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THE PREPARATION AND PROPERTIES OF LOW NITROGEN CONSTANT VISCOSITY RUBBER

By

P. A. J. Yapa

SUMMARY

A method for the preparation of a viscosity stabilised version of low nitrogen rubber is described. The process basically involves a simultaneous treatment of latex with hydroxylamine hydrochloride and papain. Hydroxylamine apparently prevents storage hardening by blocking aldehyde groups in rubber whilst papain reduces the nitrogen content usually by about 40%. In addition, the latter acts as a coagulant. Carbonyl condensing chemicals such as hydroxylamine sulphate and hydroxylamine hydrochloride can also be used in the manufacture of low nitrogen CV rubber. Preliminary studies have shown that several other commercially available proteolytic enzymes viz. *protease, trypsin, superase or esperase can be used with hydroxylamine hydrochloride to produce the same effect.*

INTRODUCTION

There has been a significant increase in consumer interest in viscosity stabilized rubber in recent years. The main attraction of this type of rubber is that it requires very little or no mastication prior to mixing in a consumer factory. Preparation of this grade of rubber involves treatment of NR latex with carbonyl condensing chemicals such as hydroxylamine hydrochloride (Chin, 1968). Deprotenization of NR latex was first reported a few decades ago. However, it was only recently that it was recognized as a specialized grade of NR. Deproteinized natural rubber (DPNR) is usually manufactured by removal of proteinaceous material in latex either by alkaline hydrolysis or enzymatic digestion (Chin & Smith 1974, Smith, 1974). Extremely low levels of ash and nitrogen contents in DPNR (0·05% and 0·06%, respectively) reduce its tendency to absorb moisture and this in turn gives it several improved characteristics such as uniformity in cure behaviour, reduced creep, superior fatigue life and superior dynamic properties (Bernard, 1973).

The use of papain as a coagulant for *Hevea* latex produces a rubber with a low nitrogen content ; the reduction usually being in the region of 40% (Nadarajah *et al.*, 1973 ; Yapa & Balasingham, 1974). The dual effect of papain on NR latex has revived interest in its use. Papain coagulated rubber has been found suitable for the manufacture of cyclised rubber by the p-toluene sulphonic acid method (Nadarajah *et al.*, 1973).

The present investigation was undertaken to see whether a viscosity stabilized low nitrogen rubber could be prepared by a combination of these two processes (viscosity stabilization and deproteinization). The possibilities of using commercially available proteolytic enzymes other than papain in this process have also been studied and the results are reported.

MATERIALS AND METHODS

Preliminary studies on a laboratory scale were carried out with latex collected from the Institute's estate and diluted (1 : 1) with water prior to treatment. White papain (oven-dried papaw milk) was used in all experiments. Hydroxylamine hydrochloride ($NH_2OH.HCl$), hydroxylamine sulphate and semicarbazide hydrochloride were purchased from British Drug Houses Ltd. (England). Alcalase, Esperase, TPN (Trypsin Pancreatic Novo) and BPN (Bacterial Protease Novo) were obtained from Novo Industri (Denmark).

Nitrogen determinations were carried out by the semi-micro Kjeldahl method and the ash content by B. S. method. The storage hardening test was carried out as described by Sekhar (1960).

Field latex was diluted (1 : 1) with water prior to treatment and papain (0·05% on volume) was added as a supsension in water followed by NH_2OH. HCl solution (0·08% on volume). The latex was stirred vigorously and continuously while adding the chemicals, and then left overnight for the enzyme to act on the latex proteins and for coagulation to take place. Serum is usually clear at the completion of the treatment period. Coagulum can then be either milled into thin laces for crepe production or granulated for block rubbers.

RESULTS AND DISCUSSION

Preliminary investigations showed that the papain concentration (0·05% on latex) which is usually used for coagulation is also suitable for the combined treatment. Experiments carried out to find the optimum concentration of hydroxylamine hydrochloride showed that 0·08% (on latex) gives the lowest nitrogen content (Fig. 1). When latex is treated with both papain and hydroxylamine hydrochloride (0·05% and 0·08% on latex, respectively) the nitrogen content of the rubber is reduced by about 50% and this shows that papain is fairly active even in the presence of this chemical. The difference in nitrogen contents obtained by papain with and without hydroxylamine hydrochloride or hydroxylamine sulphate is usually small with the exception of semicarbazide HCl where the degree of deproteinization is comparatively low, (Table 1).

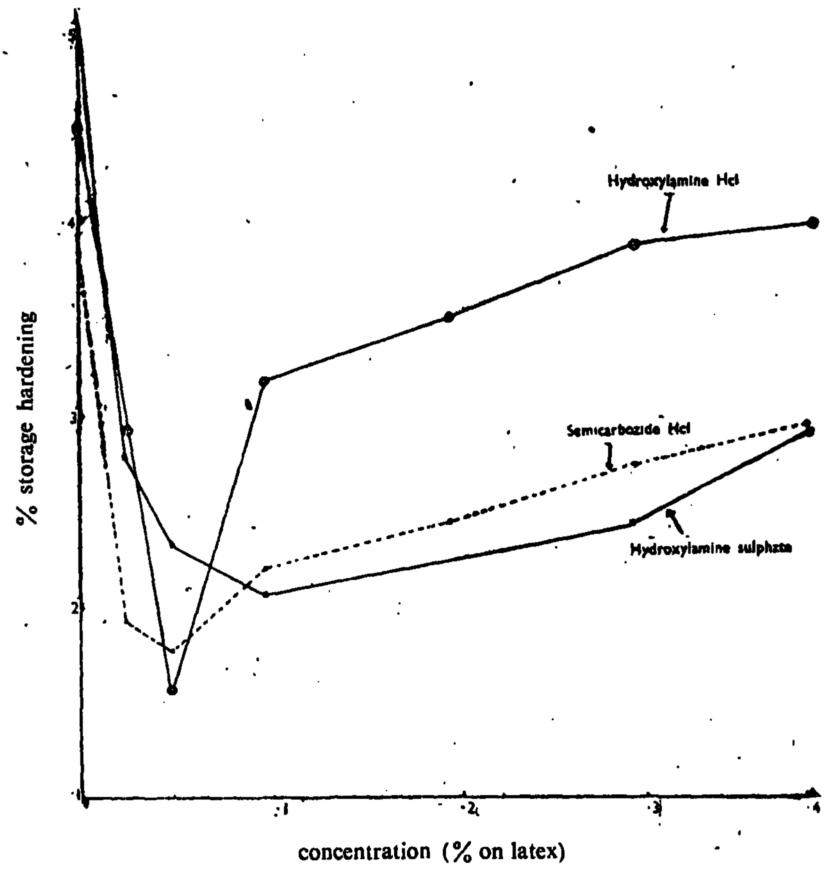

Fig 1. Effect of concentration of carbonyl condensing chemicals on storage hardening.

TABLE 1

EFFECT OF SOME CARBONYL CONDENSING CHEMICALS ON PROTEOLYTIC ACTION OF PAPAIN ON *Hevea* PROTEINS

Treatment	Nitrogen %	
	PB 86	RRIC 7
1 Control — acid	0·392	0·378
2 Papain (0·05% on Latex)	0·182	0·196
3 Papain + hydroxylamine hydrochloride (0·08% on latex)	0·182	0·210
4 Papain + hydroxylamine sulphate (0·08% on latex)	0·196	0·196
5 Papain + semicarbazide hydrochloride (0·08% on latex)	0·210	0·224

It appears from these results that the inhibitory action of hydroxylamine on the enzymes is so small that it can be used for the purpose of preparing low nitrogen-CV rubber. On the other hand, papain seems to have no effect on the blocking action by hydroxylamine of aldehyde groups which are responsible for hardening of natural rubber on storage. This type of behaviour of papain and hydroxylamine make them a suitable combination for the manufacture of low nitrogen-CV rubber. Hydroxylamine hydrochloride at a concentration of 0·075% (on latex) prevents storage hardening (Fig. 2). It may be noticed (Tables 2 & 3) that the Wallace plasticity and Mooney viscosity of hydroxylamine-papain treated rubber is also increased by a few units after the storage hardening test. We have often observed similar increases of one or two units in rubber produced by methods commonly employed for viscosity stabilization. Therefore, these slight increases which are on the other hand negligible, when compared with those of untreated rubber, cannot be attributed to combination of papain with the usual chemical treatments. The concentration of hydroxylamine hydrochloride is almost the same as the concentration used in the manufacture of CV rubber from latex. Semicarbazide hydrochloride, and hydroxylamine sulphate which are also used in the manufacture of CV rubber, were also examined in this study and it is seen from Fig. 1 that they too exert the same effect in the presence of papain. However, in the case of semicarbazide HCl the increase in Mooney values after the storage hardening test is quite marked (Table 3) and it, therefore, does not appear to be a satisfactory reagent to arrest storage hardening in the presence of papain.

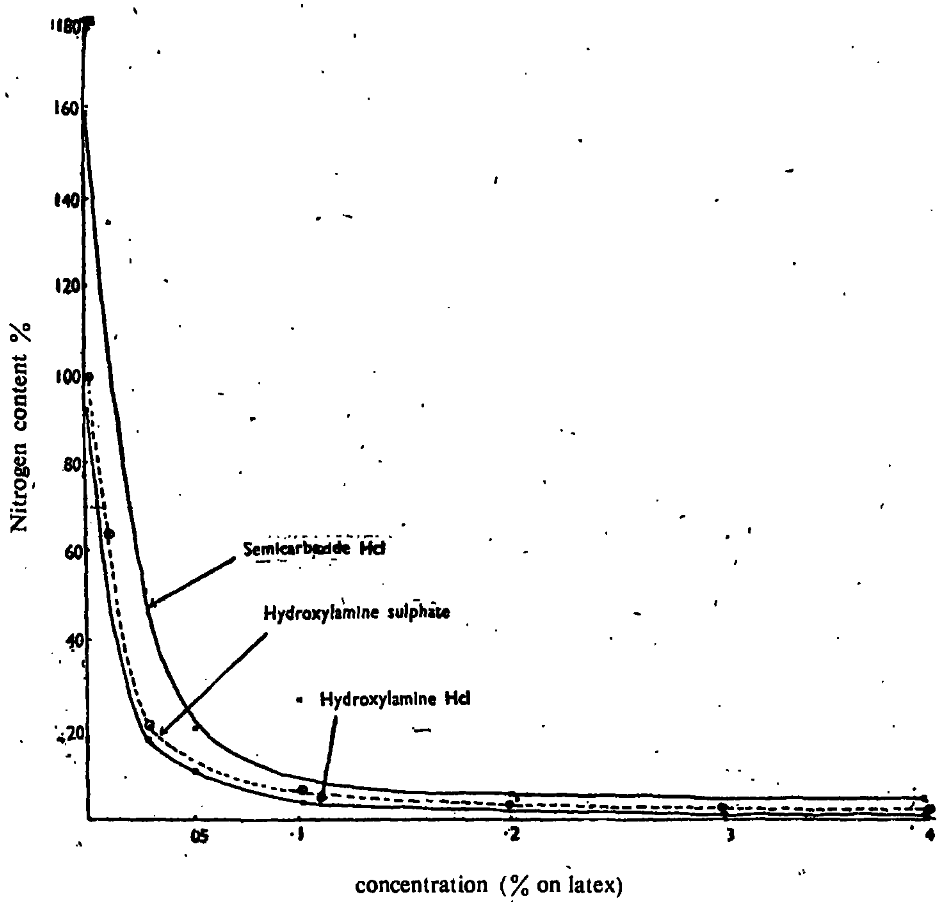

Fig. 2. Effect of carbonyl condensing chemicals on the reduction of nitrogen content.

TABLE 2

WALLACE PLASTICITY (Po) OF PAPAIN — HYDROXYLAMINE SULPHATE TREATED RUBBER, BEFORE AND AFTER STORAGE HARDENING TEST

Treatment	Wallace Plasticity					
	PB 86		RRIC 7		RRIC 45	
	before	after	before	after	before	after
1 Control (acid)	39	47	48	61	33	55
2 Papain	47	58	56	71	43.	67
3 Hydroxylamine sulphate	35	24	47	43	32	30
4 Hydroxylamine sulphate/papain	37	35	43	44	30	32

TABLE 3

MOONEY VISCOSITY OF PAPAIN ALDEHYDE-CONDENSING REAGENTS TREATED RUBBER BEFORE AND AFTER STORAGE HARDENING TEST

Treatment	Mooney viscosity			
	PB 86		RRIC 7	
	before	after	before	after
1 Control — Acid	69	96	78	88
2 Papain	84	102	93	105
3 Papain + hydroxylamine hydrochloride	66	68	76	77
4 Papain + hydroxylamine sulphate	66	68	75	77
5 Papain + semicarbazide hydrochloride	75	81	84	92

The raw rubber properties of low nitrogen-CV rubber, prepared by the papain-hydroxylamine hydrochloride treatment are given in Tables 4 & 5. The PRI of papain - hydroxylamine treated rubber is excellent and this is improved even more on storage (Table 4). This was found to be the case with all three clones PB 86, RRIC 7, RRIC 45 investigated. The reduction in nitrogen content, in this particular case, is about 50%. The MOD value of this rubber is high, and this is usually the case with rubber coagulated with this enzyme. The higher ash content is apparently one of the few drawbacks of this process, the other being the slight discolouration which needs rectifying. One possible method to overcome these is to use purified papain (Yapa & Balasingham, 1974). Physical properties of the ACS 1 Mix vulcanizate are given in Tables 3 and 4.

TABLE 4

EFFECT OF HYDROXYLAMINE SULPHATE ON PLASTICITY RETENTION INDEX (PRI) BEFORE AND AFTER STORAGE HARDENING TEST, OF PAPAIN TREATED RUBBER

Treatment	Plasticity Retention Index					
	PB 86		RRIC 7		RRIC 45	
	before	after	before	after	before	after
1 Control — Acid	71·8	68·1	72·9	70·5	98·1	76·4
2 Hydroxylamine sulphate	62·9	54·2	73·3	76·7	81·2	80·0
3 Papain	72·3	70·7	78·2	74·7	95·2	82·0
4 Hydroxylamine sulphate/papain	75·7	88·6	76·7	82·6	80·0	87·5

TABLE 5

RAW RUBBER PROPERTIES

Property	Control (2% formic acid)	Low N-CV Papain — $NH_2OH.HCl$)
Dirt %	0·015	0·014
Ash %	0·183	0·247
Nitrogen %	0·443	0·231
Mooney viscosity	72	69
Po	40	37
PRI	82	73
MOD	5·45	6·51

TABLE 6

ACS 1 MIX. VULCANIZATE PROPERTIES (CURE TIME 40 MIN. AT 140°C)

Property	Control (2% HCOOH)	Low N-CV (Papain — $NH_2OH.HCl$)
Elongation at break %	806	792
Modulus 100% Kg/cm²	4·9	7·6
Modulus 300% Kg/cm²	11·3	14·8

TABLE 7

ACS 1 MIX. VULCANIZATE PROPERTIES (CURE TIME 40 MIN. AT 140°C)

Property (after ageing at 70°C)	Control (2% HCOOH)	Low N-CV (Papain-$NH_2OH.HCl$)
Elongation at break		
7 days	754	713
14 days	754	690
Modulus 100%		
7 days	6·7	6·8
14 days	6·4	7·2
Modulus 300%		
7 days	14·4	15·5
14 days	15·4	17·0

Note :

Compound formulations

		Parts by weight
Natural rubber	..	100·0
Zinc oxide	..	6·0
Stearic acid	..	0·5
MBT	..	0·5
Sulphur	..	3·5

In this study we have concentrated mainly on one possible method of preparation of low nitrogen-CV rubber ; simultaneous treatment of latex with papain and hydroxylamine hydrochloride. The other possibility is the soaking of papain coagulated rubber in hydroxylamine hydrochloride or in any other suitable carbonyl condensing chemical such as hydroxylamine sulphate or semicarbazide hydrochloride. This is outlined in Fig. 3 and the practicability of this method is to be investigated. Semicarbazide is known to produce a rubber with a slightly higher viscosity.

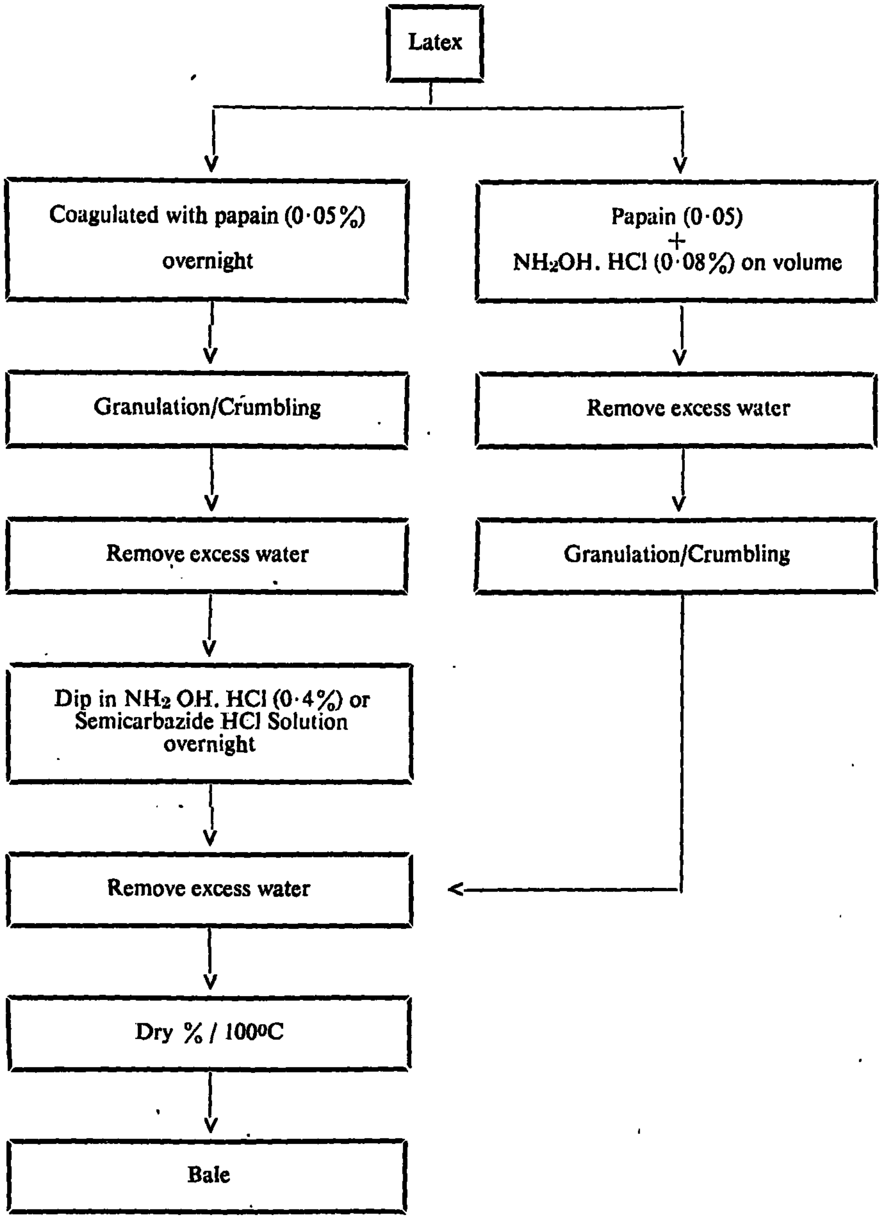

FIG. 3

SCHEME FOR THE PREPARATION OF LOW NITROGEN CV RUBBER FROM LATEX

The results of some preliminary studies carried out with several other commercially available proteolytic enzymes are indicated in Table 8. These enzymes were examined in combination with hydroxylamine hydrochloride, on field latex diluted with water (1 : 1). It is seen that the enzymes investigated have reduced the nitrogen content in the presence of NH_2OH. HCl and that the ability to prevent storage hardening has not been affected by these enzymes. The combined treatment was sufficient to bring about a complete coagulation in the case of BPN, TPN and superase. However, coagulation was found to be incomplete with alcalase and esperase.

TABLE 8

USE OF VARIOUS PROTEOLYTIC ENZYMES WITH NH_2OH. HCl (0·07% ON LATEX)

Enzyme	Initial		After storage hardening test		Nitrogen	Ash
	Po	PRI	Po	PRI	%	%
1. Alcalase 0·1%	32	78·1	37	73·0	0·194	0·210
2. Trypsin 0·1%	33	72·7	38	68·4	0·203	0·115
3. Superase 0·1%	33	72·7	38	68·4	0·187	0·203
4. Esperase 0·1%	32	84·4	37	78·4	0·235	0·189
5. Protease 0·1%	32	78·1	37	73·0	0·167	0·197
6. Papain 0·1%	33	75·8	37	75·7	0·179	0·238
7. Formic acid + NH_2OH. HCl	34	64·7	39	59·0	0·458	0·139
8. Formic acid only (control)	35	65·7	56	48·2	0·462	0·169

Hydroxylamine hydrochloride has been reported to affect the curing properties of rubber (Ong, 1973). Semicarbazide HCl is preferred in certain instances, in this respect; for it has no such adverse effect. However, when hydroxylamine HCl is used with papain a noticeable improvement of curing properties resulted, and it is seen in Table 4 that this improvement remains unchanged even after ageing.

The results reported in this paper show that it is possible to manufacture a low nitrogen-CV rubber. Treatment with proteolytic enzymes reduces the nitrogen content while retaining the viscosity, stabilized by the NH_2OH. HCl treatment. One of the additional advantages of the process is that it needs no coagulant ; with papain, TPN, BPN or superase the enzyme treatment itself is sufficient to bring about a complete coagulation overnight. Reduction in the nitrogen content is usually in the region of 40 — 50%. Further work is in progress with a view to obtaining the CV version of DPNR by a more complete deproteinization.

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