CHEMICAL SECTION.

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The Industrial Development of Indigo.

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The triumphs of chemical research in the fields of industrial life have attained such a height at the present time that the mind of the layman is no longer astonished at any marvel which may be accomplished. It requires a scientific mind and training to appreciate the numerous obstacles which must be overcome in the successful pursuit of an intricate chemical research. The outsider only sees the results in their entirety; the path by which that result was reached, though tortuous, dark and difficult to climb is not apparent except to the technologist.

Somewhat more than thirty years ago, when it was announced that the coloring matter contained in the madder root, and so extensively employed for the dyeing of red colors, had been made in the chemical laboratory from materials extracted from coal-tar, it elicted a great deal of surprise and comment, both from the laity and from men of science; and this surprise was furthermore increased when it was demonstrated that this red coloring matter, which became known as alizarin, could be manufactured not only in small experimental quantities in the chemist's test-tubes, but on a large commercial scale, and at a cost which soon drove the naturally occurring article almost completely from the market. Since then the development of the dye-stuff industry in the manufacture of numerous colors from coal-tar has had such rapid strides that people ceased to be astonished at results which would otherwise have been accounted marvelous; so that a few years ago, when it became known that the highly important coloring matter, indigo, had been successfully made from coal-tar, it only excited a passing mention, and indeed but few people outside of the profession were even aware that such a result had been accomplished. And yet, the synthetic preparation of this dyestuff was one of the most far-reaching successes that chemical research has won. It was not the result of accidental discovery nor of haphazard experiment, but the outcome of twenty years of patient labor along well-defined lines of scientific development. The successful culmination of this work is a monument to the unwavering and strong-hearted faith of the chemist to the ideals of his science.

A word now as to what indigo really is. To the ordinary individual it stands for a certain blue color which is extensively dyed on all manner of textile materials. The technologist knows it as the most extensively employed dyestuff both of past eras and of the present time. It is derived from the indigo plant botanically known as *Indigofera tinctoria*, which means, "I make things of a blue color." This plant grows extensively in certain provinces of India and in various islands situated in the Indian Ocean, though it has been cultivated with a greater or less degree of success in numerous other localities. The extraction of the dyestuff from the plant is rather a complicated and wasteful process, and depends on fermentation rendering soluble certain ingredients held in the plant which a subsequent oxidation by the air converts into indigo. The dyestuff itself does not appear to exist ready-formed in the plant, but is contained therein in combination with a sugar-like body, the resulting compound being known by the name of *indican*. The plants are harvested at the proper time and the leaves and stems are immersed in water and allowed to macerate until an active fermentation has been engendered. When this process has proceeded to a sufficient degree the turbid greenish steeping liquors are drawn off into shallow tanks usually built of masonry. There the liquor is stirred up and beaten so as to expose it very thoroughly to the action of the air, after which treatment it turns blue, and on standing for some time deposits a blue muddy sediment which is collected, freed from excess of water by means of filter presses, and finally dried and pressed into blocks. This constitutes the natural unrefined indigo which formerly was so largely brought into trade. It may be said that only from 0·2 to 0·3 per cent. of the weight of the plant is finally obtained as indigo.

The amount of coloring matter or indigotine in this crude natural product will vary from 10 to 70 per cent., according to the amount of accidental impurities, or the sophistications of unscrupulous dealers. Of late years, however, on account of the stern competition and the demand for greater purity, it has become the custom, to a great extent, to refine the crude indigo by chemical means, so that products can be obtained having as high as 90 to 95 per cent. of indigotine. The cultivation of the indigo plant, however, is a very precarious industry, so much depending upon climatic conditions for the success of the crop, in consequence of which both the quality and quantity of indigo produced were liable to great fluctuations from year to year.

It is a matter of some surprise that though indigo has been such an extensive article of commerce, and of almost universal use throughout the world, very little of scientific value was known concerning its chemical nature and constitution until comparatively recent years. The fact, however, is that its chemical constitution is a very complex one, and required the highest refinement of scientific knowledge to be brought to bear upon it before a clear insight into its molecular structure was attained. For the pursuit and final solution of the problem we are indebted to the indefatigable labors of Adolph von Baeyer, who for more than twenty years worked patiently upon this research, unraveling successfully, one after another, the many complexities with which the problem was surrounded.

It is historically interesting to know that from the study of indigo really sprung the early beginnings of the coal-tar dyestuff industry. As is well known, Unverdorben, in 1826, first discovered aniline in the products of distillation derived from indigo; and even further back than that, Haussmann, in 1788, prepared picric acid—really the first of the artificial coloring matters—from indigo, by treating the latter with nitric acid. The etymological derivation of the name aniline is also connected in an interesting manner with that of indigo. The Sanscrit term for indigo is *nila* (signifying dark blue); this was adopted into the Portuguese under the word *anil*, from which in turn is derived the word *aniline*.

A full discussion of the chemical studies involved in the demonstration of the proper formula for indigo would engender too many complexities to be considered in this paper, and a brief review only of the principal points will be given here. As already mentioned, indigo in the plant exists in the form of a glucoside known as *indican*. This is capable of being hydrolyzed, by the action of dilute acids or of suitable enzymes, into indigotine and a glucose.

$$\underset{\text{Indican.}}{2C_{26}H_{31}NO_{17}} + 4H_2O = \underset{\text{Indigotine.}}{C_{16}H_{10}N_2O_2} + \underset{\text{Indiglucin.}}{6C_6H_{10}O_6}.$$

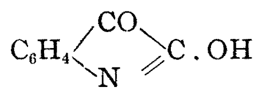
The empirical formula for indigo had been established by Crum and Laurent to be C_8H_5NO, and subsequently Sommaruga, by a study of its vapor-density, found that its proper molecular formula should be double that given by the empirical formula, or $C_{16}H_{10}N_2O_2$. Baeyer took up the investigation of its constitutional formula in 1865, and worked it faithfully to a successful conclusion. He found that indigotine was converted by oxidation in the presence of dilute alkalies into anthranilic acid; in other words:

$$C_{16}H_{10}N_2O_2 + 2H_2O + 2O_2 = 2C_6H_4\begin{cases} COOH \\ NH_2 \end{cases} + 2CO_2.$$

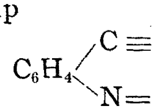
From this reaction it would seem apparent that the indigo molecule contained two phenylene groups, $C_6H_4<$, and that the nitrogen atom was probably an amido group or a residue of such. This reaction was also in keeping with the one whereby aniline was obtained by the destructive distillation of indigo with caustic alkalies, since the anthranilic acid, first formed as above indicated, would be further decomposed into aniline:

$$C_6H_4\begin{cases} COOH \\ NH_2 \end{cases} \longrightarrow C_6H_5NH_2 + CO_2.$$

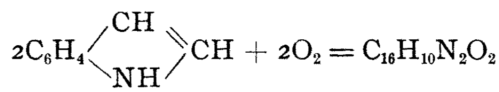
It was also found that a body known as isatin could be obtained from indigo by oxidation. The structural formula of this body was worked out carefully and found to be:



which was additional proof that the indigo molecule probably contained the group

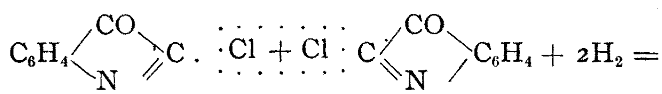


This opinion was still further strengthened when it was found that indol by simple oxidation could be converted into indigo:

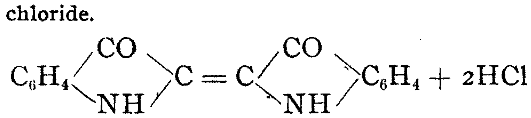


Indol.

The next step was the discovery that indigo could also be obtained from two molecules of isatin chloride by removing the chlorine, and as the new linking of the atoms of carbon would have to take place at the points occupied by the chlorine atoms, the following equation was reasoned out:



Isatin chloride.



Indigo.

In this manner the above formula was deduced for the proper structure of the indigo molecule, and all its subsequent reactions and methods of derivation have confirmed it as being true.

After its proper structural formula had been worked out, the next step was to prepare indigo synthetically. Its first synthesis had already been attained by Baeyer in the reduction of isatin chloride, as above indicated, but this was of no value from a commercial point of view. Several snytheses of minor importance were soon worked out in the succeeding few years, but they were of only theoretical interest, and may be passed over with the bare mention that one was from ortho-nitrocinnamic acid (Baeyer, 1880). This was of interest as being the first synthesis to be patented. This body was converted into ortho-nitrophenylpropriolic acid, which was used to a certain extent in printing in connection with sodium xanthate for the production of indigo directly on the fiber. The first synthesis of real importance was that discovered by Heumann (1890), who used phenyl-amido-acetic acid (otherwise known as phenyl-glycocoll). It was found that this body, on fusion with caustic potash, yielded indigo—or rather indigo white or reduced indigo was at first produced, which, on oxidation by the air, was speedily converted into indigotine itself:

$$2C_6H_5 . NH . CH_2 . COOH + O_2 = 4H_2O +$$
$$C_6H_4 \langle {CO \atop NH} \rangle C = C \langle {CO \atop NH} \rangle C_6H_4.$$

Although this reaction forms the basis of the present successful methods for preparing synthetic indigo on a commercial scale, yet it was not until it was found that naphthaline could be employed as a raw material from which to make the phenyl-glycocoll, that the process became commercially available. Naphthaline, on treatment with fuming sulphuric acid, is converted into phthalic acid, which by successive stages is converted into phthalimide, anthranilic acid, and then to phenyl-glycocoll ortho-carboxylic acid, from which the indigo is finally prepared by fusion with caustic potash. The successful commercial preparation of these successive bodies was only reached after tedious and thorough research on the part of specially trained chemists. Each step presented certain difficulties which had to be surmounted. A very large amount of fuming sulphuric acid was required, and the cost of this had to be brought down within certain limits. This led to the development of the contact process for the manufacture of highly concentrated acid. The Badische Anilin und Soda Fabrik, by whom this work was chiefly carried out, recover over 40,000 tons (in 1900) of sulphur dioxide formed in the reaction converting naphthaline into phthalic acid, and reconvert it into sulphuric acid by the contact process.

Also, monochloracetic acid had to be employed for converting the anthranilic acid into the phenyl-glycocoll compound, and it was found that this body was required of a very high degree of purity, which developed a process of making it from liquid purified chlorine and acetic acid, and in order to obtain it sufficiently cheap, the chlorine was prepared by an electrolytic process from salt, instead of the old methods of Deacon and Weldon.

The last few years (since 1897) have witnessed the successful exploitation of synthetic indigo upon the market on a large and continually increasing scale. Its manufacture has evidently proved lucrative, for several large dyestuff firms are engaged in its preparation. Besides the Badische Company, already mentioned, the Farbwerke Höchst are also large producers of indigo. These two firms for a number of years associated themselves in working out the synthesis of indigo, but since its commercial realization they have adopted certain modifications which give them slightly different methods of attaining the same end. The Société Chimique des Usines du Rhone, at Lyons, France, have also entered the field of indigo manufacture. This firm starts from toluene as the raw material and works up through ortho-nitrobenzaldehyde to indigo. Other large firms are also bending their efforts to obtain other processes to arrive at the same result. In consequence of all this activity on the part of the dyestuff manufacturers, and in view of the fact that the synthetic indigo is appearing in such large quantities on the market, and at a price which can undersell the natural product, we may soon look forward to the eventual total extinction of the natural indigo industry, in the same manner as the madder-root industry was quickly obliterated by the production of synthetic alizarin. Synthetic indigo appears to have all the essential qualities of the natural dyestuff, and can be prepared in a much purer state, so if anything it is really somewhat better in its quality than the natural product. And thus is recorded another triumph of chemistry over the clumsier processes of nature—and withal, that the very science which surpasses nature is but a science that nature makes!