STUDIES IN HEVEA RUBBER

Part I

Molecular State of the Rubber Hydrocarbon in Freshly-Tapped Latex

By

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By collecting latex straight from the tree into a solvent it can be effectively demonstrated that the rubber hydrocarbon is already present in a high-molecular condition as it leaves the tree. Marked differences in hydrocarbon intrinsic viscosity are observed between trees, but little systematic difference is found between tappings of each individual tree in regular tapping, hence the average molecular weight of rubber is a specific characteristic of the tree. No appreciable change in intrinsic viscosity occurs in the rubber hydrocarbon during tapping of latex, nor during short term storage of latex or its conversion into vacuum-dried sheet. A slight degradation is observed in the conventional methods of preparation of smoked sheet and crepe rubber.

Although the rubber hydrocarbon of *Hevea brasiliensis* has been extensively studied in Europe and America with respect to its average molecular weight, its molecular weight distribution and its molecular homogeneity, little work has been done on the rubber hydrocarbon in the tree or on the rubber hydrocarbon in fresh latex as drawn from the tree in a normal tapping operation. The European and American investigations have of necessity been confined to ammonia-preserved latex of unknown origin and age except in a few isolated instances [1, 2] where latex specially preserved has been examined immediately after its arrival in the consumer countries.

Questions which can only be answered in the producing territories are (1) whether rubber is already present in high polymer form in the tree and, if so, whether it is a mixture of polymer homologues or a material of narrow molecular weight distribution; (2) whether rubber hydrocarbon undergoes any substantial change after leaving the tree or during processing as smoked sheet or crepe, e.g. post-tapping polymerisation or cross-linking; (3) whether the tree produces a rubber of reasonable uniformity from one tapping to another, including periods of biological activity such as refoliation; (4) whether the oxygenated component [3, 4] of rubber is present in latex as it leaves the tree or whether it is formed subsequently

as a result of oxidative degradation; (5) whether rubber drawn from different parts of a tree is of different molecular type from that drawn from the tapping cut and (6) whether the hardness of raw rubber, or the modulus of its vulcanisate, can be correlated with the molecular weight or molecular weight distribution of the rubber.

In order to obtain an unequivocal answer to as many of these questions as possible, some fundamental research work on rubber was undertaken in the Laboratories of the Rubber Research Institute of Malaya by mutual co-operation with the British Rubber Producers' Research Association and the secondment of senior officers of the latter organisation for work in Malaya. These investigations are not yet completed, but it is considered desirable at this stage to put on record an interim report on methods developed and results so far obtained.

Experimental Methods

The most convenient approaches to the characterisation of high polymers are undoubtedly through viscometric and osmotic measurements in dilute solutions of the polymer, protected against the well known degrading effects of light and air which are aggravated at the temperatures prevailing in a tropical laboratory. The viscometers used were essentially those described by Gee ([5]) with a standard flow time between 70 and 80 seconds, and the osmometers used for the work described in Part III were of the Zimm-Myerson type. Viscometric work was standardised at 25°C and osmometric work at 30°C, these temperatures providing the best compromise between thermostat regulation and volatilisation of solvent; cooling water was of course essential to maintain the thermostats at these temperatures in a tropical laboratory. Benzene (pure crystallisable) was used exclusively as solvent since the less volatile toluene could not be maintained in a sufficiently peroxide-free condition under tropical storage, nor was it available in adequate quantity. Solutions of rubber were prepared by placing appropriate amounts of rubber and freshly-distilled benzene in Pyrex tubes, thoroughly out-gassing by connection to a high vacuum system and sealing under high vacuum (10^{-4} to 10^{-5} mm.). Only in the case of precipitated and, consequently, partially purified rubber (cf. p.8) was there any evidence of degradation after

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opening the sealed tubes to the atmosphere, and this was entirely suppressed by having present 0.05% of sulphur in the benzene. Well known antioxidants (e.g. hydroquinone, pyrogallol, phenyl-β-naphthylamine, as well as some commercial materials) were ineffective in preventing degradation and, moreover, owing to their polar nature, had the objectionable characteristic of lowering the viscosity of rubber solutions (Table I).

Concentration of solutions (g. per 100 ml.) for viscometric timing was adjusted to give specific viscosity ($\eta_{sp} = \frac{\text{flow-time solution} - \text{flow-time solvent}}{\text{flow-time solvent}}$) around 0.2, which, except for low viscosity rubber fractions, involved concentrations below 0.05 g. per 100 ml. A second determination was made at greater dilution, but it was found that at the prevailing concentrations the inherent viscosity $\frac{\log_e (1 + \eta_{sp})}{c}$ in benzene was independent of concentration (c) for all *normal* rubbers examined*, and consequently the inherent viscosity was numerically equal to the intrinsic viscosity $\left[\frac{\log_e (1 + \eta_{sp})}{c}\right]_{c \to o}$. All such concentration-independent inherent viscosities are reported hereinafter as intrinsic viscosities, to differentiate them from some abnormal instances (see Part VI of this series) where the inherent viscosity was not independent of concentration. (The terms specific, inherent and intrinsic viscosity are used in the sense defined by Cragg[9]).

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* In some investigations on crepe rubber in England Gee [7] found that the inherent viscosity decreased appreciably with decreasing concentration when determined in benzene, but was substantially independent of concentration in some other more polar solvents. Hauser and Le Beau [8] working with fractions of the benzene-soluble component of smoked sheet observed a similar decrease in inherent viscosity with decreasing concentration, which was enhanced in their fractions of highest inherent viscosity. In the course of the present series of investigations there became available for statistical examination 116 pairs and a smaller number of triplicate determinations at, respectively, two or three progressively reduced concentrations, of inherent viscosities of latex solutions, total rubbers and rubber fractions covering a range of inherent viscosities from 0.5 to 10. The mean of differences between the 116 paired results was $\bar{x} = .003276$ with standard error of the mean $6\bar{x} = .007413$. The mean of differences did not differ significantly from zero since $t = \bar{x}/6_{\bar{x}}$ was 0.44 with 115 degrees of freedom.

Table I. *Effect of some oxidation inhibitors on degradation of a precipitated rubber.*

Viscometer timing	Inhibitor added and proportion used in benzene				
	none	hydroquinone 0.1%	phenyl-β-naphthylamine 0.2.%	pyrogallol 0.1%	sulphur 0.05%
1st reading seconds ..	102.74	100.85	101.10	100.45	102.94
2nd „ „ ..	102.50	100.80	100.98	100.45	102.90
3rd „ „ ..	102.26	100.62	101.02	100.30	102.97
4th „ „ ..	102.16	100.55	100.88	100.21	103.00
5th „ „ ..	102.05	100.52	100.62	100.10	102.62

For the examination of the rubber hydrocarbon in freshly-tapped latex it is clearly desirable to extract the rubber phase from the latex directly into a solvent. One such method is to use a mixed solvent such as one of the "Vistex" types* used by Baker and Kolthoff (see Henderson and Legge[10]), giving a three-component system in which the water as well as the rubber phase is dissolved, and contemporaneously with the present work, van Essen in the I.N.I.R.O. Laboratories[11] developed a Vistex method using toluene-pyridine, which, with the aid of a little non-ionic stabiliser added to the latex, gave almost instantaneous solution of latex.

Since all the Vistex mixtures contain a highly polar component and consequently have the well-established property of causing coiling† of long-chain molecules thereby reducing their solution viscosity, it seemed highly desirable to work only in a non-polar solvent such as benzene, and to remove the water phase either physically or chemically. Fresh latex was indeed found to dissolve quite rapidly in benzene giving an opaque solution in which the water-content of the latex was efficiently dispersed, provided that the amount of latex did not greatly exceed 1 ml. per 100 ml. benzene, and that the rubber-content of the latex was not abnormally low. Addition of a chemical desiccant (e.g. sodium sulphate) gave a clear solution but at the same time removed a portion of the rubber by adsorption. The water could, however, be much more easily and very rapidly removed by partial evaporation at *ca.* 35°C under reduced pressure, to give a perfectly clear solution which sometimes contained a little suspended non-rubber material removable by filtration. The concentration of these solutions was determined either by evaporating an aliquot portion (giving a figure corresponding closely to that based on the total solids content of the latex), or, preferably, from knowledge of the rubber content of the latex. Since the small size of the sample frequently precluded separate determination of its rubber content, it has been found convenient to express the intrinsic viscosities of benzene

* The term "vistex" was first used by Baker *et al.* in 1943 in a private communication to the Office of Rubber Reserve in America to describe measurements of the dilute solution viscosity of polymers dissolved directly from the latex in a mixture of hydrophobic and hydrophilic liquids such as xylene and pyridine[10]. The method was, apparently, in use in Germany[12].

† Discussion of this phenomenon is deferred to Part III of this series.

solutions prepared directly from latex in terms of the total solids concentration obtained by evaporation, so including the bulk of the non-rubbers. The error so involved is not large, and is reasonably constant from sample to sample since the ratio rubber content/total solids content does not in general vary widely enough to affect the comparative magnitude of the solution viscosities. The main concern of the present work has been to establish a rapid method, applicable to rubber in fresh latex, for detecting any considerable differences between samples and between rubber in the latex and rubber in coagulated and dried sheet. A precision method, although desirable, was not essential since it could only logically be applied to purified material. In order to avoid confusion with intrinsic viscosities determined on solutions of dry rubber and, also, with the term latex viscosity defining the viscosity of the latex itself, the term "latex solution viscosity" (L.S.V.) will hereinafter be used for the intrinsic viscosities of solutions prepared as above.

The standard procedure throughout the experimental work was to determine means of four solution and four solvent timings, with one determination of concentration, in order to evaluate a single value of intrinsic viscosity. Analysis of variance of replicated determinations of the intrinsic viscosity of dry rubber and of latex solutions showed the standard errors of such single values to be $\pm$ 0.051 and $\pm$ 0.175 respectively.

In Table II are given the results of observations on some selected trees during a year. Defoliation occurred towards the end of February and refoliation was nearly completed by mid-March. As is usual during wintering, latex yields decreased very considerably but without serious depletion of the rubber content of the latex.

Table II

Individual Trees: Latex Solution Viscosities.

Tree No.	May	July	Oct.	Nov.	Dec.	Jan.	Feb.	March	April	Aug.
	←		1949		→	←		1950		→
1	—	—	—	3.2	4.6	4.7	4.8	4.5	4.7	4.9
2	—	—	—	4.7	4.7	4.7	5.1	5.3	5.1	5.1
3	4.8	—	5.3	5.3	—	—	4.6	4.6	4.6	—
4	—	4.2	4.5	—	—	—	4.5	4.5	4.4	—
5	—	4.3	4.7	—	—	—	4.4	4.8	4.7	—
6	—	4.7	4.9	—	—	—	4.8	4.9	—	—
7	—	4.8	4.5	—	—	—	5.5	5.2	5.0	—
8	—	5.2	5.2	—	—	—	5.2	5.3	—	—
9	—	5.2	5.7	—	—	—	5.4	—	5.2	—
10	—	5.4	5.2	5.2	—	5.9	5.0	5.5	—	—
11	—	5.8	5.5	—	—	5.9	5.4	—	5.5	—
12	—	5.1	5.8	—	—	—	5.4	—	5.6	—
13	—	5.5	5.9	5.7	—	6.5	5.8	—	5.7	—
14	5.8	—	5.6	5.4	5.0	5.2	5.7	5.4	—	5.3
15	6.3	—	6.0	5.5	5.3	5.6	5.7	5.6	—	5.7
16	—	—	6.2	6.4	6.1	—	6.2	6.4	—	—
17	7.3	7.1	7.6	6.9	7.0	6.8	7.5	7.6	—	7.3

Notes. Trees 4—9 and 11—12 were not tapped between October and January. The tapping of trees 10 and 11 was changed over to the panel on the opposite side of the tree in February. All trees were in half-spiral tapping. (Trees Nos. 1, 2, 14, 15 and 17 may be identified as 43/11, 54/18, 42/6, 57/12 and 14/20 in Field 2, consisting of mixed illegitimate seedlings, at the Experiment Station of the Rubber Research Institute of Malaya).

An analysis of variance on 62 observations from 7 of the trees in Table II gave the following:—

Source	d.f.	Sum of squares	Mean square	Significance
Between trees	6	48.5792	8.096	Highly sig. ($P<.001$)
Between days of same tree	55	6.2055	0.1128	
Total ..	61	54.7847		

The tree effect was thus markedly greater than any day to day effect with the same tree.

A further analysis of variance on a more restricted portion of the data, for which 5 trees were all examined on each of 6 days produced the following:—

Source	d.f.	Sum of squares	Mean square	Significance
Between trees	4	26.2967	6.5742	Highly sig. ($P<.001$)
Between days	5	1.6257	.3251	Sig. ($P<.05$)
Error ..	20	1.6393	.08197	
Total ..	29	29.5617		

Significant variation due to days and to trees is evidenced, and that due to trees was particularly marked.

Although there were significant differences in L.S.V. in a given tree from one tapping to another, it is of particular interest that no perceptible general trend or seasonal fluctuation was observed throughout the year. This is consistent with the constancy of hardness (Mooney or Williams plastimeter) observed with rubber from individual trees.

Relation between L.S.V. and intrinsic viscosity of precipitated rubbers

If the effect of non-rubbers on the L.S.V. were purely additive then precipitation of the rubber by addition of a non-solvent to the dehydrated latex solution would only be expected to increase the intrinsic viscosity by the ratio of total rubber/total rubber less soluble non-rubbers. In actual fact the viscosity increase was nearly 30 to 40%, when the rubbers were precipitated by addition of methanol, dried in high vacuum and redissolved in benzene, as will be seen by comparison of Table III with Table II.

Table III

Intrinsic viscosity of rubber precipitated from latex solutions

Tree No.	May	July	Nov.	Dec.	Jan.	Feb.	March	Aug.
	← 1949			→	← 1950			→
1	—	—	—	7.35	6.53	—	6.90	7.73
2	—	—	—	6.18	6.47	—	6.59	6.72
3	6.80	—	7.00	—	—	6.57	6.49	—
14	8.13	—	7.75	—	7.53	7.13	—	7.32
15	—	—	7.50	—	7.12	—	7.29	7.57
16	—	—	8.97	—	—	8.47	7.96	—
17	8.93	9.11	—	9.08	8.74	—	9.80	9.42

With trees in the lower L.S.V. range precipitation of the rubber tended to be incomplete (Table IV), some low molecular material remaining in solution at the prevailing dilutions. Evaporation of the solution phase in vacuo, followed by re-solution in benzene and addition of the solution to a benzene solution of the precipitated rubber closely restored the original L.S.V. showing that the intrinsic viscosity of the rubber itself was not increased by precipitation and drying.

Table IV

Precipitation of rubber from latex solutions by a standard procedure (addition of an equal volume of 30% benzene in methanol)

Tree No.	% rubber pptd.*
1	69
2	87.5
3	79
14	75
15	87
16	85
17	87

* expressed as % of total solids content of the solution.

Even when allowance is made for failure to precipitate approximately 10% of low molecular material (intrinsic viscosity <2), the intrinsic viscosity increase on precipitation, if due to purely additive effects of the eliminated non-rubber and low viscosity material, could hardly be expected to be much in excess of 20—25%, and the higher order of increase observed is attributed to a depression of the L.S.V. due to the polar character

of the non-rubber substances eliminated by precipitation of the rubber. This was confirmed by intentional addition of polar substances to a solution of a precipitated rubber; 10% of an acetone-extract of rubber reduced the intrinsic viscosity by 15%, although 10% of stearic acid effected only a 3% reduction.

Analysis of the preciptated rubbers revealed that most of the protein nitrogen and much of the mineral content of the latex were precipitated with the rubber (Found: tree 14; C, 86.0; H, 11.55; N, 0.50; ash 0.85; O, 1.59%; tree 15; C, 85.7; H, 11.9; N, 0.56; ash 0.80; O, 1.64%), but since at least the polar acetone-solubles had been eliminated the precipitated rubbers could be considered as 93—95% hydrocarbon. It is probable that the oxygenated material present could be fully accounted for in salts of carboxylic acids and in proteins; Chambers[13] some time ago reported similar oxygen contents to the above in both pale crepe and smoked sheet. The oxygen content is certainly not due to adventitious uptake of oxygen during manipulation since the intrinsic viscosity is known to be greatly reduced, and the whole character of the rubber changed, by oxidative attack involving very much smaller quantities of oxygen. Nor is the major part of the oxygen chemically combined with the rubber since it is largely removed on purification of the latex[14]. Its close association with the mineral content of the latex is evident in that precipitated rubbers with higher ash content than the above also contain more oxygen and, moreover, centrifuging the fresh latex, which is known to eliminate a substantial proportion of the mineral matter in the lutoid fraction[15], is also effective in reducing the oxygen-content (Found: pptd. rubber from total latex, C, 85.1; H, 11.5; N, 0.42; ash 1.4; O, 2.12%; $[\eta]$ 6.97; pptd. rubber from corresponding white fraction, C, 86.4; H, 11.65; N, 0.42; ash 0.55; O, 1.14%; $[\eta]$ 6.97). The identity of the intrinsic viscosities of precipitated rubbers from total latex and white fraction and of rubber precipitated from a solution of a purified latex (purified by soap addition and creaming; N, 0.09%, and 0.18% on dry rubber) has also been satisfactorily established and shows that the residual nitrogenous, mineral and oxygenated matter still present in the precipitated unpurified rubbers can have no significant influence on the intrinsic viscosity.

Comparison of a number of intrinsic viscosities of precipitated rubbers with L.S.V's showed that to a first approximation the latter could be converted to the former by multiplication by a factor of 1.35, except when the proportion of rubber precipitated fell seriously short of 80% when the factor was somewhat larger. The use of L.S.V. as a rapid comparative guide to the average molecular weight of the rubber hydrocarbon in latex is accordingly justified.

Intrinsic Viscosities of Latex Solutions in Benzene and in Toluene-Pyridine

Table V shows the results obtained by dissolution of the latex into benzene and also into toluene-pyridine (70—30 by volume) according to the procedure of van Essen(11).

Table V

Viscosities in benzene and in toluene-pyridine

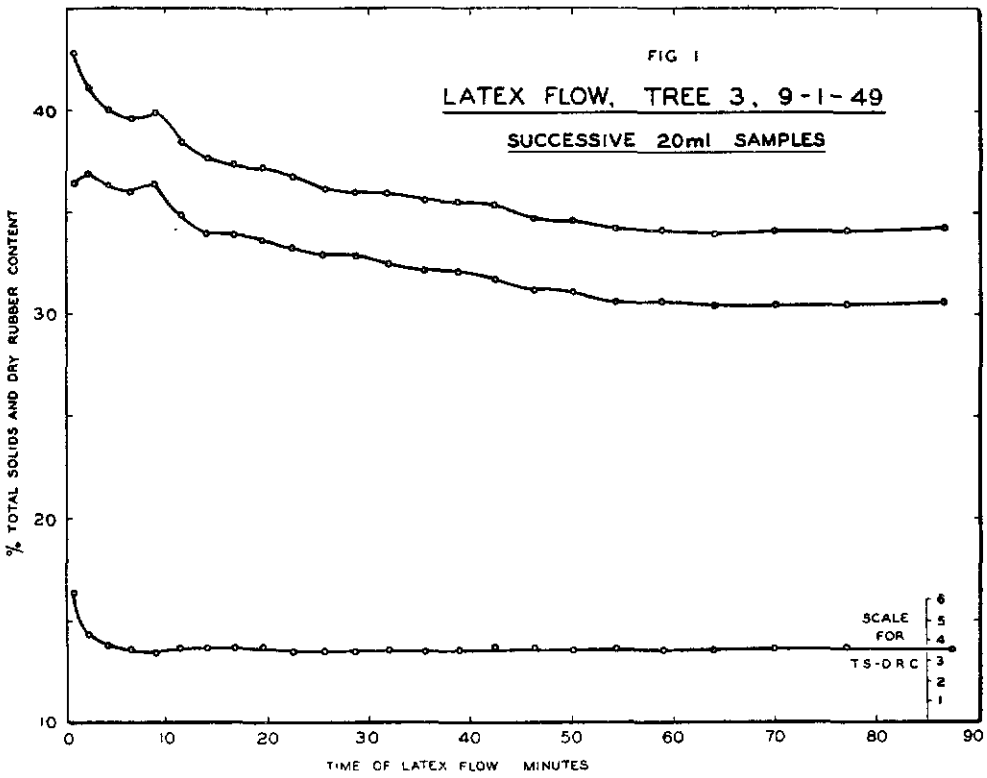
Tree No.	L.S.V. in benzene	L.S.V. in toluene-pyridine	Intrinsic Viscosity of rubber pptd. from benzene solution
14	5.7	4.25	7.70
17	7.1	5.8	9.11

Although the ratio of the L.S.V's determined by the two methods are not quite the same, possibly due to less restriction on "coiling up" in the less cross-linked sample No. 14*, it is clear that the two methods are reasonably comparable. Van Essen's tabulated results, which show considerable differences between clonal rubbers, are therefore very relevant to the present work, and it has not been considered necessary to make any additional survey of clonal rubbers in the course of the present investigations.

Variation of L.S.V. during tapping

It is known that there is considerable dilution of latex within the tree during the tapping outflow, followed by a slight recovery of concentration towards the end of

* See part III of this series.



flow (Fig. 1). Only in the very early stages of flow is there any indication of enrichment in non-rubber substances, the difference between the total solids and the dry rubber content subsequently remaining constant. Solution viscosities of samples taken at intervals during the period of latex outflow are shown in Table VI for two of the trees (Nos. 3 and 17) for which data are available for rather more than a year (Table II). The analysis of variance demonstrates that samples taken during the tapping of a given tree on a given day shows less variation than samples taken from tappings of the same tree on different days, whence it may be concluded that the intrinsic viscosity of the rubber hydrocarbon in latex does not change significantly during the period of latex outflow.

Table VI

Intrinsic viscosity of some samples taken during tapping of trees Nos. 3 and 17

TREE 3			TREE 17	
Consecutive 20 ml. portion tested	L.S.V.	[η] of pptd. rubber	Consecutive 20 ml. portion tested	L.S.V.
1st	—	6.8	2nd	7.0
3rd	4.7	6.8	10th	7.3
10th	4.8	6.75	18th	7.2
15th	4.7	6.7		
25th	4.7	6.75		
Latex yield 540 ml.			Latex yield 195 ml.	

Analysis of variance:—

Source	d.f.	Sum of squares	Mean square	Significance
Between trees	1	31.7857	31.7857	Highly sig. ($P < .001$)
Between days within trees	17	1.9567	0.1151	Sig. ($P < .05$)
Between samples within days and trees ..	5	0.0966	0.0193	
Total ..	23	33.8390		

Effect of depth of sampling on L.S.V.

In one instance a change of tapper to a less experienced individual was associated with a general reduction in both L.S.V. and yield of some trees under review, and it was noticed that his tapping was extremely shallow. Reversion to normal depth of tapping restored both yield and L.S.V.

More specific tests with deep and shallow sampling showed that there was indeed a real difference in L.S.V. and in the intrinsic viscosity of the corresponding precipitated rubbers between samples drawn from near to the surface of the bark and those taken more deeply (Table VII). The magnitude of the difference was in fact dependent upon the success with which a sample could be taken from near the surface without penetrating

more deeply-seated latex vessels. The sampling technique was to cut just above the tapping panel first a shallow groove which just reached the latex vessels, then, when flow had slowed down, to make a deeper incision within the area of the initial groove. The differences observed between the precipitated rubbers confirm that the differences in L.S.V. are real and not due to possible differences in the amount or nature of non-rubber substances.

Table VII

Influence on intrinsic viscosity of deep and shallow tapping

Tree No.	Location of sample	L.S.V.	Intrinsic viscosity of pptd. rubber
17	Outer edge of tapping cut	6.3	8.28
	Inner recess „ ..	6.45	8.42
17	Shallow groove ..	4.40	5.69
	Deep incision ..	6.65	9.02
17	Shallow groove ..	6.25	8.14
	Deep incision ..	6.7	8.68
14	Outer edge of tapping cut	5.0	—
	Inner recess „ ..	5.25	—
14	Shallow groove ..	5.3	8.05
	Deep incision ..	5.8	8.42
	Normal tapping cut ..	5.7	8.25
15	Shallow groove ..	4.85	6.71
	Deep incision ..	5.4	7.12
15	Shallow groove } Opposite tapping panel	4.65	6.81
	Deep incision } Opposite tapping panel	5.9	7.85
18*	Very shallow groove ..	2.5	—
	Shallow groove ..	2.75	—
	Deep incision ..	3.9	—

* This tree was not in tapping.

Effect of storage on L.S.V.

No changes were observed in the L.S.V. of fresh latex during the first four hours after tapping, nor during a few weeks' storage of ammoniated latex or latex preserved under neutral conditions with 1.0% sodium azide

and 0.5% Lubrol W([16]). More prolonged storage rendered the rubber partially insoluble so that the latex could no longer be taken into solution, nor could coagulated rubbers, *which had been dried in vacuo*, then be completely dissolved.

Intrinsic viscosity of rubber hydrocarbon in latex, crepe and smoked sheet

Considerable difficulty accompanies attempts to establish precisely the identity of intrinsic viscosities of rubbers in latex and in dried rubber. Logically this should be done only with purified latex, but every known method of purification has some specific disadvantage. Multi-centrifuging involves considerable loss of rubber of small-particle size([17]), so that the purified rubber is not necessarily representative of the original. Multi-stage electro-decantation, which similarly provides a rubber to which nothing has been added, is slow and difficult to operate on a small scale. Multi-creaming of necessity introduces creaming agents of high oxygen content which cannot be removed from the coagulated rubber, but is less objectionable, from the point of view of subsequent determination of L.S.V., than a more rigid purification involving displacement of surface-active materials by soap prior to creaming since this gives a latex containing residual soap which depresses the L.S.V. Moreover, vacuum-dried rubbers from such highly purified latices are invariably partially insoluble, especially after extraction with acetone or alcohol. The most satisfactory compromise accordingly appeared to be the comparison of L.S.V. with vacuum-dried coagulum using white fraction or multi-creamed latex. Only small differences in intrinsic viscosity were then observed, not greater than could be accounted for by differences in the non-rubber content, while the intrinsic viscosity characteristics of the rubbers precipitated from solutions of the latex or of the dried coagulum were practically identical. Furthermore, the differences between L.S.V. of unpurified latex and the intrinsic viscosity of the corresponding vacuum-dried rubber were not very large (Table VIII). Preparation of smoked sheet, involving several days' exposure to air at 50—65°C, or preparation of crepe, involving some machining, slightly reduced the intrinsic viscosity (Tables VIII and IX).

Table VIII

Comparison of L.S.V. with intrinsic viscosity of vacuum-dried coagulum and smoked sheet

Trees	L.S.V.	Vacuum-dried coagulum	Smoked Sheet
1 ..	4.95	4.95	4.85
2 ..	5.15	5.66	5.79
14 ..	5.25	5.64	5.50
19 ..	5.5	6.11	5.94
15 ..	5.7	6.66	6.16
17 ..	7.6	7.83	7.61
18 ..	7.3	7.4	7.44
Group A, 8 trees ..	5.7		5.53
„ B, 8 „ ..	6.4		5.59
„ C, 7 „ ..	6.1		5.61
„ D, 9 „ ..	6.8		6.18
„ E, 8 „ ..	7.5		6.73
„ F, 8 „ ..	8.0		7.25
„ G, 11 „ ..	7.0		6.35

Table IX

Comparison of L.S.V. with intrinsic viscosity of vacuum-dried crepe, and air-dried crepe prepared from estate latex

Incoming latex	L.S.V.	Intrinsic viscosity of		
		Vacuum-dried coagulum	Vacuum-dried crepe	Air-dried crepe
September 6th	6.1	6.45	5.62	5.60
September 27th	6.4	6.81	5.85	5.65
October 6th	6.0	6.25	5.90	5.63

The viscosity reduction in the crepe samples is attributed to machining rather than to drying in air since the corresponding intrinsic viscosities for vacuum-dried crepe samples were little different from the air-dried samples, whereas the intrinsic viscosities of the crepe samples were considerably lower than those of corresponding vacuum-dried coagula.

Summary and Conclusions

It is abundantly clear that the rubber hydrocarbon as it leaves the tree is already in high polymer form and that changes during estate processing are degradative, although not seriously so.

Inherent viscosities, whether determined with solutions of latex in benzene, or on dried rubbers, are independent of concentration below 0.05 gr. per 100 ml., and are therefore numerically equal to intrinsic viscosities.

Considerable differences exist in average intrinsic viscosities of rubbers from different trees and from different clones, although van Essen's work has shown that considerable tree to tree variation can also occur within a clone. Small random variations are observed in the average intrinsic viscosity of rubber from a given tree from day to day throughout the year, but there is no pronounced seasonal variability.

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Literature Cited

1. Spence and Ferry, *J. Soc. Chem. Ind.*, **58**, 345 (1939).
2. Kemp and Peters, *J. Phys. Chem.*, **43**, 923 (1939).
3. Roberts, *J. Chem. Soc.*, 215 219 (1938); 223 (1942).
4. Bloomfield and Farmer, *Trans. Inst. Rubber Ind.*, **16**, 69 (1940).
5. Gee, *Trans. Far. Soc.*, 36, 1162 (1940).
6. Zimm and Myerson, *J. Amer. Chem. Soc.*, **68**, 911 (1946).
7. Gee, *Trans. Far. Soc.*, 36, 1171 (1940).
8. Hauser and Le Beau, *J. Phys. Coll. Chem.*, **54**, 256 (1950).
9. Cragg, *J. Coll. Sci.*, **1**, 261 (1946).
10. Henderson and Legge, *Can. J. Res.*, **27 B**, 666 (1949).
11. Van Essen, *Rec. trav. chim.*, **69**, 753 (1950).
12. Marvel, F.I.A.T. Report No. 618 (B.I.O.S., 1945).
13. Chambers, *Proc. Rubber Tech. Conf.* (*1948*), p.120.
14. Martin, *ibid.*, p.319.
15. Homans and van Gils, *ibid.*, p.292.
16. McMullen, unpublished work.
17. McGavack, *Ind. Eng. Chem.*, 31 1509 (1939).