Effect of treating latex with some metal ions on storage hardening of natural rubber

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Storage hardening of natural rubber is a complex phenomenon involving crosslinking reactions due to certain abnormal groups on the rubber chains. The various mechanisms put forward can each account for certain of the experimental observations. Recently, an ionic crosslinking mechanism involving carboxylate and metal ions was proposed. It is being investigated by treating latex with a series of selected cations. While monovalent cations are found to have no effect on the crosslinking reaction, some divalent cations are able to reduce the storage hardening. Certain transition metal ions catalysed the degradation of natural rubber. Infra-red spectra show that the main chain structure remains the same after the degradation, and the abnormal groups appear unaffected.

(Keywords: storage hardening; aldehyde groups; epoxide groups; ionic crosslink; effects of metal ions; degradation)

INTRODUCTION

The progressive hardening that occurs in natural rubber with prolonged storage under ambient conditions leads to an increase in plasticity number and viscosity[1,2]. Although the technological problems have been overcome[3], the actual mechanism by which this process occurs has yet to be clearly established. There is general agreement that certain abnormal groups probably provide sites for spontaneous crosslinking, but conclusive evidence remains elusive since various aspects of the process are not completely reproducible in experimental measurements. In addition, the proportions of abnormal groups in rubber, amino acids and mineral contents of latex are subjected to clonal and seasonal variations. Different workers have variously implicated aldehyde[4–8], epoxide[9] and carboxylic groups[10–13] as the ones responsible for the crosslinking reactions in dry rubber.

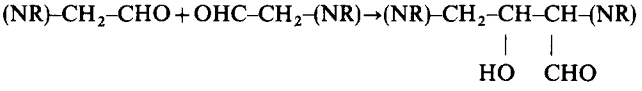
The presence of aldehyde groups was based on the inhibition of storage hardening by certain amines, such as hydroxylamine and semicarbazide[4,5]. The rubber molecules were also supposed to contain 'aldehyde condensing groups' which could react with the rubber aldehydes. The ability of bifunctional amine, such as hydrazine, to promote the hardening reaction was attributed to an azine formation i.e.

$$\begin{aligned}&2(\mathrm{NR})\text{–}\mathrm{CHO}+\mathrm{H_2N\text{–}NH_2}\\&\rightarrow(\mathrm{NR})\text{–}\mathrm{CH{=}N\text{–}N{=}CH}\text{–}(\mathrm{NR})+2\mathrm{H_2O}\end{aligned}\qquad(1)$$

Monofunctional amines could then inhibit crosslinking through the formation of aldoximes.

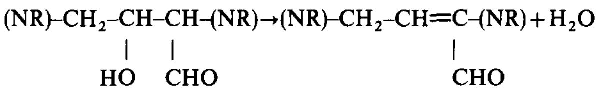
$$(\mathrm{NR})\text{–}\mathrm{CHO}+\mathrm{NH_2\text{–}R}\rightarrow(\mathrm{NR})\text{–}\mathrm{CH{=}N\text{–}R}+\mathrm{H_2O}\qquad(2)$$

To account for the observation that the hardening was accelerated by conditions of low humidities, a bimolecular aldol condensation between rubber aldehyde groups was proposed[6].



$$(\mathrm{NR})\text{–}\mathrm{CH_2\text{–}CHO}+\mathrm{OHC\text{–}CH_2}\text{–}(\mathrm{NR})\rightarrow(\mathrm{NR})\text{–}\mathrm{CH_2}\text{–}\underset{\mathrm{HO}}{\mathrm{CH}}\text{–}\underset{\mathrm{CHO}}{\mathrm{CH}}\text{–}(\mathrm{NR})$$

(3)



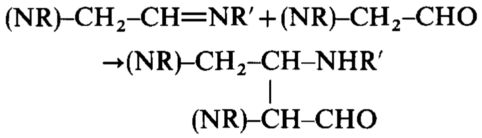
$$(\mathrm{NR})\text{–}\mathrm{CH_2}\text{–}\underset{\mathrm{HO}}{\mathrm{CH}}\text{–}\underset{\mathrm{CHO}}{\mathrm{CH}}\text{–}(\mathrm{NR})\rightarrow(\mathrm{NR})\text{–}\mathrm{CH_2\text{–}CH}{=}\underset{\mathrm{CHO}}{\mathrm{C}}\text{–}(\mathrm{NR})+\mathrm{H_2O}$$

(4)

Gorton[7] has used the same scheme to explain the increase in initial plasticity of rubber isolated from latices stored at high pH.

Gregory and Tan[8] observed that purified rubber from the ultra-centrifuged latex did not undergo storage hardening. When the bottom fraction of centrifuged latex was added back, the hardening increased with the concentration of the fraction up to a limiting value. A similar effect was noted when amino acids were added to the purified latex. Thus, these authors proposed a modified mechanism involving amino acids, i.e.

$$\begin{aligned}&(\mathrm{NR})\text{–}\mathrm{CH_2\text{–}CHO}+\mathrm{R'NH_2}\\&\rightarrow(\mathrm{NR})\text{–}\mathrm{CH_2\text{–}CH{=}NR'}+\mathrm{H_2O}\end{aligned}\qquad(5)$$



$$\begin{aligned}&(\mathrm{NR})\text{–}\mathrm{CH_2\text{–}CH{=}NR'}+(\mathrm{NR})\text{–}\mathrm{CH_2\text{–}CHO}\\&\rightarrow(\mathrm{NR})\text{–}\mathrm{CH_2}\text{–}\underset{(\mathrm{NR})\text{–}\mathrm{CH\text{–}CHO}}{\mathrm{CH}}\text{–}\mathrm{NHR'}\end{aligned}$$

(6)

where $\mathrm{R'NH_2}$ represents the conjugate base of an amino acid. They also speculated that the carboxylate group of the amino acid might participate in the following reaction:

$$(\mathrm{NR})\text{–}\mathrm{CH_2\text{–}CHO}+\mathrm{RCOO^-}\rightleftharpoons(\mathrm{NR})\text{–}\overset{-}{\mathrm{C}}\mathrm{H\text{–}CHO}+\mathrm{RCOOH}\qquad(7)$$

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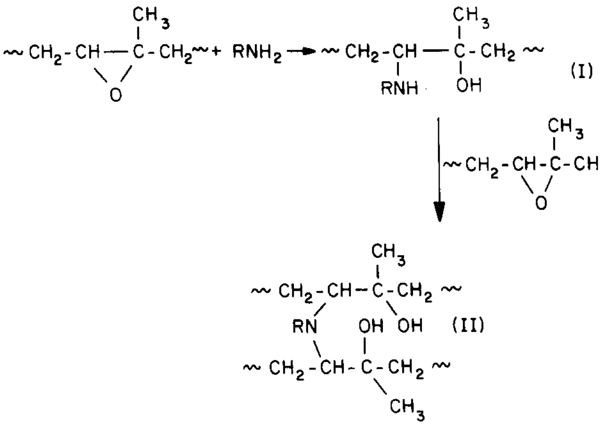
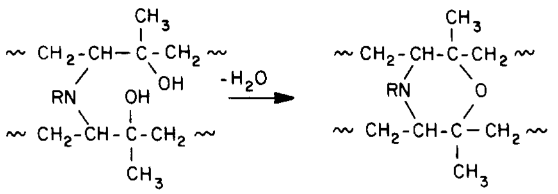
However, this scheme cannot adequately accommodate all their observations since a cyclic amino acid, proline, could accelerate storage hardening but could not be involved in imine formation as required by equation (5).

The presence of epoxide groups in natural rubber was deduced from the degradation of acid-hydrolysed rubber with $Pb(OAc)_4$ (see refs 9 and 10), and later confirmed by n.m.r. (see ref. 14). Epoxide groups can be ring-opened by naturally occurring amino compounds in latex. The resulting structure (I) can form crosslink structure (II) in subsequent reaction with another epoxide group.



(8)

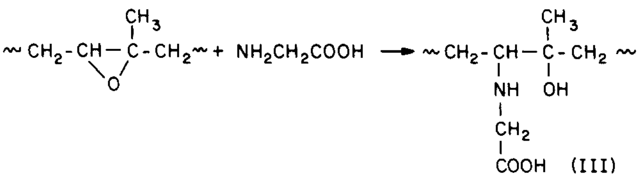
Dehydration under low humidity conditions in dry rubber is represented as follows:



(9)

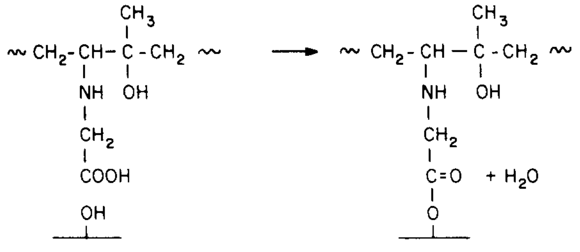
An apparent weakness of the proposal was the low reactivity of rubber epoxide in dry epoxidized rubber towards amino compounds[15–17]. Subramaniam and Wong[18] reconfirmed that the epoxide groups in epoxidized natural rubber did not enhance storage hardening. However, reactions of model compounds have demonstrated that water or β-substituted hydroxyl groups[16,17] could promote the ring-opening reactions to occur smoothly at ambient temperatures. Since reaction (9) does not increase the number of crosslinks, the mechanism cannot explain how hardening increases by the removal of water.

A revised mechanism was put forward[11,12] in order to take into account the accelerating effect of low humidity conditions and the involvement of amino acids. It was suggested that epoxide groups were ring opened by amino acids at the latex stage to give a functionalized rubber with short carboxylic side-chains, such as (III).



(10)

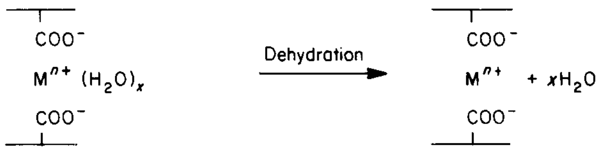
Crosslinks could subsequently form under low humidity conditions by a condensation reaction such as (11)



(11)

Evidence for reaction (10) was provided by radio-tracer studies which showed that labelled glycine added to fresh latices was incorporated into the rubber at levels close to the epoxy contents[12]. Moreover, model tri-substituted epoxides, similar to rubber epoxide, react readily with amino acids in the presence of water[16]. It is conceivable that different crosslinking processes occur under the two entirely different conditions, as in latex and dry rubber.

In a recent publication, it was proposed that the carboxylic groups in rubber, such as structure (III), could react with metal ions to form ionic crosslinks[19] and be responsible for storage hardening since the tensile strength of CaO crosslinked carboxylated rubbers increases under conditions of low humidity[20]. The formation of ionic crosslinks could be envisaged with links bridged by metal cations, as represented below:



Hydration of the ions reduces the strength of the link while drying of the rubber intensifies the ionic interactions and hence increases the hardness.

In this paper, further experiments are described to investigate the hardening behaviour of the rubber when fresh field latex is treated with a number of selected metal ions.

EXPERIMENTAL

Materials

To minimize the clonal variation in properties of the natural rubber, fresh field latex of the RRIM600 clone was collected from four selected trees and used immediately. All other chemicals were used as commercially supplied.

Reactions of rubber latex with additives

First, 30 ml of latex was diluted to 60 ml with distilled water. The pH of the solution was adjusted to 8.1 by the addition of 0.5 M NaOH. Next, 0.012 mol of metal salt in aqueous solution was added, and the final volume was made up to 300 ml with distilled water. The pH was again adjusted to 8.1 to prevent coagulation. The reaction mixture was then kept in an oven at 40±2°C for 24 h unless stated otherwise. The mixture was centrifuged at 11 400 rpm for 15 min, and the cream fraction precipitated into 150 ml methanol. The coagulum was then washed and pressed into thin sheet, soaked in distilled water for 2 h before being dried under vacuum at room temperature for 48 h.

Plasticity measurements

The dry rubber was milled on a two-roll laboratory mill to a final thickness of 1.6–1.8 mm, folded and pressed together before pellets were cut by using a Wallace Puncher. Each pellet is a disc of rubber of thickness 3.2–3.6 mm and approximately 13 mm in diameter. Eight pellets were prepared from each sheet of the sample. A Wallace Plastimeter was used for plasticity measurements. Four of the pellets were used to determine the initial plasticity, P_o, while the other four were used for the 'hardened plasticity', P_H, after subjecting the pellets to an Accelerated Storage Hardening Test (a.s.h.t.) as described in the standard procedure[21], except that molecular sieves were used as a replacement desiccant[22]. Each set of four pellets for a.s.h.t. was kept over a fixed amount of desiccant in a quick-fit glass container and left in an oven, which was set at 60°C, for 24 h. The treatment could attain an increase in plasticity which would otherwise require many months of storage to achieve under ambient conditions. The average of the measurements on each set of four pellets was reported, generally with a deviation of less than ± 2 units.

Preparation of purified latex

Fresh latex was stabilized with 1% w/w Vulcastab LW, a polyethylene oxide–fatty alcohol condensate, a non-ionic surfactant from ICI, and then centrifuged at 11 400 rpm for 15 min. The cream fraction was redispersed in distilled water containing 1% w/w Vulcastab LW. This procedure was repeated twice. At the third centrifugation, the cream was dispersed in distilled water and diluted to the original volume before using it the same way as unpurified latex in the various experiments.

Nitrogen content analysis, viscosity, and infra-red measurements

Nitrogen content in rubber was analysed by a semi-micro Kjeldahl procedure as described in the RRIM test method[21]. The rubber was oxidized by heating with a catalyst mixture and concentrated sulfuric acid, thereby converting nitrogen compounds into ammonium hydrogen sulfate. Strong alkali was then added, and ammonia was removed by steam distillation. The liberated ammonia was absorbed in boric acid solution and titrated with a standard acid. Viscosity measurements were carried out as described elsewhere[10]. Films of rubbers were cast on sodium chloride cells, and the infra-red spectra recorded on a Beckmann Acculab 4 infra-red spectrophotometer in the 600 cm^{-1} to 4000 cm^{-1} region.

RESULTS AND DISCUSSION

One problem of working with fresh latex is that its properties are subject to clonal and seasonal variations. While the former can be overcome by selecting a fixed number of trees of the same clone to obtain the requisite amount of latex per tapping, the latter is quite beyond control when fresh latex is collected, as required, in a different period. Thus, for each new series of experiments, a control measurement is made on P_o and P_H (and in certain cases %N), and the changes brought about by various treatments are then compared with the control to determine the relative magnitude of reaction in the same series. The different control values, which are normally fairly close to each other, serve to demonstrate the seasonal variation of the latex during the six month period taken by this project.

Fresh latex contains metal ions[23], and in the process of coagulation some of them might be retained in the rubber. Removal of these ions by dialysis is reported to have reduced hardening of rubber[19]. However, the result is not conclusive since amino acids which have also been implicated in the storage hardening could also be removed by dialysis[24].

Divalent cations required for ionic crosslinks can come from latex which contains Mg^{2+} (0.01–0.12%) and Ca^{2+} (0.001–0.03%) — see ref. 23. Addition of these cations in excess should have a disrupting effect. The results of adding Mg^{2+}, Ca^{2+} and Ba^{2+} at 0.04 M in diluted latex are summarized in *Table 1*. Although the initial pH was adjusted to 8.1, degradation of proteinous materials has occurred over 24 hours resulting in a drop of pH to around 5.5. In comparison with the control sample, Ba^{2+} has reduced the extent of storage hardening by about 50% while Mg^{2+} and Ca^{2+} ions have reduced storage hardening by 75%. The decreases in nitrogen content of the rubber seem to indicate that these cations are affecting the incorporation of protein or amino acids into the rubber chains.

Latex also contains K^+ and Na^+ which are incapable of ionic crosslinking. Thus, Li^+, K^+ and Na^+ were then added into latex before the rubber was isolated. The results, summarized in *Table 2*, show that storage hardening of the final rubber was not reduced. The nitrogen content of the final rubber was also not significantly affected. The finding is contradictory to the postulate of the ionic crosslinking mechanism[19] since the formation of –COOK or –COONa is expected to inhibit the hardening. The results of treating latex, collected on a different day, with CsCl also show that Cs^+ does not inhibit storage hardening.

We have decided to investigate the effect of the Mg^{2+} ion in greater detail since Mg^{2+} is present in a greater amount than Ca^{2+} in the latex. *Table 3* summarizes the effect of reacting latex with Mg^{2+} for different time

Table 1 Effect of Mg^{2+}, Ca^{2+} and Ba^{2+} on storage hardening of natural rubber

Metal salt added	Final pH	P_o	P_H	ΔP	%N[a]
Control (none)	5.5	30	90	60	0.32
$MgCl_2.6H_2O$	5.8	31	46	15	0.24
$CaCl_2$	5.7	32	46	13	0.18
$BaCl_2.2H_2O$	5.7	31	70	39	0.24

Latex diluted tenfold; [metal ion] = 0.04 M; temperature 40°C, reaction time = 24 h; $\Delta P = P_H - P_o$

[a] Nitrogen content of final rubber

Table 2 Effect of some monovalent cations on storage hardening of natural rubber

Metal salt added	Final pH	P_o	P_H	ΔP	%N[a]
Control	5.3	30	90	60	0.37
$LiNO_3.3H_2O$	5.6	31	85	54	0.38
$NaNO_3$	5.7	29	86	57	0.34
KNO_3	5.8	28	86	58	0.34
CsCl[a]	5.4	25	86	61	0.29

[a] Using fresh field latex collected on a different day

Table 3 Effect of $MgCl_2.6H_2O$ on storage hardening of natural rubber at different reaction time intervals

Reaction time (h)	Final pH	P_o	P_H	ΔP
0	5.5	29	81	52
6	5.5	32	75	43
8	5.5	31	77	46
24	5.3	28	39	11
30	4.8	29	40	11
48	4.6	27	40	12

Table 4 Effect of reacting Mg^{2+} with latex at different initial pH on storage hardening of natural rubber

Initial pH	Final pH	P_o	P_H	ΔP
6.4[a]	5.1	28	73	45
5.2	4.8	29	58	29
6.3	4.9	29	53	24
7.0	4.9	30	46	16
8.1	5.1	28	40	12
9.1	5.7	32	44	12
10.0	9.5	33	44	11
11.0	10.4	40	50	10

[a] Control, latex without Mg^{2+}

Table 5 Effect of bactericide

Sample	Final pH	P_o	P_H	ΔP	%N
Control	5.5	30	94	64	0.36
A	6.1	27	81	54	0.32
B	5.7	29	41	12	0.28

A: treated with 0.35 g dm^{-3} pentachlorophenol
B: treated with 0.35 g dm^{-3} pentachlorophenol, and 0.04 M $MgCl_2.6H_2O$

Table 6 Effect of different anions

Metal salt added	Final pH	P_o	P_H	ΔP	%N
Control	6.1	27	55	28	0.38
$MgCl_2.6H_2O$	5.8	32	46	14	0.30
MgF_2	5.9	27	35	8	0.33
$Mg(NO_3)_2.6H_2O$	5.9	35	40	5	0.28
$MgSO_4.7H_2O$	5.8	26	36	10	0.33

intervals. The reduction in storage hardening increases with reaction times. Incidentally, the maximum reduction of storage hardening is achieved after 24 hours, which is similar to the reaction time required for optimum radioactive glycine incorporation[25]. The reduction in hardening by excess Mg salt has been attributed to the 'swamping effect' on $-COO^-$ groups[19]. However, in the case of carboxyl-terminated liquid rubbers, hardening is reported to increase with the ratio of metal/COOH, and no 'swamping effect' was observed even when the Ca^{2+} or Mg^{2+} ion is in tenfold excess over the $-COOH$ group[20]. Most probably, the reaction of amino acids with the abnormal groups in the rubber chains is retarded by the presence of Mg^{2+}, as shown in *Table 1* by the drop in nitrogen content, and consequently hardening is reduced when less amino acid is incorporated into the rubber chains.

The reaction between rubber and amino acids is found to be pH sensitive[12], with the optimum conditions around pH 8.1. The reaction of a Mg^{2+} ion with latex was carried out at a different initial pH by the same procedures as described earlier. Results in *Table 4* show that Mg^{2+} ions achieve the maximum inhibition of storage hardening at pH above 8.

The drop in pH at the end of 24 hours of the reaction indicated that acidic components were formed probably through hydrolysis or through bacterial degradation of the proteinous materials of the latex. Pentachlorophenol, a known bactericide, was added to the fresh latex. The plasticity and nitrogen content of the rubbers were determined. Results in *Table 5* demonstrate that the bactericide has no effect on storage hardening. The reduction of P_H and %N can be completely attributed to the presence of Mg^{2+}. Similarly, it has been reported[24] that bacteria do not affect the incorporation of radioactive glycine and ethanolamine on rubber particles. Thus, the slight drop in pH is due to the hydrolysis of proteinous materials and saponifiable lipids of the latex particles since all bacterial activity is expected to be stopped by the added pentachlorophenol.

Up to 12 anions in significant concentrations have been identified in latex[26]. To investigate whether different anions might affect the reaction of Mg^{2+} with latex, water-soluble magnesium salts with different anions were used. The anions were arbitrarily chosen to reflect the variation in sizes and electronegativity. Results in *Table 6* show that there is no clear trend due to the different anions. The P_o and P_H values of the control are significantly different from those of others (such as in *Tables 1, 5* and *7*) due to seasonal variation of the latex, *vide supra*.

In general, when a solution of metal ions is added to the latex under alkaline conditions, direct interaction with the stabilizing carboxylate ions may occur with the formation of metallic soaps.

$$M^{n+} + nRCOO^- \rightarrow (RCOO^-)_n M \quad (12)$$

An insoluble metal hydroxide may also be precipitated in the aqueous phase, and removal of OH^- will cause the pH to drop:

$$M^{n+} + nOH^- \rightarrow M(OH)_n \quad (13)$$

Both these reactions can cause destabilization of the latex, first through collapse of the electrical double layer which surrounds the latex particles, and secondly through the adsorption of latex stabilizers on the precipitated hydroxide. To prevent coagulation of rubber as the metal ion was added, the pH of the mixture had to be readjusted to 8.1.

Since many transition metal ions can form chelating complexes with carboxylate groups, they could be involved in ionic crosslinks, although it is well known that in the case of natural rubber, many of them are strong pro-oxidants[27,28]. The effect of some of these ions are investigated and the results summarized in *Table 7*.

The multivalent hydrolysable cations tend to adsorb on the latex particles more strongly than simple divalent cations and, depending on the concentration, this absorption may lead to a neutralization of charge and eventually to charge reversal[29]. These polynuclear hydrolysable ionic species do not displace the proteinous compounds and might even induce higher absorption of proteinous materials and amino acids onto rubber particles. Thus, rubber isolated from latex treated with Co^{2+}, Cu^{2+} or Fe^{2+} appears to have a higher nitrogen content than that of the control sample. The fact that P_H

Table 7 Effect of treating latex with some transition metal salts on storage hardening of resulting rubber

Metal salt added	P_0	P_H	ΔP	[η]	%N
Control	28	89	61	6.10	0.33
$AgNO_3$	41	62	22	5.22	0.43
$NiCl_2.6H_2O$	45	49	3	3.70	0.39
$FeSO_4.7H_2O$	40	3	−37	1.18	0.39
$MnSO_4.H_2O$	25	2	−23	1.02	0.30
$CuSO_4.5H_2O$	31	1	−30	0.66	0.46
$CoSO_4.7H_2O$	46	1	−45	0.51	0.40

Table 8 Effect of Co^{2+} ions on purified latex

Purified latex treated with	P_0	P_H	ΔP	%N
–	22	28	6	0.07
$CoSO_4.7H_2O$ (0.04 M)	27	2	−25	0.07

of the rubber decreases drastically implies that these metal ions have catalysed the degradation reaction to become the predominant reaction. These ions normally exhibit two or more valency states, and can react with hydroperoxides to produce free radicals.

$$ROOH + M^{n+} \rightarrow RO^{\bullet} + {}^{-}OH + M^{(n+1)+} \quad (14)$$

$$ROOH + M^{(n+1)+} \rightarrow ROO^{\bullet} + H^{+} + M^{n+} \quad (15)$$

The overall reaction is equivalent to the bimolecular decomposition of hydroperoxides:

$$2\,ROOH \rightarrow RO^{\bullet} + ROO^{\bullet} + H_2O \quad (16)$$

Osawa *et al.*[30] have investigated the oxidation of polypropylene catalysed by metallic salts. The order of decreasing catalytic effect, assessed from oxygen absorption curves and activation energies, was Co > Mn > Cr > Fe > V > Ni > Ti > Al > Mg > Ba. In our investigation, as represented in *Table 7*, the order of decreasing catalytic activity toward degradation of natural rubber, assessed from the intrinsic viscosity, [η], of the rubber after the a.s.h.t. is Co > Cu > Mn > Fe > Ni > Ag. Although Ag is directly below Cu in the periodic table, its ion exhibits only one stable oxidation state. However, Ag^+ has been known to be a mild oxidizing agent or catalyst for certain oxidation reactions, such as in the well known silver mirror test for aldehyde and the catalysed oxidation of Cr^{3+} to Cr^{6+} by potassium persulfate.

Fresh field latex was purified to remove most of the proteinous compounds and free amino acids. It was then treated with cobalt salt. The results are summarized in *Table 8*. Obviously, the purification process could not remove the nitrogenous component already attached to the rubber molecule prior to the latex leaving the tree as reflected by 0.07% N in the rubber. Recently *FT*i.r. studies on purified Hevea rubber showed that residual amino acids were bonded to the rubber molecule[31]. Thus, a very small increase in plasticity is observed in the control purified rubber since uncatalysed degradation is very slow under the conditions of a.s.h.t. A serious degradation catalysed by cobalt ion is again clearly demonstrated.

During the storage of dry rubber, the crosslinking reactions are assumed to involve some abnormal groups such as –COOH, –OH, and –NHR, while degradation is attributed to radical reactions on the main chain of the rubber molecule. As the transition metal ions catalysed the degradation, we have no idea whether the abnormal groups were affected. With this in mind, i.r. measurements were recorded. *Figure 1* shows the overlaid spectra of rubbers from (A) unpurified latex, (B) unpurified latex treated with Co^{2+}, (C) purified latex, and (D) purified latex treated with Co^{2+}, all after a.s.h.t. The spectrum of (C) is consistent with a fairly pure hydrocarbon structure of *cis*-1,4-polyisoprene, the unpurified rubber (A) exhibits many extra minor peaks such as around 3280 cm^{-1} due to N–H or O–H stretching, and 1540–1630 cm^{-1} due to amide –N–H bending vibrations, and a larger peak at 1710–1740 cm^{-1} due to C=O stretching. The i.r. spectrum of degraded rubber (B) is remarkably similar to (A), while (D) is similar to (C). This indicates that the main characteristics of the rubber structure were not altered by the oxidative degradation. The presence of the amide and carbonyl peaks in the degraded samples are indicative that the nitrogenous and carboxylate groups on the rubber chains are not affected by the degradation catalysed by Co^{2+}.

CONCLUSIONS

The present investigations have shown that treating latex with different metal ions may produce different effects on the storage hardening of natural rubber. The soaps and hydroxides of the monovalent metals are readily soluble and ionized in water, causing minimal disturbance to the surfaces of the rubber particles. Thus, monovalent ions such as Li^+, Na^+, K^+ and Cs^+ do not affect the incorporation of nitrogenous groups into the rubber chain and consequently do not inhibit crosslinking. The results also cast some doubt over the ionic crosslinking mechanism. In the case of divalent cations, such as Ba^{2+}, Ca^{2+} and Mg^{2+}, the overall results seem to suggest that they slowly displace the proteinous materials and amino acids from the latex particles, leading to less amino acid being incorporated onto rubber, as reflected by the lower nitrogen content, and consequently reduce the extent of storage hardening. On the other hand, transition metal ions such as Co^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+} and Ag^+ promote oxidative degradation to such an extent that

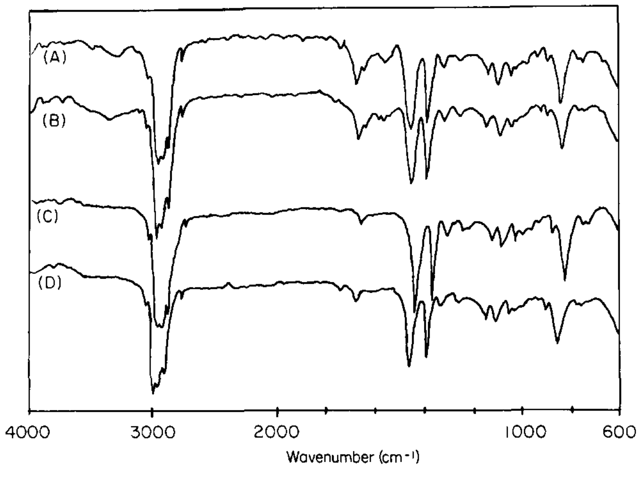


Figure 1 Infra-red spectra of rubbers from (A) unpurified latex; (B) unpurified latex treated with Co^{2+}; (C) purified latex; and (D) purified latex treated with Co^{2+}, all after being subjected to 'accelerated storage hardening test' conditions

the chain scission become the predominant reaction during the storage of dry rubber,.

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