The Accelerating Capacity of Organic Polythionates and Polysulphides

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In natural rubber bis-*p*-tolylsulphonyl sulphide, disulphide and trisulphide (the so-called organic polythionates), di-benzoyl trisulphide and tetrasulphide provoke a fair vulcanisation at 162°C preferably in combination with 2 PHR (parts per hundred rubber) sulphur. The coefficients of vulcanisation are determined by means of ^{35}S . The physical state of China Clay containing vulcanisates are intermediate and the ageing stability equals that of similar DPG-vulcanisates, the benzoyl tetrasulphide being the best.

The formal analogy of the sulphur bond in thiurams and polysulphides
 —S—S—

suggests a possibility of vulcanisation with polythionates. X-Ray investigations by Dawson *et al.*¹ of bis-*p*-tolylsulphonyl sulphide and trisulphide indicated a zig zag sulphur chain. Orientating measurements comprising bis-*p*-tolylsulphonyl sulphide and disulphide (abbrev. tol-tri, tol-tetra) and di-benzoyl trisulphide and tetrasulphide (abbrev. benz-tri, benz-tetra) revealed practically no cure in absence of sulphur, the ability to vulcanising was, however, distinct upon addition of 1 PHR of sulphur. For instance the sulphur-free tol-tetra in a clay-whiting compound showed a tensile of 55 kg/cm² and a halving time for the tensile at 70°C in air of 17 days.

The following experiments were carried out with 2 PHR of sulphur in combination with 2 PHR of accelerator. Rates of vulcanisation were indicated as moduli at 110 % elongation, measured with a 32 oz strain gage (Statham Laboratories²), operated at a strain rate of 750 mm/min. Sensitivity is about 2 g in stress.

The sulphur reaction was determined after introduction³ of ^{35}S on a micro mill (10—20 g rubber) and vulcanisation of discs, 65 mm diam., 0.75 mm thick.

From these samples discs of 25 mm (4.91 cm^2) were cut for measurement of activity using a Geiger-Müller-tube and a Frieske-Höpfner scaler counting 10 000 counts. The sulphur had an activity of about $60 \mu\text{C}$ and 2 parts gave with the 4.91 cm^2 sample about 1 500 counts per min. Afterwards the samples were wrapped in gauze and acetone-extracted for 18 h either in the bottom of an ordinary Soxhlet filled with silica Raschig rings in order to reduce the volume or in a ASTM micro extractor⁴. The samples were then airdried and the activity measured. The ratio of activities of unextracted to extracted specimens duly corrected for decay is used as a very convenient measure of gross bound sulphur. Ten or more samples are measured in a few hours and the determination of the coefficients of vulcanisation completed in 24 h.

Ageing tests were performed at 70°C ($\pm 0.5^\circ$) in air with dumbbell specimen⁵ tested with a Zwick Z.125 tensile machine at an elongation rate of 800 mm/min at 25°C .

RATE OF VULCANISATION

The basic composition of the mixes was

Smoked sheets	100	
Zinc oxide	10	
Stearic acid	1	
Whiting (Kragelund)	53	batch
China clay (Erbslöh P)	51	216.5 parts
Nonox CI	1.5	
Accelerator	2	
Sulphur	2	

The compounds were made from the batch using 108.25 g (= 50.0 g smoked sheets) and S and the accelerator was added on a micro mill ($150 \times 90 \text{ } \Phi \text{ mm}$ rollers) thermostated by water circulation at 50°C . The radioactive sulphur compounds were made on the same mill using 21.65 g batch and 0.200 g ^{35}S . The micro mill was equipped with a hood and an absorber containing active carbon (Carboraffin). A vacuum cleaner performed the suction.

The state of vulcanisation was determined as modulus at 110 % elongation 15 sec after application of the load (rate 750 mm/sec) and is shown in Table 1.

Table 1. A. Sulphurfree compounds.

Mix No.	Accelerator	Modules 110 % (kg/cm ²)		
		15'/162°C	75'/162°C	
57.295,	58.06	tol-tri	1.08 ^a	0.89 ± 0.19
	58.04	tol-tetra	2.42	1.81
	58.05	tol-penta	3.60	2.43
57.296,	58.07	benz-tri	1.35	1.05 ± 0.07
57.297,	58.08	benz-tetra	2.65	1.23 ± 0.05

a) The vulcanisate tends to porosity.

B. 2 sulphur (2 accelerator compounds).

Mix No.	57.274	57.273	57.276	57.371	57.282	57.304
acc. min. 162°C	nil	tol-tetra	tol-tri	tol-penta	benz-tri	benz-tetra
			a	b	a	b
1						3.34
2				3.97	5.70	6.82
3					7.35	9.17
4				7.15	8.31	7.12
5		7.90	6.29	4.35	9.46	10.26
8				10.48	8.08	10.53
10	4.00	10.98	10.30	8.97	9.82	8.82
12						10.03
15	5.76	12.31	12.15	9.54	13.27	8.22
20	6.05			12.40	7.95	
30	7.29			12.35	14.71	

a) Sulphur rubber grade. b) ³⁵S passed 100 mesh.Table 1 A. Bound sulphur at 162°C. 2 parts ³⁵S added.

57.274 A: nil acc.

57.305 : tol-tri

min./162°C	U ^a	E ^b	S _b ^c	min./162°C	U	E	S _b
	cpm				cpm		
15	1 429	525	0.361	5	1 559	345	0.221
60	1 453	1 490	0.027	10	1 511	671	0.443
120	1 446	1 473	1.015	20	1 522	1 113	0.731
180	1 409	1 449	0.999		1 496	1 097	0.733
				30	1 552	1 378	0.889

57.311 : benz-tri

57.317 : benz-tetra

min./162°C	U	E	S _b	min./162°C	U	E	S _b
	cpm				cpm		
2	1 223	466	0.381	1.5	1 365	338	0.248
3	1 418	575	0.406	2	1 372	388	0.282
8	1 447	776	0.536	3	1 517	542	0.357
15	1 334	803	0.602	8	1 367	664	0.486
				12	1 455	755	0.519

58.02 : tol-penta^d

min./162°C	U	E	S _b
	cpm		
1,5	706	59	0.084
2	704	72	0.102
4	690	131	0.189
8	766	256	0.334
16	673	423	0.628
32	707	682	0.964
64	710	692	0.975

a, untreated sample

b, extracted with acetone 18 h (ASTM)

c, S_b = E/U, bound S = 2 × S_b PHRd, bis-*p*-tolylsulphonyl trisulphide

cpm, counts per minute

The data are illustrated in Fig. 1.

Fig. 1. Rate of vulcanisation: Modulus 110 % elongation and percent bound sulphur vs. time of vulcanisation at 162°C.

RATES OF OXIDATION

The rates of oxidation were measured at 1 mm thick slabs as described elsewhere⁶.

In pure oxygen at 95°C the following rates were found, *cf.* Table 2. Initial rate was determined after 1 h oxidation at a starting pressure about 150 mm Hg below atmospheric pressure.

Table 2.

Mix No.	Accelerator	initial ^b	Rate ^a	final ^b
57.274	nil	674 ⁶⁸⁷		
57.312	nil 0.01 Cu	553 ⁶³⁹		469 ⁵⁵⁹
57.325 ^a	TMT	2 230 ⁷⁰¹		1 420
57.273	tol-tetra	2 500 ⁶³¹		1 800 ⁵³⁸
57.302	tol-tri	3 390 ⁵⁵⁹		1 451 ³⁵⁹
57.303	benz-tri	592 ⁶⁸⁹		558 ⁴⁵⁹
57.304	benz-tetra	897 ⁶⁶¹		881 ⁴¹¹
57.371	tol-penta	2 590 ⁶⁴⁹		1 460 ⁵⁶⁹

a, moles oxygen per h and g Smoked sheets ($\times 10^8$).

b, exp., mm Hg.

TMT, tetramethyl-thiuramdisulphide.

The graphs (height of mercury *versus* time) are collected in Fig. 2.

Fig. 2. Rate of oxidation at 95°C measured as height of mercury in the capillary of the absorber *vs.* time.

RATE OF AGEING

Ageing data are recorded in Table 3 and shown in Fig. 3.

Table 3.

Mix No.	Accelerator	TB°	$t_{\frac{1}{2}}$	σ	Ageing at 70°C		δ
					μ	ϵ	
57.274	nil	83	58	0.63	-0.35	4.0	+8 ⁴⁸
57.325 ^a	TMT	114	1.90r	30 ₀	-5 ¹	90 ¹	+2 ¹
57.276	tol-tri	131	21.1r	3 ₁₂	0.25	5.4	+1 ²⁴
57.273	tol-tetra	126	31.2	1 ₈₆	0.17	2.8	+3 ³⁶
57.282	benz-tri	108	43(r)	1 ₂₅	0.0	3.7	+1 ³⁶
57.304 ^a	benz-tetra	137	34r	2 ₀₀	0.0	4.0	+2 ³⁵
57.371	tol-penta	126	15 ₂ r	3 ₉₅	-0.15	13.5	+5 ²⁰

TB°, tensile at break before ageing.

$t_{\frac{1}{2}}$, days for half value of TB°.

σ , rate of decrease of tensile in kg/cm² per day.

μ , same for modulus at 300 % elongation.

ϵ , same for elongation at rupture in percent per day.

δ , marginal change of Shore A hardness.

r, straight line

exponents, period in days.

The ageing was only controlled until half value of the tensile was reached, at which point the samples in all cases were in fair condition. No tackiness or serious hardening was observed whereas generally a strong discoloration (brown) was noticed.

Fig. 3. Rate of ageing: Tensile strength at break vs. days at 70°C.

PREPARATIONS

Bis-*p*-tolylsulphonyl sulphide ($C_7H_7SO_2$)₂S, was prepared according to Otto and Troeger⁷ by oxidation with iodine of equimolar mixture of potassium *p*-tolylthiosulphonate and *p*-tolylsulphinate. Crystallization from glacial acetic acid gave a product with m. p. 137°C corr. (Otto and Troeger⁷ found 133–134°C, Dawson, Mathieson and Robertson¹ 138°C). (Found: S 28.5. Calc. for $C_{14}H_{14}O_4S_3$: S 28.1).

Bis-*p*-tolylsulphonyl disulphide ($C_7H_7SO_2$)₂S₂, was prepared according to Troeger and Hornung⁸ by interaction of sodium *p*-tolylthiosulphonate with disulphur dichloride in carbon tetrachloride. We have slightly modified the preparation so as to get a higher yield (ca. 60 %). The raw product of bis-*p*-tolylsulphonyl disulphide is formed as a suspension in carbon tetrachloride, which according to Troeger and Hornung is distilled off on a water bath. However, the solubility of the said compound in cold carbon tetrachloride is rather small, so we just filtered off and discarded the filtrate. The raw product was then dried, washed with water, dried, washed with carbon disulphide, again dried, and then crystallized from glacial acetic acid. M. p. 113–114°C corr. (Christiansen⁹ found 114°C). (Found: S 34.0. Calc. for $C_{14}H_{14}O_4S_4$: S 34.2).

Bis-*p*-tolylsulphonyl trisulphide ($C_7H_7SO_2$)₂S₃, was prepared according to Troeger and Hornung⁸ by interaction of sodium *p*-tolylthiosulphonate and sulphur dichloride in carbon tetrachloride. Also in this case (*cf.* bis-*p*-tolylsulphonyl disulphide) we discarded the carbon tetrachloride solution. Crystallization from glacial acetic acid gave a product with m. p. 179.5–180°C corr. Christiansen⁹ found 183°C just as Troeger and Hornung⁸; Dawson, Mathieson and Robertson¹ found 180°C). (Found: C 41.3; H 3.53; S 39.5. Calc. for $C_{14}H_{14}O_4S_5$: C 41.4; H 3.44 S 39.4).

Di-benzoyl trisulphide; $(C_6H_5CO)_2S_3$, and dibenzoyl tetrasulphide $(C_6H_5CO)_2S_4$, were prepared according to Bloch and Bergmann¹⁰ by interaction of potassium thiobenzoate and sulphur dichloride in the former case and disulphur dichloride in the latter. M. p. of the trisulphide was 160°C corr., while Bloch and Bergmann¹⁰ found 165–167°C. (Found: S 31.3. Calc. for $C_{14}H_{10}O_2S_3$: S 31.4 %). M. p. of the tetrasulphide was 68–69°C corr. while Bloch and Bergmann¹⁰ found 83–84°C. (Found: S 39.3. Calc. for $C_{14}H_{10}O_2S_4$: S 37.8).

DISCUSSION

The accelerating power is moderate but definite. As shown the tensiles are about 120 as compared with about 180 obtainable with conventional accelerators. In their behaviour the accelerators show only slight analogy to thiurams. The ability to vulcanising in absence of sulphur is not very pronounced, and the oxidation and ageing characteristics are quite different. It is interesting to note that the S-addition curves show very varying amounts of bound S corresponding to optimum moduli, *e.g.* the benzoyl sulphides show rapid cure and a low percent of chemically bound sulphur, whereas the thionates vulcanise slowly but ending at about total binding of sulphur. Benz-tetra gives the fastest cure and maximum tensile. The sulphur determination and melting point of this compound showed a small content of free sulphur. This explains the high tensile and the reduced ageing stability of benzoyl tetrasulphide as compared with the trisulphide.

The oxidation curves show some interesting features, *e.g.* the thionates have about linear curves whereas the benzoyl sulphides have obvious autocatalytic curves resembling those of peroxide-vulcanisates. This might be explained as an analogy between S and O in the —X—X— group. The rates are in agreement with the $t_{\frac{1}{2}}$ values from the ageing tests. Thus the manometric method gives a fair screening here.

Finally the ageing resembles that of diphenylguanidine vulcanisates more than that of thiuram vulcanisates both in the decreasing moduli and the magnitude of $t_{\frac{1}{2}}$ (70°C).

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Received January 29, 1958.