STUDIES IN HEVEA RUBBER

Part VI

Characteristics of Rubber in Latex of Untapped Trees and in Branches of Trees in Regular Tapping.

By

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The discovery that the latex in some untapped trees, and in the branches of some trees in regular tapping, contains a high proportion of microgel enables important conclusions to be drawn as to the area of bark affected by tapping, since, when an untapped tree is brought into production, the microgel latex contained in a considerable area of the tree is replaced by normal latex. Certain clonal species, notably P.B.186, do not contain very much microgel latex even when old untapped trees are examined.

Microgel latex has certain novel characteristics. Its rubber content can be brought into solution in benzene to give solutions of very low inherent viscosity, but only small osmotic pressure. Rubbers obtained from microgel latex are not of low molecular weight and are in fact very hard.

When two tapping cuts are opened on a single tree, the upper cut at first contains more microgel latex than the lower cut, and yields rubber which is correspondingly harder.

Experience in rubber-producing territories has established that severe increases in the intensity of tapping of *Hevea brasiliensis* give softer rubbers, with depletion of the rubber content of the tapped latex. No information is, however, available to show whether there is any corresponding change in plasticity of rubber when trees are brought into tapping for the first time or after long periods of resting, i.e. an increase of tapping intensity from zero to normal, although it is known that the rubber content of the tapped latex(1) falls progressively from an initially high value (frequently >50%) to an equilibrium value determined by the tapping system employed.

Since *Hevea brasiliensis* possesses a latex system of inter-communicating vessels, it is not surprising that withdrawal of latex at the tapping cut affects the concentration of latex over a considerable area of the bark of the tree(2-4). Estimates of the area of bark affected vary considerably, possibly depending on the tree, but a reduction in the rubber content of the latex at sampling points as remote as thirty feet above the tapping cut has

been observed after only three tappings of a newly opened tree.

When the technique of taking samples of latex into benzene (Part I) was applied to trees which had not been tapped for 8 years, as well as to some 20 years old trees which had not previously been tapped, it was immediately apparent that the latex from trees representative of several clones had different solubility characteristics compared with normal latex since, on shaking, the rubber phase first disintegrated into small, swollen particles which required considerable further shaking to bring them into solution. After dehydration the solution remained hazy and had quite low inherent viscosity which increased slightly with concentration (Table I and Fig. I); when poured from one vessel to another the solution left an insoluble rubber film on the walls of the container. In the group of trees examined, one particular clone, P.B.186, gave a normal latex, i.e. latex with solubility characteristics as described in Part I, passing into solution after a few minutes shaking to give intrinsic viscosity in the range 4-7.

Table I

Inherent viscosity of rubber in untapped and in long rested trees.

Clonal type	Inherent viscosities [a] of latex solution from 28 different trees					
Av. 49 ..	1.3	3.0	1.0	1.0	0.8	0.6
Av. 152 ..	2.2	2.8	0.8	1.4	—	—
Tj. 1 ..	1.0	1.0	1.4	0.9	0.5[b]	—
Rub. 393 ..	2.0	1.1	1.6	3.6[c]	—	—
P.B. 186[d] ..	6.2	5.6	5.4	4.4	4.5	5.0
P.B. 186[b] ..	4.4	3.2	—	—	—	—
B. 84 ..	1.1	—	—	—	—	—

Notes: (a) Inherent viscosities were determined at concentrations ca 0.1g/100 ml.

(b) These trees were 20 years old and had not previously been tapped.

(c) This tree had been badly wind-damaged.

(d) Inherent viscosities of P.B.186 samples were independent of concentration.

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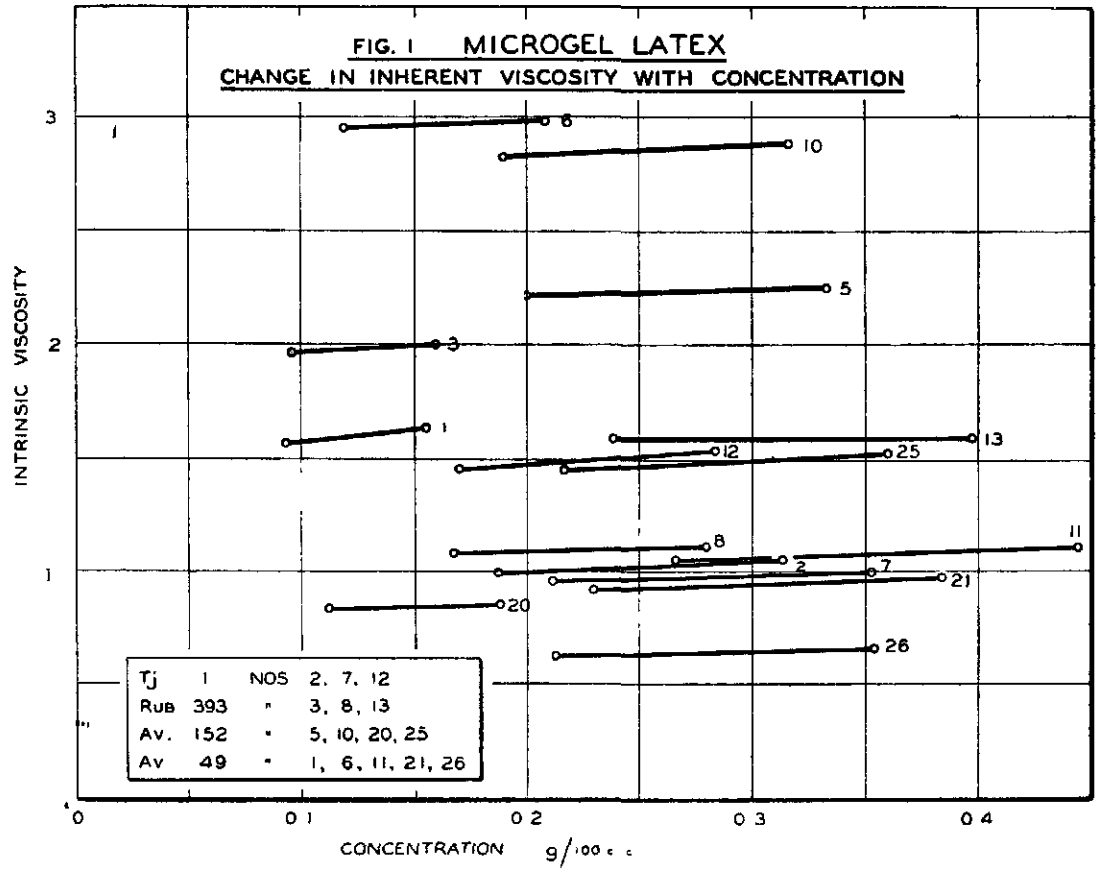
FIG. 1 MICROGEL LATEX
CHANGE IN INHERENT VISCOSITY WITH CONCENTRATION
INTRINSIC VISCOSITY
CONCENTRATION g/100 c c
3
2
1
0
0 1
0 2
0 3
0 4
1
6
10
5
3
1
13
12
25
11
8
2
7
21
20
26
Tj 1 NOS 2, 7, 12
Rub 393 " 3, 8, 13
Av. 152 " 5, 10, 20, 25
Av 49 " 1, 6, 11, 21, 26

When the rubber was precipitated from benzene solutions of latices of the above abnormal type and dried in vacuo, it could not be redissolved in either benzene or benzene-methanol. Precipitation of the rubber was practically quantitative, 88-92% of the total solids (estimated by evaporation of a portion of the solution) being found in the precipitate. The data presented in Table VII show that the non-rubber content of latex from long-rested trees is no greater than that of normal latex, consequently the low intrinsic viscosities observed could not have been due to an abnormally high proportion of non-rubber substances in these latices. The precipitated rubbers (Table II) were in fact rather less contaminated with nitrogenous and mineral impurities than precipitated rubbers derived from solutions of more normal latices (cf. Part I).

Table II

Characteristics of rubbers precipitated from solutions of latices of Av.49 and Tj.1 long-rested trees.

	Av. 49	Tj. 1
Inherent viscosity of latex solution	0.76	0.95
Proportion of total solids pptd. . .	91%	89%
Analysis of pptd. rubber: C . .	86.6	86.25
-do- H . .	11.7	11.6
-do- N . .	0.44	0.44
-do- Ash . .	0.08	0.25
-do- O* . .	1.16	1.15

* Directly determined.

The almost quantitative preciptation of the rubber from solution and the insolubility and toughness of the precipitated rubbers proved beyond doubt that the above rubbers were not of low molecular weight (cf. characteristics of fractions of comparable inherent viscosity described in Part V). Even before removing residual solvent from the precipitated rubbers, difficulty was experienced in redissolving them completely and at best, only "specky" solutions could be obtained, containing discreet swollen gel particles. The solvent-free precipitated rubbers were only swollen to a limited extent in benzene, thus resembling lightly vulcanised rubber, and estimates of

the degree of swelling were obtained by visual measurements or rapid weighing of the swollen samples. These are shown in Table III in which Qm is the swelling index expressing the volume of benzene absorbed per unit volume of rubber.

Table III

Swelling index of rubbers from long-rested trees.

Preparation of samples	Clonal type	L.S.V.	Qm.
Pptd. from solution ..	R.R.I. 514	2.1	29
„ „ „ ..	R.R.I. 513	1.9	28
„ „ „ ..	Av. 49	1.0	20
Ace-tone-extracted coagulum from purified latex ..	same tree	—	20
Pptd. from solution ..	Av. 49	0.8	11
„ „ „ ..	Tj. 1	0.5	9

Vacuum-dried films of the abnormal types of latex could be brought into solution by violently shaking with benzene within a few minutes of their preparation. The inherent viscosity (1.1) of one of these solutions was identical with that of the solution of the corresponding latex. Vacuum-dried coagula were mainly insoluble.

All the characteristics of the above abnormal latices were consistent with the conception of a cross-linked structure confined to the individual latex particles, and such a latex has accordingly been designated "microgel latex"(5) (cf. Part II). An alternative term "primary rubber", which has been used to differentiate between the rubber in an untapped tree and that synthesised subsequent to withdrawal of this rubber by bringing the tree into tapping, is too general in its implication; it does not differentiate between the normal latex in untapped P.B.186 and microgel latex, both of which contain "primary" rubbers.

Soluble components of rubber isolated from microgel latex

Although the vacuum dried coagula were substantially insoluble in a variety of solvents, relatively small amounts of soluble components were extractable when a finely-

shredded acetone-extracted rubber was immersed in solvents for several days in an atmosphere of nitrogen (Table IV). The soluble components had intrinsic viscosities considerably higher than the inherent viscosity of the original latex in solution; another point of interest is that fractionation by benzene-methanol of one of these soluble components (Table V) yielded a low-molecular fraction, characterised by its softness and ready solubility, with a rather higher oxygen content than fractions of corresponding intrinsic viscosity isolated from normal latex (cf. Part V).

Table IV

Soluble components of rubber from microgel latex. (Av. 49 + Tj. 1 mixture L.S.V. 1.3)

Solvent	Successive extraction†	% Rubber extracted	$[\eta]$ in benzene of soluble component
Benzene	1	1.5	3.26
	2	12	3.68
	3	4	3.38
Benzene + 15% methanol	1	11.4	3.03
	2	5.1	3.50
	3	2.1	—
	4	1.2	—
Benzene + 20% methanol	1	3*	0.69
	2	5	1.63

† Extractions for successive 3-day periods.

* This would be reported as "97% gel" in the R.R.I. method of gel determination. (see Table III in Part IV).

Table V

Sub-fractionation of soluble component extracted by benzene + 15% methanol.

Fraction	% in soluble component	$[\eta]$	Analysis				
			C	H	Ash	N	O
1	70	3.7	87.7	11.8	nil	nil	0.25
2	30	1.56	85.3	11.7	0.34	0.05	2.0

Osmotic Pressure of a Solution of Microgel Latex

The conception of microgel latex as a system of cross-linked particles was supported by attempts to measure the osmotic pressure of a dehydrated solution of

a microgel latex with inherent viscosity 0.62. No measurable osmotic pressure was developed by solutions of concentration less than 0.5% by weight, and at the highest concentration examined (0.89%) the osmotic pressure was only 0.111 cm., indicative of an enormous molecular weight.

Inherent Viscosity of Microgel Latex in Benzene + 15% Methanol

The restriction imposed on uncoiling of polymer molecules when passing from a poor solvent to a good one, is indicative of cross-linking. This results in a lowered ratio of the intrinsic viscosities in benzene and in benzene-methanol (Part III). Solutions of the rubber phase of several microgel latices gave a considerably lower ratio of intrinsic viscosities (1.5 to 1.8) than solutions of normal rubbers (cf. Table VII of Part III).

Plasticity of Rubber From Microgel Latex

From the considerations under discussion in Part IV, it follows that rubber of such high gel content as that obtained from microgel latex should be very hard. This is confirmed by the data in Table VI.

Table VI

Williams plasticity (D_{10}) of rubbers from microgel latex.

Treatment of latex	Av. 49 L.S.V. 1.0	Bulk Latex L.S.V. 2.1	
	D_{10} m.m.	D_{10} m.m.	Rec. m.m.
Coagulated, vacuum-dried	6.62	5.68	8.62
-do- + acetone extraction	7.77	7.49	12.5
Multi-creamed, coagulated, vacuum-dried	—	6.49	10.77
-do- + acetone extraction	—	6.52	12.07
Purified,* coagulated, vacuum-dried	6.52	6.32	10.84
-do- + acetone extraction	8.82	7.52	13.84

* Purified by soap-displacement and multi-creaming, (^{6})N-contents 0.04% and 0.06% respectively.

Table VII

Changes in latex on bringing into tapping two trees which had been rested for 18 months.

Tapping No.	R.R.I. 513					R.R.I. 514				
	Yield ml.	T.S. %	D.R.C. %	L.S.V.	D_{10} m.m.	Yield ml.	T.S. %	D.R.C. %	L.S.V.	D_{10} m.m.
1 ..	15	58.9	—	1.6	—	12	55.6	—	2.1	—
2 ..	36	—	50.7	1.7	6.01	30	50.1	—	2.1	6.10
3 ..	77	51.4	48.4	1.9	5.36	48	51.8	49.0	2.2	5.04
5 ..	98	48.0	44.1	3.7	3.21	75	50.0	47.0	3.4	4.62
7 ..	124	46.1	42.9	3.2	3.61	100	44.4	41.5	2.75	4.15
9 ..	120	44.5	41.3	3.5	3.53	98	44.0	41.0	2.9	4.36
12 ..	101	43.9	40.7	3.4	3.37	83	44.2	41.0	3.1	4.26
15 ..	23	48.8	45.7	4.0	2.89	18	47.6	43.8	3.7	3.71
21 ..	48	48.9	45.5	3.9	—	39	47.2	43.6	4.1	—

Notes: (1) Plasticity determinations on vacuum-dried coagula.

(2) *Dried* rubbers were not completely soluble until after the 10th tapping.

(3) Refoliation affected yields after the 13th tapping.

Now since the rubber-content of latex in an untapped tree gives solutions of very low inherent viscosity and also gives a very hard rubber, it follows that considerable changes must occur in the characteristics of latex and of the rubber derived from it when untapped trees are brought into regular tapping. Table VII, which records observations on two individual trees which had been out of tapping for eighteen months, and Table VIII which gives similar data for bulk latex from previously untapped trees (illegitimate seedlings, about 12 years old, from high-yielding mother trees), shows that the change from microgel to normal latex is practically complete in ten consecutive half-spiral alternate daily tappings. During this period the inherent viscosity of solutions of the latex increases while the rubber becomes progressively softer, which emphasises the point made in Part IV that there is no general correlation of intrinsic viscosity with plasticity.

Table VIII

Changes in bulked latex on bringing 114 untapped trees into production.

Tapping No.	Yield litres	L.S.V.	Vacuum-dried coagula		Smoked sheet			
			D_{10} m.m.	Rec.	D_{10} m.m.	Rec.	Mooney	% Gel*
1	1.5	2.1	5.68	8.62	5.45	9.37	120	85
2	2.0	3.2	5.40	8.46	4.56	6.48	98	84
3	2.7	3.8	4.78	7.22	3.83	5.09	88	82
4	2.8	4.3	4.95	7.51	3.78	4.80	82	82
5	3.5	4.5	4.35	6.12	3.62	4.30	77	80
6	5.7	4.6	4.31	5.25	3.42	4.07	74	77
8	5.7	4.3	3.84	4.98	3.54	4.12	67	74
9	4.5	4.2	3.92	5.08	3.51	4.13	72	72
12	8.5	4.1	3.50	4.48	3.26	3.66	58	72
25	10.2	4.1	—	—	3.28	3.76	62	66

* Gel. content was determined by the R.R.I. method (see Part IV).

Characteristics of Latex in Different Parts of a Tree

Examination of trees which had not been tapped for 8 years showed a fairly uniform distribution of microgel latex throughout the tree (Table IX) when samples were taken from small incisions in the bark.

Table IX

Microgel latex distribution in long-rested trees.

Tree	L.S.V. at height above ground:—			
	4 ft.	10 ft.	20 ft.	30 ft.
Av. 49 ..	.82	.36	.39	.44
Tj 1 ..	.83	.75	.41	.51

Determination of the area in which microgel latex is subsequently replaced by normal latex might, therefore, reveal the area of a tree affected by tapping. From a field of mixed illegitimate seedlings there were selected four high-yielding trees giving soft rubber, four high yielding trees giving hard rubber, four low-yielding trees giving soft rubber and four low-yielding trees giving hard rubber, as well as a representative selection of the trees studied in the previous parts of this series of papers. Table X shows that microgel latex is found in some parts of trees which have been in regular tapping for ten or more years, and also reveals a tendency for high-yielding trees to drain latex from a much greater area of the tree than low-yielding trees. Some low yielding trees behave similarly to the high yielders; these may, of course, be trees incapable of yielding much latex so that the small yield obtained may also be drawn from a considerable area.

There is no correlation between plasticity and area of drainage of microgel latex, and consequently, no indication that hardness and high gel content of some rubbers might be due to continual infiltration of microgel latex from more remote parts of the tree.

In the above survey three trees were included from a P.B.186 x Tj.1 clonal cross. Although rested for only a comparatively short time they seem to indicate that the capability of P.B.186 for synthesis of normal latex rather than microgel latex is inherited by the clonal cross since untapped Tj.1 latex usually shows typical microgel characteristics.

It is proposed shortly to determine the rubber content of latex in different parts of a tree by Ferrand's drop technique(4) since it follows that, if microgel latex persists in the upper regions of a tree, there can be no *rapid* transport of rubber from these parts to the tapping cut.

Consequently no loss of rubber resulting from tapping should be observed in parts of a tree where microgel latex is still present. Unfortunately the only data available(2) on the dilution effect in various parts of a tree do not differentiate between regions containing microgel and normal latex.

Table X

Characteristics of latex in different parts of trees.

Tree No. or type	Description	L.S.V. at height above ground		
		Tapping cut	20 ft.	30 ft.
	20 year old-trees in regular tapping:—			
1 ..	High yield, soft rubber	4.0	4.8	—
2 ..	„ „ hard „	5.0	2.4	1.5
14 ..	Medium „ soft „ *	5.6	0.8	0.5
15 ..	High „ hard „	5.2	3.9	4.5
17 ..	Medium „ hard „	7.1	1.5	0.35
1- 1 ..	High „ soft „	5.2	5.7	5.5
23-13 ..	„ „ „ „	5.3	6.0	4.1
41- 5 ..	„ „ „ „	5.7	3.8	2.5
52- 7 ..	„ „ „ „	6.7	3.1	1.3
10-16 ..	„ „ hard „	6.4	4.8	3.1
11- 1 ..	„ „ „ „	5.9	4.7	3.7
10-19 ..	„ „ „ „	6.4	5.1	2.4
52-12 ..	„ „ „ „	6.8	6.8	5.0
3- 7 ..	Low „ soft „	5.8	3.7	2.0
6- 4 ..	„ „ „ „	4.9	4.2	4.5
6-17 ..	„ „ „ „	6.5	1.9	2.3
6-22 ..	„ „ „ „	6.6	0.68	0.59
14- 1 ..	„ „ hard „	6.9	1.3	0.7
22- 3 ..	„ „ „ „	7.6	1.0	0.7
31- 3 ..	„ „ „ „	7.0	5.3	1.6
8- 2 ..	„ „ „ „	7.8	1.3	0.9
P.B.186 ..	High „ „ „	5.7	5.3	2.2
	Tree not previously tapped	(trunk)		
P.B.186 ..		3.2	2.2	1.7
	Trees rested two years			
(a) ..	Clonal cross P.B.186 x Tj.1	6.4	6.0	3.7
(b) ..	„ „ „ „	6.7	6.4	6.3
(c) ..	„ „ „ „	6.8	6.4	6.0

* In this tree samples taken 10 ft. above tapping cut and from a root had L.S.V. 3.8 and 5.2 respectively.

Tapping of Isolated Islands of Bark

Bobillioff([7]) and Frey-Wyssling([8]) reported that bark islands could continue to yield rubber over considerable periods of time. Recent experiments on two trees, one of which (Tj.1) had not been previously tapped, did not confirm these observations when islands approximately 3 ft. x 2 ft. were completely isolated by cutting to the wood a channel about one inch wide. The island on the untapped tree yielded latex (a few drops) only once after opening a tapping cut on the isolated island, while that containing the original half-spiral tapping cut yielded only 20 ml. of latex initially of 30% rubber content, dropping to less than 5 ml. of latex of 10% rubber content after 12 tappings. (The yield from the same tapping cut of the latter tree before isolating the island was 270 ml.).

Comparison of Rubber from Two Tapping Cuts on a Single Tree

Common practice in slaughter-tapping is to open a second tapping cut at some distance above the existing cut, both being made full spiral, resulting in a 300% increase in tapping intensity if the frequency of tapping is maintained. This is generally found to diminish the rubber content of the latex and to result in a softer rubber but no data are available in the literature for latices collected separately from the two tapping cuts. It might be expected from the foregoing that larger areas of the upper parts of the tree would be drained as a result of the increased severity of tapping, and that the latex from these regions would appear mainly in that drawn from the upper cut so that a harder rubber would be obtained therefrom. This has been confirmed by observations (Table XI) extending over 12 weeks on five trees in which the lower half-spiral tapping cut was extended to full spiral and the newly opened upper cut, located at the top of the existing tapping panel and subsequently moved progressively upwards, was made full circumference in the form of an extended "V", thus obtaining the maximum possible isolation of the lower cut from the upper part of the tree. Tapping was twice weekly, and latices from the upper and lower cuts were bulked separately. After 12 tappings serious precoagulation

occurred in the top-cut latex and it was found necessary to introduce into the latex receptacles sufficient ammonia to give 0.1% in the total volume of latex collected; smaller doses were inadequate. No precoagulation occurred in the bottom-cut latex.

Table XI

Characteristics of latex from two tapping-cuts.

Consecutive tapping No.	Yield ml.	T.S. %	D.R.C. %	L.S.V.	Vac-dried coagulum		Mooney of smoked sheet
					D_{10} m.m.	Rec. m.m.	
SAMPLES FROM TOP CUTS							
1	660	46.6	43.3	5.0	5.1	8.3	—
3	600	37.4	33.7	5.0	4.8	7.6	108
4	1,110	36.3	33.0	—	4.6	6.3	108
5	1,100	35.4	31.8	5.2	4.76	6.74	—
8	1,070	34.3	31.0	4.7	5.43	8.30	101
10	800	33.7	—	4.9	5.48	8.34	—
12*	380	33.8	29.9	4.7	4.96	7.47	—
14	1,090	31.3	27.6	4.7	5.23	7.91	99½
16	1,210	33.8	30.0	5.1	4.5	6.5	92
18	1,250	31.0	27.2	5.5	5.0	7.2	99½
20	1,250	28.0	25.0	—	—	—	—
22	1,210	31.4	28.6	6.1	5.35	7.85	—
24	1,724	33.1	29.5	6.2	5.52	8.64	—
26	1,140	33.5	29.5	6.2	4.78	7.14	—
SAMPLES FROM BOTTOM CUTS							
1	850	45.4	41.7	4.9	5.1	8.3	—
3	1,020	39.6	35.9	5.5	4.0	4.6	86½
4	1,570	36.1	33.1	—	3.85	4.65	78
5	1,350	36.2	32.6	5.4	3.69	4.30	—
8	1,120	30.7	27.7	5.2	3.52	4.87	58½
10	1,100	32.2	—	5.3	3.78	4.35	—
12*	1,110	31.9	28.2	5.1	3.72	4.30	—
14	1,120	30.3	27.0	4.7	3.69	4.13	67
16	1,240	29.4	25.9	4.8	3.1	3.4	61½
18	1,200	28.5	25.0	5.0	3.5	3.9	65½
20	1,400	23.1	20.1	4.7	—	—	—
22	1,000	23.7	21.1	4.8	3.64	4.18	—
27	1,104	24.0	20.8	4.6	3.40	3.68	—
26	940	26.1	21.4	4.8	3.21	3.56	—

* Late tapping.

The rise in intrinsic viscosity after the 17th tapping may be due to exhaustion of available microgel from the upper part of the tree, but it is of interest that the top cut rubber does not become softer at this stage. Philpott[9] observed that harder rubbers were obtained from the bark just above the tapping panel, with a sharp difference in plasticity in passing from the renewed bark of the tapping panel to the old bark just above it.

Summary and Conclusions

Untapped or long-rested trees frequently contain microgel latex which yields solutions of low intrinsic viscosity and with only very small osmotic pressure. These latices yield very hard rubbers.

When a tree containing microgel latex is brought into tapping the inherent viscosity of solutions of its latex increases steadily, while the rubber obtained from it becomes progressively softer. After about ten tappings the latex becomes more or less normal.

Trees of clone P.B.186 do not contain much microgel latex, especially when they have once been brought into tapping and then rested. This characteristic also applies to the clonal cross P.B.186 x Tj.1.

Microgel latex appears in the crown of many trees in regular tapping, and its identification assists in defining the area of a tree not affected by tapping. There is a tendency for tapping of high yielding trees to affect the latex of a greater area of the tree than low yielders.

When two tappings cuts are opened on the same tree the latex drawn from the upper cut gives much harder rubber than that from the lower cut although the intrinsic viscosities of rubber from the two cuts are not initially different.

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