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B. C. SEKHAR

The Rubber Research Institute of Malaya, Kuala Lumpur

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Chemistry and Technology of Dry Rubber 1

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Evidence is presented in further support of the hypothesis that aldehydic groups are present as an integral part of the polyisoprene chain when it leaves the tree in the form of latex. These are the groups that are mainly concerned in the gelation of rubber on dry storage. A simple method of estimating the number of aldehydic groups per molecule of rubber is described. Results of a survey of the aldehydic group contents and the extent of hardening on accelerated storage of clonal rubber are reported.

It is well known that the polyisoprene of *Hevea* latex undergoes considerable changes after its emergence from the tree. These changes take the form of chain scission or cross-linking depending on the conditions obtaining (see all References). In the solid state the predominant reaction that takes place on storage of rubber is one of cross-linking as indicated by the increase in Mooney viscosity, Williams plasticity and gel content (MESSENGER, 1933; WOOD, 1952). The plasticity of solid rubber changes continuously from the time it is prepared to the time it is used by the consuming industry. Considerable work has been carried out in the past to study this reaction (MESSENGER, 1933; WOOD, 1952; SEKHAR, 1958) with a view to controlling or inhibiting it. WOOD (1952) suggested that peroxidic or other free radical forming groups in the rubber may be responsible for the gelation of rubber on storage but gave no indication whether these groups were present in rubber as it leaves the tree or were formed subsequently. In a recent paper (SEKHAR, 1960), it was shown by the writer that reactive groups are present in the rubber molecule as it leaves the tree. These reactive groups have the characteristic property of carbonyl groups or more specifically aldehyde groups. Condensation of these groups with other groups on the rubber hydrocarbon molecule e.g. α-methyl or methylene groups, may be responsible for cross-linking of the polymer molecules. In support of this hypothesis, it was shown that reactive mono-functional amines or other carbonyl reagents are capable of inhibiting this cross-linking effectively, and that bifunctional amines can bring about cross-linking. The present investigation is an extension of this work and includes an examination of the effect of excess bifunctional amines, observations on the influence of formaldehyde in de-activating the naturally occurring amines in latex and a study of the reaction between hydroxylamine and a number of rubbers from different clones.

EXPERIMENTAL METHODS

Storage Hardening Test (Accelerated Storage Test)

This test consists in heating a 50 g sample of the rubber for 48 hours at 140°F over P_2O_5 in a vacuum. The difference in Mooney viscosity before and after treatment is a measure of the hardening which will occur on normal storage.

Mooney Viscosity: The standard test using the small rotor has been employed throughout.

Intrinsic Viscosity: The method used is as described by FREEMAN (1954). All reagent additions have been made as aqueous solutions to freshly collected latices.

RESULTS AND DISCUSSION

Effect of Increasing Concentration of Diamines

Certain aromatic and aliphatic diamines have been shown to cause cross-linking (PHILPOTT, 1947; SEKHAR, 1960) of rubber when added to latex. This was explained as due to condensation of carbonyl groups with each of the amine groups in the diamine molecule in a two-stage process. In the first stage one amino group of the diamine molecule condenses with a carbonyl group and then in the second stage the second amino group condenses with another carbonyl group. If the two carbonyl groups reacting belong to the same rubber molecule intra-molecular cross-linking results, but if they are from different rubber molecules, inter-molecular cross-linking results.

In the presence of an excess of reactive diamines, the condensation reaction should not go further than the first stage, i.e. condensation of carbonyl groups with one amine group of the diamines, as there will be sufficient diamine molecules present to react with every carbonyl group. Thus if an excess of diamines is added to rubber latex, the carbonyl groups should combine with separate diamine molecules and none remain active to cross-link and cause storage hardening. The effect of increasing concentrations of diamino ethane and diamino hexane on the storage hardening property of rubber is shown in *Figure 1*. At higher concentrations of diamine, no cross-linking of rubber takes place initially and further cross-linking on accelerated storage is inhibited contrary to the effect at low concentrations of the diamine.

Effect of Formaldehyde on Storage Hardening of Rubber

Formaldehyde has been used to de-activate the reduction activator (MORRIS AND SEKHAR, 1959) present in natural rubber latex. It has been well established that hydroperoxidised latex becomes cross-linked in the presence of such reduction activators. Since hydroperoxidation of latex can take place on storage or agitation in air (SEKHAR, 1958), it is possible that such groups may be partly responsible for the cross-linking on storage. To investigate this, samples of fresh latex were treated with increasing concentrations of formaldehyde 24 hours prior to filming and storage hardening tests. Results are presented in *Figure 2* in which the increase in hardness on accelerated storage expressed as per cent of the unhardened value is plotted against formaldehyde concentration.

Part of the cross-linking can be inhibited by treatment with formaldehyde and may be due to inactivation of reduction activators naturally present in latex. Since only part of the storage hardening can be inhibited by formaldehyde it appears likely that a substantial part of the cross-linking is due to carbonyl groups in the polymer.

Storage Hardening of Clonal Rubbers

Natural rubber is known to be variable both in initial hardness and the extent to which the hardness changes on storage. A survey was therefore carried out to determine the magnitude of these variations in clonal rubbers. Samples of latex from different clones were collected and the rubber derived from them tested for Mooney viscosity before and after accelerated storage. Results of this survey are given in *Table 1*.

There is a wide distribution in initial hardness and the extent to which the Mooney viscosity increases on storage is also variable. The variation in initial hardness of these rubbers may be due to many factors, among which, average molecular weight, micro-gel and gel contents, and non-rubber constituents, are important. Since the increase in hardness on storage has been postulated as being due to the presence of carbonyl groups in rubber, the variation in the extent of increase should also be at least partly due to variation in the average number of carbonyl groups present per polymer molecule. Any hydroperoxidation of rubber that may take place will also contribute to this variation.

Carbonyl Group Contents of Clonal Rubbers

The average number of carbonyl groups present per molecule of rubber can be estimated by determining the optimum or critical concentration of a monofunctional carbonyl reagent required to inhibit effectively the cross-linking of rubber on storage. Two suitable reagents for this purpose are hydroxylamine and dimedone (5,5 dimethyl cyclohexane 1, 3 dione. Since one hydroxylamine or 2 dimedone molecules condense with one carbonyl group, the critical concentrations of these two reagents should be in the ratio of 33 : 280 (1 mol : 2 mols) for any one sample of rubber.

Latex from different clones was collected from the R.R.I.M. Experiment Station and the critical concentration of carbonyl reagent required to inhibit hardening determined. This was carried out by treating different portions of the same latex with increasing concentrations of the reagent and testing resulting films for Mooney viscosity before and after storage hardening. A plot of the final Mooney viscosity against concentration of reagent gives an inflection point at the critical concentration as in *Figure 3*. In three cases both dimedone and hydroxylamine were used to determine the carbonyl group contents for confirmation.

The intrinsic viscosities of the rubber were also determined initially. This was carried out by latex solution in benzene method (FREEMAN, 1954). *Table 2* gives the results obtained on a number of clonal latices.

The values obtained for the average number of carbonyl group per rubber molecule estimated from the dimedone results agree very satisfactorily with those obtained using hydroxylamine. The average number of groups per polymer molecule varies from 9 to 29. Such a distribution in the number of groups can reasonably explain the variation in extent of changes in hardness obtained on storage. In *Figure 4*, the Mooney viscosity increase on accelerated storage is plotted against average carbonyl group contents for these rubbers. Although a straight line relationship was not obtained, it is clear from the figure that a strong correlation exists between the number of carbonyl groups and increase in hardness on storage. A linear relationship is not to be expected, since the net effect of cross-links on the hardness will depend not only on the number of cross-links, but also on the molecular weight and molecular weight distribution of the rubber. It should also be remembered that some hardening arises from cross-linking due to hydroperoxidation of the rubber through interaction with oxygen.

Thus the results presented in this paper are consistent with the hypothesis that reactive groups possessing characteristics of aldehyde groups are present as an integral part of the natural rubber molecule and that these groups are responsible for causing changes in the plasticity of dry rubber on storage.

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DISCUSSION

THE CHAIRMAN commented that two important points were brought out in this paper, namely the explanation for storage hardening of rubber, and the control of this hardening. The findings recorded implied that natural rubber hydrocarbon may not be a simple polymer but may have other groups.

MR DRAKE inquired about the cost of the treatment for inhibiting hardening. **MR SEKHAR** considered that, with the most effective reagents, it would be about 1 cent per lb of rubber.

MR PIDFORD asked whether the reverse application of this discovery was possible, that was, to select latices from clones that gave specially hard rubbers. This would be useful in choosing material for the manufacture of sole crepe. **MR SEKHAR** replied that these inhibiting agents might cause discolouration. Further, he could not guarantee that a particular clone would always give the same degree of hardening. This would depend on other factors, like soil, tapping methods and time of the year; a more extensive survey taking these into account would be needed before a definite answer could be given.

PROFESSOR BONNER referred to Mr Sekhar's work as an elegant contribution to the knowledge of rubber, capable of widespread ramifications. Clear evidence had been given of the presence in rubber of branch groups containing carbonyl groups, and it would be interesting to speculate on their method of origin and location in the molecule. **MR SEKHAR** said that all he could be sure about in this respect was that these groups were formed along the chains and not at the ends, because of the large amount of gel produced. Perhaps, in the light of Professor Bonner's remarks during the lecture that morning, specific enzymes could contribute to the production of these carbonyl groups after the synthesis of rubber. **PROFESSOR BONNER** confirmed that they were possibly formed after the synthesis of the rubber molecule and that they must be on side chains. He could envisage the shift of double bonds to give angular methylene groups which could be converted to carbonyl groups by oxidation and speculated on the possibility of the artificial introduction of more of these groups, to produce further cross-linking deliberately.

Dr Resing wanted to know how the gel formation on storage of latex in the presence of ammonia could be explained. **Mr Sekhar** thought that this was due to hydroperoxidation and not to carbonyl groups, the latter being responsible only for cross-linking on dry storage. He was of the opinion that ammonia would stabilise the carbonyl groups, precluding the possibility of cross-linking. Preliminary tests showed that there was no difference in carbonyl group content of the latex after a specified period of storage. Hence these were two separate mechanisms. The author had reason to believe that carbonyl groups were, however, responsible for the formation of micro-gel in newly tapped and untapped trees.

Dr Resing also asked the author whether he could discuss the influence of long-chain fatty acid amines which, when added to latex before coagulation, produced an increase in Mooney viscosity. **Mr Sekhar** replied that although these reactions were observed he had no real mechanism to propose; but one would expect these amines to affect hydroperoxidic groups in rubber latex.

Dr Cockbain had two questions. First, had the author carried out storage hardening experiments with purified rubbers, and if so, how did his results compare with normal unpurified rubbers? Second, was consideration given to the detection of carbonyl groups in purified rubbers by infra-red analysis? Answering the first question, **Mr Sekhar** mentioned that Wood had, in work done much earlier, shown that both purified and normal rubbers hardened to the same extent. He had himself confirmed these results. He had also thought of infra-red analysis, but doubted whether a straight-forward spectroscopic analysis would detect the few carbonyl groups present. A hydrazine compound might do it.

In a question which was recorded but which was not asked in the open discussion, **Mr Krishnaswamy** enquired whether formaldehyde or hydroxylamine added to ammoniated latex showed any evidence of causing storage hardening. **Mr Sekhar** commented that the results which he quoted were applicable to both fresh and freshly ammoniated latex. Formaldehyde would, of course, react with ammonia and make no contribution in the hardening reaction.

TABLE 1. EXTENT OF HARDENING OF CREPES FROM CLONAL RUBBERS ON ACCELERATED STORAGE

Clone	Mooney Viscosity (Small rotor)	
	Before accelerated storage	After accelerated storage
AVROS 152	40	59
Pil A44	53	68
PB 23	45	66
PB 186	36	56
AVROS 256	48	79
Tjir 1	56	68
Gl 1	41	61
BD 5	55	70
Pil B84	47	66
SR 9	42	68
PB 86	53	70
Rub 393	41	62
Sab 24	44	67
War 4	53	68
RRIM 501	23	44
Ulu Klang bulk latex	33	73

TABLE 2. CARBONYL GROUP CONTENTS OF CLONAL RUBBERS

CLONE	Molecular wt $\times 10^6$ from intrinsic viscosity $(\eta: 5.06 \times M^{0.67})$	% conc of NH_2OH. HCl at inflection point*	No. of carbonyl groups per molecule of rubber*
AVROS 157	0.7079	0.10	10
PB 23	1.023	0.12 (0.52)	18 (19)
Pil A44	1.00	0.10	15
Tjir 1	1.047	0.08	12
AVROS 152	0.8913	0.12	16
RRIM 501	0.7762	0.16 (0.64)	18 (18)
Gl 1	0.8511	0.16	20
War 4	0.8913	0.07	9
SR 9	0.8913	0.10	13
Rub 393	0.9550	0.12	17
PB 186	0.9772	0.10 (0.44)	14 (15)
Sab 24	1.047	0.10	15
AVROS 256	1.072	0.08	12
Ulu Klang bulk latex	1.148	0.17	29

*Values given in brackets are those obtained using dimedone as the carbonyl reagent.

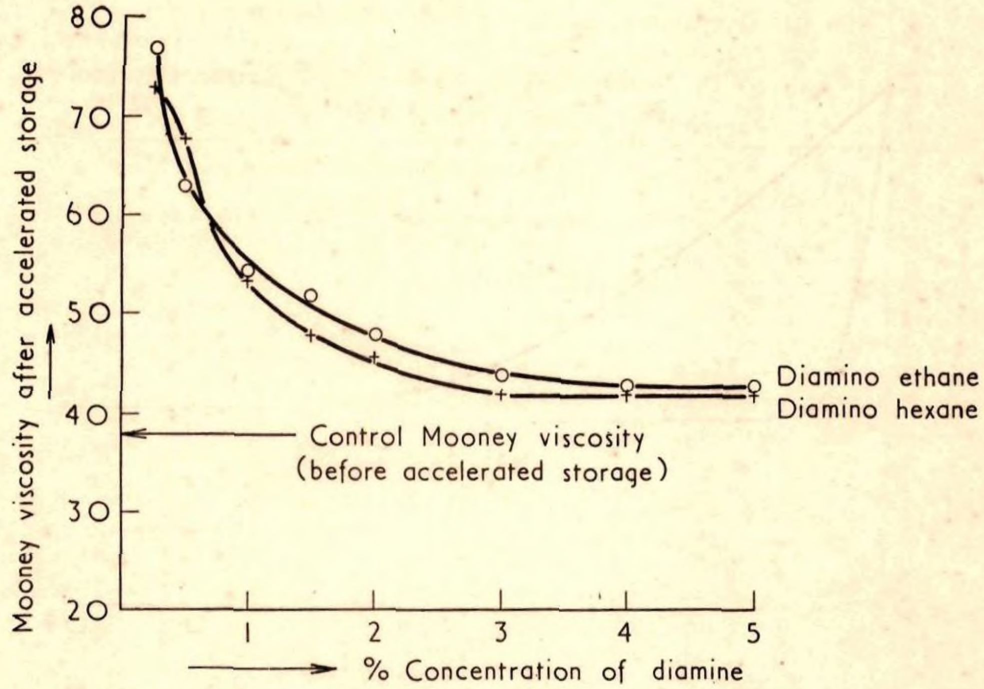

Figure 1. Effect of increasing diamine concentration on storage hardening. The concentration of diamine is based (w/w) on rubber contents and was added as an aqueous solution.

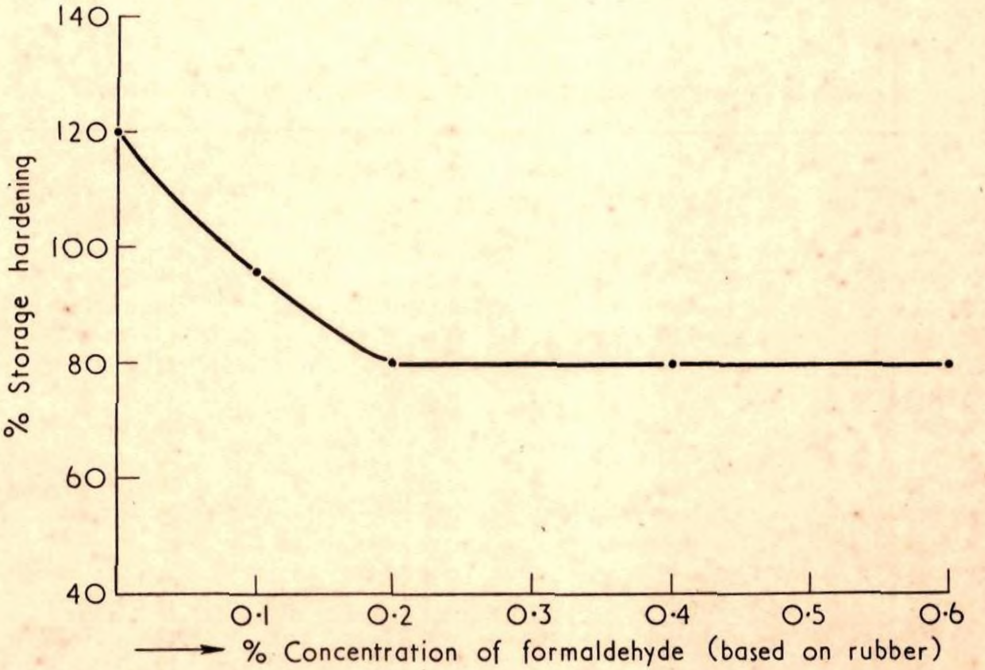

Figure 2. Effect of formaldehyde on storage hardening. The formaldehyde was added as a 10% neutralised aqueous solution. The concentration is based on (w/w) rubber contents.

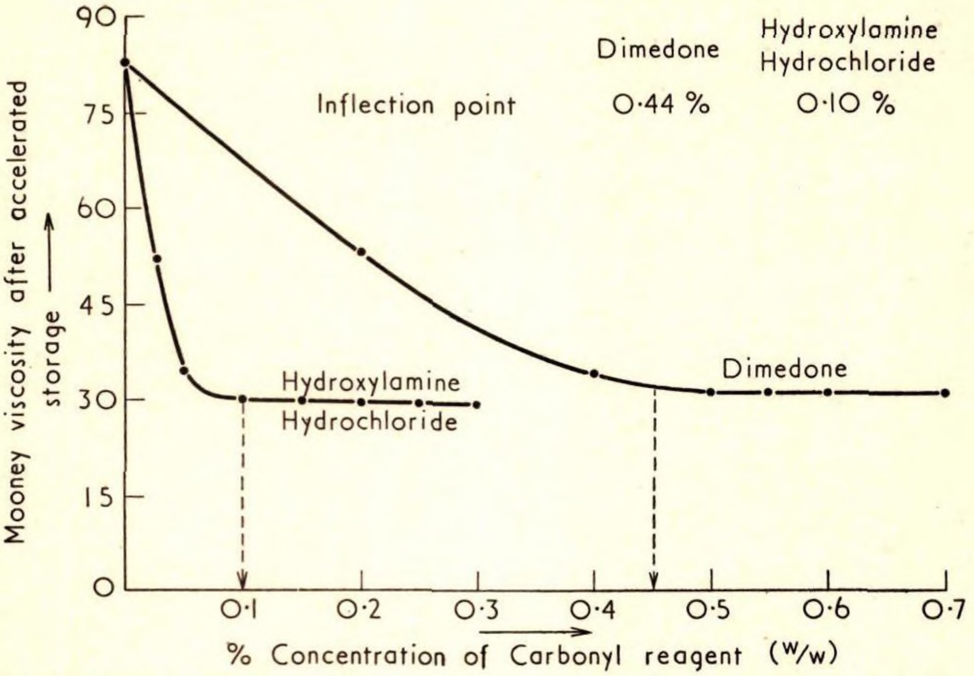

Figure 3. The effect of adding increasing concentration of monofunctional carbonyl reagents on storage hardening. The two reagents used are dimedone (5,5, dimethyl cyclohexane 1,3 dione) and hydroxylamine hydrochloride. The inflection points on each of the curve are shown by dotted lines.

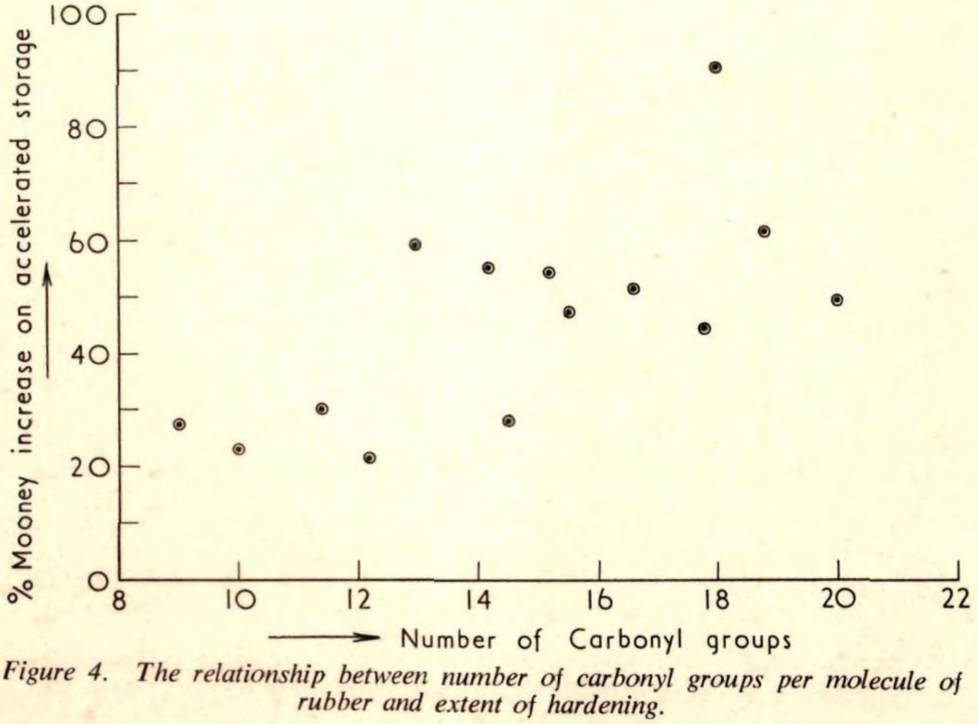

Figure 4. The relationship between number of carbonyl groups per molecule of rubber and extent of hardening.