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EFFECT OF STORAGE HARDENING ON THE *PRI* OF CHEMICALLY TREATED RUBBER

By

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Natural rubber hardens on storage resulting in an increase in viscosity, which is caused by cross linking through aldehydic groups present in the rubber molecule (Sekhar, 1953). However, treatment with chemicals which will condense with the aldehyde groups, such as hydroxylamine hydrochloride (NH_2 OH. HCl), suppresses the cross linking reaction to produce rubber with a constant viscosity (Chin, 1968). There is a definite consumer preference for such types of rubber.

Various other chemicals such as phosphoric acid, oxalic acid, pyrogallol and sodium bisulphite have been tested for the improvement of the storage stability of raw rubber. However, very little attention has been paid to the study of the effect of storage hardening on the raw rubber oxidisability (expressed as PRI) of natural rubber treated with chemicals. The observations made during the study of the production of viscosity stabilized rubber from low grades, are reported in this paper.

MATERIALS AND METHODS

Chemical treatments, viscosity determinations and accelerated storage hardening tests were all carried out as described by Karunaratne & Yapa (1969), using field coagula (cup lumps) from a number of selected clones in Dartonfield Group.

RESULTS

PRI of natural rubber is known to diminish on storage under normal conditions and this was found to be true in all the clones examined in this study (Table 1). A significant decrease in PRI after storage hardening was observed in certain instances. Of the clones investigated PB 86 and RRIM 513 showed a drop in PRI of more than 20 units whilst in RRIC 7 and AVROS 427 the reduction was only a few units.

TABLE 1

EFFECT OF STORAGE HARDENING OF SCARP RUBBER ON *PRI*

Clone	PRI	
	Initial	After storage hardening test
RRIC 7	66.6	63.4
RRIC 52	72.7	66.6
PB 86	80.0	55.5
AVROS 427	61.1	57.1
RRIM 513	94.7	58.3

Hydroxylamine hydrochloride

When cup lumps, in granulated form, were soaked in hydroxylamine hydrochloride (0.4%) a significant increase, rather than a decrease in PRI after storage hardening was observed. This improvement was recorded in all 12 clones examined in this investigation (Table 2).

TABLE 2

EFFECT OF SOAKING CUP LUMP IN $NH_2OH.HCl$ (0.4%) ON *PRI* BEFORE AND AFTER STORAGE HARDENING

Clone	PRI	
	Before	After
RRIC 5	50.0	66.6
RRIC 13	50.0	64.8
RRIC 36	57.1	63.8
RRIC 37	50.0	65.0
RRIC 40	50.0	61.9
RRIC 41	51.7	62.0
RRIC 48	19.0	36.3
RRIC 55	50.0	54.1
RRIM 501	58.3	61.5
Wagga 6278	65.5	74.1
Tjir 1	53.8	66.6
MK 3/2	18.1	25.0

Oxalic acid

It has been observed that oxalic acid improves PRI when it is used as a coagulant for latex or as a soaking medium for field coagula (Nadarajah *et al.*, 1967). Several aspects of oxalic acid treatment were examined and the results are shown in Table 3. It is seen that PRI of storage hardened rubber decreases after oxalic acid treatment (see also Table 4). Initial viscosity also shows an increase. Soaking of cuplump in oxalic acid alone yields a product with a high viscosity even prior to storage hardening but when a mixture of hydroxylamine hydrochloride and oxalic acid is used as the soaking medium, only a slight increase in viscosity was evident, before as well as after storage hardening. PRI, after storage hardening shows an improvement with increasing levels of hydroxylamine hydrochloride in the mixture.

TABLE 3

EFFECT OF ADDING OXALIC ACID (1%) TO SOAKING MEDIUM (NH_2 OH.HCl)

	Treatment	PRI		
		Initial	After storage hardening	Increase in plasticity after storage
1	Control	65.5	45.8	19
2	Soaked in NH_2 OH.HCl (0.4%)	72.7	75.0	2
3	Soaked in $H_2C_2O_4$ (1%)	90.0	65.7	16
4	Soaked in NH_2 OH. HCl + $H_2C_2O_4$ (2:1)	78.9	65.2	4
5	Soaked in NH_2 OH. HCl + $H_2C_2O_4$ (1:1)	80.9	75.0	6
6	Soaked in NH_2 OH.HCl + $H_2C_2O_4$ (1:2)	88.2	75.0	7

TABLE 4

EFFECT OF SOAKING OF CUPLUMP IN OXALIC ACID (1%) ON *PRI* BEFORE AND AFTER STORAGE HARDENING

Sample No.	PRI	
	Initial	After storage hardening
1	81.4	71.0
2	87.8	68.7
3	84.6	72.9
4	86.3	75.0
5	77.2	70.0

Sodium bisulphite

Sodium bisulphite also has been reported to improve the PRI when added to latex (Sivabalasundaram & Nadarajah, 1966). Although PRI was improved considerably when cuplumps were soaked in sodium bisulphite solution (Table 5), it dropped sharply after storage hardening. From the results it is seen that the PRI of bisulphite treated rubber is even worse than that of untreated rubber after storage hardening.

TABLE 5

EFFECT OF SOAKING CUPLUMP IN SODIUM BISULPHITE (2%) ON *PRI*

Sample No.	PRI	
	Initial	After storage hardening
1	93.3	67.3
2	100.0	63.6
3	92.8	64.7
4	96.5	62.9
5	107.4	66.0
Control	87.0	72.7

Phosphoric acid

Field coagula treated with low concentrations of phosphoric acid resulted in a slight improvement in PRI whilst higher concentrations have rather adverse effects. However, unlike sodium bisulphite it was interesting to note that nearly all the samples tested showed an relative improvement in PRI after storage hardening even though the improvement was not very significant (Table 6).

TABLE 6

EFFECT OF SOAKING OF CUPLUMP IN PHOSPHORIC ACID (1%) ON *PRI* BEFORE AND AFTER STORAGE HARDENING

Sample No.	PRI	
	Initial	After storage hardening
1	60.0	73.9
2	66.6	71.4
3	81.8	65.5
4	68.4	72.0
5	57.8	68.9
Control	80.0	72.0

Urea

Effect of increasing concentrations of urea on PRI was examined and a reduction in PRI both before and after storage hardening was observed (Table 7). This adverse effect is probably due to the removal of naturally occurring antioxidants by urea, which is well known to increase solubility of proteins.

TABLE 7

EFFECT OF SOAKING CUPLUMP IN UREA SOLUTION OF DIFFERENT CONCENTRATIONS ON *PRI*

% Urea	PRI	
	Initial	After storage hardening
1	79.4	63.4
2	79.4	66.0
3	79.4	64.4
4	77.8	63.4
5	75.0	59.6
6	75.7	60.0
7	62.5	59.6
8	60.6	58.9
9	60.6	54.9
10	51.6	49.0
Control	82.1	67.5

Addition of serum water to soaking medium

Soaking of cuplump in serum water produced rubbers with significantly higher viscosities which almost doubled after storage hardening (Table 8). The effectiveness of hydroxylamine hydrochloride appeared to be completely inhibited when serum water was used in combination with it in the soaking medium. Substantial improvement in PRI after serum water treatment (Table 8) was noticed. However it dropped markedly after storage hardening. In addition serum water treatment inhibited the ability of NH_2 OH. HCl to produce a rubber with an improved PRI after storage hardening.

TABLE 8

EFFECT OF MIXING SERUM WATER AND NH_2 OH.HCl DURING SOAKING ON *PRI*

	Treatment	Plasticity		PRI	
		Initial	After storage hardening	Initial	After storage hardening
1	Control	21	25	68.1	72.0
2	Cuplumps soaked in serum water	32	53	89.2	60.3
3	Cuplumps soaked in NH_2 OH.HCl 0.4%	23	24	68.1	75.0
4	Cuplumps soaked in serum water + NH_2 OH.HCl	33	65	78.9	53.8

DISCUSSION

This investigation deals only with the effect of chemical treatment on the storage hardening of low grades of rubber. It gives useful information on the storage stability of such rubbers. Sodium bisulphite, oxalic and phosphoric acids are all known to improve PRI of natural rubber. On storage, however, the hardening of the rubber seems to be accompanied by a weakening of the induced oxidative resistance. Sodium bisulphite treatment was the worst in this respect, yielding a product the PRI of which becomes even lower than in the case of untreated rubber. The chemical reactions leading to these changes are not known. Both cross-linking and chain scission reactions are known to occur in oxidation of rubber. This is particularly well described in synthetic substances like SBR but it is less likely in the case of NR. However, it is supposed that the loss in PRI in storage hardened rubber is due mainly to the formation of weak crosslinks, sufficient to cause an increase in the initial plasticity when the rubber is aged at 140 °C for 30 min it is believed that these crosslinks disappear, thereby resulting in a low PRI.

CONCLUSION

While bisulphite and oxalic acid treatment reduces the PRI of rubber hydroxylamine hydrochloride and, to a lesser extent, phosphoric acid bring about an increase in PRI after accelerated storage hardening. This finding may be of some importance to the producer whose aim is always to produce a rubber with a high PRI which is not reduced during storage.

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