

STUDIES IN HEVEA RUBBER

Part IV

Factors Affecting the Plasticity of Raw Rubber, and Some New Data on Hardening of Rubber by Benzidine

By

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There is no general correlation between intrinsic viscosity and plasticity of rubber apart from a tendency for rubbers of high intrinsic viscosity to be hard and for soft rubbers to have low intrinsic viscosities; the converses are not necessarily true.

Some new data on the hardening of rubber by benzidine show that this does not require the presence of oxygen, although in its absence the hardened rubbers can be brought into solution from treated latices and these solutions show no change in intrinsic viscosity as a result of the hardening reaction.

Acetone-soluble non-rubbers have a considerable influence on the plasticity of raw rubber; acetone-extraction results in considerable hardening without any indication of structural changes in the rubber. Any treatment of latex or rubber which is effective in removing some of these acetone-soluble impurities gives a harder rubber.

It has been established that progressive mill breakdown of a given rubber produces a series of rubbers of progressively reduced intrinsic viscosity and Mooney viscosity in which these two variables are closely related, but it is clear from Tables I, II and III that although there is between *different* rubbers a statistically significant correlation between plasticity and intrinsic viscosity in some cases (e.g. Table III), there are also such wide deviations revealed in the examples shown in Tables I and II that no generalisation can be attempted, and intrinsic viscosity cannot be used as a reliable guide to the plasticity of raw rubber. The sub-divisions of Group G of Table II in particular show that increasing hardness can actually be accompanied by a decrease in intrinsic viscosity.

Table I

Relation between L.S.V. and Mooney viscosity of smoked sheet.

Tree No.	L.S.V.*	Intrinsic viscosity* of pptd. rubber	Mooney* Viscosity
1	4.4	6.9	47
2	4.9	6.5	110
3	4.8	6.6	45
14	5.5	7.6	50
15	5.7	7.3	110
16	6.2	8.5	72
17	7.1	9.0	115

* Means of a year's observations.

Table II

*Intrinsic viscosities of latex solutions and of smoked sheet
with corresponding Williams plasticities (D_{10} values)
and Mooney viscosities.*

Source of Latex		L.S.V.	Smoked Sheet		
			$[\eta]$	D_{10} m.m.	Mooney
Group A,	8 trees	5.4	5.53	—	57
„ C,	8 „	5.8	5.61	—	65
„ B,	7 „	6.1	6.12	—	70
„ D,	9 „	6.5	6.18	—	93
„ E,	8 „	7.1	6.73	—	102
„ F,	8 „	7.6	7.25	—	112
„ G,	11 „	6.7	6.35	—	123
„ Ga,	4 „	6.8	—	5.61	120
„ Gb,	3 „	6.5	—	5.58	128
„ Gc,	4 „	6.2	—	5.86	130

(Ga, b, c were sub-divisions of Group G)

Table III

Individual Trees: Intrinsic viscosities of latex solutions, vacuum-dried coagula and smoked sheet, with corresponding Williams plasticities and gel contents.

Tree No.	L.S.V.	Vac-dried coagula			Smoked sheet				Gel in Dried latex
		$[\eta]$	D ₁₀ m.m.	Rec. m.m.	$[\eta]$	D ₁₀ m.m.	Rec. m.m.	Gel %*	
1 ..	4.95	4.95	2.89	3.21	4.85	2.89	3.12	51	21
2 ..	5.15	5.66	4.07	5.01	5.59	3.70	4.38	70	59
14 ..	5.25	5.64	3.28	3.67	5.50	3.11	3.35	60	27
19 ..	5.5	6.11	4.33	5.40	5.94	4.07	4.85	77	—
15 ..	5.7	6.66	5.23	7.36	6.16	4.54	5.95	88	71
17 ..	7.6	7.83	5.0	7.6	7.32	5.10	6.94	85	67

* The gel content in this column is defined as that portion of smoked sheet not dissolved on standing with an 80/20 (by volume) mixture of benzene-methanol for 3 days at 30°C., and is not to be confused with the petroleum-insoluble gel described in Part II of this series, and reproduced in the final column of the above Table.

It appears to be generally true that soft rubbers have low intrinsic viscosity, and that rubbers of high intrinsic viscosity are hard, as might be expected in view of the implied differences in molecular weight, and in all probability the range of rubbers examined by van Essen⁽³⁾ fell into these two categories since his intrinsic viscosities were correlated with Hoekstra plasticities. Some instances occur in the above tables, however, where hard rubbers have only medium or even rather low intrinsic viscosity and these particular rubbers also have high gel contents, determined either on smoked sheet by extraction with 80/20 benzene-methanol or on vacuum dried latex films by extraction with petroleum. Correlation has indeed been found between the Mooney viscosity of smoked sheet and its content of gel insoluble in 80/20 benzene-methanol⁽²⁾, and it may well be that the plasticity of rubber is very sensitive to the presence of gel whereas the interpretation of viscometric data in terms of molecular weight is greatly complicated by gel. The inverted order of hardness of the rubbers from trees 15 and 17 in relation to their gel-contents however probably reflects the greater average intrinsic viscosity of rubber from the latter tree.

Osmotic molecular weights of hard and soft rubbers of similar intrinsic viscosity

Osmotic data (Fig. I) were obtained for benzene solutions of vacuum-dried coagulated white fractions of the latices of trees 1, 2 and 14. These three rubbers were selected as having very similar intrinsic viscosities but very different plasticities and gel contents. Extrapolation of the osmotic data gave the molecular weights listed in Table IV and these showed considerable differences between the hard and soft rubbers which were not revealed by the intrinsic viscosity measurements. Other differences in the physical state of two of these rubbers, suggesting a greater restriction on uncoiling in the harder rubber, are also shown in Table VIII of Part III.

FIG. 1
OSMOTIC DATA FOR WHITE FRACTION
OF RUBBER FROM DIFFERENT TREES
GIVING SIMILAR L. S. V.

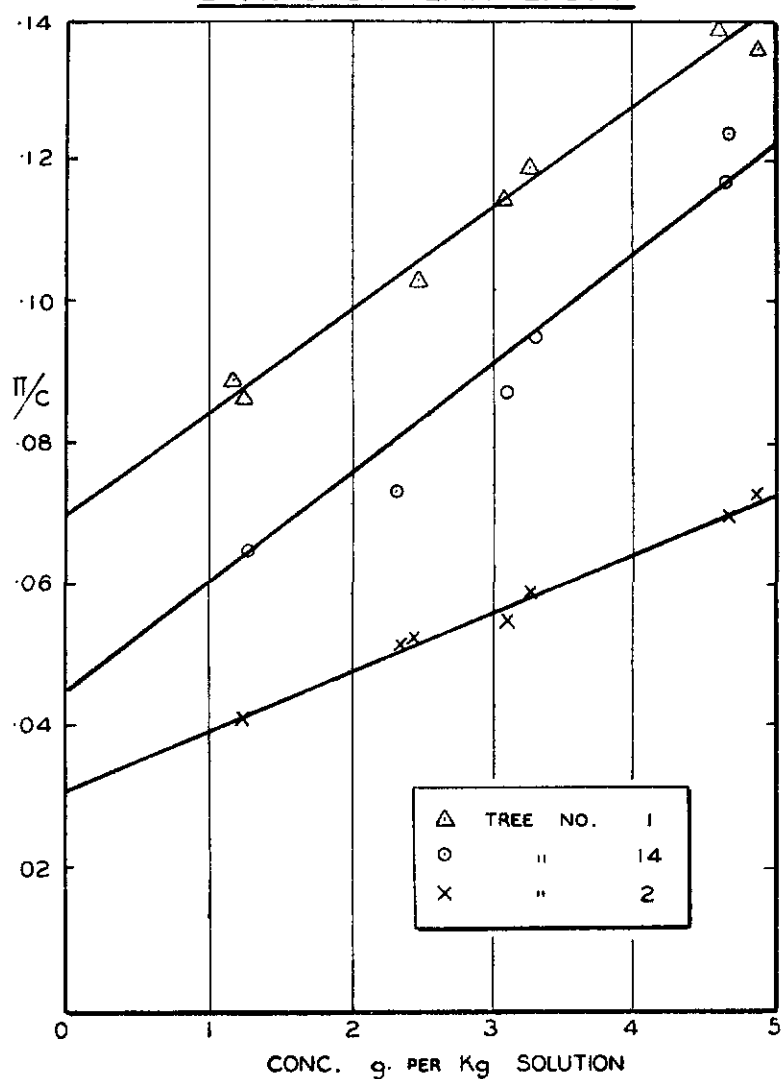


Table IV
*Osmotic data on hard and soft rubbers of similar
intrinsic viscosity.*

Source of rubber	L.S.V.*	Intrinsic viscosity of pptd. rubber*	Osmotic* molecular weight	Mooney† viscosity of smoked sheet
Tree 1	4.9	6.96	367,000	47
" 14	5.2	7.07	572,000	50
" 2	5.2	6.60	830,000	110

* Determined on white fraction of centrifuged latex.

† For comparable Williams plasticity data on these rubbers see Table III.

Benzidine-hardening of rubber

A convenient means of hardening rubber artificially is by addition of benzidine hydrochloride to latex prior to coagulation⁽⁴⁾ and it is of interest to examine this reaction in relation to changes in intrinsic viscosity and solubility brought about by the benzidine modification. Philpott has presented evidence which suggests that benzidine hardening involves cross-linking by a mechanism not yet established with certainty. If such cross-linking occurs in the latex phase without coalescence of particles it must of necessity be confined to the individual latex particles giving a microgel structure which should be dispersible in solvents on agitation, whereas if cross-linking occurs in the bulk rubber at any stage subsequent to coagulation a macrogel insoluble structure would be expected.

In the above work either benzidine hydrochloride (preferably in suspension) was added to the latex before coagulation, or benzidine was dissolved in the coagulating acid. It is of interest that free benzidine itself is now found to be equally effective when added in aqueous solution to the latex followed by drying the latex in a thin film without acidification (Table V). For comparison the degree of hardening produced by treatment with benzidine hydrochloride is also shown in this table.

Table V
Benzidine hardening of rubber.

Conditions of preparation of samples	Mooney Viscosity	Williams plasticity D ₁₀ m.m.
(1) Solution of benzidine (0.02 g. in 30 ml. water) added to latex (25 ml.).		
(a) Film dried at 70°C ..	—	6.84
(b) " " " 30°C ..	—	6.37
Control: without benzidine, film dried at 30°C	—	4.50
(2) Conventional acid coagulation and preparation of smoked sheet.		
(a) after adding benzidine (0.1 g.) in water (150 ml). to latex (100 ml.)	151	—
(b) after adding 5 ml. of 2% neutral benzidine hydrochloride solution to 100 ml. latex, followed by 145 ml. water	138	—
(c) control—without benzidine ..	82	—
(3) Conventional acid coagulation and drying of coagula in vacuo.		
(a) as 2 (a) ..	150	7.06
(b) as 2 (b) ..	146½	6.53
(c) control—without benzidine ..	78½	4.30

The effect of benzidine on the solubility of latex and of rubber derived from it is shown in Table VI. Although the latex itself could be brought into solution in benzene as readily as the untreated latex, without significant difference in inherent* viscosity of the resulting solutions, the rubber prepared from this latex, even when dried in vacuo, was difficult to disperse in benzene without violent agitation, while under static conditions it was an insoluble though fairly rigid swollen gel, so resembling a lightly-vulcanised rubber.

* The inherent viscosities of benzidine-hardened rubbers decreased (by about 0.1 units) with a decrease in concentration to 0.6 x c₁.

Table VI

Effect of benzidine on solubility and inherent viscosity.
(40 ml. of 2% neutral benzidine hydrochloride added to 1000 ml. estate latex).

Property measured	Untreated latex (control)	Benzidine-treated latex
Solubility of latex in benzene ..	soluble	soluble
L.S.V. (cf. Part I) ..	5.95	5.91
Inherent viscosity of vacuum dried coagulum	6.54	insoluble*
D ₁₀ (m.m.) -do- ..	3.88	8.0
D ₁₀ (m.m.) of smoked sheet	4.07	6.36
Mooney -do- ..	79	135

* This sample was dispersed in benzene after prolonged violent shaking. Its inherent viscosity was then 7.2.

Coagulated benzidine-treated latex rapidly develops a brown discolouration, and in the above experiment it was noticed that the discolouration in the vacuum-dried coagulum was most intense in the surface layer originally uppermost in the coagulating dish, with a gradation of colour through the thickness of the sample. This clear indication that oxidative reactions might have been playing a part in the benzidine hardening led to some trial preparations under conditions rigorously excluding access of oxygen. Tables VII and VIII show that in the absence of oxygen the benzidine-treated rubbers, whether prepared by drying whole latex films or by acid-coagulation and drying, could be brought into solution in benzene with the aid of considerable shaking although the benzene-treated products under static conditions again gave fairly rigid gels. Although soluble, the products were found to be hardened by the benzidine treatment when tested in the Williams plastimeter. From this evidence alone it could not be conclusively argued that the benzidine-treated rubber was in fact already hardened before the plasticity tests were applied since hardening might have taken place at the elevated temperature employed in determining the plasticity. No loss of solubility occurred, however, when a vacuum-dried film prepared from latex containing benzidine was heated for 3 minutes at 100°C in a sealed evacuated tube, and

initially-soluble rubbers containing benzidine were still soluble after testing, hence it seemed unlikely that any structural changes were occurring during the Williams plasticity test; moreover, in the Mooney evaluation benzidine-treated rubbers were invariably extremely hard initially and *softened* during test (cf. Table IX). It therefore appeared certain that the presence of oxygen was not necessary for the fundamental mechanism of hardening by benzidine, although in the presence of oxygen more extensive insolubilisation of the rubber occurred.

Table VII

Properties of vacuum dried film prepared from air-free latex containing benzidine hydrochloride (added as 2% solution to nitrogen-saturated latex)

Properties of dried film	Untreated latex	Benzidine-treated latex
Solubility ..	soluble	soluble
Inherent viscosity ..	6.42	6.45
D ₁₀ (m.m.) ..	4.30	5.71

Table VIII

Properties of benzidine-treated rubber prepared in absence of oxygen.

Properties of dried sheet	Untreated latex	Benzidine-treated latex, coagulated and dried	
		in air	in absence of air
Colour ..	pale yellow	brown	pale yellow
Solubility ..	soluble	insoluble	soluble on shaking
Inherent viscosity ..	5.96	—	5.99
D ₁₀ (m.m.) ..	3.75	5.75	5.55

For the coagulation experiments in absence of air, latex was first withdrawn from the tree into a nitrogen atmosphere under sterile conditions, using the apparatus of McMullen⁽⁵⁾. A wide necked bottle was fitted with nitrogen inlet and outlet tubes and a dropping funnel; after displacing the air with nitrogen 20 ml. of the latex were introduced via the dropping funnel, followed by 1 ml. of 2% neutral benzidine hydrochloride solution, 30 ml. of air-free water and 5 ml. of air-free 1% formic acid. Similar quantities of latex were coagulated in air for comparison, one after addition of an equivalent amount of benzidine hydrochloride; coagula were squeezed into thin sheets very rapidly and dried in vacuo at room temperature.

A study of the change in viscosity during test in the Mooney Viscometer, using rubbers prepared as above, showed that the sample prepared under nitrogen was initially the hardest, but gave a slightly lower viscosity after the full three-minute run than the sample prepared in air (Table IX). The addition of 'sodium bisulphite (0.5% on rubber content of latex) prior to adding the benzidine gave a non-discoloured soluble product without the necessity for excluding oxygen, but although this rubber gave initially high readings it gave a considerably lower viscosity after 3 minutes than the samples without bisulphite, although still harder than the control.

Table IX

Change in viscosity during Mooney evaluation of benzidine-treated rubbers.

Time from start secs.	Untreated latex, coagulated, and vacuum dried	Benzidine treated latex, coagulated and dried		
		in air	in absence of air	in air, after adding bisulphite to latex
11	—	251	—	—
12	—	—	—	220
13	—	—	270	—
14	147	—	—	—
15	142	190	240	216
30	108	170	196	167
45	95	160	172	143
60	87	152	155	124
90	73	147	146	105
120	71½	138	138	96½
150	73	134	127	94
180	74	132	123	95

The data in the foregoing section clearly indicate that plasticity measurements are more sensitive than solution viscosity to the cross-linking attributed to modification of rubber by benzidine.

The effect of purification of rubber on its plasticity

Many instances have been observed where acetone-extraction of rubber in an inert atmosphere, either at room temperature or at the boiling-point of acetone, has markedly increased its hardness. The hardening was accompanied by an increase in viscosity which was not greater than could be accounted for by removal of the 2.5—3.5% of acetone soluble components which are known to reduce solution viscosity (cf. Part I). Coagulation of latex by pouring it into acetone or alcohol similarly led to considerable hardening (Table X).

Table X

Effect of acetone-extraction on intrinsic viscosity and plasticity (Williams, D_{10}) of vacuum-dried coagula.

Treatment	Latex 1			Latex 2		
	$[\eta]$	D_{10} m.m.	Rec. m.m.	$[\eta]$	D_{10} m.m.	Rec. m.m.
Coagulation with formic acid ..	6.75	4.11	5.10	6.89	3.94	5.08
-do- , plus acetone-extraction	7.01	5.05	7.36	6.73	5.13	7.93
Coagulation into acetone ..	7.15	4.13	5.00	6.76	3.92	4.67
-do- , plus acetone-extraction	7.21	5.13	7.50	6.87	5.54	8.99
Coagulation into alcohol ..	—	—	—	6.87	4.57	5.92
-do- , plus acetone-extraction	—	—	—	6.98	5.71	9.19

The degree of hardening appeared at first sight to be rather large in relation to the small amount of acetone-soluble material removed, but the absence of any permanent structural change in the rubber was demonstrated by redissolving the acetone-extract in benzene-alcohol, adding it to a solution of the extracted rubber in benzene, and evaporating the solvents in vacuo, whereby the original plasticity was restored (Table XI). Also of significance was the observation that acetone-extraction did not increase the gel-content of rubber more than could be accounted for by removal of the acetone-soluble components.

Table XI

Effect of restoring the acetone-soluble component of rubber on plasticity of acetone-extracted rubber.

Treatment of rubber (Vacuum-dried coagulum)	D_{10} m.m.	Recovery m.m.
None ..	5.03	7.70
Acetone-extracted ..	5.68	9.52
Restored acetone-extract ..	5.01	6.92

The amount of hardening accompanying purification of the latex itself appeared to depend on the source of the latex (Table XII).

Table XII

*Effect of purification and acetone-extraction on plasticity
(D_{10} m.m.) of vacuum-dried coagula.*

Treatment	Tree 1 Latex		Tree 15 Latex	
Unpurified latex, acid coagulation	2.86	3.07	5.32	8.51
-do- , plus acetone-extraction	3.48	3.99	6.00	10.39
Unpurified latex, coagulated with acetone ..	—	—	5.84	9.15
-do- , plus acetone-extraction	—	—	6.36	11.00
Purified latex*, acid coagulation	3.56	4.69	4.26	6.41
-do- , plus acetone-extraction	4.85	8.91	5.29	9.63
Purified latex, coagulated with acetone ..	—	—	4.86	7.20
-do- , plus acetone-extraction	—	—	6.13	10.85

* Purification by adding ammonium oleate followed by multi-creaming. (The presence of residual soap may have had a softening effect on the unextracted samples).

Summary and Conclusions

Structural changes in rubber attributed to restricted cross-linking have a greater influence on plasticity than on solution viscosity. The interpretation of viscometric data is complicated by the presence of gel in the rubber, consequently there is no general correlation between plasticity and intrinsic viscosity and measurement of the solution viscosity cannot be used as a reliable guide to processing characteristics of the rubber.

The hardening of rubber by addition of a small proportion of benzidine to latex is not dependent on the presence of oxygen, although a rather insoluble and discoloured product is formed when air is not excluded. The inherent viscosity of samples prepared in the absence of air is not significantly affected by the hardening reaction.

Removal of acetone-soluble components of rubber gives a disproportionately large increase in hardness which is not due to any permanent structural change in the rubber.

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