

when heated to 80° the oil took out the free phenol, of which considerable quantities were contained in the Bakelite. Separation also took place if mineral matters were mixed with the base and with castor oil. He did not think that the claim of a definite compound was proved. The above observation was against the claim. As to the varnishes all the instances given were those of spirit varnishes. Was there any rival to oil varnishes? Was there any preparation which could be used in a similar way in relation to a boiled varnish? How might paper be impregnated with Bakelite G?

Dr. W. R. ORMANDY asked if the new substances were available for replacing ebonite. If the material was effectual for the coating of cast iron pipes, then the long time spent in experimental work had been well spent. As condensation was produced in the presence of small quantities of bases as well as acids and an insoluble material could be produced by using a large excess of formaldehyde in the presence of acids, were the natures of the products in the two cases physically similar? When condensation took place in the presence of a base was it possible to carry the condensation to such a state of completeness that no phenol remained in the condensed mass as it was frequently very difficult to cause condensation to proceed until all material was involved in the reaction? Finally he would like to know whether they had succeeded in making soluble condensates which were practically colourless, since for varnish making it was well known that the price of copals and other gums increased greatly as the material went lighter in colour. It would be interesting to know if the Bakelite products had been produced in this colourless and more valuable form.

Mr. REX JOHNSON inquired whether, when using Bakelite for impregnating coils for electrical work, it was possible to use it in any other form than the varnish form. There was always a difficulty in getting a solid impregnation and, with Bakelite varnish, this would be accentuated owing to the large proportion of solvent, which, when expelled, would leave air spaces. In electrical coil impregnation it was essential to have a solid job, and at the present time this was most easily effected by using a high melting point asphaltum compound. The chief drawback to the use of this material was the large coefficient of expansion. Would the lecturer kindly give his opinion as to the best method of applying Bakelite to obtain a solid filling for wire coils.

Mr. F. H. ALCOCK said having regard to the composition of one of the preparations, which included an appreciable amount of ammonia, he did not think it would be suitable as a brass lacquer. Did the material expand or contract on exposure to air, and to variable climatic conditions; and was it adhesive or elastic, so as to enable the negotiation of corners in work without cracking. What would be the effect of fats and oils (and especially turpentine) upon the material. There would be a limited application, with regard to varnishes, if it did not resist those. Was the material effective in the retention of bristles in brushes; he conceived a difficulty in relation to brushes used for oils and turpentine. Was it suitable for making reservoirs for fountain pens, for its transparency suggested its usefulness for this purpose.

Mr. W. H. H. NORRIS asked if the shrinkage resultant upon stoving the composition could be overcome. He understood that after coating iron vessels by brushing on a solution of Bakelite they needed to be stoved at a high temperature. He had failed to make a coating which did not crack owing to the shrinkage previously mentioned. It would be most valuable if cotton fibre could be made impervious to the action of acid and chlorine by means of a Bakelite coating. He found that stoving cotton fibre impregnated with a 10 per cent. Bakelite solution in alcohol, at 140° C. in an autoclave for only 10 minutes, made the cotton brittle. With a 5 per cent. solution the stoved cotton could be handled but he was unable to make it sufficiently resistant; he asked if Dr. Lebach had been more successful.

Dr. LEBACH, in reply, said that although the cost of coating pipes with Bakelite was rather high, it was not prohibitive in view of the results obtained. The mixture

used for coating contained from 20 per cent. upwards of Bakelite; the remainder consisted of sand, asbestos fibre, or some other suitable material. The shrinkage of Bakelite in moulds was very slight if a Bakelite-powder mixture was used. A vessel coated with Bakelite would stand water up to 200° C.; but it would not stand direct heating in a steam boiler, when probably it would crack off.

There was no essential chemical difference in the two qualities of Bakelite, only in the uses. By further heating Resitol (Bakelite B) would result, which had an appearance similar to that of solid Bakelite A; the principal difference was that it no longer melted or dissolved in any solvent. On application of phenol or glycerin it would swell and decompose, and on heating it became soft. The combined action of heat and pressure would weld it together and moulded articles could be manufactured in this way. It was not, however, a process which could be used largely on a commercial scale.

A certain amount of elasticity was invariably lost in impregnation. Cotton impregnated with Bakelite and used as a filtering material for alkali, was not affected by the alkali. But the Bakelite reduced the elasticity of the cellulose and made it brittle.

The ammonia in the Bakelite lacquer did not affect the brass.

If Bakelite was transformed into its final stage there was no considerable contraction or expansion, and he did not think there was any danger in its application in the open air. No oil could attack the final Bakelite. The proposal to mix oils with Resols to alter the properties, probably with a view of getting a more elastic product, was useless. He had never heard any complaint as to inefficiency when used for brushes for oils.

Bakelite had been used for bottles for hydrofluoric acid, and was not attacked. The substance was obtainable without colour; but as transparency increased the price advanced, as colourless Resites could only be made from the purest materials. Resinite enamel, for instance, was quite colourless. The patent numbers for Bakelite were 1921 and 1922 of 1908; and Resinite 28,009 of 1907 and many others. The liquid material, for coating purposes, cost 15s. 6d. per gallon; the other grades and prices were also obtainable.

## Liverpool Section.

Meeting held at the University, on Wednesday, 12th March, 1913.

PROF. F. G. DONNAN IN THE CHAIR.

## SOME PROBLEMS OF THE RUBBER INDUSTRY.

BY H. E. POTTS, M.Sc.

The ordinary raw rubber of commerce is obtained from the milk or latex of various trees, chief among which is the *Hevea Brasiliensis*. *Hevea* latex is a thick white liquid which is secreted by the tree and oozes out of incisions made in the bark. In the fresh state it is faintly alkaline. The viscosity diminishes on dilution with water in such a way as to suggest that it is an emulsion rather than a suspension. Seeing, however, that rubber is an emulsoid colloid, and therefore theoretically always a liquid, this does not enable us to draw any conclusion as to the state of polymerisation in the latex. The globules can be readily seen under the microscope; they consist of rubber plus resin. The liquid in which they are suspended contains sugars, salts, etc. The latex also contains protein, which is considered to reside on the surface of the globules as a protective colloid. This view is borne out by the fact that, generally speaking, precipitants of protein exert a coagulating action on the latex. The nature of

coagulation is not yet fully elucidated, though it is of absolutely vital importance as regards the quality of the rubber produced.

On the Amazon, the wild *Hevea* trees are tapped and the latex is coagulated by being poured from a cup on to a rotating paddle held in smoke. Successive layers of rubber are produced by the coagulating action of the heat, acetic acid, and, some say, carbon dioxide. The resulting rubber forms a loaf, shaped like a Rugby football. Clearly this contains the majority of the total solids of the latex, including protein, though not all, since some of the latex is allowed to drain away. When fine hard Para reaches this country it contains 16 per cent. of water and some dirt. It is washed between differential speed grooved rollers, then sheeted between equal speed rollers and dried at a low temperature. The product is termed technically pure Para: it contains about 94 per cent. rubber, 3 of resins, 3 of protein, and about 0.2 of water.

Turning to plantation Para rubber as a contrast, the latex is again obtained by tapping *Hevea* trees. It is coagulated, usually by the careful addition of acetic acid, washed, sheeted between diamond-studded rollers, thus giving the so-called *crêpe*, and then dried, perhaps *in vacuo*. On arrival in England it may contain 0.5 per cent. of moisture, but should contain no dirt. No washing process should thus be necessary, unless the amount of adsorbed acetic acid is appreciable, in which case it should be removed, as acid exerts a very deleterious action in rubber mixings.

We now come to the first problem to which I wish to draw attention. On comparing a sample of Plantation rubber with fine hard Para, we prefer the latter. The Para appears harder and "nervier" on the mixing rollers, and in any case it is usually more consistent in quality. Many explanations of this have been advanced, such as the youth of the trees on the Plantations, the acetic acid process of coagulation as compared with the smoking process, and so on. Many patents have been taken out, among the list of which are those of Byrne, for smoking rubber on the plantations. In any case, however, this is a causal explanation. At present no chemical explanation can be given.

Experiments have been made by Schidrowitz and others on the viscosity of solutions of rubber in benzene and these have shown that there is a certain connection between viscosity and "nerve," in the same botanical species. A good rubber gives a highly viscous solution. But even so, we know very little as to the viscosity of colloidal solutions in general, and it appears that the first thing which should be done is to discover how to interpret the viscosity results in terms of the constitution of the colloid, and to see, possibly by ultramicroscopic measurements, whether a high viscosity accompanies a coarse-grained structure or not.

Practically the only reliable way is to make a very careful mixing, to vulcanise it and then to test the vulcanised rubber by mechanical tests (e.g., with a Schopper dynamometer). A convenient method of securing standard conditions of vulcanisation, though it is a little remote from actual practice, is that proposed by Spence, who cures the rubber in very thin sheets between metal, immersed in a glycerin thermostat. Such measurements require time and a fair quantity of material. It seems certain that if they are to be done at all it will have to be by some central organisation. The present method, of buying a substance at £500 per ton on a small sample the size of a handkerchief or less, is absurd. A Conditioning House should be established to which all plantation rubber should be sent immediately on arrival. Vulcanising tests should there be made and the result sent out with the sample. In this way the manufacturer would have some guarantee that he was securing each time a product that would cure at the same speed under the same conditions. This is all important, as the manufacturer cannot afford to be continually changing his times of vulcanisation: he wants them standardised, like everything else. It is only reasonable that he should be given some sort of guarantee such as the above.

Of course, such a test would only ensure constancy of speed; it would not mean that the manufacturer

could calculate the cure required under changing conditions. This seems impossible at present owing to the complexity of the problem: the bad thermal conductivity of rubber makes it excessively difficult to say what is actually happening inside the article being cured, except by actual trial.

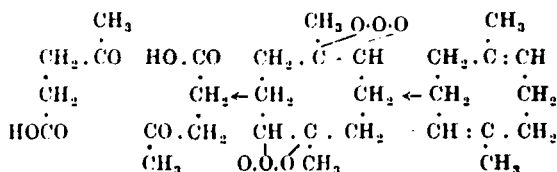
Beyond this, research is required to determine the nature of the factors affecting quality of raw rubber, and its velocity of vulcanisation.

Returning to technically pure raw rubber, from a chemical point of view, the resins may be removed by treatment with acetone, alcohol or other organic hydroxyl compounds. In the laboratory the extraction is best performed in a Soxhlet or in a Zuntz extractor, leaving behind rubber and protein. Numerous processes have been patented for removing the resins from highly resinous raw rubbers in practice. The most ingenious is perhaps that of Wildermann, who employs a resin solvent (such as alcohol) plus a rubber solvent (such as carbon bisulphide). Alcohol alone would only act superficially in a short time. Carbon bisulphide alone would dissolve all but protein. A suitably proportioned mixture will cause the rubber to "swell" just sufficiently to permit the liquid to dissolve out the resin without touching the rubber, except to a small extent.

To separate protein, the rubber is dissolved out by a solvent such as benzene, chloroform, carbon bisulphide, etc. Solution takes a long time, and filtration is exceedingly tedious. Harries has prepared pure rubber by extracting for 24 hours with acetone, dissolving in benzene, filtering, precipitating the solution with alcohol and thus obtaining rubber. The treatment was repeated twice.

The chief investigations into the constitution of rubber are those of C. Harries, and it is very interesting to note the gradual evolution of his methods. At one time he was engaged in researches on oleic acid with the object of determining the position of the double bond. He treated the acid with ozone, two molecules of which added on at the double bond, giving a diozonide. This was decomposed by water and from the products formed it was possible to deduce the point at which rupture of the chain had occurred.

He applied the same method to rubber—a hydrocarbon  $C_{10}H_{16}$  with two double bonds. He found that it duly gave an ozonide which on decomposition yielded laevulinic acid and laevulinic aldehyde. We may consider the acid alone; taking two molecules we find



Rubber is thus 1.5-dimethyleyclooctadiene 1.5.

In comparing two rubbers, it cannot be said that samples are chemically identical until derivatives of them have been made. The first compound that suggests itself is the tetrabromide,  $C_{10}H_{16}Br_4$ , which is a white body obtained by bromination. This has attained an undeserved prominence because numbers of methods of estimating rubber have been based on it, not one of which is really sound, because they all depend on the assumption that the tetrabromide is a definite compound, which, except under conditions difficult to realise in practice, it is not.

The next derivative was the nitrosite, on which Harries did a great deal of work. This does not melt sharply and the only way of comparing two nitrosites was to determine the temperatures at which they frothed on heating.

Harries then tried the ozonides and determined the relative amounts of laevulinic acid and aldehyde formed on decomposition. Differences of this kind at one time led him to believe that gutta percha and rubber were stereoisomers. This ratio depends much on the purity of the ozonide. Harries has now shown that two ozonides are formed, a diozonide and a dioxozonide,  $O_6$  and  $O_8$ , and his method of comparing two rubbers is to determine

the amounts of acid and aldehyde formed on the decomposition of the ozonides, and to determine the reaction-velocity of the decomposition. If this ratio is the same, and if the reaction-velocity curve is the same, the ozonides, and therefore the parent rubbers, are the same.

It is of great interest to note that he has adopted reaction-velocity as the final criterion for the constitution of an organic body.

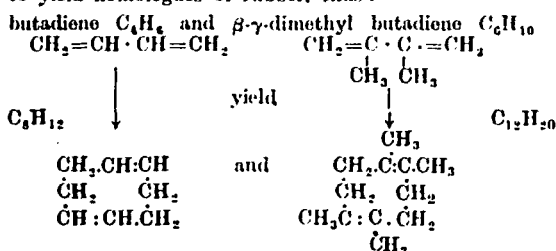
The application of these results is most fruitful in connection with synthetic rubber. The synthetic problem at once divides itself into two parts: (1) The formation of rubber by the polymerisation of isoprene. (2) The production of isoprene.

The polymerisation is perhaps of more general scientific interest and I will therefore discuss it first. The isoprene question is of primary interest from a specialised economic point of view.

This polymerisation has now been done in three ways: (1) By the firm of Bayer, Elberfeld, simply by heating isoprene in a sealed tube for a long time at about 100°. (2) By Harries, who heated the isoprene in a sealed tube with glacial acetic acid. The result is the same as (1), and I will call both these methods "heat polymerisation." (3) By the Perkin, Matthews and Strange group and also by Harries, heating with sodium. The sodium method gives a different product entirely.

All these methods have been exhaustively studied by Harries, who has applied his reaction-velocity method to the ozonides of the rubbers produced. He concludes that the product obtained by heat-polymerisation is actually identical with natural rubber, but that the product of the sodium method is not. This only refers to chemical tests, and is not to be construed as saying that the sodium method may not give as good or even better rubber than the other. Whether it does or not, the product is not chemically identical with natural rubber, as is the heat-polymerisation product. Of course, provided the physical properties are the same this does not matter commercially, because the sodium-rubber will vulcanise.

The work has been carried further than this. The homologues of isoprene have also been polymerised to yield homologues of rubber, thus:—



The constitution of these bodies has been confirmed by the ozone method. In particular the  $C_8H_{12}$  butadiene rubber has been shown, by the reaction-velocity curve, to be identical with the only other example of an eight-membered ring known in nature, a substance occurring in the bark of the pomegranate tree. Obviously these bodies are not the same as ordinary natural rubber. The fact of their constitutional difference from natural rubber is absolutely an academic point, provided they have similar technical properties. This point has not been sufficiently emphasised, obvious as it is. Of course, *a priori*, there is more chance of  $C_{10}H_{18}$  being valuable technically than  $C_{12}H_{20}$ , but in any case it is a matter for technological investigation, quite as much for synthetic  $C_{12}H_{20}$  as for  $C_{10}H_{18}$ .

Very many patents have dealt with this question of polymerisation, but it has not been elucidated very much except by the researches of Harries. These have been mainly concerned with proving the identity of the final products. There is great scope for research, both from the purely scientific as from the technical side, upon the mechanism of the polymerisation.

Before we know the conditions which lead to a product of the highest quality we must know something more as to the chemical conditions underlying "cure," the importance of which I have mentioned already.

We will thus take as proved the facts (1) that actual rubber, identical, as far as present chemical criteria go, with wild Para, can be obtained from isoprene; (2) that by treatment with sodium a pseudo-rubber can be obtained; (3) that homologues of rubber can be obtained from homologues of isoprene.

The best known method of obtaining isoprene has been the breaking down of turpentine. The yield was bad at first, only about 10 per cent. Many patents have been granted for processes to increase the yield, such as passing the vapours over heated surfaces of various metals, diluting the vapour with foreign gases, lowering its pressure, etc. (a simple application of Le Chatelier's principle, based on the fact that 1 vol. of turpentine = 2 vols. of isoprene), and so on. However, other methods have now been put forward. Bayer (Elberfeld) propose to obtain it from cresol by a series of reactions. Another process is that of the Perkin group of workers, who obtain iso-amylalcohol from fusel oil, chlorinate it, and treat the product with heated soda lime. Unfortunately fusel oil is too dear at present.

More promising processes appear to be those of preparing homologues of isoprene. The Perkin group have obtained butadiene by the action of soda-lime on chlorinated butyl alcohol. This product has been obtained by Fernbach and Strange from starch by fermentation, together with acetone as a valuable by-product.

Again, Perkin and his colleagues have started with acetaldehyde, which can be readily obtained from acetylene, transformed it into aldol by condensation, chlorinated and treated with soda-lime, giving  $\beta$ - $\gamma$ -dimethyl butadiene, which in turn can be polymerised by sodium to yield the dimethyl homologue of rubber.

Thus the chief successes of the Perkin group have been so far in the synthesis of rubber homologues, using sodium, which according to Harries does not give normal rubbers. As I have pointed out already, this does not matter technically as long as the product is satisfactory, and there seems to be no reason why it should not be. However, it may be as well to quote the statement made by Dr. Hofmann, of Elberfeld, that it will probably be a very long time before the synthetic problem will be fully solved.

We may now leave synthetic rubber for a moment to follow the technically pure natural raw rubber through the works. After drying, it is mixed with sulphur and various filling materials, appropriately selected in view of the purpose of the article. The dough so obtained is made up into the required shape by calendering and lapping, by calendering and pressing, or by spewing, moulding, etc. It must then be vulcanised or cured, and it is this process of vulcanisation which almost entirely overshadows the horizon in the rubber works.

The difficulties which arise are largely due to the great difficulty experienced in repeating a vulcanisation to give exactly the same result, it may be months later. It is at once clear that the velocity of vulcanisation depends on two very different factors, the nature of the raw rubber and the method of cure. I have already emphasised the importance of having a raw rubber which shall vulcanise at a constant speed, and, if possible, of guaranteeing this by careful tests before buying.

There is no need to describe the physical results following on vulcanisation. It is enough to say that the rubber may be made progressively harder as the coefficient of vulcanisation increases, until at length, with a sulphur content of 33 per cent. the mixing when fully cured will be perfectly black and hard ebonite. All intermediate properties may be obtained by suitably modifying the percentage of sulphur and the time and temperature of cure.

At first sight, the reaction appears a simple one. Rubber has a molecule containing two double bonds and the sulphur adds on with evolution of  $H_2S$ . Vulcanisation is thus saturation. Much controversy has arisen as to whether the sulphur is adsorbed by the rubber in vulcanisation or whether a chemical compound is produced as in the analogous cases of dyeing and tanning. The view current at the moment is that the sulphur is at

first adsorbed, and then fixed as a disulphide. We must regard all the various stages of vulcanisation as being solid solutions of disulphide in pure rubber, though it is hardly correct to speak of them as solid on account of the fact that rubber is strictly, in one sense, always a liquid.

Vulcanisation is accelerated by raising the temperature or by increasing the sulphur percentage, as would be expected. Beyond this, there is a remarkable acceleration produced by the presence of certain bases, lime, magnesia, and more especially litharge. Litharge has been shown actually to raise the temperature of the article and thus cause a higher reaction-velocity by burning up the resins and proteins contained in the rubber, which thus exert the function of fuels. This simple but ingenious explanation was only put forward quite recently; previously some mysterious catalytic action was supposed to be exerted on the rubber.

In harmony with this view, it has been found that rubber from which the resins or proteins have been removed will not vulcanise as readily as ordinary technically pure rubber. The conclusion has been drawn that synthetic rubber will be bad on the ground of being too pure. The rubber manufacturer will not be in any way embarrassed on that account and will be quite capable of putting in as much resin as is needed, consistent of course with the limits prescribed by specification work. Many of the experiments which have been published on this point are, I think, inconclusive, not only for this reason, but also because in actual practice mixings of 90 per cent. rubber + 10 per cent. sulphur are rarely used. These for some reason appear to be favoured by those making researches. It would be far better to work on a good standard mixing, containing about 50 per cent. of rubber at most.

Finally there is the question of the regeneration of waste vulcanised rubber. The patent literature shows a heterogeneous collection of processes, most of which are very little use. So far, to my knowledge, it has not proved possible to obtain from waste vulcanised rubber a product like raw rubber and containing no sulphur. The combined sulphur is bound with extraordinary strength. Hinrichsen and his co-workers have published experiments showing a decrease in combined sulphur after treating with zinc and a mixture of benzene and alcoholic soda. These results have, however, been criticised severely by Paul Alexander. What can be done is to remove the free sulphur, some or all of the mineral fillers, and the fibrous matter such as cloth, etc. The reclaimed rubber thus obtained by many processes is a valuable adjunct in cheap mixings. It can take up more sulphur on vulcanisation, since if it contains 5 per cent. combined sulphur it is still unsaturated, as the limit is 33 per cent. The usual processes consist of treatment with acids, alkalis, etc., leaving the rubber behind. Many processes have also been proposed in which the rubber is dissolved by all kinds of solvents leaving the mineral matter behind, and the solution is then precipitated with alcohol or distilled in steam and so on. Solvents are too dear usually.

A curious process is that of Bary, in which the solution in naphtha is dialysed, when the dissolved sulphur, resin, etc., pass through the membrane, leaving the colloidal rubber in solution in the dialyser.

Another group of processes are those in which the waste rubber, usually finely pulverised, is reformed under the influence of heat and pressure. Surprisingly good results can be obtained in this way.

There are thus four leading groups of problems:—

- (1) Quality of natural raw rubber.
- (2) Synthetic rubber.
- (3) Vulcanisation.
- (4) Regeneration.

In every case advance is hampered because we do not know what to aim at from a chemical point of view. We know a good article from a bad one, *after* it has been in use for six months: what we want now is to be able to foretell accurately, before the rubber has even been mixed, what the article will be like, and to do that we should be able to interpret the differences of quality in terms of chemical differences.

## DISCUSSION.

Mr. J. H. C. BROOKING said that it had been stated that Para rubber after being washed was dried at a low temperature, presumably about 60° F.; were not temperatures up to 120° F. meant? Possibly the surprisingly good results mentioned as having been got from reformed rubber were more in the nature of special tests than general commercial practice. Otherwise all rubber manufacturers would be using reformed rubber, in self defence.

Dr. A. J. ALLMAND asked what was the explanation of the differences observed by Harries with washed and unwashed ozone. How was the ozone altered by the washing and with what was it washed?

Dr. ALEX. RULE asked Mr. Potts if he could give any information on the chemical differences between the different varieties of rubber. Why was it that Para rubber would not grow in certain parts of Africa, and was the inferiority of Ceara and other rubbers due to the presence of impurities, or was it that the actual rubber was of different composition, seeing that rubber was stated to be really a series of products? Regarding the vulcanisation, the author said that 33 per cent. was the limit of the amount of sulphur taken up by the rubber. Did this percentage correspond to a definite compound or was it possible, by suitable solvents, to dissolve out a part of the sulphur and leave a definite compound behind? Had any attempt been made to prepare from the tetrabromide of rubber a sulphur compound of definite composition, and if such a one had been prepared did it bear any resemblance to vulcanised rubber?

Mr. WILLCOX asked whether the manufacture of artificial rubber was kept back wholly because of the cost, or because of the inferior quality of the artificial rubber, or for both reasons.

Mr. H. B. STOCKS said that of commercial resins some consisted principally of acids, others contained large proportions of neutral substances. Rubber resins were of the latter class. How were rubber resins formed, from the rubber itself, or from the latex?

Dr. BLACKLER asked whether, in the manufacture of rubber, lead oxide acted on the impurities of the rubber or whether it tended to oxidise the rubber and make it brittle? In regard to synthetic rubber, was it the proteid matter which gave "nerve" to the rubber? Even if synthetic rubber were made on a large scale, would it last seeing that the physical property known as "nerve" could not be given to it? Had anyone ever brought forward any proof of the constitution of the so-called "nerve" of rubber?

Mr. W. C. SMITH, in regard to the suggestion that when synthetic rubber was manufactured on a large scale resins would have to be added to it and that this was an easy matter, said that the character of rubber resins varied considerably, and that these additions might be a very difficult matter.

Mr. H. B. STOCKS remarked that a quantity of resin was extracted from low grade rubbers and waste products, and, if wanted for adding to artificial rubber, there would be no difficulty in obtaining it.

Mr. W. P. THOMPSON said that on soaking rubber in carbon bisulphide, the rubber swelled up but never completely dissolved, a skeleton being always left. What was the composition of this skeleton?

Professor F. G. DONNAN asked if the products of polymerisation of isoprene by sodium differed from the products when the other substances were used to induce polymerisation? What was the effect of keeping rubber at low temperatures?

Mr. H. E. POTTS, in reply, said that low temperatures were the best, especially for cut sheet rubber. With regard to the different chemical products as a result of polymerisation by different substances, Harries had not succeeded in explaining this. It was apparently not due to the position of the double bond, but the matter awaited further research. The skeleton to which Mr. Thompson had referred was composed of protein according to Spence, who performed some experiments on silver staining to prove this matter. Litharge did not seem to have a deleterious action on rubber because there were only the impurities which could act as a fuel.

Referring to the extraction of resins from low grade rubbers for addition to synthetic rubber, it was possible that these might not work in the same way. Para resins were optically inactive and unsaponifiable, whilst certain resins from other rubbers were optically active and saponifiable. The inactivity of the resins from Para rubber showed that they are not formed by the breaking down of the rubber itself. He had not seen any large samples of synthetic rubber but believed that two motor tyres made of synthetic rubber had run an enormous distance. Two had also been given as a present to the Kaiser. It was the expense of production, not the want of quality, which was keeping back the industry.

In regard to the growth of rubber in various parts of the world, climatic conditions affected the different species of rubber trees so that they were limited to certain parts of the globe. As regards the compounds of rubber and sulphur, this was a point upon which a great deal of research had been made. A sulphide of rubber  $C_{10}H_{16}S_2$  seemed to have been isolated but some of the sulphur might be Alexander Smith's insoluble sulphur. There seemed to be no distinctions between the actual rubbers in the different species, grown in different parts of the world. With regard to the "nerve" it was quite a different story. This "nerve" might be due to the protein, but the rubber was so knocked about in the mixing treatment that the mesh must get broken up very much. Personally he did not think that protein gave the "nerve."

In regard to the washing of ozone, strongest unwashed ozone contained 12 to 16 per cent. of ozone. After being washed by caustic soda and dilute sulphuric acid, the ozone concentration was considerably lower.

Rubber was dried at  $110^{\circ}\text{C}$ . or so, which from a chemical point of view was a low temperature.

## London Section.

Meeting held at Burlington House, on Monday, May 5th, 1913.

PROF. W. R. E. HODGKINSON IN THE CHAIR.

## METHODS AND APPARATUS USED IN PETROLEUM TESTING.

### PART II.—VISCOMETRY.

BY W. F. HIGGINS, A.R.C.Sc., B.Sc.

(Abstract.)

**Introduction.** This paper embodies the results of experiments carried out at the National Physical Laboratory, for the International Commission for the Unification of Tests on Petroleum Products, on the methods and apparatus used in petroleum testing. Apparatus used for the determination of the flash-point of illuminating oils has been dealt with in the July, August and September numbers of the "Petroleum World" for 1911.\*

The types of viscometer under consideration are those designed by Dr. C. Engler and Sir Boverton Redwood in 1884 and 1895 respectively. The latter is the instrument most commonly employed by the English oil-trade and chemists, while the former is extensively used in Germany and on the Continent generally.†

\* See also National Physical Laboratory, Collected Researches, Vol. VIII., pp. 19—30, 1912.

† Further details regarding these apparatus are given in the following publications:—

The Redwood Viscometer is described in:—  
(a) "Petroleum and its Products," by Sir Boverton Redwood vol. II., pp. 600—602; (2nd edition, 1906).

(b) "On Viscometry," Sir Boverton Redwood; this Journal, 1886, 6, 121—133.

**Definition of "Viscosity."** By the term "true viscosity" is here to be understood the usually accepted physical definition of viscosity which states that the "viscosity of a substance is measured by the tangential force on unit area of either of two horizontal planes at unit distance apart, one of the planes moving with unit velocity relatively to the other, the space between these planes being filled with the viscous substance."

In using the Redwood apparatus, the instrument is previously levelled by the aid of a small circular level which fits on the upper edge of the oil-cup, while in the Engler apparatus the adjustment is made by bringing the oil-surface into coincidence with each of three filling-points.

Experiments made on the Redwood apparatus showed that over a range of 5 mm. on either side of the normal level, the change in the time of outflow was proportional to the variation in level, the value was about 1.4 per cent. in the time for 1 mm. change of level.

**Errors in levelling the instrument.** For the Redwood instrument it is found that one degree of tilt is equivalent to a reduction of 0.3 mm. in the effective head.\* This corresponds to a change of 0.4 per cent. approximately in the resulting time of flow. The small circular levels supplied with the Redwood viscometers are sensitive to a change of tilt of about  $1/5^{\circ}$ , though not always accurate to this extent. The corresponding accuracy in the time of flow is accordingly about  $1/10$  per cent.

In the Engler instrument the accuracy under this heading is limited to about 0.2 per cent.

**Errors in the volume of the measuring flask.** It was found by experiment that in the neighbourhood of the normal volume the time of flow is directly proportional to the volume outflowing, for a range of 1 or 2 per cent. on either side of the normal value. In actual practice, however, it is quite unlikely that the measuring flask employed should have an error of as much as 1 per cent. Those employed in the present investigation were tested, and it was found that the error was so small as to be negligible.

**Description of the oils used.** The following table gives a brief summary of the properties of the oils used in the tests described later. The first column gives the reference number by which the oil is indicated throughout this paper. The second and third columns give a short description of the nature of the oil and the country of origin, if known, for the samples employed. The remaining three columns respectively give their colour, density at  $20^{\circ}\text{C}$ ., and viscosity at  $20^{\circ}\text{C}$ . in Redwood units.

TABLE I.

No.	Description.	Origin.	Colour.	Density at $20^{\circ}\text{C}$ .	Redwood Viscosity at $20^{\circ}\text{C}$ .
1	Shale oil ...	—	Dark brown	0.853	8.25
2	Fuel oil, ....	Burma	Dark brown	0.889	14.8
3	Refined machine oil	—	Pale yellow	0.863	21.8
4	Olive oil ...	—	Yellow	0.913	69.3
5	Refined spindle oil	Russia	Pale brown	0.895	76.3
6	Fuel oil, ....	Texas	Black	0.931	126
7	Engine oil (refined)	Russia	Brown	0.905	25.5
8	Fuel oil ....	Roumania	Black	0.949	579

The Engler Viscometer is dealt with in the following:—  
(c) "Prüfungsbestimmungen für Zähigkeitsmesser nach Engler"; Die Chemische Industrie, XXX., Nr. 9 1907. This is a short publication from the Physikalisch-Technische Reichsanstalt, Charlottenburg, dealing with the official test on the instrument.

(d) "Ein Apparat zur Bestimmung der sogenannten Viscosität der Schmieröle"; C. Engler; Chem.-Zeit. (1885) 9, pp. 189—190. See also this "Journal," 1893, 12, 201.

(e) "Schmiermittel und ihre Untersuchung." A. Kunkler; pp. 119—124.

\* This is a maximum value and occurs when the radius passing through the setting point coincides with the line of maximum tilt.