Results of repeat analyses carried out by independent operators.

Material.	Grs. per litre.			Operator.
Sumac "40"	15	Per cent. 0.1216 = 16.21 0.1214 = 16.18	Per cent. 0.1212 = 16.16 0.1210 = 16.13	H. Br. W. J.
Extract "54" contains Fichtenholz extract	14	0.0636 = 9.08 0.0624 = 8.91	0.0632 = 9.02 0.0610 = 8.80	S. H. H. Br.
Extract "333"	14	0.0666 = 9.51 0.0660 = 9.42	0.0658 = 9.40 0.0662 = 9.45	S. H. W. J.
Quebracho extract (solid) "2628"	6	0.0318 = 10.60 0.0330 = 11.00	0.0308 = 10.26 0.0332 = 11.06	S. H. W. J.
Quebracho extract solid "2563"	6	0.0312 = 10.40 0.0322 = 10.73	0.0318 = 10.60 0.0306 = 10.20	S. H. W. J.
Swedish Fir Bark extract	22	0.2336 = 21.23 0.2336 = 21.23	0.2334 = 21.12 —	W. J. W. J.

As a further test of the comparative accuracy of the official determination of non-tans, I applied to a number of English extract manufacturers and large dealers whom I knew to have been making extensive tests of the concordance of the results of different chemists under the new method, for information as to the results obtained; and received in all, details of the analysis of 20 different extracts each determined by two or three different chemists, of whom in many cases I do not even know the names. In order to determine the degree of concordance attained the average result on each material was determined, and the sum of the differences from these averages was taken without regard to whether + or —. One set of three analyses was rejected on account of an obvious clerical error in one analysis which added to 102.3. Of the remaining 51 analyses the average difference from the mean was 0.39 per cent. In order to compare to some extent the accuracy of the work and sampling, the water determinations of the same extracts were similarly compared, and showed an average error of 0.31 per cent. As a further check, the non-tannin results of the 66 analyses by the filter method with Prof. Paessler's "lightly chromed powder" carried out by Messrs. Arnoldi, Bosch, Moll, Philip, Siehling, Seidel, and Veit for the German Analysen-commission, and published in the report by Prof. Paessler (*Collegium* 218 *et seq.* 1908), were similarly treated; and showed an average error of 0.42 per cent. As in this case the samples were sent out as identical by Prof. Paessler himself, together with an identical hide-powder, and the names given preclude the supposition of careless or incompetent work, while those by the shake method were by ordinary commercial chemists, with commercially drawn samples, and any hide-powder, the comparison of the results is interesting.

Most of these extract manufacturers now admit that present results by the shake method show better concordance than the former with the filter, and several of the more important are warm supporters of the change; and complaints now centre rather on the defects of colour-testing than on the actual tannin determination.

In conclusion I may say that the evidence I have brought seems to me absolutely to establish the superior accuracy (or at least concordance) of results of the shake-method as compared either with the old filter-method, or with Dr. Paessler's with lightly chromed powder, and though, as Chairman of the Commission, I shall be glad to discuss any improvements which may be suggested either in accuracy or rapidity of execution, I consider that the controversy as regards the superior accuracy of the old filter method is now closed so far as I am concerned.

SOME INDIGO PRODUCTS FROM NORTHERN NIGERIA.

BY A. G. PERKIN, F.R.S.

In a previous communication (this J., 1907) an account was given of the investigation of the so-called "Gara-plant" which had been forwarded by the authorities of Sierra Leone to the Imperial Institute for an examination

of its dyeing properties. This product, which consisted of the dried and fermented stems and leaves of the *Loncho-carpus cyaneusens*, a woody climber of from 10 to 40 feet in length, contained indigotin to the extent approximately of 0.65 per cent. Somewhat more recently Prof. Dunstan forwarded to me two other indigo products also from West Africa, but this time from Northern Nigeria, one of which closely resembled the Gara plant of Sierra Leone, whereas the second consisted of specimens of indigo in the lump form.

For the examination of the former, which consisted of a mixture of leaf and stem of a dull greenish-blue colour, 200 grms. of the material was repeatedly extracted with boiling water, which removed (as had also been the case with the Gara plant) a very large quantity of a brown substance. The residue was then steeped in a large bottle repeatedly with alkaline hydrosulphite solution, the yellow extract oxidised by means of air and to render the colouring matter thus precipitated in a more granular form, the mixture was boiled and treated with an excess of salt. The product was collected, washed, first with water, and then with boiling dilute hydrochloric acid, and after removal of the acid was allowed to dry at the ordinary temperature, so that the substance thus obtained was in a porous condition and was easy to powder. For purification it was extracted with boiling nitrobenzene, and the crystals collected and weighed. By operating in this manner an approximate idea of the colouring matter present in the material was obtained, though this value is probably a little too low.

Found Indigotin = 1.3035 grms., which is equivalent to 0.65 per cent., a result curiously enough identical with that which was previously given by the "Gara" plant.

Somewhat recently the authorities of the Imperial Institute obtained for the author some quantity of the air-dried leaves of the *Loncho-carpus cyaneusens* from Sierra Leone, in order that a chemical examination of the indigo-yielding principle contained in the plant could be carried out, and also that a better knowledge could be obtained of its commercial possibilities. Unfortunately, however, the leaves on arrival were found to be devoid of colouring principle, and as they contained some indigotin it was evident that the former substance had been hydrolysed by fermentation. It is quite possible, of course, that the indigo-yielding substance of this plant may consist of the isatin which has been shown by Boyerinek (*Proc. K. Akad. Wetensch.* 1900, 3, 101) to exist in woad, and which differs from the better known indican of the *Indigofera*, by its instability, which has not yet permitted of its isolation in a pure condition. Should such be the case, an effective chemical examination of this plant can only be made on the spot. The specimen was, however, useful for reference, for as there was a considerable similarity between this and the Northern Nigerian product, it seemed likely that they were identical, and a comparison of the samples very kindly carried out by Prof. V. H. Blackman of the Leeds University, leaves little doubt that this is the case. Thus it was found by an examination of the materials in question, that the stems of both possessed a similar arrangement

of epidermis, selenchymating, vascular bundles and pith, and that in the leaves the well-marked arrangement of hairs (characteristic of the *L. cyanescens*) was present. The form and arrangement of the stomata, and of the veins and the structure of the upper and lower epidermis of the leaf was also identical in the two cases, and as a result Prof. Blackman states:—"The unnamed plant must therefore be *L. cyanescens* or some very closely related form." The specimens of indigo above referred to, and which consisted of small pyramids, weighed on the average about 7 grms., possessed in parts a coppery lustre, and were of a friable nature. For the analysis of this product in regard to its percentage of indigotin and indirubin, a somewhat novel method devised by W. P. Bloxam and the author was employed. As certain experiments which are being carried out by this process are not fully completed, the details are reserved for the full communication which will shortly be made on this subject. In addition to the amount of colouring matter which was present, a determination of the mineral matter soluble in hydrochloric acid, of the substances dissolved by alkali after this treatment, and of the amount of other impurities contained in the indigo was carried out. The results are embodied in the following table.

	I. Per cent.	II. Per cent.
Molature.....	5.38	—
Indigotin	21.47	21.65
Indirubin	1.33	1.10
Brown matter (indigo brown) soluble in sodium hydroxide	12.15	—
Organic matter, soluble in HCl	10.83	—
Organic matter (plant debris) insoluble in Nitrobenzene.....	9.59	—
Inorganic matter soluble in HCl	19.20	—
" " insoluble in HCl	20.10	—
	100.05	

A complete analysis of the mineral matter (39.3 per cent.) was not performed, but it was ascertained that whereas the portion insoluble in hydrochloric acid was quite colourless and consisted almost entirely of silica, the dissolved matter contained iron and calcium salts, the latter in considerable quantity. The existence of this very considerable amount of inorganic substances in the indigo naturally suggests adulteration, but on the other hand it is possible that this may have been added as a crude lime preparation during the process of manufacture, to assist both in the more rapid oxidation of the fermented plant solution, and to complete the precipitation of the indigo thus formed. The presence of indirubin supports this latter contention, as this colouring matter is always formed to some extent when indoxyl is oxidised in the presence of lime water, or indeed under any other faintly alkaline conditions.

To be certain that the colouring matter present in this product was in reality indigotin, and not some closely allied derivative, a nitrogen estimation of the substance isolated in the usual manner by means of nitrobenzene was carried out with the following result:—

Found N = 10.75.

$C_{16}H_{16}N_2O_2$ requires N = 10.69 per cent.

With regard to the botanical origin of this indigo, no information could be given by the Imperial Institute, but it was stated that in Northern Nigeria indigo is produced not only from the *Loncho-carpus cyanescens*, but probably also from certain species of *Indigofera*. This is in harmony with the following extract taken from the "Miscellaneous Trade Notices" of this Journal, 1880, p. 584: "Yoruba land* is famous among West Africans for its blue dyeing. Over it are found many botanical species that yield the indigo of commerce."

Fortunately, however, one of the cakes of this indigo was found to contain some fairly large fragments of stem, and these it was only reasonable to anticipate were derived from the plant which had been employed for the manufacture of this colouring matter. The examination of these was again very kindly undertaken by Professor Blackmann, who pronounced them to be very similar and probably identical with the leaf stems of the *Loncho-*

carpus cyanescens, and there is thus practically no doubt that these samples of indigo had been derived from this plant.*

It is thus interesting to find that both in Sierra Leone and Northern Nigeria, districts of Western Africa which are several hundred miles apart, the same plant *Loncho-carpus cyanescens* is employed for the manufacture of indigo. In Bancroft's "Philosophy of Permanent Colours" (Vol. I. 1813, 168) mention is made of the introduction of the "Taroom akkar," which grows in Sumatra and is probably the *L. cyanescens*, into Sierra Leone, so that whether it is really native of this part of West Africa does not seem to be certain.

A point of some interest is afforded by the occurrence of brown matter in both these West African indigo products derived from the *Loncho-carpus cyanescens*, for such appears to be always present in natural indigos, whether produced from the *Polygonum tinctorium*, the various species of *Indigofera*, or the wood plant, *Isatis tinctoria*. It has long been considered likely that these brown substances represent a "waste" of colouring principle, and recent work in the University of Leeds indicates as probable that indigo brown itself may originate in this manner. That indigo derived from such distinct varieties of plant should invariably contain indigo brown certainly lends support to this view.

In an earlier paper, "Notes on West African Indigo," by Rawson and Knecht (Jour. Soc. Dyers and Colourists, 1888, 60; this J., 1888, 420) an account has been given by these authors of some indigo products which had been sent to this country by Sir J. Goldie, Governor of the Royal Niger Co. These consisted of the leaves of a plant in ball form which contained indigotin to the extent of 0.51 per cent, and (b) small conical masses of indigo which on analysis were shown to possess the following composition:—

Indigotin, 39.12. Indirubin, 4.75 per cent.
Foreign organic matter, 29.17. Ash, 10.60 per cent.

Unfortunately the botanical origin of these specimens was lacking, and in view of the statements that indigo is produced in Nigeria from a variety of plants, it is impossible to conjecture whether these indigo samples of Rawson and Knecht had also been derived from the *L. cyanescens*. It is interesting to note in connection with the leaf product described by these authors, that it contained a large quantity of a brown substance soluble in boiling water, and the presence of this they considered was probably due to changes which had involved a loss of colouring matter.

Finally, it is to be remarked that with the exception of a patent taken out by Calmetto (this J., 1902, 38) for the production of indigo from the *L. cyanescens*, the author has been unable to discover any allusion to this plant in the literature, and information appears to be entirely lacking, as to its capabilities in this respect, as compared with those of the better known indigo plants.

ADDENDUM.

Since the communication of this paper, it has been possible, owing to the courtesy of Prof. W. Gardner, to carry out a botanical examination of the leaf product described by Rawson and Knecht, samples of which had been preserved in the museum of the Bradford Technical College. As a result it has been found that these leaf fragments possessed the same structure as those of the *L. cyanescens*, and there can thus be little doubt that they have also been derived from this plant. On the other hand, the "ball" form of this product has a very distinct appearance from the "Gara ball" of Sierra Leone, previously described (*loc. cit.*), and indicates that in Nigeria a different process of native manufacture is employed.

*Prof. Blackman states, "I see no reason for believing that it is other than the *L. cyanescens*."

†There is evidence that in such crude fermented preparations of indigo yielding plants, the presence of this brown matter is usual. A somewhat similar product to those derived from the *L. cyanescens*, and which is known as "Aldama" indigo, and is produced from a perennial bush cultivated in Southern Japan, has been examined by the author, and found to contain very large quantities of such an impurity.

* Yoruba land is a district of Nigeria.

DISCUSSION.

Prof. W. M. GARDNER said it was uncertain whether natural indigo would or would not be entirely superseded by synthetic indigo. A great deal might still be done to improve the production of natural indigo, to which end an examination of indigo-producing plants from all parts of the world would be of service. Plants yielding better supplies of the product might still be found and the possibilities of improvement by proper selection of seed and cultivation of wild species should be investigated.

Mr. F. W. RICHARDSON asked if any analytical figures were forthcoming to show the relationship between the amount of indigotin, indirubin, and brown colouring substance at different periods in the growth of the plants. Wastage by conversion of the indigotin to the brown colouring substance seemed probable and such a series of figures would locate this loss.

Mr. A. G. PERKIN, in reply, said that experiments carried out some years ago by Rawson showed that the

quantity of colouring principle present in the leaf of *I. Sumatrana*, varied according to the season; thus in one instance the leaves yielded in May 0.30 per cent. of indigotin and in August 0.76 per cent., whereas in November the quantity had fallen to 0.25 per cent. With regard to the formation of brown products during the manufacture of indigo, which appeared to represent a loss of colouring matter, a very large quantity of pure indican had been prepared in order to study this point, and it was found that though indoxyl when oxidised by air was converted mainly into indigotin, certain secondary reactions took place at the same time. From the work of Mr. Bloxam and his colleagues, there was evidence that in southern India the indigo plant contained more indican than that growing in the more northern districts. It was probable that the natural indigo industry would hold on for some time, and there was no immediate prospect of it dying out. Natural indigo might yet be more economically produced, though it appeared to him to be doubtful if synthetic indigo could be made much more cheaply than it was at present.

Journal and Patent Literature.

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I.—PLANT, APPARATUS, AND MACHINERY.

PATENTS.

Drawing liquids through other liquids of greater density, and viewing same in their passage. R. Wood, Bolton. Eng. Pat. 4834, March 3, 1908.

The lighter liquid (*e.g.*, oil or ether) enters by the pipes, O, into the box, C, and passes upwards past the ball-valve D, into the transparent sight tube, E, which is filled with the heavier liquid (*e.g.*, water), the latter being prevented from escaping from the tube, E, by the ball-valve, D. The lighter liquid rises through the water and can be seen, and the quantity passing judged, through the transparent tube, E. From the top of E, the lighter liquid escapes through the passage, g, past the ball-valve, H, to the passages, e, P, P', Q, which are connected to spaces in which there is a slight vacuum.—W. H. C.

Separating materials of different specific gravity. H. I. Lewis, Lameston, and The High Moor Syndicate, Ltd., London. Eng. Pat. 6253, March 20, 1908.

The materials to be separated are fed along with water into the upper end of a long sluice-box, a, on the bottom of which a layer of coconut matting, b, is spread. Above the matting a number of perforated plates, c, are arranged step fashion, the front of each plate overlapping the back of the next, but supported a little distance above it, so as to leave a space, e, through which the water can flow. The back of each plate is bent over or has an angle-piece fastened to it to form a weir, d. The solids are carried down by the flow of water, pass through the perforations, and are caught behind the weirs, the water flowing on. When sufficient material has collected, the plates are taken out and the solids removed, the heavier bodies being found nearer to the upper and the lighter bodies nearer to the lower end of the sluice-box.—W. H. C.

Printing inks and the like; Moving-stirrer apparatus for mixing —. E. and H. Bush, Leeds. Eng. Pat. 8623, April 18, 1908.

The vertical shaft by which the stirrer-blades are rotated in the mixing pan is made in two parts and passes through