 slabs.
[4] Crumbed on the mill.
[5] By regression.

IV. Vulcanisates with both antioxygen and copper

The investigation has been only carried out in a preliminary scale. In Table 8 are quoted measurements on a series of vulcanisates, which were very difficult to disintegrate and consequently the surface became about 50 cm^2/cm^3. For the sake of brevity the table gives simply the ratio of the rates of the base vulcanisate and the vulcanisates with addition of copper and antioxygens. The symbol 2AAN/0.05 indicates 2 parts antioxygen pro 100 rubber (AAN = aldol-a-naphtylamine) and 0.05 % copper calculated on the whole mix.

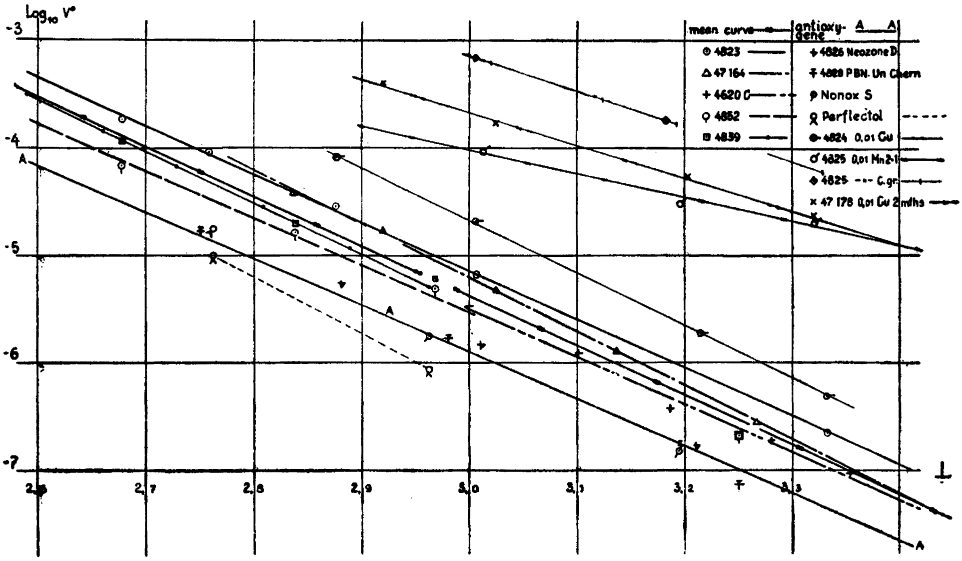

Fig. 6.

The retarding effect of the antioxygens is most pronounced at the high concentration of copper as indicated by the proportions Φ', and Φ'' in Table 8. An increase of the amount of antioxygen exceeding 2 parts per 100 rubber shows no effect as measured by the initial rate of oxygen absorption. PBN seems to give a somewhat greater protection against copper than does AAN, although the possibility of formation of complexes with copper has been stressed in case of AAN [18]. Jones and Craig [19] demonstrated the superiority of the aryl substituted phenylenediamines in combination with copper, a point of view which we are hoping to treat in a later communication. Due to the before stated instability of the copper containing vulcanisates the measurements cited in Table 8 are not quite consistent *e. g.* 2 parts PBN causes greater relative retardation than 4 parts in the samples with both 0.01 and 0.05 per cent copper.

APPENDIX

Some preliminary ageing tests

Several of the samples were aged in circulating air at 70, 95 and 130° C. The ageing tests were carried out using dumbbell specimens, cut from 2 mm thick slabs. The width of the narrow neck of the specimen was accurately

Table 7. Initial rates of oxidation for vulcanisates with 2 parts of antioxygens per 100 smoked sheets.

mols O_2 per hour and g C_5H_8. ($\times 10^8$)

No. of mix Antioxygen	47163 Antioxygène A[1]	48 33 Perflectol[2]	4826 Neozone D[3]	4828 PBN[4]	4829 Nonox S[5]	4832 Agerite[6] White
°C:						
34.9				7.4		
38.0			17.1			
39.9				17.0	15.1	
59.5			147			
64.4		87		171	178	
68.2	263					
74.4			550			
79.8	530					
88.9		1 010			1 760	1 025
89.4			1 610			
90.6				1 700		
103.3			3 125			

Mean for 47163, 4826—28—29, $\log_{10} v^\circ = 7.11 - 4.33 \cdot \frac{1}{T}$, $Q = 19.9$, $H = 12.4$

[1] Phenyl-α-naphthylsamine ∼ PAN.

[2] Blend of Flectol H, an acetone-aniline condensations product, and N—N'-diphenyl-*p*-phenylene diamine.

[3] Phenyl-β-naphthylamine ∼ PBN.

[4] From United Chemicals, Praha.

[5] Unknown composition.

[6] N—N'-di-β-naphthyl-*p*-phenylenediamine.

5 mm. Tensile strenght (TB), elongation (EB) and modulus at 300 per cent elongation was determined. Measurements of the moduli showed complications and are consequently omitted.

The values of tensiles and elongation were plotted against the time in days and the slope of the zero tagent determined graphically. Calculating the slope as per cent of the zero value we are denoting these "decrease figures" as N_{TB} and N_{EB} defined by $N_x = -\frac{\partial x}{\partial t} \cdot \frac{100}{x}$

From the ageing curves was further determined the time elapsed for the reduction of the zero value to 50 per cent, which figures are termed as $t_{\frac{1}{2}TB}$ and $t_{\frac{1}{2}EB}$. Table 9 gives some data, measured at 70° C.

Table 8. Ratios of initial rates of oxidation for combinations of antioxygen and copper at 60° C and powders with a surface about 50 cm^2/cm^3.

Mix no.:	Aox. [2]/%Cu	$\Phi = \frac{\overset{\circ}{v}_{Aox/Cu}}{v^{\circ}\%}$	$\Phi'^{1} = \frac{\Phi_L}{\Phi}$ (0.01 % Cu)	$\Phi'' = \frac{\Phi_M{}^{1}}{\Phi}$ (0.05 % Cu)
4620K	0 / 0	1.00		
» L	0 / 0.01	+ 5.8		
» M	0 / 0.05	+ 24		
» N	2PBN [3]/ 0	− 0.29		
» O	2AAN [4]/ 0	− 0.28		
» P	4PBN / 0	− 0.28		
» Q	4AAN / 0	− 0.32		
» R	2AAN / 0.01	+ 2.6	2.2	
» S	2AAN / 0.05	+ 6.6		3.6
» Y	4AAN / 0.01	+ 2.7	2.1	
» V	4AAN / 0.05	+ 6.0		4.0
» T	2PBN / 0.01	+ 1.5	3.9	
» U	2PBN / 0.05	+ 2.9		8.2
» Æ	4PBN / 0.01	+ 2.1	2.8	
» X	4PBN / 0.05	+ 4.7		5.1

[1] Φ' and Φ'' are a relative measure of the retarding power of the antioxygenes at a copper content of 0.01 and 0.05 respectively.

[2] Parts of antioxygen per 100 smoked sheets.

[3] PBN ~ phenyl-β-naphthylamine } from I. G. Farben.

[4] AAN ~ Aldol-α-naphthylamine } from I. G. Farben.

+ Denotes accelerations, — retardations.

In the column v_{70} the rate of oxidation is calculated from the average values of the Arrhenius lines. $\Phi^{v^{\circ}}$ denotes the ratio v_{-}/v_{+} + and Φ_{Ag} is the corresponding ratio for N and $t_{\frac{1}{2}}$.

It is seen that the retardation of antioxygens is very consistent whether measured as ratios of rates of oxidation or as ratios of ageing using tensile. The elongation determines a lower retardation and the $t_{\frac{1}{2}}$ value a higher retardation. The ordinary antioxygens such as Flectol H and naphthylamines give a retardation of 3—4 units, while the more effective substituted *p*-phenylenediamines give a greater retardation about 6—7 units. The value for Agerite White must be discarded as it is expected that this antioxygen and Perflectol should be equal.

Table 9. Decrease figures from ageing tests at 70° C in circulating air.

Mix. no.	Antioxygen	N_{TB}	N_{EB}	$t_{\frac{1}{2}TB}$	$v°_{70°}$	$\Phi^{v°}_{70°}$	Φ_{Ag}		
							Φ_{TB}	Φ_{EB}	$\Phi_{t\frac{1}{2}TB}$
		% per day		days					
47 161 B	÷	9.9	0.71	11.2					
48 23	÷	9.7	1.30	5.2					
48 30	÷	6.4	0.69	10.3					
Average	÷ :	8.7	0.90	8.9	1 070				
47 162	PBN I. G.[1]	2.0	0.43	41					
47 165	Antioxygene MC[1]	1.5	0.11	50					
48 26	Neozone D[1]	3.4	0.54	34					
48 28	PBN[2]	4.0	0.62	34					
Average	+ PBN	2.7	0.43	40	310	− 3.4	− 3.2	− 2.1	− 4.4
47 163	Antioxygène A[3]	2.2	0.40	(50)			− 3.9	− 2.3	
47 164	» INC[4]	—	0.36	(54)				− 2.5	
48 29	Nonox S[5]	2.0	0.50	48			− 4.4	− 1.8	− 5.4
48 31	Flectol H[6]	2.6	(0.78)	(33)			− 3.3		
48 32	Agerite White[7]	2.4	0.42	(54)			− 3.6	− 2.1	
48 33	Perflectol[8]	1.4	0.34		160	− 6.3	− 6.2	− 2.6	
48 24	− with 0.01 %Cu	55	7.7	1	5 500	+ 5.1	+ 6.3	+ 8.6	+ 8.9
						(+ : accelerations)			
						(− : retardations)			

$$\Phi^{v°} = \frac{v°_{\div}}{v°_{+}} \text{ or } \frac{v°_{\div}/\text{Cu}}{v°_{\div}} \; ; \; \Phi_{Ag} = \frac{N\div}{N+} \text{ or } \frac{t_{\frac{1}{2}}+}{t_{\frac{1}{2}}\div}$$

÷: vulcanisates without antioxygen
+: » with »

[1] PBN.
[2] From United Chemicals, Praha.
[3] Phenyl-α-naphthylamine.
[4] Aldol-α-naphthylamine.
[5] Unknown composition.
[6] Acetone-aniline condensation product.
[7] N—N′-di-β-naphthyl-p-phenylenediamine.
[8] Blend of Flectol H and N—N′-diphenyl-p-phenylenediamine.

The effect of temperature is illustrated in Table 10 giving measurements at 70°, 95° and 130° C. The data show that the retarding effect decreases with increasing temperature. The coefficients of temperature are not consistent, being too low at 95°/130°, possibly due to insufficiency of diffusion.

Table 10. A. Retardations at 70°, 95° and 130° C.

°C	Mix. no.	antioxygen[1]	N_{TB} % pr. hour	$\Phi = \frac{N-}{N+}$	$v°$
70	4830	÷	0.266		1 070
	4831	Flectol H	0.108	2.5	310
	4833	Perflectol	0.058	4.6	160
95°	4830		3.7		8 900
	4831		2.7	1.4	2 240
	4833		1.1	3.4	
130°	4830		13.3		
	4831		6.4	2.1	
	4833		5.9	2.3	

Table 10. B. Temperature coefficients.

Mix. no.	$\Phi' = \frac{N_{T_1}}{N_{T_2}}$ 95°/70°	130°/95°
4830	13.9	3.6
4831	25	2.4
4833	19	5.3
$v°_{\div}$	8.3	—
$v°_{+}$	7.2	—

[1] 2 parts per 100 smoked sheets.

Better figures would possibly result by the use of *normal rings* where the tensile properties are more strictly defined. For the reason of information the use of slabs however is very practical as little area of rubber samples is demanded for the performance of the tests.

Calculating the "index of ageing" from the rates of oxidation at 70° we find 1.2 days for the — -vulcanisate and 4.2 days for the +-vulcanisate *i. e.* about one tenth of the measured $t_{\frac{1}{2}TB}$-values, a quite reasonable magnitude taking into account the difference in surface.

When data from the course of the natural ageing are available the comparison of the N-values and the v-values at room temperature can be computed, by means of which we will obtain a final judgement of the significance of the ageing indices.

SUMMARY

An apparatus is described for the measurement of rate of the oxidation of rubber vulcanisates by means of a simple technique. Further formula for the calculation of the rate from pressure and time readings are derived *cf.* equations I and III.

For a diphenylguanidine vulcanisate some typical *s-t* graphs * are shown. If no antioxygen is added the *s-t* function becomes a straight line (in some cases with a slight increase of ds/dt) indicating approximately a zero order reaction. Duplicate runs agree very well ($\pm$ 5 %), but the reproduction of rates of samples from parallel mixes from the same base smoked sheets is very poor.

With addition of two parts of antioxygen per 100 smoked sheets the *s-t* graphs show a very pronounced decrease in slope and the order of reaction will be between zero and one. The reproduction is very good in all cases, and the measurements of mixes containing common antioxygens yields the same Arrhenius curve for the initial velocities.

Vulcanisates containing 0.01 per cent copper or manganese as soaps are very unstable. The *s-t* curve have an increasing slope in some cases after a straight line initial course. The rate is here a rather undefined property with a rapid increase with the age of the sample.

The rates of oxidation for powders of an approx. surface area about 300 cm^2/cm^2 are expressed in the following equations

without antioxygen $\log_{10} v = 8.52 - 4.63 \cdot \perp$ **

with two parts of antioxygen $\log_{10} v = 7.11 - 4.33 \cdot \perp$

(*Cf.* Tables 3, 5, 6, 7 and 8.)

Preliminary ageing test determined a factor for the retardation of the rates executed by ordinary antioxygens coninciding with the same property determined by the initial rates of oxidation.

Common antioxygens will retard the rate of oxidation 3—4 times and the aryl substituted phenylendiamines 6—7 times.

The acceleration of the rate of oxidation by copper and manganese soaps (especially in samples aged short time at room temperature in the dark) may amount to 200—500 times the velocity of the base vulcanisate. Calculated in molar concentrations the accelerating power of copper and manganese will be about 1 300 times greater than the retarding power of phenyl-β-naphthylamine.

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* *s* is the height of the mercury (mm) at time *t*. The slope $ds/dt = - dp/dt$.

** $= 1000/T$.

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