

## Viscosity-stabilised Heveacrumb

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*Treatment of first quality natural rubber latex or coagula with hydroxylamine hydrochloride during Heveacrumb manufacture results in viscosity-stabilised (abbreviated: CV) Heveacrumb. This material has been produced commercially in eleven factories in West Malaysia, within an overall range of 50 to 75 Mooney viscosity units. Each factory is, however, capable of producing CV rubber within a narrower range of viscosity after characterising the incoming sources of latex and standardising the method of manufacture. Heveacrumb CV has all the advantages of the Standard Malaysian Rubber (SMR) scheme. It should give further advantages to the consumer in pre-mastication savings and consistency of compound viscosity, while still retaining the excellent inherent properties of the natural product.*

The spontaneous and irreversible increase in the viscosity of crude natural rubber (DE VRIES, 1927; WOOD, 1952; MESSENGER, 1933) is an important physico-chemical change which occurs during manufacture and subsequent storage. This is often termed 'storage-hardening' and its unpredictable rate of change caused the elimination of the Mooney viscosity criterion for technically classified natural rubber (NEWTON, 1953). Recent elucidation (SEKHAR, 1958a and b; 1961) of this phenomenon has led to an interesting hypothesis of the presence of a few aldehyde groups distributed at random along the *cis*-1,4 polyisoprene chains. This evidence is consistent with earlier indications of the presence of oxygenated groups (WOOD, 1952; MESSENGER, 1933; BLOOMFIELD, 1951; CRAIG *et al.*, 1951; WATSON, 1953; and SCHUUR, 1958) and also provides a first indication that natural rubber can be manufactured with a pre-determined viscosity (SEKHAR, 1962) which would remain unaltered even after prolonged storage. In the course of development, many chemical compounds were screened (SEKHAR, 1964) and hydroxylamine hydrochloride was considered to be most suitable due to its ready availability, low cost and compatibility with latex. Hydroxylamine hydrochloride stabilises rubber at the viscosity at which it emerges from the tree by blocking the 'natural cross-linking

sites'. This rubber offers advantages in the consumer's factory by reducing mastication time and stock storage. This 'constant viscosity' concept was, unfortunately, considered economically unattractive for sheet and crepe rubbers and was only reviewed later for new presentation rubbers because the latex could then be coagulated at its initial rubber concentration when a lesser quantity of the chemical was required (CHIN, 1966).

This paper discusses the features affecting the Mooney viscosity variation encountered at various Malaysian factories for Heveacrumb (SEKHAR *et al.*, 1965), the procedure for minimising this variation, the commercial availability of these rubbers in West Malaysia and basic information on some of its properties.

**Terminology.** Natural rubber which has been chemically treated for inhibition of storage-hardening has been ascribed as having 'constant plasticity' (SEKHAR, 1962), or 'constant viscosity' (CHIN, 1966), or being 'Mooney viscosity-stabilised'. At present, the Rubber Research Institute of Malaya has provisionally adopted the term 'constant viscosity' and has abbreviated it 'CV'. For describing this type of rubber precisely, however, the author has preferred the term 'Mooney viscosity-stabilised'. For abbreviating this description, the 'CV' symbol is still used.

METHODS OF PREPARATION,  
SAMPLING AND TESTS*Preparation*

(i) *Mooney viscosity-stabilised Heveacrumb (CV) from latex*: Undiluted natural rubber latex which arrives at the factory is sieved through 40-mesh sieve and bulked in volumes as large as possible to ensure maximum uniformity of production. Experience has shown that 3000 gallons per bulk is adequate provided no large monoclonal areas are involved. The minimum amount of ammonia as anti-coagulant is used and added within the range of 0.01 to 0.1 per cent on the latex. The use of formalin as an anti-coagulant is avoided because of its reaction with hydroxylamine hydrochloride to form formaldoxime and sodium sulphite is also not recommended on account of its discolouring tendencies. Castor oil (0.7 per cent wt) of an approved grade (RUBBER RESEARCH INSTITUTE OF MALAYA, 1967a) or castor oil-zinc stearate (0.4 per cent wt) mixture (RUBBER RESEARCH INSTITUTE OF MALAYA, 1968) calculated on the rubber is then stirred into the latex either directly (RUBBER RESEARCH INSTITUTE OF MALAYA, 1966a) or by a plunger-masterbatch method (RUBBER RESEARCH INSTITUTE OF MALAYA, 1967b). This is followed by a 5 per cent aqueous sodium metabisulphite solution at the rate of about 0.04 per cent by wt on the rubber content to prevent enzymic discolouration. While keeping the latex mixture well stirred, aqueous 10 per cent hydroxylamine hydrochloride (0.15 per cent by wt on the rubber) is added. Stirring is continued for 3 minutes and the latex is run down to individual coagulating tanks where formic acid solution (to bring the pH to 5.0–5.2), is added for coagulation. The coagulum is left for 8–10 hours before milling through a 3- or 4-roll crumbler. The crumb is dried by hot-air circulation in a crumb drier at 100°C for about 6 hours.

(ii) *Mooney viscosity-stabilised Heveacrumb (CV) from estate field coagulum*. Estate cuplump is collected free of tree lace, leaves, twigs, bark and other contaminants. Pre-coagulum can also be included as the starting raw material. The coagulum of reasonable size is passed directly through a granulator (e.g., the U.S. Cum-

berland cutter fitted with a 1½-inch screen) for the first size reduction and dirt removal. For batch-wise production, the granules are then soaked for 16 hours in aqueous 0.4 per cent hydroxylamine hydrochloride contained in an aluminium or a ceramic-lined tank. The ratio of the weight of the wet granules to the weight of the chemical solution is kept at 1:5 for satisfactory immersion.

After this soaking treatment, 100–150 lb lots are successively removed and blended by crepeing for three passes on a medium macerator. Castor oil is then evenly applied to the crepe at the maximum rate of 0.7 lb of oil per 100 lb of dry rubber. The crepes are crumbled and dried at 100°C. The hydroxylamine hydrochloride soak solution can generally be used for five times in succession. Small volume changes are adjusted by addition of 0.4 per cent hydroxylamine hydrochloride solution to the tank.

*Sampling*

The sampling procedure depends on the method of addition of hydroxylamine hydrochloride at the processing unit. Normally, it is added in the bulking tank, and for each bulk of latex processed, all the bales derived from any one coagulating tank are sampled in addition to taking one sample for every ten bales produced. The former constitutes 100 per cent sampling and indicates the efficiency of mixing. The latter represents 10 per cent sampling of one production lot. Such extensive sampling is carried out for fourteen days. If the results confirm efficient distribution of chemicals, then only the 10 per cent sampling procedure is continued. Sometimes the hydroxylamine hydrochloride solution is added to individual coagulating tanks and, for such a method, two samples are taken from each of the tanks processed. This represents about 30 per cent sampling intensity. In addition, all the bales derived from one coagulating tank are sampled to check the efficiency of mixing.

For the production of Heveacrumb CV, a corner bale sample taken for SMR specification testing is representative of the whole bale in Mooney viscosity.

*Preparation of sample for testing*. Each sample is homogenised by six passes through the

rolls on a cold mill moving at even speeds at a nip setting of 0.065 inch.

#### Tests

(i) *Mooney viscosity.* Viscosity of the test sample is determined by *A.S.T.M. Method D-927-55T* or *B.S.1673, Part 3 (1964)* using the standard large ( $1\frac{1}{2}$  inch) rotor and the result is expressed as ML 1+4' at 100°C.

(ii) *Accelerated storage-hardening test.* A test portion of approximately 50 g from the homogenised sample is placed, without further preparation, in a desiccator over phosphorus pentoxide and evacuated to 0.1 mm mercury pressure for 1 hour and the evacuated desiccator is then placed in an oven at 60°C for 48 hours. At the end of this period, the rubber is cooled to room temperature before determining its Mooney viscosity. This value is compared with the value obtained on an unhardened test portion from the same homogenised sample.

### RESULTS AND DISCUSSION

#### Choice of Mooney Viscosity Determination

Although the processibility of raw rubber cannot be assessed by a single determination of Mooney viscosity (VEITH, 1953), the choice for this particular determination was made on account of its almost universal usage in consumer countries and its ease of conversion to other measurements obtained with compression plastimeters like the Williams, Goodrich, Defo and the Wallace Rapid. The value obtained gives an indication of the amount of mechanical work required of the crude rubber, before the addition of fillers and accelerators can take place. Such determination is often made on rubbers from different batches before they are submitted to standard plastication and mixing schedules to obtain compounds with similar rheological properties. This determines, for example, their behaviour in an extruder, where uniformity will avoid rejection of compounded stocks.

#### Factors Influencing Mooney of Heveacrumb

Natural rubber as produced at the plantations is derived from multiple sources of planting materials and processing conditions. Each of these factors may cause, during manufacture, variation in its viscosity, composition and

curing characteristics. In West Malaysia, for instance, there are still about 130 clones of known commercial interest (PAARDEKOOPER, 1965). Table 1 shows that the typical Mooney viscosity of Heveacrumb rubbers prepared

TABLE 1. TYPICAL MOONEY VISCOSITY VALUES OF MONOCLONAL HEVEACRUMB RUBBERS

Clone	Mooney viscosity, ML 1+4' at 100°C		
	Untreated rubbers		Rubbers treated with hydroxylamine hydrochloride
	Initial	After accelerated storage-hardening	
I. Soft			
RRIM 501	43	74	37
RRIM 707	59	84	44
RRIM 526	65	89	46
RRIM 701	56	90	49
II. Medium			
RRIM 519	70	99	50
RRIM 605	58	110	52
TR 3702	65	85	52
RRIM 603	66	92	52
Gl 1	57	84	54
RRIC 45	67	102	54
RRIM 513	68	102	57
RRIM 610	75	87	58
RRIM 623	70	101	59
Ch 32	74	100	59
RRIM 625	67	111	60
PR 107	68	126	61
GT 1	73	92	62
RRIM 600	65	101	63
RRIC 5	74	91	65
Ch 30	74	103	65
RRIM 612	77	96	65
AVROS 1734	75	98	65
Ch 26	80	121	65
RRIM 614	73	89	66
AVROS 2012	78	93	67
III. Hard			
PB 5/51	78	102	75
PB 86	78	106	76
RRIM 607	85	104	76
Tjir 1	86	117	80
RRIC 41	86	98	80
PB 28/59	87	102	81
AVROS 1279	87	100	82
WR 101	86	100	82
RRIC 7	92	102	84
RRIC 36	96	104	90
AVROS 529	100	110	99

from some of the more popular clones varies from 43 to 100 Mooney units.

Data shown in *Table 1* are typical values of Heveacrumb prepared from monoclonal latices selected from the Experiment Station of the Rubber Research Institute of Malaya at Sungei Buloh. For production convenience, the rubbers can be divided into three arbitrary ranges: soft (with a ML 1+4' of less than 50), medium (with a ML 1+4' between 50 and 75) and hard (with a ML 1+4' of higher than 75). Apart from this wide range of Mooney viscosity values among the different clones, a comparison of *Columns 1 and 2 in Table 1* shows that the untreated rubbers cross-link to different extents during the storage-hardening test. The test is designed to check the hardening behaviour within a practical period of 48 hours and the values obtained therefrom indicate the maximum value which the rubber will attain on long-term storage. By such means, the initial range of 57 Mooney units has been extended to 83. *Table 1* also shows the trend that rubbers with high initial Mooney viscosity exhibit a smaller increment in viscosity on storage-hardening than those with low initial Mooney values (ALLEN AND BLOOMFIELD, 1963).

Cross-linking reactions of rubber do not occur only during storage but also occur in field latex preserved with ammonia. Though less well understood, these cross-linking reactions may well take place in a manner similar to that observed with latex concentrates preserved with 0.7 per cent ammonia (BEVILACQUA, 1956). When the time interval between collection and coagulation is 8 hours, up to 5 Mooney units increase is observed for latices ammoniated up to 0.3 per cent. Such cross-linking reactions have not been detected for latices in which sodium sulphite or formalin is added as anti-coagulant. Additional factors which cause Mooney viscosity increase are listed in *Table 2*. It is noted that prolonged coagulum maturation and higher drying temperature contribute more to Mooney viscosity increase than change in pH of coagulation or dilution of the latex.

These processing variables can account for differences of up to 26 Mooney viscosity units for a given latex. When such latex is treated with 0.15 per cent hydroxylamine hydrochloride be-

TABLE 2. FACTORS INFLUENCING MOONEY VISCOSITY VARIATION OF HEVEACRUMB RUBBER

Item	Factor	Range of operating conditions	Increase in Mooney viscosity
1	Dilution of latex (% d.r.c.)	10 - 35	0 - 3
2	pH of coagulation	4.5 - 5.5	0 - 3
3	Maturation of wet coagulum before milling (h)	8 - 48	0 - 6
4	Maturation of wet crumb before drying (h)	1 - 24	0 - 3
5	Drying temperature (°C)	50 - 100	0 - 6

fore coagulation (*i.e.*, when the latex is converted to Heveacrumb CV), the rubber obtained therefrom is not subjected to variation by the processing variables described but results in a rubber with a Mooney viscosity close to that obtained from the tree. The Mooney viscosity of Heveacrumb CV will therefore depend only on the clonal latices which are being processed and should fall within the range of 37 to 99. This wide Mooney range will not be desirable despite the uniformity in other respects as provided by the Standard Malaysian Rubber scheme (RUBBER RESEARCH INSTITUTE OF MALAYA, 1965a and b; 1966b and c). For example, rubber with a particularly high Mooney viscosity may require long mastication times or need expensive peptisers to obtain a product of a workable and consistent viscosity while the soft rubbers require no prior mastication.

#### *Methods of Controlling Viscosity Variation*

(a) *Latex sources.* Natural rubber latices of different clonal origins can be adequately mixed to yield intermediate properties. Normally some blending of the latices occurs during collections in the field as well as on arrival at the processing factory. The effect of mixing two clonal latices which, by themselves, will

TABLE 3. EFFECT OF MIXING CLONAL LATICES ON PROPERTIES OF HEVEACRUMB

Percentage wt mixture		Mooney viscosity		Acetone extract, % weight	ACS 1	
Tjir 1	RRIM 501	Initial	After accelerated storage-hardening		TC strain, %	Compound Mooney viscosity
100	0	83	109	2.77	70	40
85	15	77	103	3.14	73	37
75	25	72	101	3.37	74	36
65	35	68	92	3.60	76	33
50	50	63	89	3.93	75	31
35	65	56	86	4.37	72	28
25	75	52	81	4.47	67	25
15	85	49	79	4.73	69	26
0	100	45	75	4.84	67	22

give rise to a soft and hard rubber (*e.g.*, from RRIM 501 and Tjir 1) is illustrated in Table 3 which shows that the contribution of each clonal latex in a mixture is *pro rata*, in respect of non-rubber contents, viscosity and curing characteristics of the resultant rubber.

The same effect is shown in Table 4 for two rubbers which, by themselves, are of medium viscosity. Thus satisfactory production with average properties is possible after characterisation of the latex sources and judicious blending of those *known* sources. The application of this approach was studied in two cases. The first case involved an estate which maintained good records of their planting materials, distribution of their clonal acreages and/or yield as well as their tapping systems. From such data and the information in Table 1, the Mooney viscosity of each collecting station was calculated. Experimental rubbers were then prepared from each collection for a week and the results obtained agreed with those calculated. It is possible from these results to work out a method of latex blending for a correct and uniform viscosity.

The second case involved smallholdings where the clones were not known. For such a

case, each collecting centre of latex was characterised for its Mooney viscosity for a week. In six schemes, the Mooney viscosity of rubber from all known collecting centres of each scheme was reasonably uniform. In one scheme where the settlers were extensively sited, the rubber type was related to the geographical location of the smallholdings as shown in Table 5. For this particular scheme, the rubber from the collecting centres varied from 43 to 67 but blending at the factory resulted in commercial production within the range of 52 to 62.

(b) *Drying conditions.* For a factory which proceeds on a discontinuous production basis, it is important that the drying conditions for each production lot are not varied because even slight over-heating can cause hardening (cross-linking). Gross over-heating leads to softening. Over-heating has been found to be the reason for an odd result within a production lot derived from a thoroughly blended latex.

(c) *Accuracy.* The weighing of chemicals, estimation of the dry rubber content and volume measurement of latex are performed accurately to achieve satisfactory production. Excess hydroxylamine hydrochloride does not

TABLE 4. EFFECT OF MIXING CLONAL LATICES ON THE PROPERTIES OF HEVEACRUMB RUBBERS

Percentage wt mixture		Mooney viscosity		Acetone extract, % weight	ACS 1	
Glenshiel 1	PR 107	Initial	After accelerated storage-hardening		TC strain, %	Compound Mooney viscosity
100	0	57	84	3.24	67	29
85	15	58	77	3.33	66	30
75	25	59	81	3.54	69	30
65	35	59	87	3.60	68	30
50	50	60	89	3.70	68	31
35	65	61	86	3.24	69	32
25	75	61	88	3.27	70	31
15	85	62	93	3.28	70	33
0	100	63	94	3.22	67	33

TABLE 5. SMALLHOLDERS' HEVEACRUMB RUBBERS PREPARED ON FOUR SUCCESSIVE DAYS

Latex collecting centre	Mooney viscosity of Heveacrumb rubber prepared on				Mean
	Day 1	Day 2	Day 3	Day 4	
A	49	48½	54	44½	49
B	55½	58	57	54½	56
C	63½	60	62	63½	62

affect the storage-hardening test but reduces the rate of cure of the final rubber. A gross excess of hydroxylamine (e.g., 2 per cent) causes corrosion of the mill during blending procedure.

(d) *Brown colouration.* This occurs more readily with Heveacrumb CV than with non-stabilised crumb, because of several factors. At 100°C, the colour of Heveacrumb CV is usually in the SMR colour test, 1 to 2 Lovibond units darker than non-stabilised Heveacrumb

made from the same latex. Increasing the drying temperature to over 100°C increases the darkening effect. Increasing ammoniation of the field latex increases the brown colouration and this is also intensified with increasing temperature. Sodium sulphite anti-coagulant gives rise to an even more intense pigment formation. Similarly, the dosage of sodium metabisulphite should be applied only in sufficient amount to arrest the black polyphenol oxidase enzymic discolouration since it intensifies browning. The brown colouration of Heveacrumb CV can therefore be minimised by using low ammonia preservation and adjustment of the drying temperature to 100°C.

#### *Commercial Production of Heveacrumb CV*

The R.R.I.M. Experiment Station at Sungei Buloh commenced commercial production of Heveacrumb CV in August 1966 from latex purchased from one commercial source. Subsequently, latices purchased from two other commercial sources as well as latex collected from its own plantings were included. The rubbers processed from each source were differentiated and those derived from the Experiment Station,

and two commercial sources had Mooney viscosities within the range 55 to 65, whereas those from the first commercial source were slightly higher, within a range of 60 to 70. Up to the end of 1966, this factory had shipped a total\* of 484 tons of Heveacrub CV. In 1967, eight other factories manufactured CV rubber (continuously or otherwise), to ship in all about 2200 tons\*. By mid-1968, eleven factories were in production; between January and May 1968, about 2900 tons\* of Heveacrub CV were shipped. The eleven factories together represent a production potential of about 28 900 tons per year when working at maximum capacity.

The Mooney viscosity values of these production lots are shown in *Table 6*. On the basis of experience gained so far, it is clear that the eleven factories have satisfactorily produced Heveacrub CV within a range of 50 to 75 units despite the variety of clonal latices available. Additionally, it is possible for each factory to manufacture the same type of rubber within a viscosity range of 10 Mooney units, by carefully selecting and blending latices.

Except for the two factories at Meru and Rantau which represent a production potential of about 4800 tons per year, and also Estate A with a potential of 2200 tons per year, the bulk of Heveacrub CV is being produced within a Mooney range of 55 to 70.

Heveacrub CV produced from field coagula treated with hydroxylamine hydrochloride is not yet in commercial production, but experimental trial lots have been produced.

### *Seasonal Variation*

Changes in the dry rubber and total solids contents of latices are known to occur near the onset of wintering (usually February, March and April), and when the trees have completely shed and renewed their leaves the susceptibility to such changes is dependent on the clonal type. For the manufacture of Heveacrub CV, seasonal variation may therefore affect the yield and final composition of the latex bulk resulting in a change in the Mooney viscosity of the final rubber. In practice, the effect of wintering on the Mooney viscosity of Heveacrub from monoclonal latices is variable but low. For example, in one estate,

RRIM 501 decreased by 5 Mooney units and Glenshiel 1 by 3 units though PR 107, RRIM 513 and PB 86 were not affected. For some factories, this decrease in the yield may balance the variation in the Mooney viscosity of the latex sources and, as shown in *Table 7*, the variation of Mooney viscosity of production lots from the R.R.I.M. Experiment Station for one year is low. On the other hand, there can be factories where these factors of variation may not balance each other and necessitate the more careful selection and blending of sources for the viscosity range required of the final rubber.

### *Effect of Age of Tree on Mooney Viscosity of Heveacrub CV*

Maturity of trees is important in the assessment of suitability of clonal types for Heveacrub CV manufacture as it is known (BLOOMFIELD, 1951; SEKHAR, 1963) that microgel is present to an extent of 60 to 80% in rubber obtained from newly tapped or long rested trees. Such rubbers then show a corresponding high Mooney viscosity value which diminishes as the period of tapping is prolonged. This effect is illustrated by the example of a smallholders' processing centre receiving latex from newly opened RRIM 605 and RRIM 623. Rubber from this latex blend had an average Mooney viscosity of 80 during the first week of tapping and the value decreased rapidly to 39 after three months of tapping. In comparison, these clones in maturity and regularly tapped have typical values of 52 and 59 respectively when processed from the R.R.I.M. Experiment Station. These results would then be misleading in any assessment on the suitability of the latex source as, in the first instance, the rubber was hard, while in the second instance it was low. The difference is probably attributable to the age of trees as the latter were of twelve years of age. The effect of maturity on the Mooney viscosity of the rubber is illustrated by the results obtained from Tjir 1 latex collected from 12-year-old trees which had a Mooney viscosity

\* Includes a small proportion of a modified version of viscosity-stabilised Heveacrub which contains 4 per cent of a non-staining process oil.

TABLE 6. VISCOSITY DATA ON HEVEACRUMB CV FROM DIFFERENT FACTORIES

Factory	Production potential in tons per year (estimated)	Period of production	Mooney viscosity of production lots			
			Maximum	Minimum	Mean	S.D.
R.R.I.M. Experiment Station, Sungei Buloh	2000	21. 8.1966 to 12.6.1968	61.0	55.0	58.3	1.53
		22. 2.1966 to 29.5.1967	71.0	61.0	68.0	2.50
		24.10.1966 to 8.1.1968	61.5	57.5	59.5	1.72
		20. 8.1966 to 9.1.1968	68.0	60.5	64.2	1.74
R.R.I.M. Factory at Meru	1800	2. 8.1967 to 1.6.1968	64.0	51.0	56.7	1.87
R.R.I.M. Factory at Rantau	3000	1.10.1967 to 28.5.1968	64.5	50.5	53.5	1.25
A	2200	18. 7.1967 to 26.5.1968	66.0	48.5	55.5	2.61
B	2200	4. 5.1967 to 22.5.1968	68.5	61.0	65.1	2.32
C	2200	15. 8.1967 to 3.6.1968	62.0	54.5	58.7	1.51
D	4500	6.12.1967 to 1.6.1968	70.0	57.5	62.4	1.07
E	3500	11. 1.1968 to 31.5.1968	67.5	60.5	63.9	1.06
F	2200	15. 1.1968 to 25.5.1968	67.5	60.0	65.6	1.84
G	1800	15. 4.1968 to 30.5.1968	62.0	57.0	58.6	1.57
H	3500	9. 5.1968 to 25.5.1968	72.0	65.0	67.0	1.97



TABLE 7. MEAN MONTHLY VISCOSITY VARIATION OF HEVEACRUMB CV

Factory	1966					1967												1968				
	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May
R.R.I.M. Expt. Station	58.0	58.0	59.0	60.0	59.0	61.0	59.0	58.0	*	58.0	58.5	59.5	58.5	58.5	58.0	60.0	59.5	*	*	*	58.5	57.8
R.R.I.M., Meru													52.6	57.0	57.2	58.0	57.0	58.2	57.9	54.5	56.1	57.3
R.R.I.M., Rantau													54.7	54.5	55.5	57.5	56.5	58.0	56.7	56.2	56.5	54.9
A								60.7	57.1	57.5	54.7	54.6	56.3	55.5	58.6	56.2	58.6	58.7	61.9	62.4	52.9	48.3
B										67.4	68.5	69.8	*	*	62.5	64.3	68.4	65.7	65.1	63.4	64.3	66.5
C													59.4	59.5	60.1	60.7	59.8	58.8	56.8	56.5	59.4	58.6
D																	65.8	60.8	60.5	62.5	61.9	62.0
E																		64.9	66.8	64.3	62.7	62.4
F																		66.9	66.9	61.0	62.0	62.2
G																					57.9	58.4
H																						67.0

\* No production

of 80 whereas latex from 18-year-old trees had a Mooney viscosity of 84 and latex from 22-year-old trees had a Mooney viscosity of 90.

#### *Properties of Heveacrumb CV*

Factory supervision during the manufacture of Heveacrumb CV is generally more stringent than that for normal Heveacrumb production and therefore leads to a rubber of high consistency. All Heveacrumb CV from field latex has so far been consistently manufactured to SMR 5 specifications without difficulty. The change-over to this type of rubber has not affected the dirt, nitrogen, ash, volatile matter, copper and manganese contents. Colour, however, is often observed to be darker (brownish) than usual as it is affected by factors described earlier. Although colour does not form part of the specifications for Heveacrumb CV, it is possible to select and blend latices with the least enzymic discolouration to be processed at factories with ready access to the latex sources so that the ammonia used

as a preservative can be kept to a minimum. As an illustration of some of the typical properties of Heveacrumb CV, *Table 8* shows the test data obtained from rubbers prepared at the R.R.I.M. Experiment Station.

These results, which are in SMR 5 category, represent the first six months of the production lots. Further, the rubbers have their PRI maintained at a consistently high level even after the accelerated storage-hardening test and the Mooney viscosity of the production lots was within a range of 10 Mooney units. Cure behaviour of these rubbers, as traced in an ACS 1 compound (BRITISH STANDARDS INSTITUTION, 1953), are also consistent and usually fall within the Red Circle classification of the TC scheme.

#### *Uniformity of Mooney Viscosity within Heveacrumb Bales*

Examination of many bales of Heveacrumb CV shows that samples taken from different portions of a bale, after standard procedure

TABLE 8. TEST DATA ON HEVEACRUMB CV PRODUCED AT THE R.R.I.M. EXPERIMENT STATION

Property	Range	Mean	Specification limit for SMR 5
Mooney viscosity, initial	59–71	63	–
Mooney viscosity, after storage-hardening	64–75	68	–
Acetone extract, % wt	2.62–3.50	3.13	–
TC strain, %	86–112	93	–
<b>SMR tests</b>			
Dirt*, %	0.000–0.020	0.004	0.05 max.
Volatile matter, % wt	0.13–0.36	0.22	1.0 max.
Nitrogen, % wt	0.34–0.50	0.43	0.7 max.
Copper, p.p.m.	1.0–2.0	1	8 max.
Manganese, p.p.m.	1.0–1.2	1	10 max.
PRI, initial	83–93	89	–
PRI, after storage-hardening	80–92	86	–

\* Retained on A.S.T.M. 325 mesh

TABLE 9. EFFECT OF TROPICAL STORAGE OF HEVEACRUMB RUBBER BALES ON MOONEY VISCOSITY

Type of rubber	Conditions of storage	Mooney viscosity of rubber bales after storage (Months)					After accelerated storage-hardening test
		0	1	2	3	4	
Heveacrubm	21.5 to 35.5°C and 70 to 93 per cent relative humidity	75	78	79	80	82	95
Heveacrubm CV		60	60	61	62	62	64
Heveacrubm	45 to 50°C and 2 to 5 per cent relative humidity	75	84	90	90	89	95
Heveacrubm CV		60	62	63	61	60	64

of homogenisation, fall within a range of 2 Mooney units.

#### *Changes in Mooney Viscosity of Heveacrubm on Storage*

The effect of storage on the Mooney viscosity change of Heveacrubm bales was studied by subjecting them to two sets of conditions: (1) normal tropical storage (21.5–35.5°C and 70–93 per cent relative humidity); and (2) fairly high temperature and low humidity (45–50°C and 2–5 per cent relative humidity). The results in *Table 9* show that a change of 6 Mooney units is observed on corner samples from a bale of normal Heveacrubm compared to a constant figure for its corresponding Heveacrubm CV rubber after four months' storage at normal tropical conditions. Higher temperatures and lower humidities can accelerate the process of hardening.

The rubbers on being subjected to the accelerated storage-hardening test showed an increase of 20 and 4 units respectively.

#### *Vulcanisate Properties*

Heveacrubm CV rubbers (with hydroxylamine hydrochloride treatment) are found to be slightly slower curing than the corresponding untreated rubber when they are tested in a pure gum ACS I compound. This is shown in

*Table 10* by a lower TC strain value of the treated rubber when compared at similar compound viscosities with the untreated rubber. When compounded to a standard CBS/S formulation\*, Heveacrubm CV shows greater processing safety, is slightly slower curing at the initial stages and attains a somewhat lower modulus than the normal Heveacrubm at optimum cure time. Oven-ageing resistance of both Heveacrubm rubbers are equivalent. A detailed comparative evaluation will be published in due course.

#### CONCLUSIONS

The economic manufacture of Heveacrubm CV involving the use of hydroxylamine hydrochloride is a commercial reality. For latex rubbers, an aqueous solution of the chemical is added to the latex prior to coagulation and for field coagula, a soaking procedure is feasible. Such treatments are easily incorporated in the normal procedures for Heveacrubm manufacture. Controlled production leads to a rubber which consistently meets SMR specifications and has a uniform Mooney viscosity

Base formulation	Parts by dry wt
Rubber	100
Zinc oxide	5
Stearic acid	2
CBS	0.5
Sulphur	2.5

and cure behaviour. Although the multiple clones now available in West Malaysian plantations can cause the viscosity of

TABLE 10. RAW RUBBER AND VULCANISATE PROPERTIES OF HEVEACRUMB RUBBER

Property	Cure time, min	Heveacrumb	Heveacrumb CV
Tensile strength, kg/cm <sup>2</sup>	20	212	*
	30	265	260
	40	264	256
	50	232	210
Elongation at break, %	20	610	*
	30	540	600
	40	550	560
	50	520	550
Modulus at 300%, kg/cm <sup>2</sup>	20	11	*
	30	22	15
	40	25	21
	50	23	22
Relaxed modulus MR 100, kg/cm <sup>2</sup>	20	6.1	*
	30	8.2	7.2
	40	8.6	8.2
	50	8.6	8.3
Retention after 7 days oven-ageing at 70°C, %			
Tensile strength, kg/cm <sup>2</sup>	40	89	82
Elongation at break, %	40	97	90
Modulus at 300%, kg/cm <sup>2</sup>	40	113	129
Mooney viscosity, raw		87.5	67.5
Mooney viscosity, compound		50.5	42.5
Mooney scorch (T <sub>5</sub> , 120°C)		62.3	71.2
TC strain corrected to compound viscosity 40		67.0	86.0

\*Undercure

Heveacrumb CV to fall within a broad range of 37 to 100 Mooney units, the practice of judicious blending of characterised latex sources has now shown that each factory can be geared to produce the same rubber within a range of 10 Mooney units. Experience gained so far from eleven factories in West Malaysia shows that the bulk of Heveacrumb CV is coming forward within the 55 to 70 range and can therefore be compounded usually without pre-mastication.

Heveacrumb CV is slightly slower curing and gives lower modulus vulcanisates. This can be remedied, if necessary, by a small increase in the dosage of curatives. The oven-ageing resistance of this rubber is excellent.

Thus, Heveacrumb CV is a high quality natural rubber with consistent properties and it has the further attribute of usually requiring no pre-mastication during compounding.

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## DISCUSSION

Chairman: Mr. B. C. Sekhar

Mr. C.W. Thompson enquired if there were any other means of controlling the final viscosity than by large-scale bulking and blending. Mr. Chin said bulking was the only method suitable for application with the factory practices prevailing in the region today. Chemicals could be used to raise the viscosities of some latices, but there were practical limitations on this. The Chairman added that bulking was necessary to process rubber to any specification as well as to CV.

Dr. J.S. Lowe reported that trypsin completely eliminated the effect of hydroxylamine in an attempt to produce a special high polyisoprene rubber, which might indicate that protein rather than rubber hydrocarbon cross-links were involved. He enquired if the effect of peptisers had been tried at either the latex or the wet solids stages. The author said he had not tried these, but he considered the role of the aldehyde groups in cross-linkage to be proven although non-rubbers might also play a part.

In answer to Dr. W.L. Resing, he said that the neutral and acid sulphates of hydroxylamine had been compared with the hydrochloride and he found all three inhibited hardening of natural rubber in storage, their

effectiveness being dependent on their hydroxylamine content. Dr. Resing asked whether the low initial Mooney viscosity of rubber from RRIM 501 was due more to the high proportion of acetone extract or to the supposedly lower mean molecular weight. Mr. Chin said lipids could act as plasticisers for elastomers. The molecular weight distribution in RRIM 501 rubber different slightly from that of Tjir 1, for example; hence, both factors might contribute but their relative importance was still conjectural. The author had not yet tried the addition of cationic soaps to latex in CV rubber production (which, Dr. Resing suggested, might improve cure rate), instead of or in conjunction with small additions of accelerator to the mix.

Dr. C.H. Tan said the condensation of an amine with an aldehyde involved the lone pair of electrons on the nitrogen atom, but these were not available when the hydroxylamine was in the form of a hydrochloride. He enquired if the hydrochloride was more effective than the free basic forms in trials of this and other amines. Mr. Chin said the acid salts were more soluble in aqueous media and the acid had a well-known catalytic effect on the condensation of amine and aldehyde. The Chairman added that in addition to alpha methyl groups there are 100 to 300 sites per rubber molecule which can condense with the aldehyde groups; these may not be integrally associated with the polymer molecule but with non-rubbers. The hardening of natural rubber could be inhibited by removal of the non-rubbers so that the aldehyde groups could not condense with them, as suggested by Dr. Lowe in the use of trypsin; but purified rubbers were not acceptable to the consumers, who obtained many necessary properties by the association of natural rubber with non-rubbers. The hydroxylamine reaction with other condensing groups was still under investigation.

Mr. P. van Gelder enquired about the toxicity effects of hydroxylamine in the product especially in causing dermatitis. The Chairman said the nature of the reaction was such that very little hydroxylamine was left after 4 hours' drying at 100°C. No adverse effects were reported from use of hydroxylamine hydrochloride in the polymerisation of some synthetic rubbers. Independent investigations had so far found only very small residues of hydroxylamine in rubber.