SCIENCE

A WEEKLY JOURNAL DEVOTED TO THE ADVANCEMENT OF SCIENCE, PUBLISHING THE OFFICIAL NOTICES AND PROCEEDINGS OF THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

FRIDAY, OCTOBER 19, 1906.

CONTENTS.

MSS. intended for publication and books, etc., intended for review should be sent to the Editor of SCIENCE, Garrison-on-Hudson, N. Y.

THE JUBILEE OF THE COAL TAR COLOR INDUSTRY.

THE INFLUENCE OF SIR WILLIAM HENRY PERKIN'S DISCOVERY UPON OUR SCIENCE.[1]

I NEED hardly assure you how highly honored I feel to be permitted to speak here to-night. Yet I am fully aware that the committee did not select me because it considered me the most competent of our chemists to respond to this subject, but because so many of our colleagues refused to be heard, fearing the arduous labor of condensing this vast material within the limits of a fifteen-minute address, when fifteen hours could be devoted to it with much less difficulty and work. With me, however, it was a labor of love, and I accepted with pride and pleasure, inspired by the wonderful development of this industry in which I have been an attentive watcher and a modest coworker, it being just twenty years since, in collaboration with Professor Bernthsen, I began the investigations which finally culminated in the discovery of the constitution of the dyestuffs of the safranine series. Above all, I have been inspired in my task by the genial personality and refined modesty of our distinguished guest, Sir William Henry Perkin, with whom I had the pleasure of becoming more intimately acquainted during last year's meeting of the Society of Chemical Industry in London. It must be a sincere source of congratula-

[1] Given at the banquet given to Sir William Henry Perkin, at Delmonico's, New York City, October 6, 1906.

tion to us that he has braved the perils of a long ocean voyage to honor us with his presence at our celebration of the semicentennial of the coal tar industry, initiated by the discovery of Perkin's mauve. Only fifty years ago, while engaged in research, having for its object the artificial production of quinine, Perkin, then an eighteen-year old assistant of Hofmann, obtained a muddy, dark precipitate, from which he first endeavored to extract certain colorless crystalline substances which might adequately explain the reaction under observation. One day, however, the thought occurred to him to utilize this colored precipitate itself for the dyeing of silk. It is hard to realize to-day what an epoch-making idea it was at that time to dye fabrics with a substance evolved in the laboratory and having no relation whatever to the dyestuffs then known. It was truly the spark of genius which led Perkin to investigate the dyeing properties of that dark-colored precipitate which would have been cast away by any other scientist of that period and particularly by his master, Hofmann, who objected to experimenting with anything which did not crystallize and who had at that time a strong aversion to working with substances which were colored. For the latter, when produced in reactions, were generally regarded as secondary products and every endeavor was made to get rid of them, so that the other substances associated with them might be examined.

But however great the discovery of mauve, and however much we must admire the courage of the youth who undertook its technical production, yet these steps were only trivial incidents in the immense revolution brought about by Perkin's genius. The greatest obstacles encountered by him, and the most difficult task to be performed, was when he attempted to sell the color to dyers and printers. At that time men of this class worked by the rule of thumb with secret recipes, mostly inherited from their forefathers, and their formulæ, although applicable to natural colors, were not suitable for mauve. Thus Perkin and his associates had to prepare new directions for dyeing and printing and to induce those ultra conservative dyers to adopt the new methods. It has been almost forgotten that Perkin was the first to introduce the method of dyeing silk in a soap bath which is commonly employed to-day for all artificial dyestuffs, and that he and Pullar first made use of the mordanting of cotton with the insoluble inorganic compounds of tannin.

Thus the introduction of mauve completely changed the art of dyeing and printing, simplifying the processes and substituting for the old time formulæ, the scientific recipes furnished by the color manufacturers of the present day. After Perkin had thus removed the obstacles in the path of practical application, it became comparatively easy to introduce other coal tar colors.

But Perkin also paved the way for the discovery of the later coal tar colors by creating commercially aniline and benzole, which up to his time had only been laboratory curiosities. Of the three methods available for obtaining aniline he selected as the most promising the reduction of nitrobenzol, made by nitration of coal tar benzol, and the production of aniline from this source led, shortly after the discovery of mauve, to the discovery of magenta, which opened up a new and immense field for this industry. Aniline from benzole was later found to contain toluidine, which is not present in aniline from indigo or that obtained directly from coal tar, and Perkin truly said in a lecture delivered December 7, 1868:

Had the aniline contained in coal tar or the aniline obtained from indigo been employed for the preparation of mauve, instead of that prepared from commercial benzol, magenta and its train of colored derivatives would in all probability have remained unknown to the present day from the simple fact that magenta can not be produced from pure aniline, a second body being also required.

The industry thus initiated with a violent impetus soon showed its revolutionizing tendencies and its vitalizing power in almost every branch of human endeavor. To-day about 2,000 individual dyestuffs are known, giving the whole range of the colors of the rainbow, and complying with every demand of taste, fashion and stability. They surpass in beauty and brilliancy the colors supplied by nature, and, contrary to the impression prevailing among the public, the shades obtained with some of them are faster to the influence of time, light and chemicals than the fastest which nature produces.

The greatest triumph of this branch of the industry was the artificial production of alizarine and indigo. In the technical production of the former our distinguished guest has played a prominent part, solving the problem of its manufacture simultaneously with Graebe, Liebermann and Caro, whose English patent antedates that of Perkin by one day, and for the first synthesis of indigo cinnamic acid was successfully employed which was originally obtained from coal tar by Perkin.

Coal tar colors, however, are not only used for the dyeing of textile fibers, like wool, silk, cotton, linen, jute, ramie, etc., but for a host of other materials.

The lady's hair is gray, or of a hue not fashionable at the time—coal tar colors will assist her in appearing youthful and gay. In eating the luscious frankfurter your soul rejoices to see the sanguineous liquid oozing from the meat—alas coal tar colors have done it, and friend Wiley can prove it. The housewife selects a bright green broom, on account of its anticipated good wearing quality, but finds, to her sorrow, that coal tar colors furnished the freshness. The product of the hen is replaced by yellow coal tar colors in custard powders, and butter is colored yellow when the dyestuff laboratory of the cow is on a strike. Leather, paper, bones, ivory, feathers, straw, grasses, are all colored, and one of the most interesting applications is the dyeing of whole pieces of even the bulkiest furniture by dipping them in large tanks containing the dyestuffs, which transforms the wood into walnut, mahogony at your command, as carried out in our big factories in Grand Rapids and elsewhere.

As coal tar colors are used on this enormous scale, so they are also employed in a liliputian manner, for staining specimens for examination under the microscope, enabling us to detect and identify bacteria, the finest nerve-ends and other minute elements of animal tissues, and by means of such staining methods, especially with methylene blue, Koch discovered the bacillus of tuberculosis and cholera, and initiated the modern battle against preventable infectious diseases. In reciprocation for the excellent reagents supplied him by the dye industry, the histologist brought about the discovery of a new and very important class of colors, and as this instance is one of the most striking demonstrations of the interdependence of practise and theory, I shall relate it to you. In 1886 Ehrlich observed that methylene blue and some of its congeners were the only colors which stained the living nerve tissue, and in order to determine whether this remarkable property was due to the peculiar constitution of methylene blue or to the presence of sulfur, he found it desirable to experiment with a substance analogous to methylene blue, but in which the sulfur was replaced by oxygen. He applied to Dr. Caro requesting him to assist him in his work by furnishing him the material necessary for his experiments.

As a substance of this constitution was then unknown, it was made to order, and in the course of this research the valuable class of rhodamine colors was discovered. Thus experiments with nerve tissues gave birth to the manufacture of coal tar colors of the greatest importance in the textile industries.

The dyestuffs methylene blue and some others are also of great value as internal remedies, and the former is strongly recommended by one of the greatest American authorities for the relief of pain in that horrible disease—cancer.

The medicinal properties of the coal tar colors lead us to that branch of the industry which is next in importance, namely, the coal tar remedies. Incidentally, it may be mentioned here that before these so-called synthetics were introduced, Kolbe had succeeded in 1874 in artificially preparing from coal tar salicylic acid, which up to that time was exclusively a product of nature. Salicylic acid has been, and is still to-day, used extensively as a remedy against rheumatism.

The industry of synthetic drugs owed its origin also to the efforts of chemists to produce quinine artificially. Experiments had shown that by decomposing quinine a substance called quinolin was formed, and the latter was likewise found to exist in coal tar. It was then assumed that quinine must in some way be derived from quinolin, and that perhaps other derivatives of quinolin might possess properties similar to quinine. This trend of thought led to the discovery of the quinolin derivatives, thallin and kairin, which, however, were soon discarded on account of their drastic action and to-day possess only historical interest.

In 1883 Knorr, starting from erroneous deductions concerning the constitution of quinine, and also misinterpreting the constitution of some of the products obtained in his research, inspired the pharmacological study of a substance afterwards called antipyrin. This product proved to be of the greatest value in medicine and was the first successful synthetic coal tar remedy in the market.

Shortly after the introduction of antipyrin a fortunate accident gave this modern art an unexpected stimulus, diverting the investigation from quinine and uncovering an entirely new field. Kahn and Hepp, two physicians connected with the Strassburg University, were on terms of friendship with a chemist of the Hoechst Works, where Knorr's antipyrin was being manufactured, and requested him, in 1886, to send them some chemically pure naphthalene, which they desired to use internally in the case of a patient suffering with some skin disease. They received the substance, and on administering it found that while it failed to exhibit the expected effect, it promptly reduced the existing fever. When the supply of naphthalene was almost exhausted, they wrote for a further quantity; but, to their great astonishment, the second supply, unlike the first, did not manifest any antipyretic action, and on comparing the two, they soon discovered that a mistake had occurred somewhere. An investigation showed that when the first request was received the laboratory boy was directed by the chemist to fill a bottle with naphthalene and mail it to his friends, but through an error some acetanilid was sent instead, while the second time the chemist himself filled the bottle correctly. Thus through an accident acetanilid was introduced into medicine, a remedy which to-day is used by the ton as an antipyretic and antineuralgic, and through the irony of fate the most powerful competitor of antipyrin was discovered as the result of a mistake made in the very factory which was realizing enormous profits from the production of antipyrin.

When it was recognized that the acetylization of an amine produced a body of so much value, this process was tried with many amines and other suitable substances, and in consequence such important remedies as phenacetin were obtained, while by substituting lactic acid for acetic acid, lactophenin was prepared, and by means of amidoacetic acid, a drug named phenocoll.

After chemical researches had shown that the active principles of vegetable purgatives, such as rhubarb, senna, cascara-sagrada and aloes were anthraquinone derivatives, synthetic preparations of this class, which therefore are closely related to the alizarine colors, are now brought into the market. These new remedies have the advantage over the crude drugs of greater uniformity of action and exactness in the dosage.

The active principle of the suprarenal gland first isolated and investigated by an American scientist, a substance of surprisingly simple chemical constitution, has been obtained from coal tar, and it is said that this synthetic product is now marketed, and from experiments carried out in Europe and in the large works of Parke, Davis & Company in this country, we may expect that derivatives of this body will soon appear which will be even superior in their pharmacological effect to nature's product.

About the time that the first synthetics were brought out, a very curious chemical was discovered also by American ingenuity, which is to-day not only used for medicinal, but also on a large scale for industrial purposes. I refer to saccharine, a substance derived from coal tar, which is 550 times sweeter than sugar, and is the first representative of the class of artificial sweeteners. It may be of interest to relate an instance showing how purely theoretical investigations may lead to the building up of an important industry.

Dr. Fahlberg, working under the direction of Professor Ira Remsen at Johns Hopkins, was experimenting with coal tar derivatives from a purely scientific point of view. Before leaving the laboratory one evening, he thoroughly washed his hands, and was under the impression that he had taken every pains in doing so. He was, therefore, greatly surprised on finding that, during his meal, when carrying bread to his mouth, the hands had a sweet taste. He suspected that his landlady had unintentionally sweetened the bread and called her to account. They had a little discussion, from which she emerged the victor. It was not the bread that tasted sweet, but his hands, and, much to his surprise, he noted that not only his hands but also his arms had a sweet taste. The only explanation that he could think of was that, notwithstanding the thorough washing, he had brought some chemical along from the laboratory. Rushing back to it and carefully investigating the taste of all the goblets, glasses and dishes standing on the working table, he finally came across one whose contents seemed to possess a remarkably sweet taste. *Thus was made this important discovery.* What remained to be done was accomplished by later researches with this substance. He found very soon that saccharine, as the product was named, when diluted assumed the taste of cane sugar. In watery solution, for instance, its taste was as pleasant as sugar water. The product seemed to be worthy of utilization, provided its other properties were not objectionable.

Physiological experiments were now made on animals, and then on human beings, which showed that it was eliminated undecomposed, and that therefore the human organism behaved indifferently towards the substance. Furthermore, as no perceptible disturbance of the general condition could be observed, it could be assumed that saccharine had no deleterious influence whatsoever upon the general health.

With the introduction of this artificial sweetener, a new industrial field was opened up, and the significance of this discovery can be easily imagined when you consider that four pounds of this material are equivalent in sweetening power to one ton of cane or beet sugar. It was soon manufactured on such a large scale that it seriously threatened the beet sugar industry of the continent, and as the latter was of much more economic importance than the production of saccharine, laws were enacted which prohibited the industrial use of the sweetener as a substitute for sugar, permitting its employment solely for medical purposes, the German government even going so far as to make a sort of state monopoly of the manufacture of this material.

Still another industry has undergone vast changes through Perkin's discoveries and since the beginning of the coal tar epoch—the manufacture of artificial perfumes. Nitrobenzol, under the name of mirbaneoil, was in the market as artificial oil of bitter almonds even before Perkin's mauve. It was used to some extent for scenting soaps. To-day a great variety of synthetic perfumes are manufactured. The odor of musk is successfully imitated by a nitrated hydrocarbon derived from coal tar; the odor of violets, of roses, of jasmine, of heliotrope, is reproduced artificially by synthetic substances, and the favorite American flavor, the oil of wintergreen, is manufactured from coal tar. And in this art also the hand of the master is seen in what is called the Perkin Reaction, through which he first succeeded in preparing from coal tar, coumarin and cinnamic acid.

The singular correlation of all these coal tar products appears from the fact that the odoriferous principle of jasmine is derived from the same mother substance which furnishes synthetic indigo, namely, anthranilic acid.

Between the products giving the sweet odors of flowers and the death dealing explosives there would seem to be a broad chasm, but not for the synthetic coal tar chemist. In fact the same nitrobenzol which was the first artificial perfume is used to-day with nitroglycerin as a safety explosive. The latter has the disadvantage of congealing when exposed to the cold and then becoming highly dangerous; the admixture of nitrobenzol keeps it liquid at very much lower temperatures. Trinitrobenzol and its homologues, especially trinitrocarbolic acid, or picric acid, are to-day employed as safety explosives by the miner and in proper mixtures as smokeless powder by the armies of the civilized world.

While coal tar preparations thus destroy life, so they likewise sustain life, for by the use of salicylic and benzoic acids, both products of nature but now derived chiefly from this source, it becomes possible to preserve the canned foods so indispensable to the soldier, sailor and explorer.

In conclusion, mention must be made of the use of coal tar colors and preparations in the reproductive arts, in which they play a most important part. Inks for printing and writing are made with coal tar colors and in photography coal tar preparations are now used almost exclusively for the development of the latent pictures on films, plates and paper. By the addition of certain coal tar colors to the photographic emulsion the latter becomes extremely sensitive to light and can then be used for instantaneous exposures, as in snapshots, and thus kodak fiends are the direct offshoots of the coal-tar industry.

By means of coal tar colors even one of the greatest of all problems—photography in natural colors—has been realized.

Curious to relate, with all these successes to its credit, the problem which has occupied the attention of master minds now for almost a century, and which was the incentive of Perkin's research, so fruitful in other fields—the artificial production of quinine—remains unsolved up to the present day.

While thus new arts were constantly developed, the chemical industries, existing at the time of Perkin's discovery, were also eminently benefited. The production of aniline required at once large quantities of sulfuric and nitric acids for the nitration of benzol, and the demand of the new industry for highly concentrated sulfuric acid gave to the world the contact process in which the sulfurous acid gas, formed, for example, in roasting zinc and iron pyrites, which heretofore was allowed to escape and then vitiated the atmosphere and destroyed vegetation, is converted into sulfuric acid by the oxygen of the air. The manufacture of alizarin consumed enormous quantities of caustic soda. Bromine and iodine became staple articles of commerce. The electrolysis of salt solution was economically perfected, and together with the contact process and the liquefaction of chlorine is employed on an immense scale for the synthesis of indigo. The experience gained in electric methods is being applied to the problem of utilizing the nitrogen of the air, and to judge from past successes, it will not be many years before the Badische Anilin and Soda Fabrik, in whose laboratories experiments in this direction are being conducted, will bring to the market nitrates, nitrites and nitric acid made from atmospheric nitrogen, instead of Chile saltpeter, the supply of which is calculated to last no longer than about twenty years, and as Chile saltpeter is indispensable in agriculture, especially in the raising of cereals, its artificial production in the manner indicated will remove the anxiety expressed by writers on economics concerning the difficulties of feeding an ever-increasing population owing to the gradual exhaustion of the soil.

The distillation of coal tar itself was changed in every respect to comply with the new developments. All its by-products are utilized, and one of them, sulfate of ammonia, is produced so economically that it is commonly employed as a fertilizer.

In the cooking processes, of so great importance in the manufacture of iron and steel, the gaseous products are not allowed to go to waste any more, but are recovered and utilized to furnish benzol, etc., in addition to illuminating gas—in fact, the United Coke and Gas Company operates some of its plants in such a manner that the gases are the principal products and coke only a by-product.

In the treatment of these gases, cyanide of potassium is obtained at such low cost that it is used for extracting low class gold ores which hitherto were useless. Hence this substance plays an important part in the monetary system, as its cheap production has disposed of the fear that there would not be enough of the precious metal to maintain the gold standard of the civilized nations.

The chemistry of benzol gave us our modern theories, especially that of Kékulé, which in its application led to marvelous prophesies of experimental results and is recognized to be one of the most remarkable achievements of the human mind.

The coal-tar industry gave us our modern chemical institutes, the wonderful equipments of which were first utilized in the laboratories of the factories, and above all it gave us the intimate cooperation of technics and science which is in fact at the root of all this magnificent success.

In closing permit me to say that it is unique in the history of civilization that the honor and credit for the creation of this enormous material and spiritual wealth is unanimously and ungrudgingly accorded to Sir William Henry Perkin. It is unique that the creator of this vast industry has been so fortunate as to witness its wonderful development during fifty years. It is unique that when no longer engaged in the industrial part of our science, he undertook a series of theoretical investigations of the utmost difficulty, which only the most gifted have the courage to attempt, and that in this branch, too, he has conquered a position as lofty as his fame as a manufacturing chemist.

The world can not spare such an extraordinary man. May he live for many years to come and may his life be replete with health and happiness.

Hugo Schweitzer.

ADDRESS OF SIR WILLIAM HENRY PERKIN.[1]

It is now twenty-two years since I visited the United States. I was attending the first British Association meeting that was held at Montreal and then extended my visit to Yellowstone Park, returning by Chicago, Washington, Baltimore, Philadelphia, New York and Boston back to Montreal. At that time I certainly never anticipated that in twenty-two years' time I should be in this city at a jubilee celebration of the discovery of mauve and the foundation of the coal tar color industry. It was, indeed, quite unexpected and a matter of surprise to me when I heard that an international celebration was about to be inaugurated in my own country, which took place in July last. This included nations on both sides of the world, as you sent Dr. Baekeland as a delegate to represent America, but it was a still greater surprise to find that you were not satisfied to merely join the English jubilee, but had determined on having a jubilee celebration of your own in this city, which I should be invited to attend. I can only say how greatly honored I feel and how gratified I am at being present here to-night at this banquet, and meeting so many fellow workers in the field of science, and other friends. From the very cordial and friendly reception you have given me, I do not feel at all strange in coming amongst you, especially as I realize how closely we are related to each other by race and language, which naturally engenders a strong feeling of sympathy between us, a feeling which has been so heartily manifested this evening by the warm welcome given by the City of New York, through the Hon. Patrick McGowan, president of the Board of Aldermen, and also in a practical manner by the presentations given by Dr. Nichols, Mr. Kuttroff and Dr. Hillebrand.

The foundation of a medal bearing my name to be annually awarded to an American chemist, I feel to be a great honor, especially as I have all my life insisted on the importance of research work, and if this medal should help to encourage and stimulate some chemists to increased activity in this direction, this jubilee celebration will have accomplished a valuable result. And when we consider the advantages you fortunately have in this country by the existence of a very large research fund, we can not but believe that this will be the case. I thank you very sincerely for presenting me with this beautiful medal, the first that has been struck, which I value very highly.

With respect to the beautiful personal token you have presented to me, I scarcely know how to express myself. I am sure it will always be greatly valued not only by

[1] Given at the banquet tendered to him at Delmonico's, New York City, October 6, 1906.