THE EFFECT OF THE CONDITIONS OF DRYING ON THE AGEING PROPERTIES OF SHEET RUBBER

BY

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Part I

Introduction

The amount of rubber exported from the East in liquid form as concentrated or normal latex has increased steadily during recent years, but it is still small in comparison with that exported as sheet and crepe. The producer will convert his crop into sheet rather than crepe unless the market demand is sufficiently high to allow him to sell crepe at a price which will compensate for the extra expense and trouble involved in its manufacture. Since it is in the form of sheet that the consumer continues to receive the major portion of his raw rubber it is important that the effect on physical properties of any alteration in the preparation or treatment be fully understood. It has been shewn by numerous investigators that considerable variation in the vulcanising properties of plantation sheet does occur, and the influence of the methods of preparation have been extensively studied. An investigation has been started at this Institute to ascertain the effect of the drying conditions on the properties of the sheet rubber, with special reference to recent tendencies towards rapid drying. The results described here are concerned with the ageing properties.

Previous Work

The successive operations which occur in the preparation of sheet rubber may be regarded as stages in a manufacturing process, of which the object is the removal of water from latex, and production of dry rubber in a form easily handled and shipped. The last stage in this process is concerned with the drying of the wet machined sheets. In order that the time required to dry the sheet shall not be unduly prolonged, the sheets are dried at temperatures higher than normal, and usually in some form of smoke-house. Smoke-drying has been used since the very earliest days of the industry and was started as an attempt to imitate the smoke-drying of thin films of latex in the preparation of "Fine Hard

Para" when plantation rubber had not established its market. Its use has persisted, however, and has in fact several advantages, but it is not unreasonable to believe that other methods of drying could be devised which would eliminate entirely the need for smoke.

Considerable quantities of firewood are used in the smoke-drying of sheet rubber. In anticipation of a serious shortage of firewood arising in rubber-producing countries several investigations concerned with the possibility of its elimination in the drying process have been made. Eaton (1) investigated the utilisation of wood in the rubber industry in Malaya in 1924. He considered that it might be possible to substitute unsmoked for smoked sheet since smoking is not advantageous so far as the intrinsic vulcanisation properties of the rubber are concerned. Unsmoked sheet may even be superior when dried at very slightly elevated temperatures. O'Brien (2) considered alternative methods of sheet preparation in Ceylon on account of the serious shortage of firewood which was feared, and prepared a number of samples of sheet air-dried under different conditions, together with corresponding smoked sheet controls. These samples were examined in the laboratories of the London Advisory Committee for Rubber Research. The results showed that the air-dried sheet was invariably inferior in ageing properties to the smoked controls, particularly when dried at temperatures above 90°F. All the air-dried sheet, however, was made from latex to which paranitrophenol had been added to prevent mould development in the dry sheet; it was suggested that this might account for the inferior ageing, and further experiments were made. As a result of these tests O'Brien (3) states that sheet, without paranitrophenol and air-dried at 100°F., has better ageing properties than the smoked sheet controls, whereas that containing paranitrophenol is distinctly inferior. Martin (4) states that, although drying sheet in smoke is a relic of the days when "Fine Hard Para" was more widely used, it does appear to make the rubber more plastic and to prevent mould development. He states, however, that there is no intrinsic difficulty in drying sheet in air at somewhat higher temperatures, that this improves plasticity and decreases mould development, and that air-dried sheet is a comparatively new product, the demand for which is believed to be increasing.

The necessity for the strictest economy in the plantation industry during the recent difficult times has compelled the producer to consider very carefully any alterations or improvements which may reduce costs in the process of preparation. Improved designs for new smoke-houses and attention to ventilation systems, with slight structural alterations in many of the present smoke-houses of the older type, have effected considerable reductions in the time

required to dry sheet rubber. A drying period of four days is now quite common in Malaya and there are few estates today taking 10 days or more to dry their sheet, a period considered quite normal a few years ago. Recent developments have been directed towards reducing the time of drying still more and there are some estates in Malaya equipped with the latest type of driers in which sheet is dried regularly in two days. The temperatures used for rapid drying are of course considerably higher than those used in the smoke-houses of previous days, and in general the sheet is much lighter in colour. The air-dried and smoked sheet prepared by O'Brien (*loc. cit.*) for his ageing comparisons was dried at temperatures lower than those in general use today and was also dried more slowly. In view of this tendency to speed up the drying process it is pertinent to enquire whether the intrinsic properties of the rubber are affected by these alterations in the drying conditions.

Experimental

The accelerated ageing test used in these experiments was the well-known Bierer-Davis oxygen bomb test, in which rings of vulcanised rubber are tested for tensile strength after exposure to oxygen under pressure and at an elevated temperature. The details of the test adopted are given below.

Mixing — The standard mix consists of 20 grams of sulphur and 200 grams of rubber mixed for 20 minutes.

Curing — The mixings are kept for a period of 24 hours after which they are cured in moulds in a steam autoclave at 149°C. using a N.P.L. thermometer to control the temperature.

Time of Cure — The mixings are cured for a time sufficient to give a load of approximately 0.80 kg./sq.mm. at an elongation of 890 per cent. This point represents a period of cure about 20 minutes shorter than the arbitrarily chosen optimum. The cure taken as optimum in these experiments is that which gives a curve passing through the point, elongation 890 per cent, load 1.30 kilograms per square millimetre. As intervals of less than five minutes are not considered in the vulcanisation process the cure adopted for ageing may be sometimes 15, 20 or 25 minutes shorter than the optimum.

Ageing conditions Schopper rings are cut and aged in the bomb at an oxygen pressure of 300 lb. per square inch and a temperature of 60°C, for periods of 24, 48 and 72 hours. All rings are kept for 24 hours at atmospheric temperature after removal from the bomb before they are tested on the Schopper tester. Four rings are broken in each case to obtain an average result for tensile strength at break.

The conditions of oxygen pressure and temperature under which the tests are carried out are those normally used in bomb-ageing work, but the state of cure to which the mixings are taken prior to ageing is an arbitrary one. It was adopted here from a consideration of the results of a number of ageing tests which were made to ascertain at what state of cure differences in the ageing properties of various rubbers could best be distinguished.

It was found that there was considerable difference in the ageing behaviour of rubber from different estates when tested under the conditions described above, and that hot-air-dried sheet did not appear to age so well as smoked sheet.

A comparison was then made of the ageing properties of hot-air-dried and smoked sheet prepared from the same latex in identical manner up to the drying stage. The preparation of the wet sheet was that given to our standard acid controls which are prepared in the following manner: Field latex is diluted to 1½lb. per gallon dry rubber content and coagulated in pans with 1 per cent formic acid at the rate of 7½ fluid ounces per gallon of latex. The coagulum is machined the following morning and passes through the machines five times, four times through the smooth and once through the marking rolls. It is then soaked in running water for two hours, drained for two hours and dried. The air-dried sheet was dried in an electrically-heated, thermostatically-controlled drying cabinet and the smoked sheet was dried in a neighbouring estate smoke-house. The time of drying was three and four days at temperatures of 120° — 130° F. and 120° — 140°F. respectively. The ageing figures are given in Table I.

The rate of deterioration of the air-dried sheet is greater than that of the smoked sheet. Similar results were obtained when other direct comparisons were made with sheet dried in hot air and in smoke.

An experiment was then carried out in which sheet was made from the same crop of latex, diluted to different dry rubber contents before coagulation, and the sheet dried in the hot-air cabinet and the estate smoke-house as before. The preparation of the sheet, prior to the drying stage, from the latex diluted to various strengths was that adopted as standard for the particular D.R.C.

TABLE I

Smoked and Air-Dried Standard Control Sheet

Vulcanised rings aged in oxygen at 300 lb./sq. inch pressure
Temperature 60°C.

Sample.	Time of Cure to give 1.30 kg./sq.mm. at an Elongation of 890% min.	Ageing Cure min.	Tensile Strength at break after ageing for hours :— k.g./sq.mm.			
			0	24	48	72
Hot Air-dried Sheet	102	80	1.26	1.26	0.79	0.06
Smoked Sheet	104	85	1.13	1.27	1.26	1.24

and differs only from that given to standard sheet in the quantity of acid used and number of machinings given to the coagulum. The ageing results of the sheet are given in Table II.

TABLE II

Sheet prepared under Standard Conditions

Vulcanised rings aged in oxygen at 300 lb./sq. inch pressure
Temperature 60°C.

Sample No.	D.R.C. lb. per gallon	Air-dried Sheet or Smoked Sheet	Time of Cure to give 1.30 kg./sq.mm. at an Elongation of 890% min.	Ageing Cure min.	Tension Strength at break after ageing for hours:— kg./sq.mm.			
					0	24	48	72
L 194/1/1	2½	Air-dried Sheet	98	75	1.28	1.48	1.28	0.35
L 195/1/1	1½	"	109	95	1.34	1.34	0.15	0.03
L 196/1/1	½	"	103	85	1.48	1.34	0.79	0.07
L 194/1/2	2½	Smoked Sheet	108	90	1.29	1.38	1.24	1.13
L 195/1/2	1½	"	109	95	1.30	1.49	1.31	1.15
L 196/1/2	½	"	125	105	1.32	1.34	1.28	0.57

The smoked sheet prepared from latex coagulated at all three dry rubber contents ages better than the corresponding air-dried sheet. That prepared from latex of low D.R.C., however, does not appear to retain its tensile strength so well as that prepared from the latex of higher D.R.C.

Air-dried and smoked sheet was also prepared from the same latex diluted similarly, but from coagulum which was soaked for 24 hours before machining. The ageing figures given in Table III again show the smoked sheet to age better than the air-dried sheet.

TABLE III

Sheet prepared from Coagulum soaked for 24 hours before machining

Vulcanised rings aged in oxygen at 300 lb./sq. inch pressure
Temperature 60° C.

Sample No.	D.R.C. lb. per gallon	Air-dried Sheet or Smoked Sheet	Time of Cure to give 1.30 kg./sq.mm. at an Elongation of 890% min.	Ageing Cure min.	Tensile Strength at break after ageing for hours :— kg./sq.mm. 0	24	48	72
L 194/1/3	2½	Air-dried Sheet	101	85	1.41	1.34	0.86	0.06
L 195/1/3	1½	"	106	90	1.34	1.34	0.80	0.06
L 196/1/3	½	"	110	90	1.43	1.19	0.08	0.05
L 194/1/4	2½	Smoked Sheet	95	95	1.27	1.45	1.32	1.01
L 195/1/4	1½	"	90	90	1.21	1.36	1.28	1.18
L 196/1/4	½	"	105	105	1.36	1.45	1.08	0.13

In connection with other experiments, further samples of air-dried and smoked sheet were made from this same bulk of latex under similar conditions, except for the amount of acid used for coagulation, which was 50 per cent more than normal. Ageing tests were carried out and the results for sheet made under normal conditions and after the coagulum had soaked for 24 hours are given in Tables IV and V.

The figures given in Tables II, III, IV and V are shown graphically in figures 1, 2 and 3 in which the preparation treatments for each D.R.C. at which coagulation was made are brought together. The smoked sheet is superior to the air-dried sheet in all experiments in which the rubber is prepared from latex of

TABLE IV

Sheet prepared from Latex coagulated with Excess Acid

Vulcanised rings aged in oxygen at 300 lb./sq. inch pressure
Temperature 60°C.

Sample No.	D.R.C. lb. per gallon	Air-dried Sheet or Smoked Sheet	Time of Cure to give 1.30 kg./sq.mm. at an Elongation of 890% min.	Ageing Cure min.	Tensile Strength at break after ageing for hours :— kg./sq.mm. 0	24	48	72
L 194/2/1	2½	Air-dried Sheet	112	90	1.30	1.35	1.16	0.10
L 195/2/1	1½	"	113	90	1.31	1.36	1.08	0.09
L 196/2/1	½	"	117	95	1.35	1.25	0.48	0.05
L 194/2/2	2½	Smoked Sheet	116	95	1.31	1.44	1.38	1.24
L 195/2/2	1½	"	117	100	1.36	1.48	1.32	1.04
L 196/2/2	½	"	124	105	1.39	1.31	0.97	0.08

TABLE V

Sheet prepared from Latex coagulated with Excess Acid, Coagulum soaked 24 hours before machining

Vulcanised rings aged in oxygen at 300 lb./sq. inch pressure
Temperature 60°C.

Sample No.	D.R.C. lb. per gallon	Air-dried Sheet or Smoked Sheet	Time of Cure to give 1.30 kg./sq.mm. at an Elongation of 890% min.	Ageing Cure min.	Tensile Strength at break after ageing for hours :— kg./sq.mm. 0	24	48	72
L 194/2/3	2½	Air-dried Sheet	111	90	1.48	1.42	0.80	0.06
L 195/2/3	1½	"	114	95	1.34	1.22	0.61	0.07
L 196/2/3	½	"	118	100	1.34	1.36	0.07	0.05
L 194/2/4	2½	Smoked Sheet	119	100	1.44	1.42	1.35	1.09
L 195/2/4	1½	"	119	100	1.24	1.26	1.12	0.88
L 196/2/4	½	"	126	105	1.32	1.43	1.24	1.20

D.R.C. 2½ and 1½ lb. per gallon. With very dilute latex of ½ lb. per gallon D.R.C., the smoked sheet is not superior in all cases, although the rate of deterioration is not quite so fast as for the corresponding air-dried samples.

Sheet dried in Estate Smoke-houses

An experiment was made to ascertain whether sheet prepared and hot-air-dried at the Institute, was inferior to that prepared at the Institute and dried in estate smoke-houses other than the particular house used for the smoke-drying of the sheet tested in the previous experiments. A number of standard control wet sheets were prepared at the Institute from the same crop. Some were hot-air-dried and some taken to a number of estates where they were dried in the estate smoke-houses by kind permission of the managers. There was considerable variation in the type of smoke-house in which these sheets were dried and the dry rubber differed in colour from house to house. The details concerned with the drying of these sheets are given in Table VI and the ageing figures in Table VII and figure 4.

TABLE VI

Details of Drying Conditions

Sample No.	Air-dried Sheet or Smoked Sheet	Where dried	Time of drying hours	Temperature of drying °F.	Colour of dry Sheet
L 251/1	Air-dried Sheet	R. R. I.	92	120 – 130	Light yellow
/2	Smoked Sheet	Estate A	144	„	Brown
/3	„	„ B	64	„	Blue black
/4	„	„ C	92	120 – 140	Brown
/5	„	„ D	72	130 – 140	Brown
/6	„	„ E	43	130 – 145	Orange brown
/7	„	„ F	264	130	Light orange

As was expected, the air-dried sheet shows poor ageing figures, but it is also noted that the rubber dried in the different smoke-houses varies in its ageing resistance. As a rough classification it may be said that these sheets fall into two groups having good and poor ageing properties. The sheet dried on Estates A, B and C has good ageing properties while that from D, E and F has inferior ageing properties, Estate F being particularly poor.

TABLE VII

Standard Sheet dried in different Smoke-houses

Vulcanised rings aged in oxygen at 300 lb./sq. inch pressure Temperature 60°C.

Sample No.	Air-dried Sheet or Smoked Sheet	Where dried	Time of Cure to give load of 1.30 kg./sq.mm at Elongation of 890% min.	Ageing Cure min.	Tensile Strength at break after ageing for hours :— kg./sq.mm.			
					0	24	48	72
L 251/1	Air-dried Sheet	R. R. I.	115	95	1.25	1.28	0.34	0.05
/2	Smoked Sheet	Estate A	120	100	1.23	1.19	1.33	0.99
/3	"	" B	126	105	1.24	1.43	1.31	1.34
/4	"	" C	120	100	1.41	1.25	1 29	1.20
/5	"	" D	118	100	1.28	1.33	1.23	0.63
/6	"	" E	124	100	1.31	1.45	1.26	0.14
/7	"	" F	115	95	1.27	1.25	0.09	0.05

Discussion

Apart from the figures in Table VII, which are discussed separately, the results indicate that sheet dried in hot air, in a time commensurate with modern drying practice, is invariably inferior in ageing properties to that dried in smoke, unless the latex be diluted to a low D.R.C. before coagulation. Since in these experiments the sheet was made from the same latex and in identical manner up to the drying stage it is evident that the process of smoking improves the ageing properties. It may be argued that the results in Table VII are not in accordance with this conclusion. An examination of Table VI giving the conditions under which the sheet was dried is of considerable interest in this connection and an explanation of the anomalies is suggested. Estates A, B and C which produce sheet with satisfactory ageing properties have smoke-houses which are of the older type but dry rubber in a reasonable time. The sheet dried in these houses is of brown colour, that dried on Estate B being particularly dark. Estates D and E, which fall into the group giving inferior ageing, have rapid-drying houses of a patented design, and sheet dried in these houses is not dried in smoke through the whole drying period.

Their construction is such that after an initial period of smoke-drying the operation is finished in a hot-air chamber without smoke at a more elevated temperature. Estate F, which gives sheet with ageing figures inferior even to those for sheet dried in hot air, has an old type of smoke-house but it will be observed that the time of drying is much longer than any of the other estates. On inquiry into the reason for this it was found that the sheet was actually dry in a shorter time but the colour was so light that it was left in the smoke-house for some longer time to darken. It was still, however, very light even after 11 days drying. The possibilities of impairing the ageing properties by prolonged heating are at once apparent.

Until more information is available on a number of points which are now under investigation it is not proposed to suggest any explanation for the differences in ageing properties between hot-air-dried and smoked sheet. Experiments concerned with the effects of different preparation treatments at different dilutions, in conjunction with variations in time and temperature of drying are in progress. Further experiments concerned with the humidity at which drying takes place and time during which the sheet is in an atmosphere of smoke will give information from which more definite conclusions on the effect of the drying conditions on the ageing properties may be drawn.

Summary

An examination of sheet rubber prepared in identical manner up to the drying stage shows that hot-air-dried sheet and smoked sheet have different ageing properties.

Hot-air-dried sheet is invariably inferior to smoked sheet except when prepared from very dilute latex. Further work is required before any explanation is offered.

Acknowledgement

The preliminary work of my late colleague, Dr. Wiltshire, on the ageing properties of clonal and estate rubber led him to express the opinion that it was impossible to compare the ageing properties unless the details of preparation were known and that they would most likely determine the ageing properties. The work described in this paper developed from these ideas and grateful acknowledgement is made.

Thanks are due to the managers of the various estates who kindly co-operated in the drying experiments, and particularly to the manager of Kepong Estate who has so kindly permitted us to use his factory on many occasions.

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FIGURE 1

SHEET FROM LATEX OF D.R.C. 2½ lb. PER GALLON

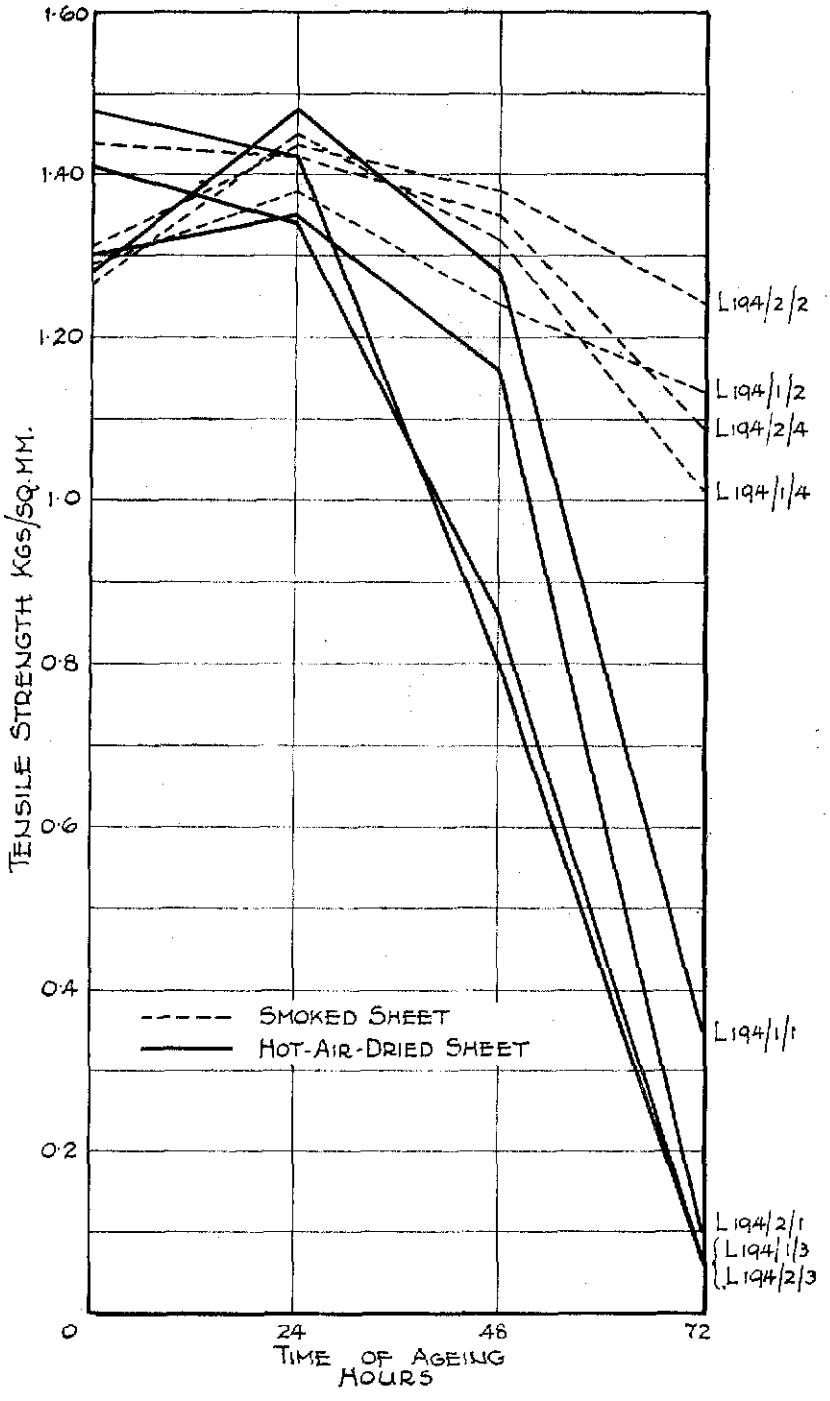


FIGURE 2

SHEET FROM LATEX OF D.R.C. 1½ lb. PER GALLON

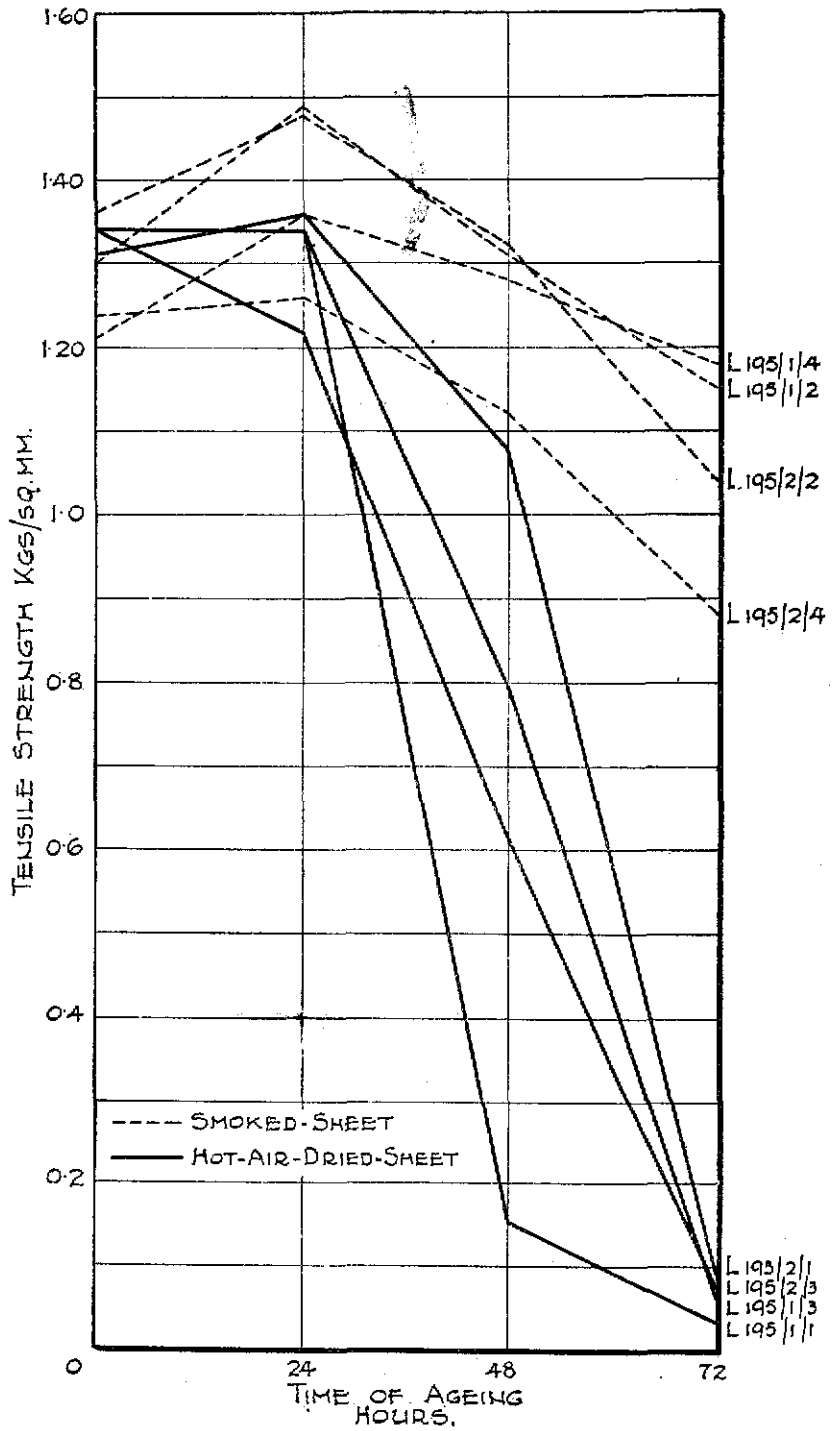


FIGURE 3

SHEET FROM LATEX OF D.R.C. ½ lb. PER GALLON

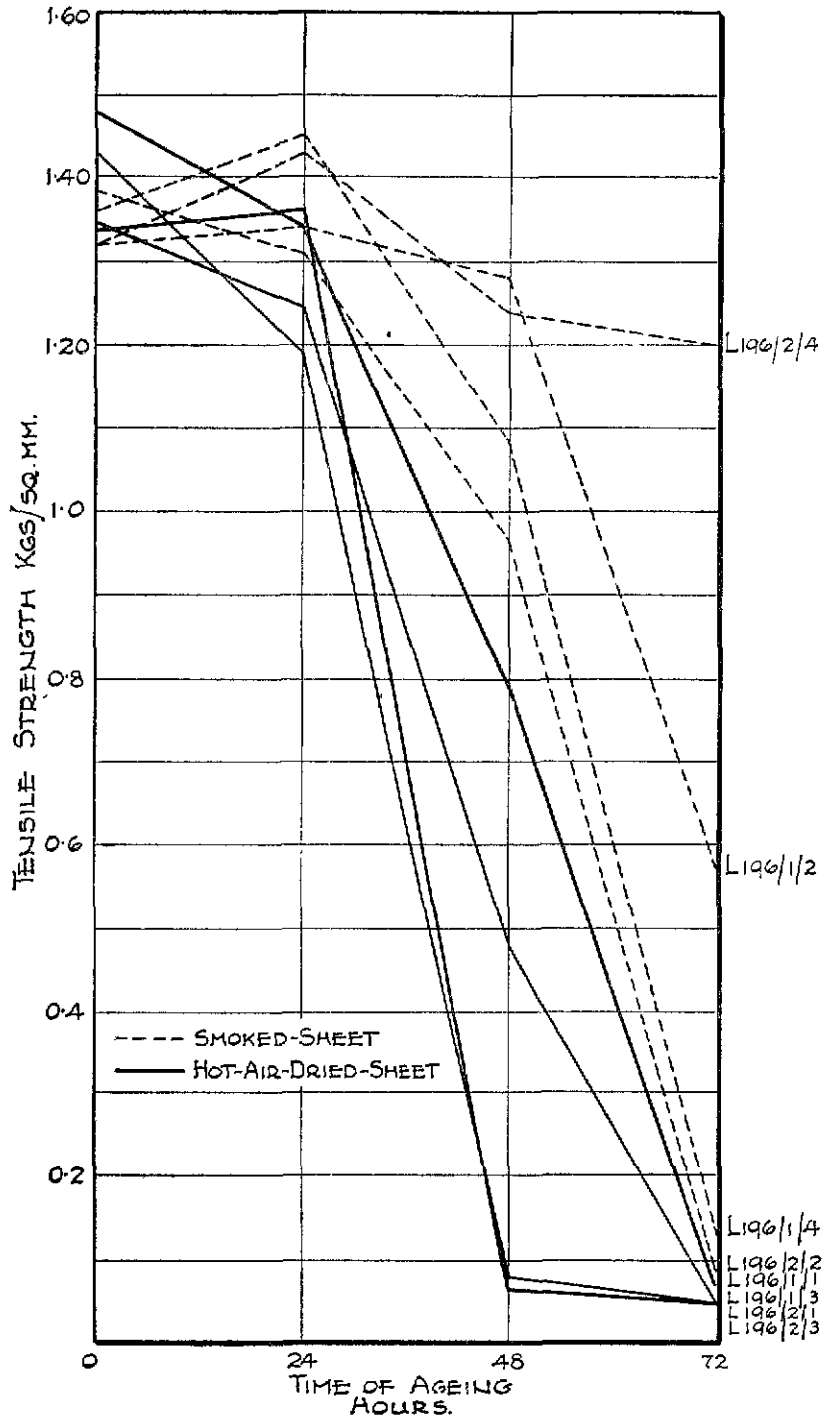
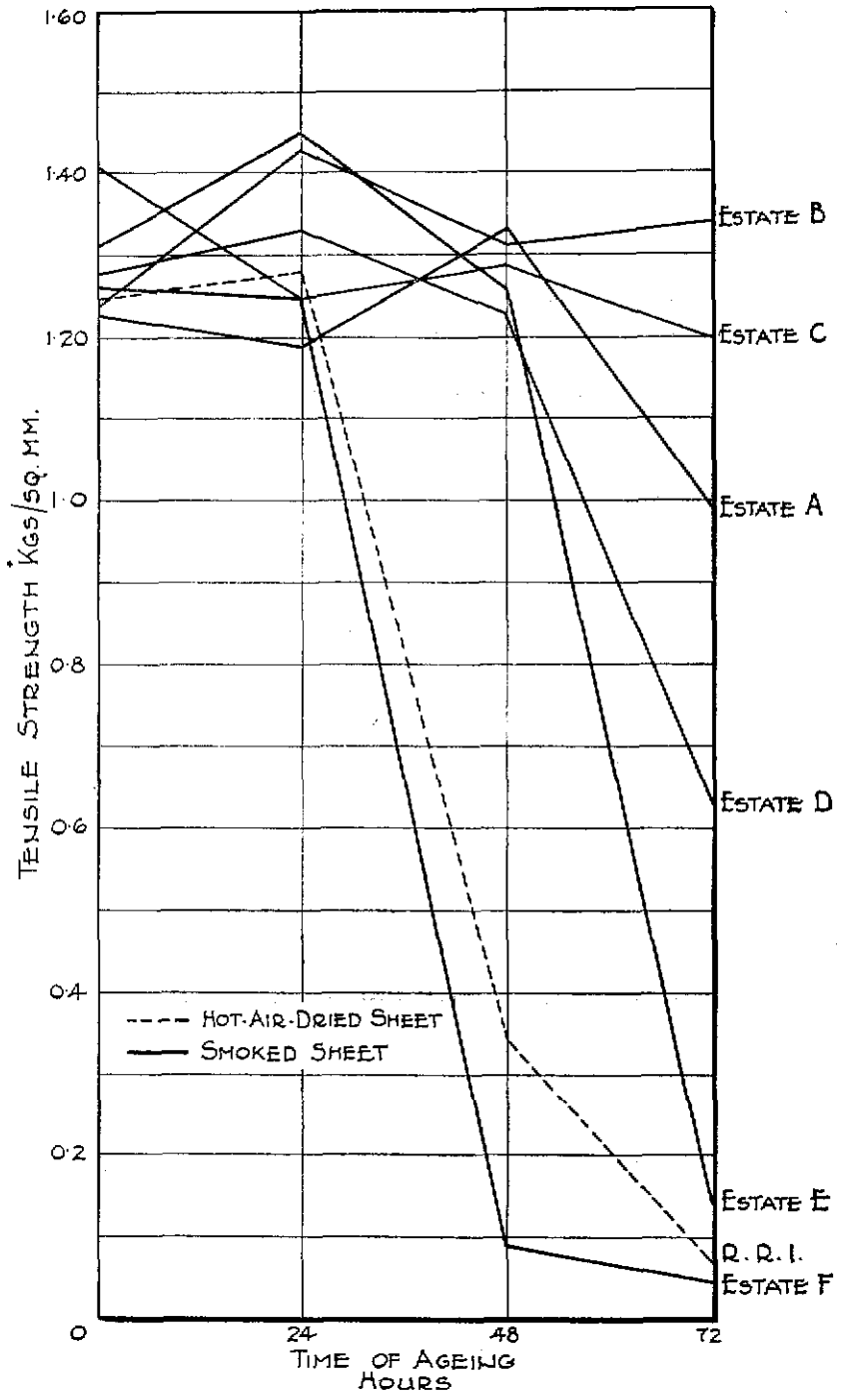


FIGURE 4

STANDARD SHEET DRIED IN ESTATE SMOKE-HOUSES