Contributions from the Ceylon Rubber Research Scheme.

Explanatory Notes on Vulcanisation Testing of Rubber.

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ESTATE Superintendents and others have frequently asked for a simple explanation of the meaning of figures given in reports dealing with the vulcanising properties of rubber samples. It is thought that the following notes may increase the value of such reports to non-technical readers.

With the exception of crepe soles and one or two minor products rubber is always used in the vulcanised form, and it has not been found possible by examination of raw rubber to predict what its properties will be after vulcanisation. Consequently in order to test the quality of a sample of rubber, it is necessary to vulcanise it under suitable conditions and then submit it to certain tests. Of recent years the question of " plasticity " of raw rubber has become of increased importance. This property is judged before vulcanisation, but can conveniently be included under the heading of vulcanisation tests.

From the point of view of the layman it is fairly accurate to say that " vulcanisation " or " curing " consists of causing rubber to combine with a certain proportion of sulphur. Under certain conditions this can be done without heat, being known as " cold vulcanisation," but more usually it is effected by heating a mixture of rubber and sulphur at a temperature of 140-150°C. If certain substances known as " accelerators " are added to the rubber the process takes place more rapidly, or alternatively can be carried out at a lower temperature.

For commercial purposes, rubber before vulcanisation is almost invariably " compounded " with various ingredients in addition to sulphur, which have the effect of modifying the properties of the vulcanised rubber to make it suitable for various uses. For testing purposes it was usual until recently to make the tests on rubber vulcanised with sulphur only, as this brings out differences between various samples of rubber. Since the introduction of organic accelerators it has been found advisable to make comparative tests of samples when vulcanised with sulphur only, and when vulcanised in presence of an accelerator. Certain accelerators only function in the presence of compounding ingredients so it is necessary for a suitable substance (usually

zinc oxide) to be added to the accelerator mix. Thus in a typical report from the Imperial Institute (see table I.) we find the tests given under two headings.

A. **Mixing** 90 Rubber, 10 Sulphur,

B **Accelerator Mixing** 90 Rubber, 5 Sulphur, 90 Zinc oxide, I Hexamine (accelerator).

Mastication Mixing.

Preparation of the raw rubber for vulcanisation consists of rolling through heated differentially geared rollers until the rubber becomes sufficiently soft and plastic to mix in the sulphur, etc. This process is known as " mastication." The sulphur and any other compounding ingredients are then added gradually and rolling is continued until they are thoroughly mixed with the rubber. Samples of plantation rubber vary in the amount of working required to soften the rubber, or in other words they vary in plasticity. This variability causes great inconvenience in manufacturing process. For many purposes such as manufacture of tubing, solid tyres, etc., the rubber after being mixed is " extruded " or forced through dies of the required shape, and if insufficiently plastic it emerges from the machine with a rough and uneven surface instead of being smooth and even. It has then to be sent back and reworked.

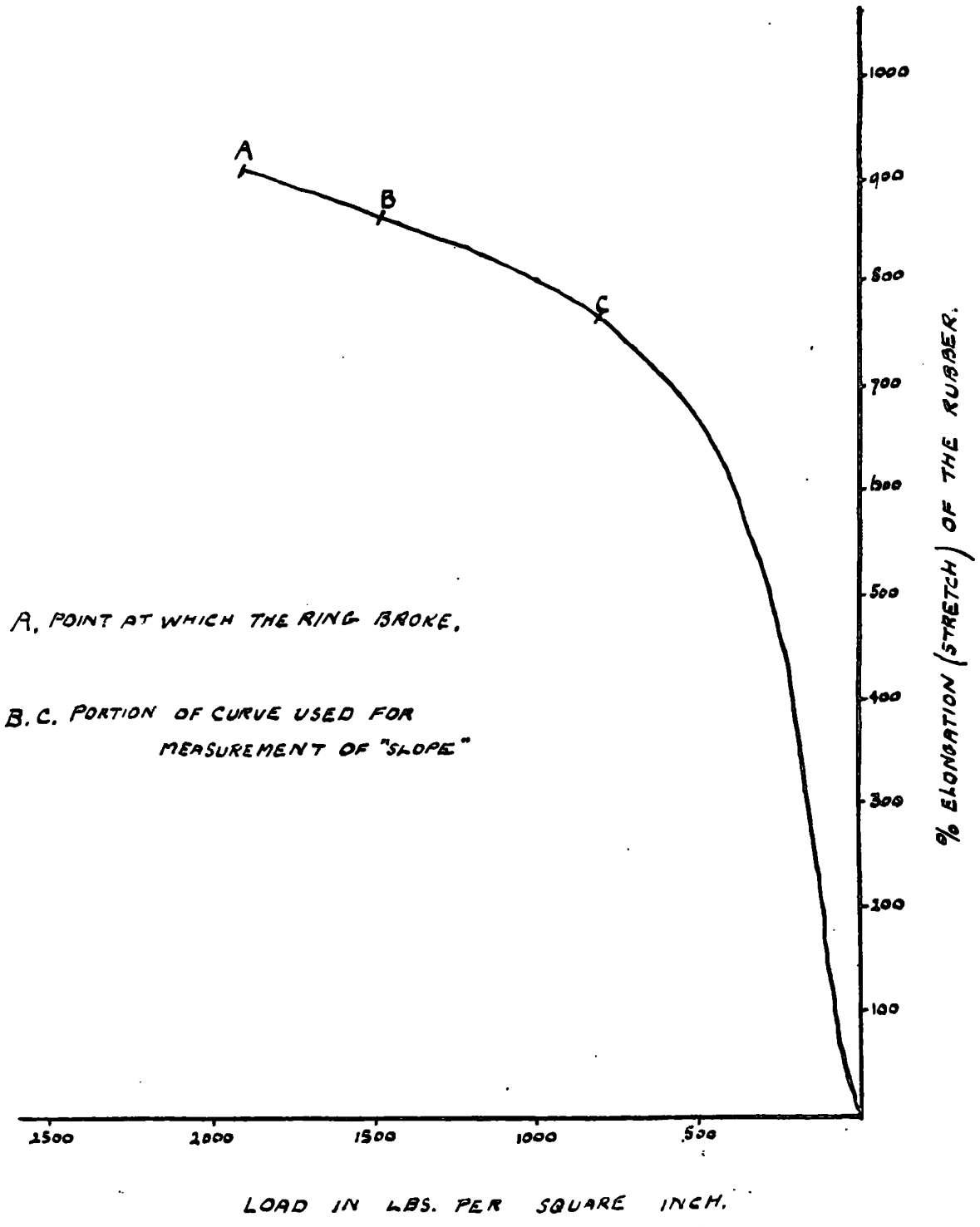
Plasticity Tests.

Two methods of measuring plasticity are in use at the Imperial Institute. In the first case a small piece of rubber of known size is heated to 100° C. and submitted to a known pressure for 30 minutes. The thickness of the sample after this treatment is a measure of the plasticity. Referring to Table 2 it will be seen that the figure for this test is given under the heading " D 30 " (D 30 can be taken to mean diameter after 30 minutes.) In this test the lower the figure obtained, the more plastic the rubber. It will be noticed that this test is made on the raw rubber and also after masticating and finally after mixing. Another test of plasticity which is now adopted, and which is much more sensitive than the foregoing, consists of extruding or forcing the rubber through a hole of given size under given pressure. The time taken to extrude a given weight is a measure of the plasticity of the rubber. In the table referred to, figures for this test are given under the heading "E.t." (E.t. can be taken to mean time of extrusion). This test is made after mastication and after mixing. In this case again a low figure represents rubber of good plasticity.

The amount of power consumed in masticating and mixing the rubber is also to some extent a measure of plasticity and in preparing the samples for plasticity tests mastication is carried out on rollers driven by an electric motor of which the power

DIAGRAM 1.

GRAPH DRAWN BY "SCHOPPER" TESTING MACHINE.



A. POINT AT WHICH THE RING BROKE.

B. C. PORTION OF CURVE USED FOR MEASUREMENT OF "SLOPE"

consumption can be measured. Rolling is continued until a certain fixed amount of current has been consumed. In Table 2, under the appropriate heading, is given the number of minutes required by each sample to consume the fixed amount of power. A high figure under this heading represents an easily workable rubber.

Time of Vulcanisation.

To turn from plasticity to vulcanisation tests, the first factor on which information is required is the rate of vulcanisation of the sample, *i.e.*, the length of time which the rubber must be heated with a fixed amount of sulphur at a fixed temperature in order to develop its maximum strength. Variability in rate of vulcanisation is a feature of plantation rubber and previously caused great inconvenience to the manufacturer, but since the introduction of organic accelerators it has lost some of its significance as suitable accelerators tend to equalise the rate of vulcanisation of different samples.

In Table I. it will be noted that there are two headings " standard cure " and " tensile optimum cure." Before explaining the meaning of these terms it is necessary to proceed to the next stage and describe the way in which the rubber is tested after vulcanisation.

Tensile Strength.

When vulcanisation is completed the sheets of rubber are allowed to stand for 24 hours, after which ring test pieces of accurately measured diameter and thickness are cut by means of a machine. The ring is placed in a machine known as the "Schopper" testing machine, and is stretched by applying a gradually increasing load. Stretching is continued until the ring breaks and the machine records the load required to break it, and also the amount which the rubber stretched before breaking. The thickness of the ring used for the test is only about $\frac{1}{4}$ inch but by calculation the breaking load or " tensile strength " per sq. inch is calculated. The amount of stretch is recorded under the heading " Elongation (per cent.) at break." While the ring is being stretched the Schopper machine automatically draws a graph representing the amount that the rubber stretches as the load is gradually increased, and a typical curve is shown in diagram I. The end of the curve represents the point at which the ring broke.

Under-vulcanised rubber stretches very easily. As vulcanisation proceeds, so the rubber becomes tougher, *i.e.*, to stretch it to a given extent a greater load is required. When over-vulcanised it becomes brittle. Vulcanisation to " standard cure " (in a rubber-sulphur mixing) is defined as vulcanising to a stage at which a load of 1,500 lb. per sq. inch (1·04 kg. per sq. mm) is required to stretch the rubber to 775 per cent. of its original length. " Tensile optimum cure," as the name implies,

consists of vulcanising to a stage at which the sample gives the highest tensile strength. For most purposes of comparison standard cure gives all the information that is required, and entails less work than the tensile optimum cure.

In general the tensile strength of a correctly vulcanised sample of plantation rubber will exceed 2,000 lb. per sq. inch. When a low figure for tensile strength is given in a report it must be studied in connection with the figure for "Elongation (stretch) at standard load." If this figure is higher than 775 per cent. it implies that the sample is under-vulcanised, and it is then known that if the time of vucanisation had been increased, improved figures for tensile strength would result. For example in Table 3 a result is given for a sample in which the tensile strength is 1,570 lb. per square inch which is a very low figure. The figure for " elongation at standard load " however is very high—943 per cent., showing that the sample is under-vulcanised and would have developed better tensile strength if vulcanised for a longer period. In this case it was not necessary to repeat the vulcanisation as the two samples under comparison were vulcanised to approximately the same extent (stretch at standard load 943 per cent. and 957 per cent. respectively) and could thus fairly be compared.

Slope.

Another heading given in reports is "slope" (see Table 3). Actually "slope" refers to the slope of the Schopper machine curve at a certain stage of stretching, shown in diagram I. It has been shown by Investigators that the slope of the curve at this stage of the test is to some extent an index of the quality of the rubber. A low figure for slope indicates rubber of good quality and "slope" figures for good quality plantation rubber in a rubber-sulphur mix are usually not higher than 40. In an accelerator mixing (Table I.) the "slope" figure has a different value

Ageing Tests.

Another heading in reports is " Ageing Tests." It is common knowledge to every user that rubber gradually perishes, particularly when exposed to light and air, and it will be appreciated that it is of importance to compare the properties of different samples of rubber in this respect. Perishing of rubber takes place slowly and it would be a great handicap if the Investigator had to wait 12 or 18 months to observe the effects of keeping the rubber, in addition to the fact that conditions of storage would have a considerable influence on the result. It has been found that if the sample is heated in an oven at 70° C. in a current of air, a change in tensile strength takes place similar to that which occurs during ordinary storage or use, and this is known as " artificial ageing." Heating in the oven for 24 hours has

approximately the same effect as 6 months natural ageing. From Table 4 it will be seen that tests are made after 48, 96, and 144 hours' artificial ageing. An average sample of plantation rubber begins to show some deterioration in tensile strength after 96 hours' ageing. It will be noted in this case that the samples actually showed improvement of strength after 48 hours' ageing and it is necessary to explain that for ageing tests the samples are purposely somewhat under-vulcanised. This corresponds with commercial practice, as full vulcanisation to the standard used for physical testing would give a product with impaired ageing properties.

It is hoped that the above notes will be of assistance in explaining in a general way the meaning of the figures given in reports of vulcanisation tests. In certain respects the explanations are necessarily incomplete, as full explanation would involve technical discussion which would not be of interest to the reader for whom these notes are intended.

Table I.

(Extract from "First report on rubber prepared with sodium silico fluoride as a coagulant." R.R.S. 4th Quarterly Circular for 1924, p. 8).

A. Mixing 90 Rubber, 10 Sulphur.

	Time of cure (mins.)	Tensile strength (lbs./sq. in)	*Elongation.* At Break. per cent.	*Elongation.* At standard load per cent.	Slope.
Standard Cure (Elongation at load of 1·04 kgs sq. mm. = 775 per cent.)					
Present sample ..	150	2,390	874	784	39
(Smoked Sheet average of 5 recent samples) ..	107	2,440	867	777	40
Tensile Optimum Cure (Maximum tensile strength developed 72 hours after vulcanisation.) ...					
Present sample ..	150	2,390	—	784	—
Smoked Sheet (average of 5 recent samples) ...	113	2.510	—	754	—

B. Accelerator Mixing.

90 Rubber, 5 Sulphur, 90 Zinc oxide, 1 Hexamine.

	Time of Cure (mins)	Tensile strength (lbs./sq. in)	*Elongation.* At Break per cent.	*Elongation.* At standard load per cent.	Slope.
Standard Cure (Elongation at load of 1·04 kgs/sq. mm. = 480 per cent.)					
Present sample ...	60	2,850	633	475	46
Smoked Sheet (average of 5 recent samples ...	37	2,420	604	481	47
Tensile Optimum Cure (Maximum tensile strength developed 72 hours after vulcanisation).					
Present Sample ...	50	2,960	—	495	—
Smoked Sheet (average of 5 recent samples.) ...	45	2,760	—	458	—

Table II.

(Extract from "Report on the effect of para-nitrophenol on the plasticity, vulcanising, and ageing properties of blanket crepe." R.R.S. 4th Quarterly Circular for 1926, p. 11.)

(I). Plasticity Tests.

Sample No.	Form of Rubber	Time of mastication for power consumption of 450 watt hours	Time of mixing for power consumption of 150 watt hours	Plasticity: Raw Rubber	Plasticity: Masticated Rubber	Plasticity: Rubber sulphur Mixing (90·10)
		(mins)	(mins)	D 30	D30 E t	D30 E.t.
1261	Blanket crepe (control) ...	23½	11	167	80 70·8	72 43·6
1262	Blanket crepe soaked in 0·1 per cent. para-nitrophenol for 30 minutes ...	23½	11	171	86 72·5	73 46·6
1263	Blanket crepe from latex coagulated with acetic acid and 0·1 per cent. para-nitrophenol (calculated on dry rubber) ...	22½	10½	174	87 75·3	72 46·5

D 30 = Thickness (in hundredths of a millimetre) of sphere 0·4 gram in weight after pressing in plasticity press at 100°C for 30 minutes.

E. t. = Time (in minutes) required to extrude fixed volume at 90°C

Table III.

(Extract from "Third report on rubber prepared with sodium silico fluoride as a coagulant." R.R.S. 4th Quarterly Circular for 1924, p. 12).

Rubber Sulphur Mixing: 90: 10.

Coagulant.	Time of cure (mins)	when tested	Tensile strength (lb. sq. in)	Elongation		
				At Break (per cent.)	At standard load (percent.)	slope
Sodium-silico fluoride	92	Before ageing	1,570	953	943	40
		After ageing	1,930*	931	877	39
Acetic acid (control)	80	Before ageing	1,480	960	957	41
		After ageing	2,070*	957	893	40

* By heating for 20 hours at 70°C. in a current of air.

Table IV.

(Extract from "Report on the effect of para-nitrophenol on the plasticity, vulcanising, and ageing properties of blanket crepe." R.R.S. 4th Quarterly Circular for 1926, p. 12).

Vulcanising and Ageing Tests.

Sample No.	Form of Rubber	Time of vulcanisation.	Period of ageing at 70°C	Tensile strength	Elongation at load of 1·04 kgs. /sq mm.
		(mins)	(hrs)	(lbs. /sq. in)	(per cent.)
1261	Blanket crepe (control)	120	nil	1780	890
			48	2240	793
			96	1880	749
			144	280	—
1262	Blanket crepe soaked in 0·1 per cent. para-nitrophenol for 30 minutes.	120	nil	1910	887
			48	2080	786
			96	1790	744
			144	340	—
1263	Blanket crepe from latex coagulated with acetic acid and 0·1 per cent. para-nitrophenol (calculated on dry rubber)	120	nil	2120	860
			48	2390	768
			96	1680	726
			144	330	—