

processes. In some early experiments a mixture of carbide and borax, or carbide and sodium chloride was found to be a most efficient de-oxidising flux for copper and some copper alloys—as bronzes—cupro-nickel, &c., perfectly bubble-free castings being obtained. About one ounce of carbide to the usual amount of borax, was quite sufficient for each 10 lb. pot of metal when added before the last stirring. With bronzes, bronzes, or cupro-nickel, a good time to add the carbide-borax was found to be at the first melt when the last portions of copper, &c., were being added.

A considerable number of metallic oxides are reduced to the metallic state by carbide, but unless the metal is very fusible or a large amount of flux—borax—sodium or magnesium or barium chlorides—be employed, the infusible calcium oxide and any separated carbon or free carbide hold up the metal in shots or globules.

Attempts to reduce some of the rarer oxides, as those of cerium, zirconium, &c., and form alloys with copper failed at ordinary coke-furnace temperatures.

It appeared probable, however, that the halides of these rarer metals might be reduced by carbide which would at the same time form a calcium halide capable of acting as a flux. Trials with copper, lead, silver, zinc, and other metallic halides proved that, at suitable temperatures, reduction was complete and the calcium halide (chloride) formed a fairly efficient flux but the separation of the metal was retarded by the liberated carbon. The addition of salt, barium chloride, or borax (none of which has any action on carbide) overcame this difficulty.

The liberated carbon sometimes takes the graphitic form. Experiments with cerium chloride (CeCl_2), carbide, and metallic copper showed that cerium was reduced and taken up by the copper, alloys containing 6 per cent. and more of cerium being obtained.

It may here be noted that a convenient method of obtaining metallic chlorides in a state ready for further metallurgical work is to drop a mixture of metallic oxide and ammonium chloride into a red hot crucible, in small portions at a time. A very slight excess only of the ammonium chloride is necessary. In most cases the chloride is obtained in the melted state.

Two methods have been employed for obtaining alloys; one in which the main constituent—say copper—was melted and a mixture of the halide of the alloying metal and carbide then added; and, a better plan, where both, or all, metals for the alloy were in the form of halides roughly mixed with the calculated amount of carbide and in the case of low melting point metals some additional flux—as borax or salt. For alloys of high melting point, such as nickel and manganese, the carbide alone acted perfectly.

The chlorides and fluorides of most of the common metals react energetically with carbide provided the starting temperature is high enough—somewhat like the aluminium thermite reaction. As far as has been ascertained, the best starting temperature is one a little higher than the melting point of calcium chloride or other halide employed. The results have certainly been better where the carbide—metallic halide mixture has been introduced in successive moderate quantities into an already hot crucible than by slowly heating up a cold charge.

Employing this method—the hot crucible—no difficulty has been found in making copper—manganese or copper—nickel of almost any desired content of Mn or Ni, using manganese chloride or nickel chloride and either copper turnings or copper chloride. Similarly with nickel—manganese, or cobalt—manganese, both metals as chlorides.

Tantalum, titanium, zirconium, and other metals which form salts of the types, K_2TaF_6 or K_2TiF_6 , have been reduced and alloyed with copper. From one product containing above 20 per cent. Ta most of the tantalum segregated out during cooling and was left as a metallic powder on solution of the alloy in dilute acid.

From manganese chloride alloys have been obtained with tin, bismuth, antimony, and lead, employing these metals in the metallic state. The first product with lead, using the metal, contained 5.6 per cent. Mn: using PbCl_2 , higher proportions of manganese were obtained. (These products from the microstructure seem to be suspensions of metallic manganese in lead.)

The tin and bismuth “mixtures” or solutions of manganese are only so far interesting that with more than 10 per cent. Mn they show decided magnetic properties.*

In cases where iron and aluminium free alloys are required the carbide reduction may be of value. Only in the cases of nickel, cobalt and iron with manganese did there appear to be any carbon taken up. A manganese-cobalt alloy for instance, contained, Mn 38. Co. 59 and graphite 3 per cent.

The method and some of the products are being further investigated.

Specimens of alloys, such as Cu-Mn, Cu-Ce, Cu-Ta, Cu-Ti, Bi-Mn, Sn-Mn, Sb-Mn, Co-Mn, Ni-Mn, prepared by the process, and having in most cases atomic proportions of each element, and micro-photographs, were shown at the meeting.

I am indebted to Capts. Hunter and Macrae for analysis and other help.

DISCUSSION.

Mr. E. GRANT HOOPER said Professor Hodgkinson had struck out a new line in this utilization of calcium carbide in the preparation of alloys. He thought the paper introduced an interesting and he trusted an important departure in connection with the preparation of alloys.

Professor HODGKINSON said he was reserving an account of the properties of some of the alloys. He only spoke of the method because he thought it would be useful, and he was sure there was room for its development. There was a difficulty. Some of the halides were volatile, necessitating a careful adjustment of temperatures, but he thought it was possible in most cases to arrange matters and obtain the product with little loss.

Meeting held at Burlington House, on Monday April 6th, 1914.

PROF. W. R. HODGKINSON IN THE CHAIR.

THE VISCOSITY OF RUBBER SOLUTIONS:

BY R. GAUNT, M.Sc., PH.D.

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Considerable interest attaches to the viscosity of rubber solutions, not only because they are colloidal solutions, but also on account of the suggestion put forward first by Axelrod¹ and afterwards by Schidrowitz and Goldsborough² that the viscosity of a rubber solution stands in intimate relationship with the quality and technical value of the rubber.

Schidrowitz³ regards the so-called “nerve” of rubber as due to three factors:—(a) Mechanical structure as indicated by the film structure of fine hard Para, and brought about by the method of conglutination; (b) physical structure or colloidal aggregation of the rubber particles; (c) chemical structure or molecular complexity.

The mechanical structure of crude rubber is largely broken down in the washing and mixing operations, and is therefore only a small factor in the quality of manufactured rubber. Schidrowitz suggests that viscosity measurements connote the physical and chemical structure of rubber although the exact relation is uncertain. He states⁴ that within the same species viscosity measurements are a means of determining strength and vulcanising capacity; comparing species with species, however, this does not hold directly.

Beadle and Stevens⁵ however, found that although some relationships can be detected, the general results of viscosity determinations are not in accordance with those obtained by vulcanisation.

* Their properties will be described in a further communication.

¹ Gummi Zeitung, 1905, 10, 1053, and 20, 105.

² This Journal, 1909, 22, 3, “The Rubber Industry,” p. 260. (The International Rubber and Allied Trades Exhibition, Ltd., 1911).

³ “Rubber,” p. 163 (Methuen and Co., 1911).

⁴ “Rubber,” p. 165.

⁵ “The Rubber Industry,” pp. 260 and 270.

Recently the viscosity of rubber solutions has been submitted to systematic study by G. S. Fol⁶ who points out several precautions that must be taken in making viscosity determinations:—

(1) Comparative results can only be obtained by using a viscometer of standard dimensions, the differences in the results obtained with two different viscometers being much greater in the case of concentrated solutions than in the case of dilute solutions.

(2) The determinations must be made at a fixed temperature. The absolute viscosity of a rubber solution diminishes with rise of temperature. The relative viscosity however remains practically constant between 20° and 70° C.

(3) The rubber should be dissolved as completely as possible.⁷ When the rubber is only partially dissolved the solution has for the same concentration a slightly less viscosity than when the rubber has been dissolved as completely as possible. This, Fol thinks, is probably due to the fact that the resins dissolve most readily and have very probably a lower viscosity than rubber itself.

(4) Viscosity is influenced by strongly shaking when preparing the solution, presumably, according to Fol, in consequence of the insoluble constituents being suspended in such a finely divided condition in the solution that they cannot be segregated by filtration through glass wool. He concludes that these particles contribute to viscosity in a larger measure than if one introduced into the solution the same weight of rubber.

Recently⁸ H. P. Stevens by fractionally dissolving rubber in benzene, obtained fractions of different viscosity but he attributes the variations to differences in the resin content of the various fractions.

In the following experiments on the viscosity of rubber solutions the method of procedure was almost identical with that suggested by Fol. The majority of the experiments were made with the following different kinds of rubber:—

- (a) A pale thin plantation crêpe Hevea, coagulated by means of acetic acid.
- (b) Fine hard Para,
- (c) Castilloa, prepared by centrifugalisation,
- (d) Funtumia sheet,
- (e) Ceara biscuits.

These rubbers had the following composition in the dry state:—

	Plan- ta- tion Hevea.	Fine hard Para.	Cast- illoa.	Fun- tumia.	Ceara.
	per cent.	per cent.	per cent.	per cent.	per cent.
Caoutchouc	93.8	91.0	85.8	86.2	91.2
Resin	3.1	3.3	13.8	11.0	4.8
Protein	2.7	1.8	0.3	1.7	3.0
Ash	0.4	0.3	0.1	0.2	1.0

The dry rubber was comminuted as finely as possible by means of scissors. A weighed quantity was placed in a stoppered bottle with a definite volume of solvent, shaken for two or more hours, and then allowed to stand over night. Next morning the solution was filtered through cotton wool and the concentration was determined by evaporating 10 c.cm. of the filtered solution *in vacuo* in a tared weighing bottle.

The viscosity was determined by means of an O-twald viscometer in a thermostat which was maintained at a temperature of 20° C. \pm 0.1° C.

The solvents employed were:—

Benzene, purified by repeated shaking with concentrated sulphuric acid, washing with water and alkali, finally drying and redistilling. In some cases the benzene was further purified by freezing.

Ether, purified by shaking with water, then drying by means of calcium chloride, and finally distilling over sodium.

Petrol, redistilled, the fraction distilling below 50° C. was employed.

Toluene, purified by repeated shaking with concentrated sulphuric acid, washing with alkali and water, drying by means of calcium chloride, and redistilling. The fraction distilling between 110° and 111° C. was employed.

Commercial xylene.

Chloroform purified by washing with water, drying and redistilling.

The Solubility of Rubber.

Rubber shows considerable variation in the extent to which it will go into "solution." Thus whereas the Castilloa and Funtumia rubbers examined mix with solvents in all proportions, the Para and Ceara rubbers are only partially "soluble." This fact is of considerable moment when one is drawing conclusions from the viscosity of rubber solutions as to the properties of the original rubber.

The following table shows the extent to which the Para and Ceara rubbers went into solution when the comminuted rubber was shaken with solvents for 2–3 hours and the concentration of the solution determined next day.

Solvent.	Weight of rubber per 100 c.cm. solvent.	Concentration of solution produced (grams per 100 c.cm.).			
		Fine hard Para.	Fine hard Para creped 45 min. in the cold.	Plan- ta- tion Para.	Ceara.
Benzene	0.5 grm.	0.21	0.26	—	0.30
	1.0 grm.	0.48	0.56	0.92	0.74
Ether	1.0 grm.	0.41	0.51	—	0.72
	2.0 grms.	0.84	1.03	—	1.43
Petrol	1.0 grm.	0.27	0.46	0.32	0.67
	2.0 grms.	0.72	0.99	—	1.59

A noticeable feature of the above results is that the greater quantities of rubber yield a rather more than proportionate amount of dissolved matter to the same quantity of solvent. It would appear therefore that the dissolved rubber causes a partial solution of the insoluble constituent.⁹

Fine hard Para is the most insoluble of rubbers, especially in the unwashed condition. In an experiment in which two grams of resin-extracted fine hard Para were extracted in a Soxhlet with benzene only 1.03 grams went into solution.

As will be seen, however, from the above results passing fine hard Para through the washer for 45 minutes in a stream of cold water raises the solubility considerably. Heating with solvents also increases the amount going into solution, as the following results show:—

	Concentration of solution produced, per cent.
0.5 gram Fine hard Para was shaken with 50 c.cm. xylene	0.49
0.5 gram Fine hard Para was heated to 100° C. for several hours with 50 c.cm. xylene	0.65
0.5 gram Fine hard Para which had been creped for 45 minutes in a stream of cold water was heated to 100° C. for several hours with 50 c.c. xylene ..	0.75

To explain the partial solubility of rubber in solvents Caspari has recently¹⁰ revived the view of Gladstone and Hibbert¹¹ and Soeligmann¹² that rubber contains a soluble and an insoluble caoutchouc. According to Weber¹³, however, the amount of insoluble matter in rubber can be reduced by successive extractions with chloroform, to a very small percentage, and according to

⁶ India Rubber Journal 1913, 45, 578 *et seq.*

⁷ Fol made all his experiments with a sample of Hevea Plantation Rubber from Java.

⁸ India Rubber Journ., 1913, 40, 345.

⁹ Cf. this Journal, 1912, 31, 518.

¹⁰ This Journal, 1913, 32, 1041.

¹¹ Journ. Chem. Soc., 1888, 63, 670.

¹² Le Caoutchouc et la Gutta Percha, 1896.

¹³ This Journal, 1900, 19, 680.

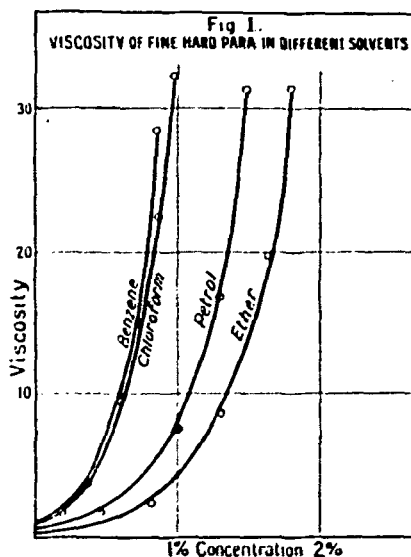
Spence¹⁴ it consists largely of protein. Even Caspari admits that his "pectous form" of caoutchouc "may conceivably be simply a residue of sol-forming rubber which has failed to burst its way out of a micellular framework possibly consisting of the rubber constituent commonly referred to as protein," but he maintains that there is no proof that the nitrogenous matter encloses rubber particles. And indeed it seems remarkable at first sight that the small amount of protein, if it is actually protein, should prevent twenty to thirty times its weight of caoutchouc from going into solution. However, there is yet no convincing proof that an insoluble pectous form of caoutchouc exists. Indeed the *Castilloa* and *Funtumia* rubbers examined mix completely with solvents and a priori one would hardly expect the pectous form of caoutchouc to exist in some species of rubber and not in others. Moreover there is no sharp line of demarcation between the soluble and insoluble forms of caoutchouc, for as is apparent from the above results, crepeing the rubber as well as heating with xylene causes more caoutchouc to pass into solution; from which one may conclude that the partial solubility of Para and Ceara rubbers is due, at any rate to some extent, to the structure of the rubber or state of aggregation of the caoutchouc.

The fact however that part of some rubbers remains undissolved in the usual method of making solutions for viscosity experiments considerably detracts from the value of viscosity determinations unless one can assume that the undissolved portion has the same viscosity as the dissolved caoutchouc. An attempt to ascertain if this was the case by treating the insoluble residue with fresh solvent failed owing to the very slow rate of solution of the residual rubber. H. P. Stevens,¹⁵ however, has determined the viscosity of different fractions of rubber in benzene and finds only small differences which he explains was due to the varying amounts of resin present.

Viscosity of Rubber in Different Solvents.

Rubber produces with different solvents "solutions" of different viscosity. In the following experiments the viscosity of solutions of various rubbers in benzene, chloroform, petrol and ether was determined at different concentrations.

The relation between the viscosity in the different solvents is shown in the adjoined curves (Figs. I.—III.).¹⁶ It will be seen that ether produces solutions of least viscosity. Benzene and chloroform, on the other hand, produce solutions of greatest viscosity. The plantation Para rubber examined gave a solution in benzene of low viscosity; this difference is shown in a greater degree in ethereal solution.



Viscosity of different Rubbers in Benzene Solution.

In order to compare the viscosity of caoutchouc in different rubbers it is necessary to make a correction for the amount of resin (which may be considerable in the case of *Castilloa* and *Funtumia* rubbers). When this is

Rubber.	Benzene.		Petrol.		Ether.		Chloroform.	
	Concentration (grms. per 100 c.cm.).	Viscosity (water=1).	Concentration (grms. per 100 c.cm.).	Viscosity (water=1).	Concentration (grms. per 100 c.cm.).	Viscosity (water=1).	Concentration (grms. per 100 c.cm.).	Viscosity (water=1).
Fine hard Para....	0.20	23.32	1.52	35.81	1.95	40.68	1.00	32.27
	0.71	13.87	1.30	10.65	1.64	19.72	0.86	22.35
	0.61	9.64	1.00	7.45	1.31	8.63	0.51	—
	0.44	5.12	0.48	1.31	0.85	2.04	0.37	3.74
	0.25	2.23	—	—	—	—	—	—
Castilloa.....	1.00	27.12	1.65	29.37	2.05	36.98	0.94	39.24
	0.83	16.56	1.36	13.15	1.85	22.18	0.87	28.31
	0.61	8.13	1.04	7.23	1.53	12.36	0.70	15.09
	0.38	2.70	0.54	1.31	0.67	1.60	0.41	4.63
Funtumia	1.14	36.14	1.67	35.08	1.57	18.34	1.12	44.70
	0.93	17.04	1.34	15.35	1.24	8.63	0.95	24.40
	0.67	9.34	1.19	10.03	0.95	3.94	0.78	14.20
	0.33	2.77	1.00	0.14	0.40	1.13	0.33	3.40
Plantation Para ..	1.45	33.75	2.72	17.62	3.17	41.42	1.34	34.32
	1.20	19.30	2.32	10.78	2.42	14.10	1.17	20.55
	0.88	9.34	1.77	4.82	1.72	4.88	0.86	9.45
	0.43	2.89	0.96	1.36	0.51	1.48	—	—

Solvent.	Fine hard Para after 45 min. crepeing in cold water.		Castilloa after 45 min. crepeing in cold water.	
	Concentration (grms. per 100 c.cm.)	Viscosity (water=1)	Concentration (grms. per 100 c.cm.)	Viscosity (water=1)
Benzene	2.06	32.90	1.67	31.30
	1.80	22.13	1.38	19.11
	1.26	9.64	1.05	10.19
	0.75	3.87	0.54	3.08

¹⁴ Journ. Inst. Comm. Res. Tropics, 1907, No. 13.

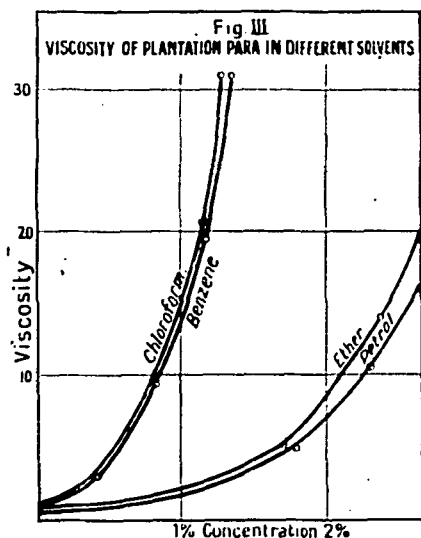
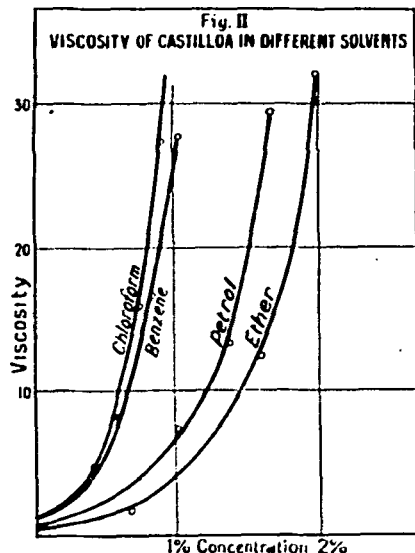
¹⁵ Loc. cit.

done and the viscosity is plotted against the concentration, the curves shown in Figure IV. are obtained. The fine hard Para and *Castilloa* curves practically coincide, from which one might conclude that the caoutchouc in the *Castilloa* sample and the soluble caoutchouc in the fine hard Para are of equal quality. When the fine hard Para, however, had been passed through the washing machine for 45 minutes in a stream of cold water it produced solutions of much less viscosity. The *Castilloa* rubber, after washing under the same conditions,

¹⁶ The curves for Funtumia rubber are similar to those for *Castilloa*, and are omitted.

produced solutions of lower viscosity, but the change was not so marked as in the case of fine hard Para.

In order to compare numerically the viscosities of different rubber solutions two methods have been suggested. Schidrowitz suggested drawing a tangent to the curve at 1 per cent. concentration and taking the tangent of the angle which this line makes with the abscissa as a measure of the viscosity. Fol on the other hand suggests taking the area enclosed by the curve, ordinate, abscissa, and a line drawn from the curve at 1 per cent. concentration perpendicular to the abscissa. Both these methods are arbitrary, and moreover it will be seen from the curves (Fig. IV.)



that in the case of the fine hard Para and Castilloa rubbers the viscosity of the solution will become practically infinite before 1 per cent. concentration is reached.

A simpler method of comparing the results would be to find the relation between viscosity and concentration and express this as a straight line.

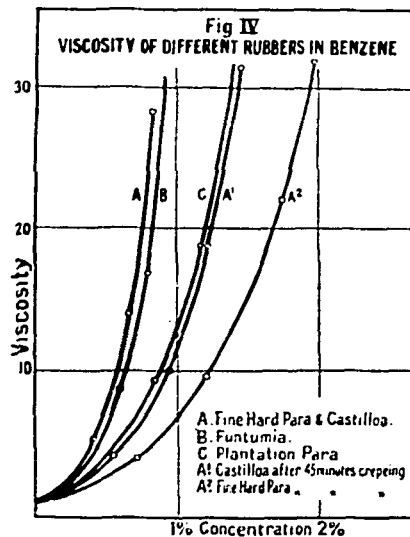
Various formulæ¹⁷ have been proposed for connecting

the viscosity of solutions with the concentration, but they have had only a limited application.¹⁸

The viscosity of rubber solutions, however, appears to obey a logarithmic equation, such as¹⁹

$$\eta = Kx$$

(where η_x = viscosity at concentration x , x = concentration, and K = constant), for when the log. viscosity is plotted against the concentration in benzene solution in the case of the rubbers examined the straight lines shown in Fig. V. are obtained.



The inclination of these lines with the abscissa would seem to be the simplest way of numerically comparing the viscosity of rubber solutions.

The actual figures given by the three methods are the following:—

	Schidrowitz.	Fol.	Proposed method.
Fine hard Para	∞	∞	68
Castilloa	∞	∞	66
Funtumia	6000	300	65
Plantation Para	1300	180	55
Fine hard Para after 45 min. washing	1000	120	43

It will be noticed that the proposed method does not show such great differences between the rubbers examined as the other two methods. If viscosity connotes the quality of rubber one would expect small differences, as the rubbers were all of very good quality. Judging from the viscosity of fine hard Para after washing, the plantation Para probably owes its position to the fact that it had been creped.

Change in Viscosity of Rubber Solutions.

It is well known that rubber solutions are liable to change in viscosity. The first mention of the fact was made by Woudstra,²⁰ who observed that toluene solutions diminished in viscosity on standing. Fol²¹ attributes this change to the gradual deposition of insoluble matter in suspension which passes through the filter. Gorter²² observed that solutions of rubber in benzene exposed to sunlight diminished rapidly in viscosity, and showed that this was accompanied by oxidation. He found also that

¹⁷ Vide Powell, Journ. Chem. Soc., 1914, 106, 8.

¹⁸ Arrhenius, loc. cit.

¹⁹ Z. Chem. Ind. Kolloide, 1900, 5, 31.

²⁰ Loc. cit.

²¹ Mededeelingen over Rubber Nos. 1 (1911) and 2 (1912) (Departement van Landbouw, Nijverheid en Handel, Java).

²² Arrhenius, Zetsch. physikal. Chem., 1887, 1, 285; Rudorff Zetsch. physikal. Chem., 1903, 43, 257; Fawcitt, Proc. Roy. Soc. Edin., 1904, 25; Dunstan and Wilson, Journ. Chem. Soc., 1837, 91, 83; Hatschek, Zetsch. Chem. Ind. Kolloide, 1913, 12, 238.

benzene solutions of rubber diminish slowly in viscosity even in the dark and when access of air is prevented.

In a preliminary experiment the writer observed a solution of rubber in commercial benzene left exposed in the laboratory to diminish 30 per cent. in viscosity at ordinary summer temperatures.

Heat as well as light appears to increase the diminution in viscosity of rubber solutions.

A solution of plantation rubber in commercial toluene was divided into two portions, each of which was maintained at 40° C. in a thermostat, one portion being protected from the light. It was found that the viscosity diminished as follows:—

	Times of efflux in seconds.	
	Protected solution.	Exposed solution.
Initial	200	200
After 6 days	150	110
After 12 days	129	83

At higher temperatures the diminution in viscosity is more rapid. Schidrowitz and Goldsbrough²³ found that the viscosity of benzene solutions of rubber in some cases sinks to half its original value on heating for two hours on the water-bath.

At high temperatures the effect of light, or at any rate of ordinary daylight, on the viscosity of rubber solutions appears to be less marked than that of heat.

A solution of plantation rubber in commercial toluene was divided into two portions, each of which was heated in a conical flask under a reflux condenser on the water-bath, one of the flasks being protected from the light by means of a tin cone. The viscosity of each portion was determined at the commencement and at stated intervals with the following results:—

	Times of efflux in seconds.	
	Exposed solution.	Protected solution.
Initial	80.5	81.0
After 30 minutes	63.0	63.0
After 2 hours	53.0	55.0
After 4 hours	46.0	51.0
After 14 hours	39.0	45.0

The effect of light only begins to make itself felt after two hours; at the commencement the solutions diminished in viscosity with the same velocity.

In the following experiments a solution of plantation rubber in commercial toluene²⁴ contained in a conical flask and protected from the light by means of a metal cone was heated under a reflux condenser on the water-bath. At the commencement of the experiment and at stated intervals the viscosity was determined at 20° C. The following results were obtained:—

	Times of efflux in seconds.					
	I.	II.	III.	IV.	V.	VI.
Initial	84	86	77	78	82	82
After 1 hour	62.5	61	60	58	61	60.5
After 3 hours	49.5	50	51	50	52	49
After 5 hours	44.5	46	47	46	47	42.5
Concentration (grams per 100 ccm.)	0.48	0.49	0.44	0.44	0.45	0.45

At higher temperatures the fall in viscosity is still more marked. A solution of rubber in toluene was heated

in a sealed tube at 125—130° C. for six hours. The time of efflux fell from 220 seconds before heating to 29 seconds after heating.

In Gorter's experiments on the diminution of viscosity under the influence of light the rubber underwent oxidation. Bernstein²⁵ states however that xylene solutions of rubber diminished in viscosity under the influence of an ultra-violet light even in the absence of oxygen.

It was also found that heat alone in the absence of air caused diminution in viscosity of rubber solutions, as the following experiment shows:—

Test tubes were completely filled with xylene solutions of rubber, and closed with corks through which passed small glass tubes to allow for the expansion of the solution. They were then placed in boiling water and as soon as the expansion had ceased the openings of the glass tubes were closed by rubber caps. The solution thus out of contact with air was heated for two hours and the viscosity determined.²⁶

	Times of efflux in seconds.		
	Fine hard Para.	Plantation Para.	Ceara.
Before heating	87	125	313
After heating	27	41	96

Rubber solutions therefore on heating diminish considerably in viscosity, apart from any oxidation which the caoutchouc may undergo.

Considering the magnitude of the change it is also difficult to believe that it is due to the separation of adventitious insoluble particles which have passed through the filter.

The phenomenon seems most easily explained by assuming that rubber in solution tends to undergo a physical change, the so-called "depolymerisation," slowly at ordinary temperatures, but much more rapidly as the temperature rises.

The rate of diminution of viscosity also varies with the time of heating, being greatest at the commencement. This is shown in the following experiments where the viscosity was measured at regular half hour intervals.

A was a solution of plantation Para rubber in toluene, heated under reflux on the water bath and protected from the light

B was a solution of *Castilloa* rubber in xylene heated in boiling water and also protected from the light.

	Times of efflux in seconds.	
	A.	B.
Initial	80.0	160
After heating 30 minutes	50.5	135
After heating 60 minutes	41.5	124
After heating 90 minutes	38.0	117
After heating 120 minutes	35.0	110
After heating 150 minutes	33.0	107
After heating 180 minutes	32.0	104

These results are shown graphically in Fig. VI.

The change in viscosity appears to follow the law:

$$x = a + b \log t$$

(where x = diminution in viscosity in time t ,

a = diminution in the first time unit, 30 minutes,

b = increment of diminution with time).

For when the viscosity is plotted against the logarithmic value of the time straight lines are obtained (Fig. VII.). It is interesting that this relation is the same as that given by Schwartz²⁷ between extensibility and time in hysteresis measurements, namely the increment of extension plotted against the logarithm of the number of the cycle is a straight line.

²³ The Rubber Industry, p. 260.

²⁴ Toluene was used for studying change in viscosity at high temperatures in preference to benzene, because the ebullition of the latter is a disturbing factor.

²⁵ These results are not comparable amongst themselves as the concentrations (undetermined) are obviously very different.

²⁶ Zetschl. Chem. und Ind. Koll. 1913, 12, 193.

²⁷ The Electrician, 1910, 54, 585 and 620.

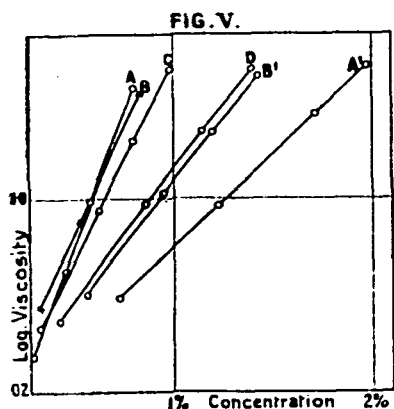
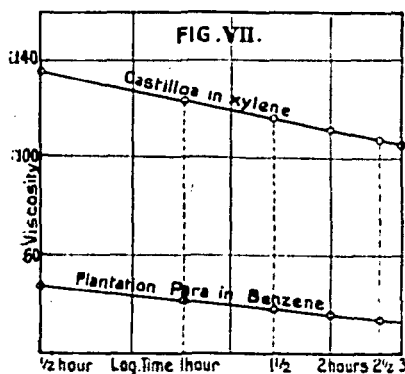
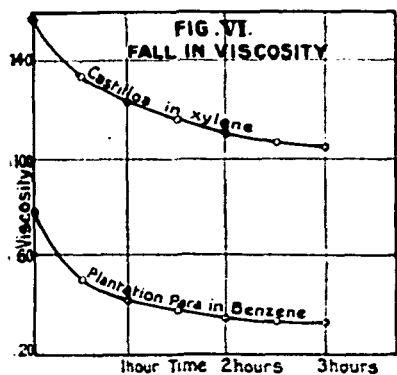


Fig. V—A. Fine hard Para, B. Castillo, C. Funtum, D. Plantation.

A¹ Fine hard Para after 45 minutes crepeing in cold water.
B¹ Castillo after 45 minutes crepeing in cold water.



This is not surprising seeing that both phenomena are the result of internal work performed on the rubber, but the point of interest is that Schwartz found that when he examined various samples of rubber, and plotted the maximum extension per cycle against the logarithm of number of cycles, the rubbers arranged themselves in the order of their quality, the maximum extension with succeeding cycles being greatest in the case of fine hard Para. It would appear that the phenomenon is due to a property of rubber which persists not only in solution but also throughout vulcanisation.

Effect of Concentration on the Change in Viscosity.

The following experiments show the relationship of change in viscosity to the concentration.

Solutions of plantation Para in commercial xylene at different concentrations were heated in small flasks (closed with corks) in a water bath maintained at a temperature of 80° C. The viscosity was determined at the commencement and at stated intervals with the following results:—

Times of efflux.						
Initial	61.5	73.0	87.0	104.5	138.0	137.0
After 30 min...	53.0	62.0	74.0	80.5	120.0	161.0
After 1 hour..	51.0	60.0	70.0	81.5	111.5	148.0
After 2 hours	46.5	57.0	64.0	73.5	105.0	132.0
After 3 hours	44.0	56.0	62.0	69.0	95.0	124.5
Concentration (grams per 100 ccm)	0.4	0.48	0.54	0.60	0.73	0.82

The relation between these results is best seen in Fig. VIII., where the times of outflow are plotted against the logarithmic value of time of heating.

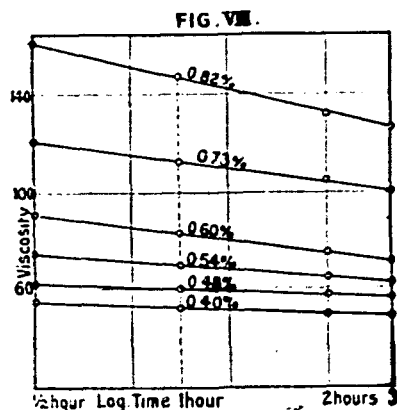


Fig. VIII. Showing rate of diminution of viscosity at different concentrations (Plantation Para in xylene at 80° C.)

Change in Viscosity of Rubber in different Solvents.

The following experimental results show the change in viscosity of plantation Para in different solvents, when heated to 80° C.

Times of efflux.						
	Purified benzene solutions.		Purified toluene solutions.		Commercial xylene solutions.	
	I.	II.	I.	II.	I.	II.
Initial	87.5	75.0	87	84.5	91	87.0
After 1 hour..	74.5	67.0	—	—	69	70.0
After 2 hours..	72.5	66.5	77	70.5	61	64.0
After 3 hours..	72.0	66.0	73	72.5	57	60.0
Concentration (grams per 100 c.c.)	0.43	0.40	0.42	0.44	0.50	0.51

It is noteworthy that the change is more marked in the case of xylene solutions than in the case of the benzene and toluene solutions. In purified toluene solutions the diminution in viscosity appears less than in commercial toluene (cf. the results on p. 450) though this may be explained by the fact that toluene solutions on the water-bath will attain a higher temperature than 80° C. A similar difference is observed between solutions in pure

benzene and solutions in "90 per cent. benzol" on the water bath, as is seen in the following results:—

	Times of efflux.	
	Pure benzene.	Commercial benzene.
Initial	80	77
After heating 1 hour	73	64
After heating 2 hours	71	62
Concentration (grams per 100 ccm.)	0.40	0.40

The effect of the addition of small quantities of the usual impurities in benzene (carbon bisulphide, thiophen xylene) was also studied. With the exception of xylene they did not cause any increased diminution in viscosity.

A solution of rubber in pure benzene was divided into two portions. To one portion 0.5 per cent. commercial xylene was added, and both heated on the water bath.

	Times of efflux.	
	Pure benzene.	Pure benzene + 0.5% of xylene.
Initial	71.5	71.5
After 1 hour	65	61
After 2 hours	63	58

It would seem therefore that the presence of xylene or higher hydrocarbons in commercial benzene may affect the viscosity of rubber solutions. Hence the importance first indicated by Schidrowitz, of working with pure solvents.

Change in viscosity of different rubbers in solution.

The simplest way of comparing the diminution in viscosity of different rubbers is to take solutions of equal or approximately equal viscosity and to determine the extent to which the viscosity is destroyed by heat.

This has been done for the rubbers examined. Care was taken that the solutions were made under as near as possible the same conditions. The comminuted rubber was shaken 2½–3 hours in a rotatory shaker with the quantity of xylene necessary for the production of a solution of definite viscosity. The same sample of xylene was used throughout.

After determining the viscosity the solutions were heated in boiling water for two hours and the viscosity redetermined. The following results were obtained:—

	Time of efflux in seconds.		Percentage diminution.
	Before.	After.	
Fine hard Para	{ 103 111 105 }	{ 46 46.5 48 }	57
Plantation Para	{ 108 109 115 }	{ 68 65 72 }	37
Fine hard Para which had been creped 45 minutes in the cold	118	81	30
Funtumia	{ 104 101 100 }	{ 78 70 81 }	26–30
Castilloa	{ 111 107 }	{ 80.5 78.0 }	28
Ceara	118	90	23

The order in these results is quite different from that obtained when comparing the viscosity of rubber solutions at different concentrations, all the Hevea rubbers showing higher percentage diminution in viscosity than the other species.

The explanation of the change in viscosity of rubber solutions depends on the one hand on the nature of the viscosity and on the other hand on the structure of the rubber gel. Assuming as is generally supposed that viscosity is due to friction of the ultimate particles²⁸, and assuming also that rubber consists of aggregated caoutchouc micelles²⁹, it is only necessary to suppose that the caoutchouc goes into "solution" in a more or less aggregated condition, with a tendency to de-aggregate or "depolymerise."³⁰ In this case the high viscosity of rubber solutions is due to the presence of large aggregates, which are disrupted by heat, and the percentage diminution in viscosity of different rubbers on heating will be a measure of the proportion of large aggregates in the solution. The larger the aggregates the more heterogeneous the "solution," hence the difficulty of obtaining absolutely concordant results for the initial viscosities of solutions even of the same rubber and of the same concentration unless one works under absolutely uniform conditions.

The phenomenon of "de-aggregation" is not limited to the solution.³¹ Bernstein has shown that when rubber is heated in the absence of air, the viscosity of the solution is less than that of the solution of the initial rubber. Creeping brings about "de-aggregation" in the same way.

The so-called hysteresis of vulcanised rubber is probably due to "de-aggregation," for it follows the same law, which would give some theoretical justification for supposing that the diminution in viscosity which a rubber solution undergoes on heating indicates at any rate one important factor in the quality of rubber, for one might conclude from Schwartz' results that although during washing and mixing the rubber may become "de-aggregated," the better rubbers do not do so to the same extent as the inferior rubbers or that, during vulcanisation, the better rubbers return to a higher state of aggregation.

Manchester Section.

Meeting held at the Municipal School of Technology, on Friday, April 24th, 1914.

MR. JULIUS HÜBNER IN THE CHAIR.

A CONTRIBUTION TO THE HISTORY OF DYEING, WITH SPECIAL REFERENCE TO SCOTLAND.*

BY JULIUS HÜBNER, M.Sc.TECH., F.I.C.

When I concluded my first paper on the History of Dyeing†, I had some doubt as to whether research with regard to the history of industries would be appreciated. Soon after its publication, however, any such doubt was dispelled by the many kind and complimentary comments which I received, and nothing could have more strengthened my decision to proceed with this work than the letter addressed to me by Mr. Rhys Jenkins of the Patent Office, in which he not only expressed his appreciation but showed his sincere interest and sympathy in this work by placing at my disposal a large amount of information upon the history of dyeing in England which he had collected during many years. The new sources of information which had thus to be

²⁸ Vide Powell, Journ. Chem. Soc., 1914, 108, 1.

²⁹ Vide Svedberg Ber. d. d. Chem. Gesell., 1914, 47, 12.

³⁰ The use of the term "depolymerisation" for denoting this change is open to criticism, because one generally understands by the expression a quite different phenomenon. For this reason the writer suggests the use of the word "de-aggregation" instead.

* See this Journal, Nov. 29, 1913, pp. 1043 seq.

† A Glossary and the complete titles of publications from which extracts have been quoted will be found at the end of the paper. The latter are referred to in the text by corresponding numbers.