Q. Jl. Rubb. Res. Inst. Ceylon (1971) 47, 20—29.

SOME SUGGESTED IMPROVEMENTS IN THE GRADING OF PALE CREPE*

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SUMMARY

In marketing pale crepe, it is suggested that in addition to the Green Book grading based on colour, other information which has an influence on technological properties be also specified.

INTRODUCTION

Pale crepe due to its white colour and high level of cleanliness can be considered as a special type of natural rubber, and is generally used where light colour and purity are important *e.g.* in the manufacture of surgical goods, pharmaceutical goods such as nipples for infants' bottles, cut thread, rubber solutions, adhesives, particularly adhesive tapes and chemical derivatives of rubber such as chlorinated rubber and cyclised rubber. Ceylon is the world's largest producer of pale crepe, producing about 40,000 tons annually. Ceylon also produces about 2,000 tons of sole crepe annually. Malaysia which is the world's largest producer of natural rubber, produces only about 20,000 tons of pale crepe and about 9,000 tons of sole crepe annually. Table 1 gives the amount of pale crepe, sole crepe and sole crepe cuttings exported by Ceylon and Malaysia in the years 1964—1970. India imports about 500 tons of pale crepe annually from Ceylon.

TABLE 1

EXPORT OF PALE CREPE AND SOLE CREPE IN TONS FROM CEYLON AND MALAYSIA

Country	Type of crepe	Year						
		1964	1965	1966	1967	1968	1969	1970
Ceylon	Pale crepe	31,560	32,989	32,384	35,745	37,527	39,977	41,728
Malaysia	Pale crepe	26,064	19,019	19,472	18,978	20,721	20,474	—
Ceylon	Sole crepe	1,234	1,112	1,133	1,245	1,203	1,058	2,160
Malaysia	Sole crepe	8,970	7,202	9,686	8,650	8,328	8,480	—
Malaysia	Sole crepe cuttings	—	—	—	—	—	1,211	—

* Paper presented at the Indian Rubber Manufacturers' Research Association 5th Technical Seminar held in Bombay in January 1971.

Pale crepe is marketed according to the type and grade descriptions in the manual of " International standards of quality and packing for natural rubber grades " called the Green Book (1968). The Green Book states that the grades of pale crepe must be produced from the fresh coagula of natural latex under conditions where all processes are carefully and uniformly controlled. The different grades are Nos. 1X, 1, 2 and 3 thick and thin pale crepe. The main difference between these grades is colour. Pale crepe No. 1X is of very light uniform colour compared with No. 3 which is yellowish and variable in colour.

The above system of grading on the basis of visual inspection is of importance to the consumer in preventing markedly inferior rubber being sold against a given grade. There is also some justification for penalising visual defects, as long as appearance remains the basis of market valuation since they indicate irregularity in processing. Defects in colour, texture and visible contamination need not arise if standard methods are followed and suitable equipment is used. It would however be better if the system of grading was simplified to conform more closely to the end use of the rubber.

The properties of the field latex depend on the clones used. Field latex to be used for the preparation of pale crepe should be relatively free from yellow pigments (Nadarajah & Karunaratne, 1963), should not have a marked tendency to undergo enzymic discolouration (Nadarajah & Karunaratne, 1964) and the hardness of the rubber should be sufficient to give a satisfactory product (Nadarajah, 1964). Hence pale crepe producing estates must look into the properties of the clone to give the best results for pale crepe manufacture. Until now these properties have been a white, (*i.e.* free of carotenoids) non-discolouring latex giving a hard rubber. The colour, tendency to discolouration and hardness of crepe made from the clones recommended for large scale planting in Ceylon, namely RRIC 45, Wagga 6278, Gl 1, PB 86 and RRIC 36 (Anon, 1968) and from clone Nab 15 are given in Table 2.

TABLE 2

PROPERTIES OF PALE CREPE MADE FROM RECOMMENDED CLONES

Clone	Properties		
	Crepe colour	Tendency to enzymic discolouration	Hardness of crepe
RRIC 45	Pale yellow	Discoloured	Medium
Wagga 6278	White	Discoloured	Hard
Gl 1	Pale yellow	No discolouration	Medium
PB 86	White	No discolouration	Hard
RRIC 36	White	No discolouration	Hard
Nab 15	Pale yellow	No discolouration	Very hard

From Table 2 it is evident that PB 86 and RRIC 36 are the best clones for crepe manufacture and PB 86 is the clone which constitutes the largest acreage in the pale crepe producing estates in Ceylon. There is no standard recommended procedure for the preparation of pale crepe. The latex is diluted to 1¼, 1½ or 2 lb dry rubber content (DRC) per gallon, a fraction is or is not taken, the bleaching agent which is xylyl mercaptan is added before or after taking a fraction: the coagulant is oxalic acid, formic acid or a mixture of both.

Though pale crepe is sold on the Green Book grading where colour is the main requirement, there are additional requirements which the consumer is interested in, *viz.* (i) gel content, (ii) mill breakdown, and (iii) vulcanisation characteristics of the pale crepe.

Gel content

The gel phase is the proportion of any commercial sample of *Hevea* rubber insoluble in rubber solvents. Kemp & Peters (1941) have shown that the gel content varied with the source and type of rubber and with the nature of the solvent. Since the gel phase is partially soluble in some solvents, it cannot be a crosslinked phase, but must have a more complex structure. The gel phase according to them, contains the greater part of the nitrogeneous impurities. Allen & Bristow (1963) have shown that the true gel phase in natural rubber is composed of small crosslinked particles (microgel) whose presence is revealed by light scattering and electron microscopy. They have also shown that on mastication of pale crepe in oxygen the amount of gel component is progressively reduced until the rubber becomes completely soluble. The amount of microgel present would be a clonal characteristic (Freeman, 1954), varying between 5% and 30%, and would depend on whether the tree is in regular tapping (Bloomfield, 1951). Sekhar (1962) has stated that the usual concentration of microgel in normal *Hevea* latex is of the order of 7—30%, but in long rested and particularly newly opened trees, the concentration of the insoluble fraction in the latex is as much as 60—80%. It is a well known fact that crepe rubber undergoes hardening on storage : Wood (1952) and Sekhar (1963) have shown that this process is the result of a crosslinking reaction between aldehydic groups in the polyisoprene molecule with aldehydic condensing groups of another polyisoprene molecule. There is rather scanty evidence that the apparent gel content increases during storage hardening (Wood, 1952). The addition of hydroxylamine hydrochloride at 0·5 parts per 10 rubber to the diluted latex before coagulation, inhibits storage hardening.

Fractional or partial coagulation consists of coagulating the latex in two stages and obtaining first the yellow fraction with low acid or no acid as coagulant and then the white fraction with the addition of the required amount of acid as coagulant. Morris (1965) has stated that fractionation concentrates the gel into the first fraction. We have confirmed these findings and also found that when RPA No. 3 (xylyl mercaptan) is used for bleaching the rubber which is a common practice in Ceylon (Anon, 1970 a), the gel content is reduced considerably (Table 3). Further, bleached fractionated pale crepe has little or no gel content. The addition of hydroxylamine hydrochloride to the latex reduces to some extent the gel content in the unfractioned rubber and in the yellow fraction (Table 3). The gel content was determined by immersing 0·3 g of pale crepe which had been cut into small pieces, in 25 ml of benzene for 48 hr in the dark without shaking or stirring, removing aliquots and their concentration determined after filtration through lens tissue and by evaporation to dryness.

TABLE 3

GEL CONTENT OF THICK PALE CREPE PREPARED BY DIFFERENT METHODS

Sample	Gel content %	N%
Latex coagulated with formic acid	9·5	0·28
Latex mixed with hydroxylamine hydrochloride and coagulated with formic acid	7·3	—
Yellow fraction	17·3	0·39
Yellow fraction — RPA No. 3 added to latex before fractionation	5·3	—
Yellow fraction — hydroxylamine hydrochloride and RPA No. 3 added before fractionation	3·8	—
White fraction — RPA No. 3 added to latex before fractionation and coagulated with formic acid	0	0·22
White fraction — RPA No. 3 added to latex after fractionation and coagulated with formic acid	0	—

Krol (1968), has stated that because of its high purity and uniformity, cis-polyisoprene is being increasingly used as starting material for chemical modifications and that 92% cis-material has an additional advantage in that the absence of gel simplifies the preparation of reaction solutions. Our work has shown that pale crepe is competitive with 92% cis- 1,4-polyisoprene if bleached, fractionated pale crepe is used, in which the gel content is nil. Consumers of pale crepe must be made aware of this fact to prevent further encroachments in this application where pale crepe is already being used.

After considerable work by the Natural Rubber Producers' Research Association, England, in testing samples of pale crepe suitable as starting material for chemical modifications, it was found that pale crepe of high viscosity, preferably from clone PB 86, and a high PRI is suitable. A very pale colour is preferred and crepe bleached with RPA No. 3 is satisfactory (Watson, 1970).

One of the main uses of pale crepe is in rubber thread. It has been claimed that Natsyn 405 (synthetic cis- 1,4-polyisoprene) which is Natsyn 400 with the gel particles reduced to a negligible level, can be cut into fine thread with no fear of resinous gel particles causing weak spots. It has also been claimed that Natsyn 405 can be calendered into extremely thin sheeting with no specks or pinholes or other irregularities *e.g.* in surgical sheeting (Anon, 1969 a). We would recommend that in the above applications bleached, fractioned pale crepe is the most suitable type of pale crepe to be used.

Mill breakdown

Although mills are giving way to other more effective mixing equipment, the units in operation today are still scheduled to play key roles in the industry. The first prerequisite in mill mixing is the formation of a polymer band around the front roll and a polymer bank. One of the attractive characteristics of Natsyn 400 (synthetic cis- 1,4-polyisoprene) when compared with NR and other synthetic polymers is its rapid breakdown during milling and mixing (O'Mahoney, 1970). Pale crepe should have consistent mill breakdown properties and the consumer should know if there are any abnormal deviations.

Pale crepe normally does not show rapid or slow mill breakdown, but if it does so, it must be so specified to consumers who use it. Otherwise they may masticate the crepe rubber in the normal way, and the rubber may breakdown too quickly allowing insufficient time for incorporation of the compounding ingredients such as sulphur, accelerators, antioxidants *etc.* or may breakdown too slowly.

The test for mill breakdown was done on the mixing schedule suggested by Anon (1970 b) and the amount of mill breakdown assessed by Wallace plasticity determinations at various intervals of time. The mixing was done on a 6″ × 12″ laboratory mill with friction ratio 1 : 1·4 and roll speeds 22 rev/min front and 31 rev/min back. 100 g of rubber were used on the full width of the roller, at a roll temperature of 70 ± 5°C and at a gap of 0·75 mm (0·03 in.). The results obtained for different grades of commercial pale crepe rubber are given in Table 4.

TABLE 4

MILL BREAKDOWN OF COMMERCIAL CREPE SAMPLES

Time of milling in minutes	Wallace plasticity of samples						
	Dartonfield Group		Pimbura Group			Remilled sole crepe	
	No fractionation	White fraction	No fractionation	Yellow fraction	White fraction	Estate No. 1	Estate No. 2
0	58	51	47	47	46	51	48
½	48	36	39	38	39	38	37
1	45	34	34	33	33	33	29
1½	37	29	29	30	31	29	25
2	33	27	27	28	27	23	23
2½	28	24	25	25	23	21	21
3	26	22	23	23	21	18	17
PRI	72	55	65	69	64	63	58

It will be seen from the results that the remilled sole crepe has a much greater rate of mill breakdown than unfractioned, yellow or white fraction crepe. This is because remilled sole crepe has undergone much more millings than pale crepe in its manufacture. It is interesting to note that Malaysia has marketed sole crepe cuttings as a separate grade in 1969. Inadequate washing of the coagulum to remove excess thiol or the aerobically oxidised disulphide from the bleaching agent, RPA No. 3 can also cause rapid mill breakdown. Exposure of the pale crepe during preparation or during storage to sunlight can also cause rapid mill breakdown.

Preliminary work done by us has shown that the rate of mill breakdown may also be a clonal characteristic. Table 5 gives the rate of mill breakdown of crepe made from clones PB 86, RRIC 45 and RRIC 36 by coagulation at initial concentration. It will be seen that the rate of mill breakdown of rubber from clone RRIC 36 and Wagga 6278 is slower than that of clone PB 86.

TABLE 5

MILL BREAKDOWN OF CREPE FROM FOUR CLONES GIVEN AS WALLACE PLASTICITY OF SAMPLE

Time of milling in minutes	Clone			
	PB 86	RRIC 45	RRIC 36	Wagga 6278
0	56	34	59	58
¼	50	32	—	48
½	—	31	51	46
¾	45	30	47	45
1	42	28	43	44
1½	38	26	42	38
2	33	22	40	36
2½	29	20	38	34
3	24	18	34	31
PRI	82	88	81	86

Vulcanization characteristics

Information on vulcanization behaviour is of prime importance in the manufacture of rubber articles. Generally consumers require consistency in cure to be able to fit rubbers into specified schedules. Because of clonal variations and of the different coagulation and treatment methods of the latex, there is a variability in cure behaviour in cure sensitive mixes. In black mixes, the differenccs in curing behaviour is not large, but this could be large in non-black applications where pale crepe is used. Hence it would be advantageous for pale crepe producers to modify processing operations and device treatment methods for ensuring consistency of cure.

The ACS 1 mix used in specifying cure behaviour in the technical classified (TC) scheme accentuates quite small differences in vulcanization behaviour and is thus well suited to production control. In the TC scheme, classification was based on a measurement of strain at a fixed stress (5 kg/cm^2) on the ACS 1 mix cured for 40 min at 140°C. There are three classes namely fast curing, (strain 55—73), medium curing (strain 73—85) and slow curing (strain 85—103) each indicated respectively by a blue, yellow and red circle.

(a) Clonal variation

Vulcanization characteristics vary with the clones and with the age of the trees. Table 6 gives strain values for crepe samples made from undiluted latex with an excess of formic acid to complete coagulation within half an hour, collected monthly during 1961 and 1962 (Nadarajah, 1965).

TABLE 6

STRAIN VALUES FOR RUBBER FROM CLONAL LATEX SAMPLES

Clone	Strain at 5 kg/cm²	
	Year 1961	Year 1962
PB 86 (old)	90	93
PB 86 (young)	84	87
Nab 15	95	93
Wagga 6278	75	81
Gl 1	83	92
RRIC 45	—	90
AVROS 352	69	73

It will be seen that latex from young trees is faster curing than that from older trees, that rubber from clone AVROS 352 is fast curing and that the clones recommended for planting in pale crepe producing estates generally give rubbers which are slow curing.

(*b*) *Different coagulation conditions*

In the preparation of pale crepe the latex is diluted to 1¼, 1½ or 2 lb DRC per gallon. The original DRC of the latex also varies from about 2½ lb to 4 lb per gallon. The more the latex is diluted before coagulation, the lower will be the rate of cure of the final pale crepe. The bleaching agent RPA No. 3 has no effect on cure rate but the use of oxalic acid as the coagulant will lower the rate of cure slightly. When a fraction is taken, the naturally present accelerators are present more in it; hence fraction rubber will have a faster rate of cure and is more scorchy. Table 7 gives the vulcanization characteristics of commercially prepared pale crepe at Dartonfield Group, Agalawatte and Pimbura Group, Agalawatte.

TABLE 7

VULCANIZATION CHARACTERISTICS OF PALE CREPE

Name of estate	Sample of crepe	Strain 5 kg/cm²	Scorch at 250°F	Nitrogen content %
Dartonfield Group	No fractionation	70	12	—
	White fraction	97	19	—
Pimbura Group	No fractionation	100	15	0·28
	Yellow fraction	47·5	11	0·36
	White fraction	107	16	0·22

It will be seen that unfractioned pale crepe is a yellow circle or a red circle and that fractionated white pale crepe is a red circle and fractionated yellow pale crepe is a blue circle.

(*c*) *Treatment methods for ensuring consistency of cure*

Consumers prefer medium and fast curing rubbers, as these rubbers are more suited towards high speed manufacturing processes. Work done in the Rubber Research Institute of Malaya has shown that it is possible to modify the cure behaviour of raw rubber by using rubber activators. Four known cure activators and the amount needed to change a yellow circle to a blue circle (Sin & Hong, 1969) are as follows :— lauric acid (1%), lecithin (1·5%), Fixanol VR which is tetradecyl pyridinium bromide (0·01%) and ethanolamine (0·6%). Considerations of cost favour the use of Fixanol VR which can be added as a 10% solution into the latex just prior to acid coagulation. Fixanol VR has no deleterious effect on raw rubber or vulcanisate properties; the processing behaviour of treated rubbers is normal and they are no more prone to scorch than normal rubbers of equivalent cure rates.

(*d*) *Whiteness of the vulcanized product*

Synthetic cis-polyisoprene is being advertised by its manufacturers as a replacement of pale crepe in high whiteness compounds. Hence pale crepe manufacturers should take steps to limit encroachments in this application. We have observed that the white fraction pale crepe gives a whiter vulcanized product than when no fractionation is done in the preparation of the pale crepe. The yellow fraction crepe on vulcanization gives a greyish colour. Anon (1969 b) states that pale crepe produced by bleaching with RPA No. 3 generally darkens more on heating than pale crepe produced by fractionation. This according to them appears to be due to a combined effect of the bleaching agent and sodium metabisulphite used to prevent polyphenol oxidase darkening. If oxalic acid is used as the coagulant and RPA No. 3 as the bleaching agent, then no sodium metabisulphite need be added to prevent polyphenol oxidase darkening (Nadarajah & Karunaratne, 1964). Hence to obtain the maximum whiteness in the vulcanized product, a fraction should be taken, RPA No. 3 should be used for bleaching, no sodium metabisulphite should be used and oxalic acid should be used as the coagulant in the manufacture of pale crepe. The use of latex from clone PB 86 which has in it inhibitors of polyphenol oxidase darkening would be an added advantage.

DISCUSSION

It is suggested that the grading of pale crepe be dependent, in addition to the present visual system, on the method of preparation and on technological properties with a view to satisfying the requirements of the consumer.

Thus pale crepe No. 1X should be made after taking at least a 10% yellow fraction and should be bleached with RPA No. 3. This pale crepe would be suitable for solution purposes, for making rubber thread and where maximum whiteness in the vulcanized product is desired. This rubber is normally slow curing but could be made to be medium curing, if so desired.

Where a fraction is not taken, the pale crepe would be No. 1 or No. 2 or No. 3 depending on the colour. The rubber is slow or medium curing and could be made to be consistently medium curing if so desired. Care should be taken not to market as No. 1 or No. 2 or No. 3 pale crepe, any rubber that would show rapid or slow mill breakdown, without stating this fact.

The yellow fraction rubber would be graded as No. 3 or more often as off-grade or No. 4 pale crepe and is normally fast curing. Ceylon produces about 2,250 tons of this type of rubber annually. Consideration is being given in Ceylon to manufacture new process rubbers from fraction rubber (Karunaratne, 1970) and to market it as high tensile strength rubber. Since yellow fraction rubber is often sold as off-grade pale crepe, it is better to have a grading in the Green Book to characterise this type of crepe.

The Rubber Research Institute of Malaya has been aware of the need for technical specifications and has introduced amongst other grades, SMR 5L which however has not been a serious competitor to pale crepe but has been only a competitor to air-dried sheet and RSS. The price fetched by it has been only a few cents above RSS 1 whilst pale crepe fetches a price of more than 25 cents above RSS 1. To compete with pale crepe, the RRIM expects to initiate in 1971 a new specialized grade called SMR EQ which will have a dirt content below 0·02%, a maximum colour of Lovibond 3·5, and an indication of cure similar to but not identical with the present technical classification scheme. Such requirements will be met from latex origin rubber prepared under careful supervision either by a crumb process or as conventional pale crepe. All the precautions normally used in pale crepe production such as the use of sodium bisulphite, avoidance of enzymic discolouration, thorough washing of coagulum, avoidance of clones giving very yellow rubber, using bleaching agents and fractionation would be essential to meet the tight specification. This grade of rubber would be expected to have a limited but important demand of about 60,000 tons/year for an extra clean, extra light-coloured grade of rubber that could be used, say in surgicals or rubber thread manufacture and would be expected to offer strong competition to Ceylon pale crepe.

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