London Section.

Meeting held at Burlington House on Saturday,
Nov. 7, 1908.

DR. LEWKOWITSCH IN THE CHAIR.

THE VISCOSITY OF INDIA-RUBBER AND INDIA-RUBBER SOLUTIONS: WITH SPECIAL REFERENCE TO ITS BEARING ON THE STRENGTH OR "NERVE" OF CRUDE RUBBER.*

BY DR. P. SCHIDROWITZ AND H. A. GOLDSBROUGH.

1.—PRELIMINARY COMMUNICATION.

(a) *Introductory.*—The present communication is a record of some preliminary experiments which were undertaken with a view (1) to studying the viscosity of india-rubber solutions; (2) to ascertaining whether there is any correlation between the viscosity of india-rubber (studied in solution) and its strength or "nerve" generally, and what the nature of such correlation may be; (3) to devising, in the event of the experiments under (2) resulting affirmatively, a method for the measurement of india-rubber "nerve" either wholly or partly by means of viscosity estimations.

Our preliminary experiments in this direction have so far proved satisfactory, inasmuch as they appear to indicate that there is a connection between the condition of the soluble rubber substance (as measured by the viscosity of its solution) on the one hand, and the "nerve" of the original crude rubber on the other hand.

We did not anticipate that the results which we might obtain by physical measurements on solutions of rubber could bear a direct relationship to the total "nerve" of the original crude rubber, because it appears to be beyond reasonable doubt that the "nerve" is at least partly due to the mechanical structure or texture, if we may so call it, of the material. It follows, therefore, and we believe that this has not been pointed out by any previous observer, that there are at least two main groups of factors to which the qualities summarised by the term "nerve" are due, namely that which we will, for convenience, call "mechanical" or "structural" "nerve," and that which may be termed "physical" or "chemical" "nerve."

(b) *The Viscosity of India-rubber Solutions.*—We have not been able in the literature of the subject to find any record of any determinations of an exact nature of the viscosity of india-rubber solutions. The instrument employed by us was an Ostwald capillary double bulb viscometer (Fig. 1) of the approximate dimensions:—Total height of apparatus, 24 cm. Capacity of Bulb A, 11 c.c. Capacity of Bulb B, 10 c.c. Length of capillary, 4.5 cm. Bore of capillary (approx.), 1 mm.

In the experiments made so far we have employed only one solvent, namely pure benzene, and the solutions examined have been of a relatively dilute nature, containing, as a maximum 1 to 1.5 per cent. of the solute. The standard temperature at which the experiments were conducted was 20° C.

The rubber solutions were prepared by weighing a definite quantity of rubber (generally one gm.) cut into very small pieces and exposing these to the action, at the required temperature, of a measured volume of solvent. After solution had taken place the sometimes bright, but occasionally turbid solutions were filtered through a plug of glass wool in order to remove mechanical impurities. In our earlier experiments in the cases in which solution appeared to be practically complete the concentration of the solution was calculated from the quantity of rubber and solvent originally employed.† In our later experi-

Fig. 1.

ments—and this is the method which we now always employ—the actual quantity of rubber in solution was estimated by evaporating a known volume of the filtered liquid and weighing the residue. In the experiments conducted at the ordinary temperature of the laboratory the samples together with the solvent were placed in glass bottles, protected from the action of light and shaken (as little as possible) at regular intervals and in a regular manner.*

Series 1.—The rubbers examined consisted of six samples of *Funtumia elastica* (Nos. 1–5 and 7); three samples of *Hevea Braziliensis* from Eastern Plantations (Nos. 8, 9, and 10), and a sample of "Fine hard Para" (*Hevea B.* from Brazil).

The *Funtumia* samples 1–5 consisted of somewhat dark, but clear, corrugated sheets which appeared to be strong and normal in character. No. 1 was perhaps rather weaker than the others. No. 7 was a thin light brown sheet rubber, obviously of a somewhat abnormal character. None of the samples were "indigenous" rubbers; that is to say, they had all been prepared from fresh latex under skilled European superintendence. We are indebted for these samples to the Mabira Forest Company of Uganda. The general analytical figures, on analysis, were as follows:—

TABLE I.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 7.
Moisture	per cent. 0.50	per cent. 0.72	per cent. 0.61	per cent. 0.36	per cent. 0.34	per cent. 1.74
Resin	7.59	7.41	7.69	8.18	9.80	6.79
Ash	0.41	0.60	0.43	0.52	0.64	1.22

Judging by our previous experience of *Funtumia* rubbers these figures are fairly normal, excepting that the resin in No. 5 is rather high, and in No. 7 rather low. The latter sample also contained a rather high percentage of ash. The three samples 8–10 were plantation *Hevea* "crêpes" (from Ceylon or Malaya) obtained on the London market. No. 8 was a greyish yellow, No. 9 of a light yellow, and No. 10 of a very pale cream colour. They were practically dry. The sample of "Fine hard Para" employed as a control—inasmuch as this variety of rubber is the standard of industrial quality—was of considerable age, and therefore, perhaps, not quite so satisfactory as a fresher sample might have been, but the reasons for

* Taken as read.

† It is possible that, for this reason, some of our earlier figures may be rather too low.

* Full details of the method of work, the limits and influence of temperature, &c., are reserved for a future communication.

using this particular specimen were (1) that it was practically dry, (2) that it had dried naturally, (3) that the dimensions of the clear, translucent layers were such as to make the cutting of test strips for the mechanical tests (*cf. infra*) a practical possibility. The amount of resin in the sample was rather high, namely, 3.46 per cent. The following table shows the results of the viscosity determinations carried out with the rubbers described above.

TABLE II.

No. or mark.	Nature of rubber.	Concentration of benzene solution per cent.	Relative viscosity (benzene = 1).
1	<i>Funtumia elastica</i> (Corrugated sheet)	1.0	19.1
		0.5	5.3
		0.25	2.2
2	" "	1.0	35.3
		0.5	7.6
		0.25	2.7
3	" "	1.0	27.3
		0.5	6.1
		0.25	2.5
4	" "	1.0	37.0
		0.5	7.2
		0.25	2.7
5	" "	1.0	37.6
		0.5	7.8
		0.25	2.9
7	(sheet)	1.0	16.6
		0.5	2.9
		0.25	1.6
8	Plantation <i>Hevea</i> (crepe)	1.0	6.7
		0.5	2.7
		0.25	1.6
9	" "	1.0	9.3
		0.5	3.3
		0.25	1.6
10	" "	1.0	9.1
		0.5	3.1
		0.25	1.7
Flac hard Para	Brazilian <i>Hevea</i>	1.2	40.6
"	" "	1.0 (calculated)	26.2
"	" "	0.55	7.1
"	" "	0.24	1.7

Of considerable interest in the above table are the very low figures shown by the plantation *Hevea* specimens as compared with the Brazilian *Hevea* and the *Funtumia* specimens. Graphically represented (Fig. 2) the results are still more striking. No. 7, which was known to be of a somewhat abnormal character, gives an abnormal curve.

The flat nature of the curves shown by Nos. 8—10 as compared with the other rubbers induced us to make an attempt to ascertain the comparative strengths of these typical samples by some direct physical method. If the rubbers had been in homogeneous sheet form, this would have been a comparatively easy matter, but as it is obviously impossible to cut strips for tension experiments from corrugated sheet or "crêpe," some other expedient had to be adopted.

The method employed by us was to dip strips of "quantitative" filter paper 60 by 10 mm. into 1 per cent. benzene solutions of the rubbers, to allow the strips to dry and then to ascertain the breaking strain. The figures obtained were as follows, the results denote grams and in each case represents the mean of a number of determinations:—

No.	Breaking strain.
Paper alone (undipped).....	700
Rubber No. 1	950
" No. 8	860
" No. 10	860

The results, naturally, can only be regarded as a rough approximation, but they serve to indicate that there is a connection between the viscosity curves and the strength of the rubbers in question. The increased strength imparted by the relatively viscous rubber No. 1 to the paper compared with that imparted by the rubbers of low viscosity (8 and 10) is roughly as 25 : 16.

Further confirmation of the connection between viscosity and strength in these particular samples was afforded by considerations of a purely empirical, though to some extent of a highly practical nature. In brief, Nos. 8—10 were decidedly brittle or "short," whereas the other rubbers gave satisfactory indications in response to the crude but by no means useless "hand-pulling" test.

Nature of the viscosity curves.—It will be observed, on referring to Fig. 2, that beyond a certain viscosity, the

FIG. 2.

curves become straight lines. This was confirmed by subsequent experiments. If, for the sake of convenience, the point at which the curve becomes a straight line, is termed the *critical point*, it follows that for all readings above the critical point, the viscosity is directly proportional to the concentration. If it were found, on producing the part of the curve above the critical point downwards, that all the straight lines thus produced met in a common point, it would follow, taking the viscosity of the rubber itself as equal to that of a 100 per cent. solution, that the viscosities of different rubbers would be inversely proportional to the concentration of the solutions at a fixed viscosity above the critical point and *vice versa*. This, however, is not the case, and the conclusion which, we think, is of some importance, is that although for any given rubber the viscosity of a solution (naturally at a fixed temperature) is proportional to the concentration at any given point above the critical point, yet the viscosity of the rubber itself cannot be ascertained by reference to such a point, and consequently the viscosities of two rubbers cannot be compared by ascertaining the viscosities of their solutions at a fixed concentration.

In order to compare different rubbers in regard to their viscosity we took two points (above the critical point) on each curve, and, inserting the values successively in the linear equation, $y = mx + c$, (where x = concentration and y = viscosity), obtained m and c . By inserting m and c in the equation where $x = 100$, we obtained y , the viscosity of a 100 per cent. solution—i.e., of the rubber.

The error involved in this method of calculating viscosity is, we think, small, provided that the concentration of the solution examined is ascertained with accuracy. Assuming that the concentration is in the neighbourhood of 1 per cent., at least 50 c.c. of the solution should be taken for the determination of the quantity of the rubber contained.

The values calculated by this method for Nos. 1—5 and "Fine Para" were as follows:—

No.	Viscosity (benzene = 1.0).
1	4966
2	8046
3	7551
4	9343
5	9940
Fine Para	7253
8	1000 (approx.)
9	1400 "
10	1400 "

It is obvious from the curve why the values for Nos. 8, 9, and 10 could not be calculated. It is probable that if we had been in a position to obtain readings at higher concentrations this might have been done. With regard to these three rubbers, we were not satisfied that we had reached the critical point, and we were unfortunately not in a position to determine the viscosities at higher concentrations. In any case it is quite obvious that the values for these three specimens must be very low.

Second series.—This series consisted of three rubbers concerning which the origin, nature, and age of the trees (at the time of tapping), were accurately known. In addition, the specimens were all in sheet form, and ordinary tension experiments could therefore be applied and the results compared with the viscosity numbers and "practical" opinion concerning their quality.

With regard to the "nerve" or strength of these rubbers judged by the ordinary method of pulling by hand, the remarks were made that A was rather lacking in strength, B was fairly strong, and C was very strong.

Viscosity experiments.—The numbers obtained with specimens A, B, and C were as follows:—

TABLE III.

Mark.	Ceylon <i>Hevea</i> rubber.	Concentration of benzene solution per cent.	Relative viscosity of solution (benzene = 1).
	Age of tree, years.	per cent.	
A	8	0.86	6.6
		0.43	2.6
		0.21	1.5
B	6-13	1.00	21.4
		0.50	5.2
		0.25	2.2
C	30	1.00	32.3
		0.50	6.8
		0.25	2.5

The results obtained are shown graphically in Fig. 2. The most interesting feature of the figure is the very flat nature of curve A as compared with B and C.

By calculation (*cf. supra*) viscosity values for the actual rubbers (*i.e.*, of 100 per cent. solutions) were obtained as follows:—

Mark.	Viscosity of rubber (benzene = 1).
A	1250 (approx.)
B	6653
C	8843

Tension experiments.—Strips of a cross-sectional area as nearly as possible 40 sq. mm. and sufficiently long to

allow a distance of 30 mm. between grips, were cut for rubbers A, B and C, and for comparative purposes also from the sample of "Fine Para" referred to above. The strips were then broken in a vertical, direct pull machine,* the breaking strain and elongation at break being observed. The units taken were: for the breaking strain, grams per sq. mm. of cross-sectional area; for the elongation, the original length of the strip between lines drawn between the grips. Each figure represents the average of a number of determinations. A second series of experiments was made with similar strips in order to determine the minimum weight per unit of cross-sectional area which would, under certain conditions, cause a permanent distension of the material. The figure so obtained we call the "co-efficient of resiliency," although possibly a better term might be "limit of elasticity."

The results of the tension experiments will be found below in Table IV. We have added the details concerning the nature, &c., of the rubbers and also the viscosity figures, so that a comprehensive view of the whole results in regard to Series II. may be obtained.

TABLE IV.

Mark.	<i>Hevea</i> rubber.	Elongation at break.	Break- ing strain.†	Co- efficient of resiliency.†	Viscosity (benzene = 1).
A	Ceylon, from 8 year old trees, weak.	4.5	58	21.6	1000 (approx.)
B	Ceylon, from 6-13 year old trees, fairly strong.	8.0	52	24	6653
C	Ceylon, from a 30 year old tree, very strong.	9.75	218	57	8843
Fine Para	Brazilian, fair, but old specimen.	10.0	406	75	7253

† Grms. per sq. mm. of cross-sectional area.

The general superiority of C and the Brazilian specimen over A and B is obvious. The inferiority of B is not so marked, however, in regard to viscosity as with respect to the other factors, and we suggest that it is possible that we have here a case where a rubber is relatively weak as regards its mechanical structure, but fairly satisfactory with respect to the chemical or physical structure of its mass. It will be noticed also, that whereas C is inferior to the Brazilian specimen with regard to breaking strain and resilience, that its viscosity is superior to that of the latter. We think that in the case of the Brazilian product there is not the slightest doubt that a considerable proportion of its mechanical strength is due to purely mechanical causes, and that comparing it with C, the viscosity figures are probably a better criterion of the relative "nerve" of the actual rubber substance of the two specimens than the tension results.

Another point of interest is that the specimen A, which is inferior to B in every other respect, shows a rather higher figure for breaking strain. We think the explanation of this point is not far to seek. This specimen (A) contained a good deal of insoluble matter, and experience has led us to know that the presence of a certain type of insoluble matter in rubbers indicates that they have gained somewhat in toughness at the cost of elasticity and resilience. In such cases the breaking strain may be comparatively high, but the elongation and resilience are always low. We have referred above to "a certain type" of insoluble matter, because it appears to us that it is necessary to differentiate between the insoluble matter present in old or exposed rubbers which is probably an oxidation or hydration product,‡ or a mixture of both,

* We may add—although this does not apply to the experiments here recorded—that we have in our most recent work discarded, for general work, tension apparatus of the ordinary "grip" type, as we have found that more accurate and rapid results may be obtained with the new Schopper apparatus, in which a ring shaped test body (obtained by double punching) working over revolving rollers is subjected to vertical tension by means of hydraulic power.

† Weber, "The Chemistry of India-Rubber," pp. 7-12, and Spiller, J. Chem. Soc., 1865, 44.

and the insoluble matter present in the fresh "hard cure" Brazilian *Hevea*, which according to Spence* consists mainly or largely of fibrous proteid substance. The insoluble matter to which we have referred in connection with sample A shows the characteristics of the former and not of the latter variety. We may also call attention to the fact that the viscosity figures for A, B, and C are in accord with "practical opinion" regarding the relative strength of these three specimens. At the same time, we do not wish, before having accumulated further data, to lay any undue stress on the fact, nor should we be justified in concluding at all positively that the differences observable are due primarily to the relative ages of the trees from which these rubbers were obtained. It is an undoubted fact that the method of coagulation† plays an important part in connection with the question of "nerve," and that variations in the quality of latices obtained from trees of the same species may be due to other causes than that of age.

Meeting held at Burlington House on Monday, Dec. 7, 1908.

DR. LEWKOWITSCH IN THE CHAIR.

THE STRUCTURE OF CRUDE INDIA-RUBBER.

BY PHILIP SCHIDROWITZ, PH.D.

Preliminary Note.

According to W. B. Hardy‡, "common black india-rubber" in sections cut with the freezing microtome displays the structure common to many organic gels, namely, that of an open net or fine open sponge. Now, the ordinary "black india-rubber" of commerce is vulcanised rubber, and it is therefore a little difficult to know whether Hardy referred to ordinary black vulcanised rubber or to some particular variety of black crude (i.e., unvulcanised) rubber.

Apart from this "open net" structure, which may or may not be an attribute of the crude variety¶, it has been assumed that the main substance of ordinary crude, dry india-rubber is a structureless mass§, and that after coagulation has taken place, and certainly after the coagulated rubber has become dry, that the original globular condition of the rubber particles as seen in the latex disappears; indeed, there has been a serious discussion as to whether the globules in the latex were actually rubber or some substance which, at the moment of coagulation, polymerises into the rubber hydrocarbon,|| after the globules containing it have first burst their envelopes, and discharged their contents. I have found from observations made on two different species, namely, *Hevea Braziliensis* and *Funtumia elastica* :—

* *Loc. cit.*

† Schidrowitz and Kaye, *India-Rubber Journal*, 23rd Sept., 1907, and V. Henri, *loc. cit.*

‡ *J. of Physiology*, 24, 189.

§ I have not been able to observe "net" structure in films of crude rubber obtained either (a) by squeegeeing on to a slide solid rubber softened with a solvent; (b) by evaporating off the solvent from a benzene solution; (c) or by coagulating a film of latex between a slide and cover glass; but it is possible that microtome cut sections might show the structure referred to. If, however, a film, obtained by evaporating off a few drops of a 1 per cent. benzene "solution" on a slide, is subjected to the action of a dilute solution of sulphur chloride in benzene (1:100) for a few seconds, I have found that (after removing excess of the reagent by means of acetone, and subsequent drying) a pronounced net structure is formed. If the treatment with sulphur chloride is continued for some minutes, the net structure becomes much more pronounced and presents a really remarkable appearance. Whether this net formation is an essential or an accessory feature of the process of "cold curing"—as vulcanisation with solutions of sulphur chloride is termed technically—or of vulcanisation in general, is a matter well worth investigation, and I propose to do so in the future.

¶ Cf. Weber, "The Chemistry of India-Rubber," p. 17, and D. Spence, *Inst. Comm. Research in the Tropics J.*, No. 13, 1907.

|| Weber, *Ber.*, 1903, 36, 3108—3115; *Gummi-Zeit.*, 19, 101—104; A. W. de Jong and W. R. Tromp de Haas, *Ber.*, 1904, 3298—3301; Esch and Chwolle, *Gummi-Zeit.*, 19, 165—166; &c.

(1) That if a thin preparation* of transparent dry rubber is examined under the microscope with magnifications of about 900 and upwards, it is seen to contain very numerous globules, similar in appearance and size to the globules present in the latex.

(2) That if such dry rubber is dissolved in benzene (cf. preceding communication) and examined in solutions of 1 to 5 per cent. strength with reflected light by means of the Leitz dark ground illumination and parabolic condenser, that is to say, on the principle of the ultra-microscopic method, the "solutions" are seen to contain numerous globular particles, these again being similar to those present in the latex.

(3) That if a drop of such a benzene "solution" is allowed to evaporate on a slide, the resultant film presents much the same appearance as a drop of diluted and dried latex, or of a drop of diluted latex coagulated by suitable means, the only difference being that the reticulated structure is not visible to any marked extent. The globular particles are, however, visible in large numbers in every case.

(4) That if a drop of diluted (*funtumia*) latex is coagulated by means of heat between two cover-glasses, the reticulation is seen to consist of branches of more or less structureless matter in which chains of and single globules are enmeshed in large number.

In connection with the films obtained by squeegeeing or from "solutions," those which were quite transparent showed the globules less distinctly than those which were slightly opaque. When, however, such a transparent film is touched or irritated with a glass rod or otherwise, the portions touched become less transparent, and at the same time the globules appear much more sharply defined. When a clear film, showing the globular structure somewhat imperfectly, is treated with a dilute sulphur chloride solution, the resultant preparation, in addition to showing very pronounced "net" structure, exhibits the globules distinctly. Such preparations are slightly opaque. It is possible that the clear film is an approximation to a solid solution of the globules, the opaque film to an irreversible gel.

In conclusion, then, it appears that the globules are not destroyed by coagulation of the latex, but that they continue to exist in the dry rubber and are not removed even by "solution" in benzene.

I take this opportunity of expressing my thanks to Messrs. Leitz for placing at my disposal some of the special optical instruments necessary for this work.

* *Note.*—The methods employed for obtaining preparations were :—(1) Squeegeeing a thin (hand cut) section on to a slide after softening with chloroform; (2) evaporation of a few drops of a benzene solution, so forming a film; (3) a homogeneous strip was punched from a very thin transparent sheet. This strip was then drawn out until very thin, and a part fixed, while under tension, on to a slide by means of shellac.

Newcastle Section.

Meeting held at Armstrong College on Thursday, Dec. 10, 1908.

MR. C. J. POTTER IN THE CHAIR.

CHEMICAL CHANGES IN PORTLAND CEMENT CONCRETE, AND THE ACTION OF SEA WATER THEREON.

BY CHARLES J. POTTER.

Some years ago the failure of the Portland cement concrete in a dock was brought to my notice; the work had stood well in the sea water for two or three years after completion, after which the walls commenced to show signs of failure, the concrete turning quite soft in places and showing great expansion, and this serious action went on so rapidly that reconstruction was necessary. This failure and several others of a similar nature, induced me to make experiments to try and find out the cause with the hope that I would be able to discover some method of prevention.