The Origin of the Coal-Tar Colour Industry, and the Contributions of Hofmann and his Pupils.

By W. H. PERKIN, Ph.D., D.C.L., F.R.S.

The illustrious man whose lifework we are called on to commemorate, was well known to very many of us, especially those who had the privilege of being his students and assistants. We can all recall the pleasure and interest with which we listened to the lucid and graphic accounts of his researches which he used to bring before the Chemical Society in years gone by; and great was felt to be the loss, not only to us, but also to the country, when he left it for his fatherland: but now we mourn a far greater loss, and one which we realise more and more deeply as we consider the incidents of his remarkable career—a career of such incessant activity and brilliant achievement.

I am charged with a duty which I wish had been placed in more capable hands than mine: to give an account of the rise and progress of the coal-tar colour industry, and its relation to the Hofmann school; and, as being connected with its commencement, I am requested to make the account to a large extent autobiographical—a part of my task which it would have been more agreeable to me to have seen undertaken by others rather than myself.

This industry holds an unique position in the history of chemical industries, as it was entirely the outcome of scientific research. We have to go back to 1825, when Faraday discovered benzene, or, as he then termed it "bicarburetted hydrogen," for the first investigation which clearly bears upon the subject. Faraday separated the hydrocarbon from the liquid products condensed on compressing the gas obtained from oil. A year later (1826), Unverdorben obtained aniline by the mere distillation of indigo, and called it "crystalline." Runge afterwards obtained it from coal-tar oil, and having observed that it produced a violet-blue coloration with chloride of lime, called it "kyanol." It was subsequently obtained from indigo by Fritsche by distilling this colouring matter with caustic alkali. We then come to the important work of Mitscherlich, who obtained the hydrocarbon benzene from a new source, namely, benzoic acid,—whence the name, and produced from this nitrobenzene. Zinin subsequently found that *benzidam*, as he termed it, could be produced by the action of sulphuretted hydrogen in presence of ammonia on an alcoholic solution of nitrobenzene.

This brings us to the commencement of Hofmann's researches on aniline, a substance which he used sometimes to speak of as his "first love." In his first published paper he showed that Unverdorben's crystalline, Runge's kyanol, Fritsche's aniline, and Zinin's benzidam were all the same compound, for which he afterwards selected Fritsche's name, aniline. Later on, Hofmann and Muspratt prepared toluidine from toluene from tolu balsam.

The work on the separation of aniline from tar was done before the date of Hofmann's coming to this country, viz., in 1843. After his arrival here in 1845, he continued his researches, and, to realise something of his indomitable perseverance, it is necessary to remember that, until the coal-tar colour industry was established, practically all the aniline he used in his numerous enquiries was procured by the laborious and costly process of distilling indigo with potash.

In 1843, organic chemistry was still in its infancy, and coal-tar naphtha had not yet been investigated. Runge had isolated carbolic acid, pyrrol, kyanol or aniline, and leucol or quinoline. Naphthalene was well known to exist in tar, having been separated by

Garden, as early as 1820. Dumas had discovered paranaphthalene or anthracene, and chrysene and pyrene had been referred to by Laurent, but these were very doubtful compounds. This was about all that was known of the composition of coal-tar at that time. Hofmann showed, in 1845, that benzene must exist in the naphtha, as he found that aniline could be produced from it, but he never separated this hydrocarbon; shortly afterwards, however, he induced his pupil, Charles Mansfield—of whom he always spoke in the highest terms—to undertake the investigation of the liquid hydrocarbons of coal-tar.

On reading over the account of Mansfield's investigation, and bearing in mind that in those days fractional distillation was conducted in old fashioned glass retorts with the thermometer in the liquid, it is impossible not to admire the patience and perseverance he exercised, as well as the systematic and skilful manner in which he worked.

All who have undertaken fractional distillations, even with all our present knowledge and improved apparatus, know how difficult it is to detect and isolate products in a mixture such as coal-tar naphtha. Yet Mansfield obtained benzene in a pure state, and toluene sufficiently so for Hofmann to prepare toluidine from it. He also obtained pseudocumene, and was led to believe in the existence of xylene. In describing his work, he modestly remarks:—

> "It has been perhaps the tedium of the methods necessary to effect a separation of mixed hydrocarbons from each other, which has deterred experienced chemists from devoting their time to disentangling the oils here treated of: and perhaps to have conducted the innumerable distillations necessary for this purpose in a laboratory imperfectly furnished with gas and other conveniences, would have been a task too laborious to have been persisted in." (*J. Chem. Soc.*, 1849, 1, 246.)

Amongst the enquiries carried on by Hofmann, in the early days of the Royal College of Chemistry, were those classical "researches regarding the molecular constitution of the volatile organic bases," in which he succeeded in displacing the hydrogen of the NH_2-group by different alcohol radicles, eventually obtaining also the ammonium compounds. In the first of these (*J. Chem. Soc.*, **3**, 1851) he describes ethylaniline (p. 284), and diethylaniline (p. 288), also methylaniline (p. 295). The method used in these researches, of substituting hydrogen in amines by means of the iodides and bromides of the alcohol radicles, and also the substituted anilines which were obtained, although not connected with the foundation of the coal-tar colour industry, have been of great value in its after development. These few references to observations on the early work carried on at the Royal College of Chemistry, for the sake of science *only*, show, in fact, what valuable material was produced for the coming new industry; indeed, without the research of Mansfield, it could never have become an industry.

The foregoing brings the work of the Royal College of Chemistry up to near the date when I became a student there, and it will, perhaps, be well if I here refer to my young days, and state how it came to pass that I had the good fortune to study under Hofmann, especially as it will enable me to say a few words in reference to one of his old pupils who has done much for the cause of science.

As long ago as I can remember, the question what pursuit I should follow was constantly before me. Even when very young, I interested myself in several subjects of a mechanical kind, and worked at them to the best of my ability; and elementary as the experience then gained was, it had a lasting influence upon me. When I was between 12 and 13 years of age, a young friend was good enough to show me some chemical experiments; amongst these were some on crystallisation, which seemed to me most marvellous phenomena: as a result, my choice was fixed, and it became my desire to be a chemist, if possible, as I saw that there was in this science something far beyond the mechanical and other pursuits I had been previously occupied with. At this time I left the school I was attending, and entered the City of London School, of which Dr. Mortimer was then head master. Here lectures were given on chemistry and natural philosophy; indeed, I believe this was the first school in which experimental science was taught. The lecturer was one of the masters, Mr. Thomas Hall, B.A. (Lond.), an old sudent of Hofmann's, who had obtained all the chemical knowledge he possessed by working at the Royal College of Chemistry. To attend these lectures was a source of great pleasure to me. There was also a yearly examination in science, and the examiner was also one of Hofmann's pupils, and his first assistant, none other than my friend Mr., now Sir, Frederick Abel. In the City of London School I was consequently brought directly under Hofmannic influence, if I may so term it, for all who came in contact with those who worked with him had infused into them by induction his enthusiasm for chemistry. Mr. Hall very soon took an interest in me, and installed me as one of his lecture assistants. Science, however, was not allowed to interfere with the ordinary school curriculum, so that the lectures, and the preparations for them, were delegated to the interval for dinner, and being very much interested in preparing the experiments, I not unfrequently found this interval had passed before I had left off work; but, fortunately, I never found that the abstinence thus caused acted prejudicially upon me. Whilst with Mr. Hall, I heard much of the Royal College of Chemistry and its Professor, and after my master had very kindly had several interviews with my father—who wished me to be an architect and not a chemist—it was my good fortune to be allowed to follow my bent, and go to the Royal College of Chemistry, in Oxford Street.

Before passing from my schooldays, I feel I must say a few more words about my old school-master, to whose kindness I owe so much. Thomas Hall was a born teacher, who took an individual interest in his scholars, studying their characters, and stimulating any special qualities he saw they possessed, and, at the same time, inculcating the highest moral qualities. He hated anything that was mean or underhand, and, at the same time, was very genial and kind-hearted; this may be gathered from the fact that the boys used to speak of him as *Tommy Hall.* His influence on behalf of science, especially the science of chemistry, was great; it appears, from a list of old City of London School boys, kindly given me by Mr. John Spiller, that more than 30 boys in whom he had taken an interest afterwards worked at the Royal College of Chemistry, and of these I may mention the following as having contributed papers to our Transactions:

J. J. Bowrey, J. T. Brown, Frank Clowes, W. H. Deering, Edward Divers, J. A. Newlands, F. J. M. Page, W. H. Perkin, Alexander Pedler, J. Spiller, and W. Thorp.

I entered the Royal College of Chemistry when I was in my fifteenth year, at the time when that institution became part of the School of Mines, but I only took up the study of chemistry. After seeing Dr. Hofmann with my father, the first person I encountered in the laboratory was the Assistant, Mr. W. Crookes, who set me to study the reactions of the metals.

There was no theatre at the Royal College then, and the students had to go to the Museum of Practical Geology in Jermyn Street to hear the lectures on chemistry, which involved a rather serious loss of time; but the lectures made up for this, as Hofmann spared no pains in making them as interesting, instructive, and perfect as he possibly could, illustrating, as far as practicable, everything by experiment, so that the facts were firmly impressed upon the mind. At that time he also had a very efficient lecture assistant, the late Mr. Witt. Hofmann was good enough to let me attend these lectures a second time.

When going through the ordinary course of qualitative and quantitative analysis, the students working at research appeared to me to be superior beings, something beyond ordinary persons; and being possessed with a desire to join their ranks, the ordinary course, and also gas analysis by Bunsen's method, was quickly gone through. Hofmann then set me to work at research, and very curiously gave me as a subject the hydrocarbon anthracene, or, as it was generally called in those days, paranaphthalene. To obtain this, pitch was taken as the starting point, but as it was found that this method of preparation was a very tedious one to carry out in the laboratory, Hofmann kindly obtained some of the crude product for me from Mr. Cliff, of Bethels Tar Works. As is well known, Hofmann—especially at that period—was much interested in the formation of organic bases from hydrocarbons, and the object of my investigation was to produce, if possible, a nitro-compound, and then convert this into a base by reduction. However, anthracene refused to give a nitro-compound, and consequently no base could be obtained, but, in the course of my work, I prepared the compound we now know as anthraquinone, and also the chlorine and bromine derivatives of anthracene. But these substances could not be got to yield intelligible results on analysis, and at that time it never occurred either to Hofmann or myself that there was any likelihood of Dumas and Laurent's formulæ for the hydrocarbon (*i.e.*, $C_{15}H_{12}$) being incorrect. The consequence was that this research was set aside, but I shall show further on that the experience I then gained was of great importance to me several years later, when I commenced to work at the production of alizarin.

Hofmann next set me to work to study the action of chloride of cyanogen on naphthylamine in the same way that he had examined the action of this gas on aniline. In those days there were no depôts where pure products for research could be obtained as there now are, and for this inquiry even the naphthalene had to be purified in the laboratory; this research was soon completed, but was not written out and published until nearly 12 months afterwards. It was brought before this Society when the meetings were held in Mr. Pepper's house in Cavendish Square.

Hofmann had a marvellous power of stimulating his students, and of imparting to them his own enthusiasm; he took the strongest personal interest in their work, visiting three or four times in the week even those who were going through the reactions, while those engaged in research work were seen daily by him, and if anything of special interest was going on, more than once in the day. His power of directing research was also most remarkable; with the aid of a few watch glasses, a glass rod, and a small gas flame he would make a number of experiments, and from the information thus gained tell his students how to proceed with their work. I well remember how one day, when the work was going on very satisfactorily with most of us and several new products had been obtained, he came up and commenced examining a product of the nitration of phenol one of the students had obtained by steam distillation; taking a little of the substance in a watch glass, he treated it with caustic alkali, and at once obtained a beautiful scarlet salt of what we now know to be orthonitrophenol Several of us were standing by at the time, and, looking up at us in his characteristic and enthusiastic way, he at once exclaimed, "Gentlemen, new bodies are *floating* in the air." I mention this just as an example of the way in which he used to stimulate us by his own example.

After I had completed the research on the action of chloride of cyanogen on naphthylamine, Hofmann promoted me to the position of an assistant in his research laboratory; I was then 17 years of age. Mr. A. H. Church, now Professor Church, was among the assistants in the laboratory. This position proved most valuable to me.

At this time Professor Cahours came over from Paris to work with Hofmann on the allyl compounds, a research in which Professor Church and I had to assist. They then commenced their splendid work on the phosphorus bases, and I well remember the excitement and interest which prevailed when Paul Thénard's triethylphosphine was first produced by the action of zinc ethyl on phosphorus trichloride, and Hofmann's delight when he found it was vigorously acted on by methyl and also ethyl iodide, producing white, crystalline, phosphonium iodides. I was occupied with this research until I left the Royal College.

I may here refer to an incident which shows how greatly Hofmann was interested in his scientific work. One day, when he was going his usual rounds in the general laboratory, a student standing not far from him poured a quantity of concentrated sulphuric acid into a thick glass bottle he was holding in his hand, which contained a small quantity of water; the consequence was that the heat evolved caused it to crack and the bottom to fall out. Some of the acid splashed up from the floor into Hofmann's eye, and we feared would have a permanently injurious effect upon it. Hofmann was sent home in a cab, and had to be kept in bed in a dark room during several weeks, his old friend, Dr. Bence Jones, attending him. But during this time, and notwithstanding his sufferings, he was so anxious about his work that we used to have to visit him in his darkened bedroom, to report progress and also to receive any instructions he had to give.

Whilst in the research laboratory I had the privilege of meeting St. Claire Deville, who came to London for the purpose of exhibiting specimens of sodium and aluminium at a lecture given by the Rev. T. Barlow at the Royal Institution, of which the lecturer was Secretary.

Whilst assistant under Hofmann, I had but little time for private work in the daytime; as, however, I wished to continue research work, part of a room at home was fitted up as a rough laboratory, and there I was able to work in the evenings or during vacations.

In this laboratory a research was carried on conjointly with Mr. Church on some colouring matters derived from dinitrobenzene and dinitronaphthalene. One of the products we then obtained afterwards proved to be amidoazonaphthalene, or, as we called it, azodinaphthyldiamine. This appears to have been the first case of a definite compound being obtained of the azo-class and shown to possess dyeing powers. As Dr. Caro has referred to this in his notice in the *Berichte* of the late Peter Griess, I need not make any further observations on the subject here (*Ber*., 1892, **25**, 4, 1011).

At this period much interest was taken in the artificial formation of natural organic substances; but at the time I was at the Royal College of Chemistry, although the theory of compound radicles, the doctrine of substitution, &c., were occupying much attention, very little was known of the internal structure of compounds and the conceptions as to the method by which one compound might be formed from another was necessarily very crude.

Thus, in the Report of the Royal College of Chemistry, published in 1849, Hofmann refers to the artificial formation of quinine as a great desideratum, and then states

> "It is a remarkable fact that naphthalene, the beautiful hydrocarbon of which immense quantities are annually produced in the manufacture of coal gas, when subjected to a series of chemical processes, may be converted into a crystalline alkaloïd. This substance, which has received the name of naphthalidine, contains 20 equivalents of carbon, 9 equivalents of hydrogen, and 1 equivalent of nitrogen." (C = 6. O = 8.)

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> "Now if we take 20 equivalents of carbon, 11 equivalents of hydrogen, 1 equivalent of nitrogen, and 2 equivalents of oxygen, as the composition of quinine, it will be obvious that naphthalidine, differing only by the elements of two equivalents of water, might pass into the former alkaloid simply by an assumption of water. We cannot, of course, expect to induce the water to enter merely by placing it in contact, but a happy experiment may attain this end by the discovery of an appropriate metamorphic process."

In fact there was but little other ground to work upon in many instances than this kind of speculation.

As a young chemist I was ambitious enough to wish to work on this subject of the artificial formation of natural organic compounds. Probably from reading the above remarks on the importance of forming quinine, I began to think how it might be accomplished, and was led by the then popular additive and subtractive method to the idea that it might be formed from toluidine by first adding to its composition C_3H_4 by substituting allyl for hydrogen, thus forming allyltoluidine, and then removing two hydrogen atoms and adding 2 atoms of oxygen, thus

$$\underbrace{2(C_{10}H_{13}N)}_{\text{Allyltoluidine.}} + 3O = \underbrace{C_{20}H_{24}N_2O_2}_{\text{Quinine.}} + H_2O$$

The allyltoluidine having been prepared by the action of allyl iodide on toluidine, was converted into a salt and treated with potassium dichromate; no quinine was formed, but only a dirty reddish-brown precipitate. Unpromising though this result was, I was interested in the action, and thought it desirable to treat a more simple base in the same manner. Aniline was selected, and its sulphate was treated with potassium dichromate; in this instance a black precipitate was obtained, and, on examination, this precipitate was found to contain the colouring matter since so well known as *aniline purple* or *mauve*, and by a number of other names. All these experiments were made during the Easter vacation of 1856 in my rough laboratory at home. Very soon after the discovery of this colouring matter, I found that it had the properties of a dye, and that it resisted the action of light remarkably well.

After the vacation, experiments were continued in the evenings when I had returned from the Royal College of Chemistry, and combustions were made of the colouring matter. I showed it to my friend Church, with whom I had been working, on his visiting my laboratory, and who, from his artistic tastes, had a great interest in colouring matters, and he thought it might be valuable and encouraged me to continue to work upon it; but its evident costliness and the difficulties of preparing aniline on the large scale, made the probability of its proving of practical value appear very doubtful. Through a friend, I then got an introduction to Messrs. Pullar, of Perth, and sent them some specimens of dyed silk. On June 12, 1856, I received the following reply :—

> "If your discovery does not make the goods too expensive, it is decidedly one of the most valuable that has come out for a very long time. This colour is one which has been very much wanted in all classes of goods, and could not be obtained fast on silks, and only at great expense on cotton yarns. I enclose you pattern of the *best* lilac we have on cotton—it is dyed only by one house in the United Kingdom, but even this is not quite fast, and does not stand the tests that yours does, and fades by exposure to air. On silk the colour has always been fugitive: it is done with cudbear or archil, and then blued to shade."

This somewhat lengthy extract is quoted because it gives a glimpse at the state of the dyeing trade in reference to this shade of colour at that period.

This first report was very satisfactory; the "if" with which it commenced was, however, a doubtful point.

During the summer vacation, however, the preparation of the colouring matter on a very small, technical scale was undertaken, my brother (the late T. D. Perkin) assisting me in the operations, and, after preparing a few ounces of product, the results were thought sufficiently promising to make it desirable to patent the process for the preparation of this colouring matter. This was done on August 26, 1856 (Patent No. 1984). A visit was then made to Messrs. Pullar's, and experiments on cotton dyeing were made, but, as no suitable mordants were known for this colouring matter, only the pale shades of colour, produced by the natural affinity of the dye for the vegetable fibre, were obtained; these, however, were admired. Experiments on calico printing were also made at some print works, but fears were entertained that it would be too dear, and, although it proved to be one of the most serviceable colours as regards fastness, yet the printers were not satisfied with it because it would not resist the action of chloride of lime like madder purple.

Although the results were not so encouraging as could be wished, I was persuaded of the importance of the colouring matter, and the result was that, in October, I sought an interview with my old master, Hofmann, and told him of the discovery of this dye, showing him patterns dyed with it, at the same time saying that as I was going to undertake its manufacture, I was sorry that I should have to leave the Royal College of Chemistry. At this he appeared much annoyed, and spoke in a very discouraging manner, making me feel that perhaps I might be taking a false step which might ruin my future prospects. I have sometimes thought that, appreciating the difficulties of producing such compounds as aniline and this colouring matter on the large scale, Hofmann perhaps anticipated that the undertaking would be a failure, and was sorry to think that I should be so foolish as to leave my scientific work for such an object, especially as I was then but a lad of 18 years of age; and I must confess that one of my great fears on entering into technical work was that it might prevent my continuing research work, but I determined that, as far as possible, this should not be the case.

Still, having faith in the results I had obtained, I left the College of Chemistry and continued my experiments, and found that not only aniline, but also toluidine, xylidine, and cumidine gave a purple colouring matter when oxidised.

The following is a copy of the principal part of the complete specification of the patent I took out at this time:—

"*Dyeing Fabrics.*

"The nature of my invention consists in producing a new colouring matter for dyeing with a lilac or purple colour stuffs or silk, cotton, wool, and other materials in the manner following:—

"I take a cold solution of sulphate of aniline, or a cold solution of sulphate of toluidine, or a cold solution of sulphate of xylidine, or a cold solution of sulphate of cumidine, or a mixture of any one of such solutions with any others or other of them, and as much of a cold solution of a soluble bichromate as contains base enough to convert the sulphuric acid in any of the above-mentioned solutions into a neutral sulphate. I then mix the solutions and allow them to stand for 10 or 12 hours, when the mixture will consist of a black powder and a solution of a neutral sulphate. I then throw this mixture upon a fine filter, and wash it with water till free from the neutral sulphate. I then dry the substance thus obtained at a temperature of 100° C., or 212° F., and digest it repeatedly with coal-tar naphtha, until it is free from a brown substance which is extracted by the naphtha. Any other substance than coal-tar naphtha may be used in which the brown substance is soluble and the colouring matter is not soluble. I then free the residue from the naphtha by evaporation, and digest it with methylated spirit, or any other liquid in which the colouring matter is soluble, which dissolves out the new colouring matter. I then separate the methylated spirit from the colouring matter by distillation, at a temperature of 100° C. or 212° F."

Fresh quantities of colouring matter were prepared and taken to Scotland, and, although the method of applying it by means of lacterine (casein) was then found to give very good results, yet the printers who tried it did not show any great enthusiasm; and even Messrs. Pullar began to fluctuate in their opinion as to the advisability of erecting plant for its manufacture, and wrote:—"Should it appear that it will not be of service to printers, it will be questionable whether it would be wise to erect works for the quantity dyers alone will require." In January, 1867, Mr. R. Pullar, however, advised me to see Mr. Thos. Keith, a silk dyer of Bethnal Green, London, and, after making a few experiments with the colouring matter, and exposing the specimens he dyed to the light for some time, he was much pleased with the result, and encouraged me to go on with its production.

I was then joined in the undertaking by my father—who was a builder, and had sufficient faith in the project to risk the necessary capital—and also by my brother, who also had a good knowledge of building, and, as he had taken part in the preliminary experiments on the preparation of the dye, his assistance proved most valuable, especially as he was possessed of good business capabilities. Plans were prepared and a site obtained at Greenford Green, near Harrow, and in June, 1857, the building of the works was commenced.

At this time, neither I nor my friends had seen the inside of a chemical works, and whatever knowledge I had was obtained from books. This, however, was not so serious a drawback as at first it might appear to be, as the kind of apparatus required and the character of the operations to be performed were so entirely different from any in use that there was but little to copy from.

In commencing this manufacture, it was absolutely necessary to proceed tentatively, as most of the operations required new kinds of apparatus to be devised and tried before more could be ordered to carry out the work on any scale.

But the mechanical were not the only difficulties. Benzene at this time was only made to a very limited extent, as there was but little use for it, and it was only after making several inquiries that it was ascertained where it could be obtained. That used at first came from Messrs. Miller and Co., of Glasgow. It was also of very unequal quality, and required refractionating before use; its price was 5*s*. per gallon. No nitric acid sufficiently strong for the preparation of nitrobenzene could be obtained commercially, and, as we did not want to complicate our works by manufacturing the substance, experiments were made with a mixture of sodium nitrate and sulphuric acid, using the latter in rather larger proportions than necessary to give an acid sodium sulphate. This method was found to succeed on the small scale, but, when working with large quantities, special apparatus had to be devised, and a great many precautions had to be taken to regulate the operation; however, very large quantities of nitrobenzene were made by it. Nitrobenzene had never been prepared in iron vessels before this time.

It was only three years before the works were started that Bechamp had made the interesting discovery that finely divided iron and acetic acid were capable of converting nitrobenzene into aniline; had it not been for this discovery, the coal-tar colour industry could not have been started. To carry this process out on the large scale, special apparatus was also required, and, on account of the energy of the action which takes place, special precautions had to be adopted; but no great difficulties were encountered in this operation. Potassium bichromate at that date fluctuated between 9¾*d*. and 11*d*. per lb., and was therefore a costly product.

Many more details might be gone into in reference to the difficulties to be contended against at the starting of the industry, but sufficient has been said to give some idea of them; however, in less than six months after the building of the works was commenced, namely, in December, 1857, aniline purple, or Tyrian purple, as it at first was called, was in use for silk dyeing in Mr. Keith's dye-house.

But in dyeing large quantities of silk, difficulties were again encountered, on account of the great affinity of the colouring matter for the fibre causing unevenness, and some time was taken up in experimenting on this subject, until eventually it was found that by dyeing in a soap bath a very pure and even colour could be produced. This process was afterwards found to be the most suitable for dyeing silk with magenta, Hofmann's violet, and many other colouring matters.

Aniline purple having now been proved to be an important colouring matter, which could be produced on a manufacturing scale, it attracted much attention, and, as a consequence, many others commenced its manufacture, and also to experiment with aniline, especially in France; all kinds of oxidising agents were used, but potassium dichromate still proved to be the best, the next best being chloride of copper, the use of which was patented by Dale and Caro, in 1860.

The French manufacturers were not long before they succeeded in producing the colouring matter (the French patent being invalid, owing to a mistake as to the date it was necessary to take it out in reference to that of the English patent), and in using it in dyeing their goods, both silk and cotton. The calico printers of this country then began to be alive to the necessity of following them, and this made the demand for the aniline purple—which the French now began to call mauve—so great that, notwithstanding the continued increase which had been taking place in the works at Greenford Green, it could not be kept pace with. At this time, a very beautiful archil colour had been produced by Messrs. Guinon, Marnas, and Bonney, called French purple; this also was applied to calico printing, and the printers in this country who could not get a supply of aniline purple used this until their requirements could be met. A little before this, Mr. Pullar and I separately discovered a process for mordanting cotton, so that it could be dyed with aniline purple to any depth of colour, and thus it became of much more value to the cotton dyer than it was so long as its natural affinity for the fibre could alone be relied upon. The process consisted in the use of tannin and a metallic oxide.

For calico printing, the colouring matter was first applied in combination with lacterin, albumin, or gluten, but endeavours were soon made to find some new method by which these might be dispensed with, and I worked for some considerable time on this subject at the Dalmonach Print Works, Alexandria, Dumbartonshire, where the colour was first practically used for printing in this country. I devised a process, which consisted in printing on a lead salt, converting this into a salt containing a fatty acid by means of soap, and then dyeing in a soap bath containing the colouring matter; the fatty lead salt then took up the colouring matter, whilst the soap prevented the white from being stained; this process was patented by myself and Mr. Mathew Grey. It produced beautiful shades of colour, but could not be used where combinations with other colours were required, and therefore did not prove useful.

Printers then experimented on the use of tannin and a metallic oxide, the process used in cotton dyeing devised by Mr. Pullar and myself; a modified form of this process has become the most important used. Another process was also very largely used, patented by M. Schultz and myself, which consisted in forming an insoluble arsenite of alumina and colouring matter on the fibre, the colours produced in this way being very brilliant, as well as fast to washing. Before the aniline purple could be introduced for dyeing woollen and mixed fabrics, some weeks were also spent at Bradford in finding out suitable methods of applying it.

Thus it will be seen that, in the case of this new colouring matter, not only had the difficulties incident to its manufacture to be grappled with, and the prejudices of the consumer overcome, but, owing to the fact that it belonged to a new class of dye stuffs, a large amount of time had to be devoted to the study of its applications to dyeing, calico printing, &c. It was, in fact, all pioneering work—clearing the road, as it were, for the introduction of all the colouring matters which followed, all the processes worked out for dyeing silk, cotton, and wool, and also for calico printing, afterwards proving suitable for magenta, Hofmann violet, &c.

All this time a host of experimentalists continued making trials with aniline and all kinds of chemicals, and early in 1859, three years after the discovery of aniline purple, or mauve, M. Verquin discovered fuchsine, also called magenta and roseine, and, later on, rosaniline by Hofmann.

From what has been said above, it will be seen that the discovery of this colouring matter was made under more favourable auspices than that of mauve: everything was ready for its production and application, it was also an easier product to manufacture and relatively to the aniline used was formed in much larger quantities than mauve was, but it was not nearly so fast against light, and when first experimented with I thought this would have been very detrimental to its extensive use, remembering the experience that I had gone through with mauve; but things had changed, and the love of brilliancy had begun to outrun the regard for durability, indeed, as is well known, magenta has proved to be one of the most successful of the coal-tar colours ever discovered. M. Verquin's process was a very remarkable one, and it has never transpired whether he was led to it by any scientific reasoning or not; it will be remembered that it consists in heating commercial aniline and anhydrous tetrachloride of tin nearly up to the boiling point of the mixture; it was first carried out by Messrs. Reynard Bros., of Lyons.

We were thus indebted to France for the second step in the coal-tar colour industry. Soon other processes were invented for the production of magenta, but the most practical one, after M. Verquin's, was that in which mercury nitrate was used; large quantities of colouring matter were made by this method.

The fuchsine, or magenta, first made in France, was but very imperfectly purified, and a good deal of that afterwards made in

Germany simply consisted of the "melt" produced by heating aniline with mercury nitrate.

Being naturally interested in this new colouring matter, I made many experiments with it, and in a lecture I delivered before this Society, on May 16, 1861 (*J. Chem. Soc.*, 1862, **14**, 230) (when I was honoured by the presence of Michael Faraday), an account of some of the results obtained by its examination was given, in which it was shown that it was the salt of an organic base (a fact at that time believed in by some, but doubted by others) precipitated by alkalis and at the same time dissolved by them to some extent, yielding colourless solutions, and that its nitrate could be obtained in the form of octahedrons, having a beautiful green metallic reflection; this was the first occasion, I believe, on which it was described as a crystalline compound. Attention was also called to the fact that its salts could not contain oxygen, which was afterwards confirmed by Hofmann; and it was further pointed out that other products were formed along with it, one possessing an orange colour (chrysaniline), and another a purple colour (violaniline, mauve aniline, &c.).

In speaking of the manufacture of rosaniline in this country, I must first refer to another of Hofmann's pupils, Edward Chambers Nicholson, of the firm of Simpson, Maule and Nicholson, who brought the manufacture of this compound to a state of perfection, which, I believe, has not been surpassed—so far as purity is concerned—up to the present time.

It is of interest to trace the manner in which Messrs. Simpson, Maule and Nicholson, became connected with the coal-tar colour industry. They were originally manufacturers of fine chemicals, &c. When aniline purple was found to be successful, and was exciting a great deal of interest, this and other firms were anxious to manufacture it, and consequently wished to have a licence for the purpose, but no agreement could be come to. They were then very desirous of manufacturing nitrobenzene for our use in producing aniline. At first they could not do this at a sufficiently low price, but eventually succeeded in producing it cheaply enough to make it worth our while to supplement our own make by theirs, as the demand for aniline purple was then so rapidly increasing. In this way they soon became considerable producers of nitrobenzene; they then set to work to prepare aniline, which after a time they succeeded in doing. In this manner they leisurely, as it were, became fully prepared to go a step further, and become manufacturers of colouring matters.

Dr. David Price at this time joined the firm, and Nicholson and he apparently experimented with the products he had patented in 1859, namely violin, purpurin, and roseine, obtained by oxidising aniline with lead peroxide; these colouring matters, however, were not found to be of practical value. They then turned their attention to the newly discovered colouring matter, fuchsine. This they commenced manufacturing, giving it the name of one of Dr. Price's products "roseine."

H. Medlock, another of Hofmann's pupils at the Royal College ot Chemistry, took out a patent on January 18, 1860, for the production of magenta, by heating aniline with arsenic acid; eight days later, Nicholson filed a similar patent, but did not proceed with it when he learnt what Medlock had done. Medlock's patent is notorious for the amount of litigation that arose owing to the occurrence in it of the word "anhydrous." The formation of magenta by the use of arsenic acid proved in the hands of Nicholson, and also of others, a great improvement on the previous processes, and for a long time was *the* process for the production of this colouring matter, until, in fact, it was superseded by the use of nitrobenzene instead of arsenic acid.

One of the things Hofmann used to impress on those of his students who were engaged at research work was the great importance of preparing their products in as nearly pure a condition as possible—especially those which were to be submitted to analysis; some of us used to think that we should get as good results by examining the substances when crystallised fewer times than he required, especially when the products were difficult to obtain and the quantities became smaller and smaller on each recrystallisation; but he was right. Nicholson, when at the Royal College, made several investigations under Hofmann's direction, studying the compounds of phosphoric acid with aniline; the formation of cumidine from cumene from cuminic acid; also caffeïne and some of its compounds; and, in conjunction with F. A. Abel, he investigated strychnine. He also appears to have been an adept at combustions, as he made the combustion of benzene for Mansfield; his name appearing also in de la Rue's paper on cochineal as having made one of the combustions of nitrococcusic acid. There is no doubt that Hofmann's teaching as to the importance of working with pure materials was strongly impressed upon Nicholson when carrying on these researches, and that it greatly influenced him when he became engaged in the manufacture of colouring matters. It is only right to add that Dr. D. Price, with whom he was for some time associated in this industry, and whom I knew when at the Royal College of Chemistry as a most thorough, painstaking, and careful worker, would also second his efforts in this respect. I may also add that I feel sure Hofmann's influence in this direction had also a considerable influence on my own after career as a chemist.

At first Messrs. Simpson, Maule, and Nicholson supplied magenta, or roseine, as they called it, to the dyers in alcoholic solution, but afterwards, when they had obtained it in a pure condition, they sold it in crystals (usually the oxalate). In their process of purification they boiled the crude solution of the colouring matter with milk of lime, and collected the base which deposited from the clear solution thus obtained, and from this prepared the desired salts.

By this time the coal-tar colour industry had become one of no mean dimensions in this country, and also in France, and it was quickly developing in Germany and elsewhere. The number of colours was also increasing, for not only had mauve or aniline purple and fuchsine been discovered, but Gerard and Delaire had made their remarkable discovery of *Imperial violet* and *Blue de Lyon* by heating aniline with fuchsine, thereby—as is now known—*phenylating* this colouring matter.

When first speaking of fuchsine, I mentioned that it was discovered by M. Verquin, and, from a practical point of view, this may be considered correct. Nevertheless it appears to have been first seen as far back as 1856, when Natanson (*Annalen der Chemie und Pharmacie*, 1856, **98**, 297) observed that in heating aniline and chloride of ethylene in a sealed tube to 200°, the mixture becomes of a rich blood-red colour; Hofmann also, in 1858, when acting on aniline with carbon tetrachloride obtained, besides carbotriphenyltriamine, a small quantity of this substance as a secondary product, which he describes as "a very soluble substance of a magnificent crimson colour."*

In the Report of the Exhibition of 1862 (Class II, sec. A, p. 126), Hofmann, in speaking of the discovery of this colouring matter, says:—"It may be said to have been discovered at two different times according as the question is considered from a scientific or industrial point of view;" and at p. 126:—"Industrially, the discovery of aniline red was made by Messrs. Verquin and Renard Brothers of Lyons."

The investigation Hofmann made with the Nicholson products soon set at rest the conflicting views which at first existed in reference to this colouring matter, and proved that it was a well defined triamine —which he re-named *rosaniline*—forming salts free from oxygen. He then regarded the base, which had the formula $C_{20}H_{21}N_3O$, as a

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* About two years after M. Verquin's discovery of fuchsine, the use of carbon tetrachloride and aniline as a means of preparing this colouring matter was tried, for reasons connected with patent rights, by MM. Monnet and Drury of Lyons. They first employed a temperature of 116—118° until the reaction between these two substances was over, and then heated the product up to 170° or 180°. By this means of working, they apparently obtained a larger yield than Hofmann, but the process never became a practical one. See *Moniteur Scientifique*, T. III, 15 Jan., 1861.

hydrate of the anhydrous compound $C_{20}H_{19}N_3$. Hofmann examined many of the salts of rosaniline—those with one molecule of acid, the ordinary salts used in dyeing, and the hydrochloride with 3 mols. of acid. He also obtained the interesting compound, leucaniline, by treating rosaniline with reducing agents, a compound which has its representation in all triphenylmethane colouring matters. The investigation is a memorable one, as being the first investigation which gave correct information respecting the formula of a coal-tar colouring matter.

It had been observed by manufacturers that some varieties of aniline yield much more rosaniline than others, samples boiling at temperatures much higher than the boiling point of the pure compound being found particularly adapted for the production of the red; and it appears that Nicholson had ascertained that pure aniline was incapable of yielding rosaniline. Hofmann studied this subject, using aniline prepared from indigo and from pure benzene, and his experiments confirmed Nicholson's. The idea then naturally suggested itself, that the toluidine contained in commercial aniline might be the source of the colouring matter. But, on making experiments with toluidine (orthotoluidine was not then known) it was found that this base also was incapable of producing the dyestuff; on taking a mixture of aniline and toluidine, however, it was at once produced in quantity, showing that both bases were necessary for its production (Report, International Exhibition, 1862, Class II, sec. A, 130).

This discovery was of great importance and interest, and explained most of the facts connected with the use of anilines of different boiling points. In the case of mauveïne, this discovery was not of so great importance as in the case of rosaniline, because pure aniline yields a purple colouring matter (pseudomauveïne), as well as mixtures of aniline and toluidine.

Mauve had also been obtained in a pure crystallised condition, but technically this was not found of much advantage, as the colours obtained with it in this condition were only slightly superior to those obtained with the less expensive precipitated colouring matter which was usually supplied to the consumer.

Having examined aniline red or rosaniline, Hofmann was also desirous of investigating aniline purple or mauve, but when he spoke to me on the subject, the colouring matter was already under investigation in my own laboratory.

The crystallised aniline purple sent into the market was the acetate of the base to which I gave the name mauveïne. This base is remarkable for its stability and tinctorial power. Its investigation (1864, *Proc. Roy. Soc.*, **12**, 713) showed that it possesses the formula $C_{27}H_{24}N_4$, and that, unlike rosaniline, it is not a hydroxy-compound. Moreover, the base is a strongly coloured compound of a blue-violet colour. When treated with reducing agents, it yields a leuco-compound, but this is so sensitive to the action of oxygen that on exposure to the air it instantly changes back to mauveïne. Its ordinary salts are produced from 1 mol. of base and 1 mol. of acid. From a more recent research on this colouring matter (*J. Chem. Soc.*, 1879, 717), I have shown that a dihydrochloride and corresponding platinum salt can be obtained, and from the characteristic changes which a solution of this substance, in concentrated sulphuric acid, undergoes on dilution, namely, from a dull green to a blue, and lastly to a purple, shows that probably salts formed by the union of mauveïne with more than 2 mols. of acid exist. The ordinary commercial product has also been shown to consist of two colouring matters, one forming very soluble and apparently uncrystallisable salts called pseudomauveïne, having the formula $C_{24}H_{20}N_4$, and produced from pure aniline; the other forming less soluble and beautifully crystalline salts of the formula $C_{27}H_{24}N_4$, derived from paratoluidine and aniline. This colouring matter, unlike rosaniline, does not freely undergo changes with reagents on account of its great stability, so that few derivatives have been obtained from it serving to elucidate its constitution, which is still unknown.

Messrs. Simpson, Maule, and Nicholson, after engaging in the manufacture of rosaniline for some time, undertook that of Girard and Delaire's Imperial Violet and Blue de Lyon, obtained by heating a salt of rosaniline with aniline (Pat., January, 1861).

Mr. Nicholson spent much time in studying the conditions most favourable to the production of these compounds, especially the blue, so as to obtain it in a pure condition, and in this he was very successful. This was due to his knowledge of the importance of using pure materials in its manufacture. The rosaniline base he used was not merely the best he produced for the preparation of rosaniline salts, but he purified it much further by means of methylated spirit; the aniline was prepared for the purpose from the purest benzene he could obtain; he also paid much attention to the selection of the best acid to use in combination with rosaniline, and found that weak organic acids, such as acetic and benzoic acids, were the most suitable. In this way he eventually obtained the blue in a condition of purification unequalled by others.

Provided with the purified blue by Nicholson, Hofmann soon discovered that the base had the formula $C_{38}H_{33}N_3O$; this he regarded as a hydrate of the compound $C_{38}H_{31}N_3$, of which he obtained a hydrochloride of the composition $C_{38}H_{31}N_3HCl$. The blue was converted by reducing agents into a leuco-compound.

As far back as 1850 (*Phil. Trans.*, **1**, 93, *J. Chem. Soc.*, **3**, 283), when engaged in his researches on the molecular constitution of the volatile organic bases, Hofmann had endeavoured to displace the hydrogen in aniline by phenyl, by heating it with phenol, but was unsuccessful; we can, therefore, easily understand his delight when he found that on boiling rosaniline with aniline the colouring matter became phenylated. The long desired method of effecting the displacement of hydrogen by phenyl had, in fact, been discovered, and we find that no sooner had he recognised that the blue was a triphenyl rosaniline than he telegraphed the result to Paris.* The *Comptes rendus* of the sitting of the Academy of May 18th, 1863, contains the following note :

"M. Le Secrétaire Perpétuel communique une Courte Note de M. Hofmann conçue dans les terms suivants.

"Bleu d'Aniline.—En poursuivante mes recherches sur les couleurs d'aniline, je suis arrivé à un résultat très simple ; le bleu d'aniline est la rosaniline triphénylique : une molécule de rosaniline et trois molécules d'aniline renferment les éléments d'une molécule de bleu d'aniline et trois molécules d'ammoniaque."

The paper, communicating fuller details of his results on this colouring matter, was read on July 6th of the same year (*Compt. rend.*, 1863, **57**, 25). Speaking in this paper of Nicholson, he pays him this tribute: "That in him was united the genius of the manufacturer and the habits of a scientific investigator."

We find the discovery of the phenylation of rosaniline afterwards bearing fresh fruit in the hands of Delaire, Gerard, and Chapoteaut, who established the remarkable fact that when boiled with its own hydrochloride, aniline acted in a similar manner, producing diphenylamine and ammonia; by using aniline hydrochloride and toluidine, they, in like manner, obtained phenyltoluylamine (*Compt. rend.*, 1866, **63**, 91).

Aniline blue having proved to be triphenylrosaniline, it was soon seen that the different shades of violet imperial were rosanilines more or less phenylated.

Nicholson also found that, on heating acetate of rosaniline to 200—215°, ammonia was disengaged, and a purple colouring matter produced, which he called regina purple. This substance was found to be a monophenylrosaniline (patented January 20, 1862).

One of the great obstacles in the way of the application of aniline

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* Hofmann had made this discovery apparently on the same day, for Professor McLeod who was his assistant at that time, gives me an entry from his diary dated May 18th, 1863, which runs thus: "The doctor told me that he had made a fine discovery, and that aniline blue is the triphenylated rosaniline. Rosaniline, $C_{20}H_{19}N_3H_2O$; aniline blue, $C_{20}H_{16}(C_6H_5)_3N_3H_2O$."

blue was its slight solubility in water, which rendered the dyeing operations unsatisfactory; this also militated against its use in calico printing for some time (the most suitable process for its use for this purpose first found being that of Schultz and myself with arsenate of alumina, but with this long steaming and afterwards clearing in a soap bath was required; the colours thus obtained, however, were very pure and very durable). Nicholson naturally was very desirous of overcoming this obstacle, and no doubt the well known process of rendering indigo soluble by dissolving it in sulphuric acid, and then converting it into a sulphonic acid, occurred to him; at any rate, by experimenting in this direction, he succeeded in obtaining the desired result and patented the process (June 1, 1862). Nicholson obtained two sulphonic acids—a mono- and a tri—the first being known as Nicholson's blue, and the latter as soluble blue, and it is owing to the discovery of these derivatives of aniline blue or triphenylrosaniline that this colouring matter became of such importance.

This method of treating aniline blue was very interesting as being the first instance of sulphonating an aniline colour, a process which of late years has become of so much importance, not only in rendering difficultly soluble dyes soluble, but also in changing the chemical nature of the colouring matters, and thus extending their applications as dyes, as in the case of rosanilinesulphonic acid.

It was Nicholson who succeeded in isolating the yellow or orange colouring matter which is formed in the manufacture of rosaniline; he prepared it in a pure state, and called it "phosphine." Hofmann undertook the examination of this dye, and showed that it is represented by the formula $C_{20}H_{17}N_3$, differing from that of rosaniline in containing 2 atoms of hydrogen less; the base is capable of forming salts with 1 or 2 mols. of hydrochloric acid, the nitrate being remarkable for its insolubility.

After discovering that aniline blue or bleu de Lyon was a triphenylrosaniline, Hofmann was very naturally inclined to experiment on rosaniline with the agents he had used so successfully in his experiments on the molecular constitution of the volatile organic bases, namely, the haloïd compounds of the alcohol radicles, to see what influence these radicles would have if introduced into the base: he found that they had, like phenyl, though not to the same extent, a blueing effect, the colour changing from red to purple, and then to violet as the hydrogen atoms were gradually displaced, colouring matters being produced which were found to be of great beauty when applied to silk, &c. In his first paper on these products (*Compt. rend.*, 1863, **57**, 30), he gives an account of the action of methyl, ethyl, and amyl iodides on rosaniline, and amongst the products he obtained at that time describes the highest ethylated derivative he had succeeded in producing as the iodethylate of triethylrosaniline, $C_{20}H_{16}(C_2H_5)_3N_3{\cdot}C_2H_5I$.

He patented the method of producing these colouring matters on May 22, 1863.

It is easy to see how Hofmann was led to the production of these compounds in the regular sequence of his work, but it is curious that E. Kopp had evidently prepared some of them as long back as 1861. E. Kopp remarks in his paper in the *Comptes rendus*, 1861, **52**, 363, "I have only stated in my notice these substitutions as a hypothesis, but their existence is very real; I have already obtained some of them, and it is a remarkable thing that the red shade disappears, and is converted into a violet, becoming bluer and bluer as the hydrogen is displaced by the hydrocarbons." It appears that he sent some specimens of his products to M. Dumas.

When Hofmann patented the use of methyl, ethyl, and amyl iodides for the preparation of these colouring matters, it seemed almost incredible that substances such as these, which had hitherto only been used in research, should be employed in the manufacture of a dye; but such circumstances have constantly arisen in the history of this remarkable industry—aniline itself, the parent of artificial colours, being an example—and nothing now appears to be too rare or difficult to prepare, to be used in its development.

It is difficult to understand why E. Kopp did not go on with his work on these substitution compounds, unless it was owing to the fact that rosaniline was expensive in his days, and he considered the alcoholic haloïds too costly to employ for practical purposes.

The Hofmann violets were the most brilliant in colour of any which had been produced, and proved not to be so costly as might be anticipated, as the iodine from the ethyl iodide used could be mostly recovered; but these colouring matters have not the stability of mauve or imperial violet, and at first it was thought that their use would be limited, but the increasing desire for brilliancy was still superseding that for stability, and the result was, that these colouring matters were very largely used, and interfered very considerably with the sale of the mauve and imperial violets, except for pale shades of colour, when, unless the colouring matter used be stable, the goods fade so quickly as to be of little value.

The products formed on heating mauveïne salts with aniline apparently are not comparable with those obtained from rosaniline, and although the product becomes bluer no ammonia is evolved; from my later experiments, it seems most likely that the aniline used takes no part in the change, the blueing being a change in the colouring matter, the consequence of the temperature employed.

When treated with ethyl iodide, mauveïne behaves unlike rosaniline, yielding a beautiful colouring matter, which is of a *redder* shade, and not bluer as in the latter case. This colouring matter, called *dahlia* (patented on November 6, 1863), consists of a monethylic derivative of mauveïne, its hydrochloride being represented by the formula, $C_{27}H_{23}(C_2H_5)N_4,HCl$. No further change is effected by ethyl iodide, and it is uncertain whether the product is a substitution or an addition compound (it may be remarked here that at times some quantity of a dark, blue-black, almost insoluble substance containing iodine is also produced).

This dahlia or ethylmauveïne was used by the calico printers and dyers to some extent, though not largely, on account of its costliness. It is, however, a colouring matter, which gives shades of very considerable stability on exposure to light.

The discovery that the introduction of such radicles as phenyl or ethyl altered the colour of rosaniline so greatly, made it of interest to see whether other kinds of hydrocarbon groups could be introduced to modify its tint. Amongst other products, brominated turpentine was used, and on heating it with rosaniline hydrochloride dissolved in methylated spirit or methyl alcohol under pressure, it was found that a very beautiful purple or violet colouring matter could be produced; the process was patented in 1864, and large quantities of a colouring matter, known as *Britannia violet*, were prepared in this manner. At first it was thought that the hydrocarbon radicle of the brominated turpentine entered the rosaniline, but it now appears most probable that the product consisted of methylrosanilines produced by the action of methyl bromide formed from hydrogen bromide resulting from the decomposition of the bromo-compound. The colouring matter was more soluble than Hofmann's ethyl violet, but I could not succeed in crystallising it, and, therefore, it was not subjected to analysis.

When the base of Britannia violet is acted on by acetyl chloride, two products are obtained, namely, a violet colouring matter much bluer in shade than the original violet, and a bluish-green compound. The base of this latter has a very feeble affinity for acids, and does not combine with acetic acid, whilst the base of the violet compound does so freely, and in virtue of these different properties the two colouring matters are easily separated. The green dye proved to be of practical value, and considerable quantities of it were prepared for the calico printers, and was known as "Perkins green;" but after a time it was displaced by iodine green. It has not hitherto been investigated. For its manufacture, large quantities of terchloride of phosphorus were prepared, from which and acetic acid large quantities of acetyl chloride were made—another instance of the use of a research reagent on the large scale.

The last investigation relating to colouring matters carried out by Hofmann in this country was that of the very interesting substance known as *chinoline blue*, discovered by Greville Williams, of which the latter gave an account in the *Chemical News* for October 11, 1860 (p. 219). A beautiful specimen of the crystallised substance was displayed in the exhibition of 1862 under the name of *Cyanin*. Chinoline blue was of a very pure shade of colour, and, although an expensive product, attempts were made to introduce it as a dye; unfortunately, although produced from bases of remarkable stability, it was very fugitive, goods dyed with it fading very quickly indeed when exposed to the light—its sensitiveness being so great that on placing it under a glass positive photograph and exposing to sunlight, after only a short time, a chinoline blue positive picture was produced.

Hofmann separated from chinoline two blue compounds, to one of which he gave the formula $C_{30}H_{39}N_2I$, and to the other the formula $C_{28}H_{35}N_2I$. According to later researches, the blue is a condensation product derived from chinoline amyliodide and lepidine amyliodide.

$$\underset{\text{Chinoline amyl iodide.}}{C_9H_7N{\cdot}C_5H_{11}I} + \underset{\text{Lepidine amyl iodide.}}{C_{10}H_9N{\cdot}C_5H_{11}I} + O = \underset{\text{Cyanine or diamyl cyanine iodide.}}{C_{29}H_{35}N_2I} + H_2O + HI$$

This formula differs from that given by Hofmann to one of the products he examined by an atom of carbon only.

After I left the Royal College of Chemistry, the researches on the phosphorus bases in which I had been helping were continued by Drs. Leibius and Holzmann, to whose able assistance Hofmann refers in one of his papers; but in carrying out the part of this work relating to the phosphammonium, phospharsonium, and arsammonium compounds, another assistant was active who is referred to by Hofmann in the following words:—

"I conclude this memoir with the expression of my best thanks for the untiring patience with which Mr. Peter Griess has assisted me in the performance of my experiments on the phosphorus bases. The truly philosophical spirit in which this talented chemist has accompanied me through the varying fortunes of this inquiry, will always be one of my pleasing recollections."

We know how the high opinion thus expressed by Hofmann of Griess not only lasted, but became enhanced as time went on; and although Griess was not one of Hofmann's pupils, I cannot refrain from thus referring to him here, as several of his most important early researches on the diazo-compounds were made within the walls of the Royal College of Chemistry, thereby connecting this Institution with work which of late years has had such a marvellous influence on the development of the coal-tar colour industry. But it is not my intention, nor indeed is it necessary for me, to go into the history of the diazo-compounds, as this has been so very ably done by my friend Caro in his memoir of Peter Griess, whom he held in such high esteem, and who was also one of his greatest friends.

Hofmann's departure was not only a cause of regret to those who had worked under him and to all his friends; it was a heavy loss also to the country at large, as no one had ever done so much for the cause of chemical science in the kingdom as Hofmann did, nor had any one exercised to such an extent that wonderful power he possessed of stimulating the enthusiasm of his students and of inciting in them a love of chemistry and of scientific research. His success is especially striking when the early history of the Royal College of Chemistry is taken into account—especially its financial difficulties, the dissatisfaction of some of the subscribers, and the want of understanding as to the value of scientific research shown both by them and the public at large. When all these circumstances are considered, we cannot but marvel at the courage and indomitable determination he displayed, which enabled him to overcome all difficulties and to persevere in maintaining the high standard of teaching he adopted at the beginning, as well as to continue the prosecution of scientific research for its own sake.

Notwithstanding the immense amount of work Hofmann must have had to attend to in connection with the building and fitting up of the new chemical laboratories of the Frederick William University of Berlin, which took place during the first four years after he left England, namely, from May, 1865, to May, 1869, no break occurred in his scientific activity, each year producing accounts of fresh work accomplished. It was not, however, until 1869 that he published anything fresh in connection with the coal-tar colours, but in this year several communications appeared.

Having found that the production of rosaniline depended on the presence of two bases, aniline and toluidine, he naturally carried his investigation of the subject further, and experimented with xylidine (meta). However, on heating this base with oxidising agents, either alone or in presence of toluidine, no colouring matter was obtained; but when it was heated with pure aniline, a red was formed, which he called xylidine red, which was supposed to be a homologue of rosaniline, probably of the composition $C_{22}H_{25}N_3O$. The colour produced on wool and silk by this dye-stuff was almost as bright as that of rosaniline itself (*Ber.*, **2**, 377). In a second paper relating to this subject, published in conjunction with Martius (*Ber.*, **2**, 411), an account is given of similar experiments with an isomer of xylidine, amidoethylbenzene, which, from the more recent researches of Beilstein and Kuhlberg (*Zeitsch. f. Chem.*, [2], **5**, 524), we now know must have been a mixture of the ortho- and para-compounds. No red colouring matter was formed from this on boiling it with an oxidising agent, either alone or mixed with toluidine or even with aniline, thus affording proof of the interesting fact that an ethyl group cannot take the place of a methyl group in the interaction which is involved in the production of colouring matters of the rosaniline class.

After the discovery of mauve and magenta, many experiments were made with α-naphthylamine, as a source of colouring matter, and a variety of products were obtained and patented; but it is unnecessary for me to enter into an account of these here, as most of them were found to be of no technical value. I may, however, allude to two naphthalene derivatives which have proved useful; the first of these, naphthazarin, was discovered by Roussin in 1861, who thought it was artificial alizarin; this beautiful substance, which is now known to be a dihydroxy-β-naphthaquinone, lay dormant for a long time, but, owing to the discovery of improved methods of producing it, has of late come into use for dyeing black on wool. The second was discovered by Martius, and is known as "Martius yellow" or dinitro-α-naphthol. These were the principal colouring matters derived from naphthalene known prior to 1867, when Schiendl discovered the naphthalene red now known by the name of Magdala red, a substance remarkable for the beautiful fluorescence of its solution. The original process for its preparation consisted in heating naphthylamine, acetic acid, and potassium nitrite together, and then adding more naphthylamine and again heating until the desired colouring matter was produced.

Hofmann investigated this red, and assigned to it the formula $C_{30}H_{21}N_3$ (*Ber.*, 1869, **2**, 374).

As this colouring matter and the above formula appeared to be related to an old friend of mine, azodinaphthyldiamine (amidoazonaphthalene), I made it the subject of experiments, and found that it was easily produced on heating amidoazonaphthylene with an acid and naphthylamine, an action taking place which it was thought involved the displacement of an atom of hydrogen by naphthyl and the formation of ammonia:

$$\underset{\text{Azoamido-naphthaline.}}{C_{20}H_{15}N_3} + C_{10}H_9N = \underset{\text{Magdala red.}}{C_{30}H_{21}N_3} + NH_3$$

The colouring matter was called azotrinaphthyldiamine (*Proc. Roy. Inst.*, 1869, May 14).

In a second paper, published in July of the same year, on the nature of naphthalene red, Hofmann confirms my observation (*Ber.*, **2**, 413).

It has since been shown, however, by Julius (*Ber.*, 1886, **19**, 1365), that the action which occurs when amidoazonaphthalene is treated with naphthylamine is not nearly so simple as above indicated, and that the formula of the hydrochloride of Magdala red is $C_{30}H_{21}N_4Cl$, not $C_{30}H_{22}N_3Cl$.

The research on Magdala red led Hofmann to study the compound produced by the action of aniline on amidoazobenzene, a substance described by Martius and Griess, but discovered by Dale and Caro in 1863, and called by them *induline*. The examination of this product was afterwards continued by Hofmann in conjunction with Geyger, under the heading of colouring matters obtained from aromatic azodiamines, and published in 1872 (*Ber.*, **5**, 472). They called this substance azodiphenyl blue, and showed that its hydrochloride had the formula $C_{18}H_{16}N_3Cl$.

In 1869 Hofmann also continued his researches on chrysaniline, studying the action of methyl and ethyl iodide on the base; he obtained trimethyl and triethyl substitution products (*Ber.*, **2**, 378).

In preparing Hofmann violet, it was found that on precipitating the colouring matter from its aqueous solution by means of sodium chloride, a certain quantity of a bluish-green product remained in solution which could not be separated (though improved in colour) by the addition of sodium carbonate; this was precipitated by means of picric acid, and as it proved to be a valuable green dye, it, after a time, was supplied in small quantities to dyers under the name of iodine green. It was then found by J. Keisser (French patent, April 18, 1866) that the colouring matter could be obtained in much larger quantities by methylating rosaniline, dissolved in methyl alcohol, with methyl iodide, the operation being completed at a comparatively low temperature, and eventually it was obtained in a pure crystallised state. This substance being evidently related to the methylrosanilines, Hofmann was naturally interested in it, and with Girard undertook its investigation (*Ber.*, **2**, 440).

The results they obtained, on analysing the iodo-compound, led them to represent it by the formula
$$\left.\begin{matrix}C_{20}H_{16}\\(CH_3)_3\end{matrix}\right\}N_3\left\{\begin{matrix}CH_3I\\CH_3\cdot I\cdot H_2O.\end{matrix}\right.$$

They found that this compound decomposes when heated at the temperature of boiling water for a few hours, and instantly at 130—150°, becoming changed into a violet colouring matter; in fact, it behaves like an ammonium or addition product. As the complicated history of the methyl and ethyl derivatives developed, it was found that the formula above given required to be modified to some extent; but this is in no way surprising, as it is practically impossible by analysis alone to arrive at a true conclusion as to the constitution of a compound of such high molecular weight, so unstable and so difficult to obtain pure.

Another green dye-stuff to which Hofmann directed his attention at this time was aldehyde green, produced by the action of aldehyde on rosaniline in presence of sulphuric acid whereby a blue colouring matter is formed, which is transformed into the green by the action of an aqueous solution of sodium thiosulphate. Lauth, apparently, was the first to produce the blue compound, in 1861, by subjecting a solution of rosaniline in alcohol, methyl alcohol, acetic acid, or acetone to the action of zinc chloride and other metallic salts, but the conversion of the blue into the green was accomplished by Cherpin in 1862. This was the first aniline green dye discovered (emeraldine, which was of no value, excepted), and was much used. Hofmann showed that aldehyde green contained sulphur, and assigned to it the composition indicated by the formula $C_{22}H_{27}N_3S_2O$, representing its formation by the following equation,

$$C_{20}H_{19}N_3 + C_2H_4O + 2H_2S = C_{22}H_{27}N_3S_2O$$

(*Ber.*, 1870, **3**, 761).

The next researches it will be most convenient to refer to, though not quite the next as to date, are those on the methyl violets; but, before considering these it may be mentioned that, in continuation of his researches on rosaniline derivatives, Hofmann, in 1873 (*Ber.*, **6**, 263), examined the violet obtained by Hobrecker by the action of benzyl chloride and methyl iodide on a solution of rosaniline in methyl alcohol, assigning to it the formula $C_{20}H_{16}(C_7H_7)_3N_3,CH_3I$.

Until long after the commencement of the coal-tar colour industry, chemists and experimenters directed their attention chiefly to aniline as a source of colouring matter; but in 1861 Lauth made some experiments on the product Hofmann obtained by acting with methyl iodide on aniline, which he described as methylaniline (*J. Chem. Soc.*, 1851, **3**, 296), but which recent researches have shown is a mixture of methylaniline and dimethylaniline, and by oxidising this he obtained violet colouring matters. Writing of these in 1867, Lauth says (*Laboratory*, 1867, 138), "The violets obtained from methylaniline possess a richness and purity which leave nothing to be desired . . . . Nevertheless, they were not adopted by manufacturers, who, indeed, at the time mentioned (1861) attached less importance to the beauty of a colour than to its permanence. In this latter respect the methylaniline violets do not excel, and, consequently, dyers would have nothing to do with them.

"Gradually, however, people have become accustomed to colours which fade on exposure to the solar rays . . . . Accordingly, two years after the experiment made by myself, Dr. Hofmann succeeded in introducing these results." These remarks confirm those already made in reference to the gradual change in public opinion which led to the disregard of permanency in favour of brilliancy of colour.

Lauth further remarks that Hofmann's method of producing these colouring matters is the inverse of that proposed by him; the aniline being first converted into rosaniline and then methylated, whilst in his case this operation is first performed on the aniline.

It would, however, not have been practicable to carry out this process if the aniline had to be methylated with methyl iodide, because the base thus prepared would be too expensive to use as the raw material for the preparation of colouring matters. On account of the success of the Hofmann violet, experiments were made in France with the object of preparing methylaniline by a different and more economical process, so as to commercially produce Lauth's violet, and this was at that time considered especially desirable by some manufacturers, because the production of rosaniline in France was the monopoly of one house, and, therefore, derivatives of this colouring matter could not be economically made by others.

Eventually a successful process was discovered by M. Bardy, chemist to the firm of Poirier and Chapat, which consists in heating a mixture of aniline hydrochloride and methyl alcohol in a closed vessel to a high temperature. As is now well known, though not at first recognised, this process yields a mixture of mono- and di-methylaniline, consisting chiefly of the latter. Large quantities of methylated aniline were soon produced by this process, and used in the preparation of a violet colouring matter which was manufactured by Messrs. Poirier and Chapat, and called by them violet de Paris; a large block of this, weighing about 150 kilos., was exhibited in the Paris Exhibition of 1867 (?). The question then arose as to whether violet de Paris was identical or isomeric with methylrosaniline violet. Lauth considered that it was isomeric, and remarks: "Hofmann violets consist of methylated and ethylated rosaniline, and rosaniline is derived from a molecule of aniline and two molecules of toluidine. The violet de Paris, on the contrary, is produced from pure aniline free from toluidine, transformed into methylaniline, which is isomeric with toluidine. This methylaniline when oxidised is converted into the violet which may have a composition analogous to that of methylated rosaniline, but must differ from the latter in the same manner as methylaniline differs from toluidine."

Hofmann, being naturally interested in the relationship of these colouring matters, investigated the subject, and published his results in 1873 (*Ber.*, **6**, 352). He first studied the conditions under which the colouring matter could be formed, showing that violet could be produced from pure dimethylaniline obtained by the distillation of trimethylphenylammonium hydrate; he also came to the conclusion from the examination of the colouring matter that it was a methylchlorhydrate of trimethylrosaniline.

$C_{20}H_{16}(CH_3)_3N_3{\cdot}CH_3{\cdot}Cl$, the base being
$C_{20}H_{16}(CH_3)_3N_3{\cdot}CH_3{\cdot}HO$.

He prepared iodine green by methylating this compound; also its leuco-compound.

This research must have been a very difficult and laborious piece of work, and although Hofmann's views as to the constitution of the dimethylaniline violet are not those now accepted, the accuracy of his work has not been impugned.

The long controversy which arose, soon after the time when Hofmann published his constitutional formula of rosaniline, as to the constitution of this colouring matter belongs to another chapter, and need not be referred to here.

Mention has already been made of the process for methylating aniline discovered by Bardy, which consisted in heating this base with hydrochloric acid and methyl alcohol. In 1871 Hofmann and Martius (*Ber.*, **4**, 742) made some experiments in reference to this method, working at higher temperatures than those usually employed (280—300°), and continuing the heating for a considerable time; in this way they obtained, besides methyl and dimethylaniline, a quantity of basic oil of higher boiling point, which eventually proved to be a complex mixture of methylated homologues of dimethylaniline, the products of an intramolecular change or atomic wandering.

These remarkable researches, like so many other purely scientific discoveries, ere many years had passed, were found to be of technical value in connection with the coal-tar colour industry, the cumidine that is so extensively used in the preparation of some of the diazo-colours being made by the method of Hofmann and Martius by heating xylidine with hydrochloric acid and methyl alcohol to a high temperature, about 300°.

Reverting once more to the early days of the coal-tar colour industry, I may now mention that the liquors from which mauve was precipitated were found to contain a red colouring matter which I succeeded in separating, although the amount obtainable was very small. This proved to be a beautiful dye producing crimson-red shades on silk. It was afterwards discovered that it could be produced by the oxidation of mauveine, and it was prepared in considerable quantity in this way, but was a very expensive product, and therefore not very largely used. This dye-stuff was known first as "aniline pink," and afterwards as "safranine." In 1865 a colouring matter having the properties of safranine was produced without the use of mauveine by F. Duprey, by heating commercial aniline dissolved in acetic acid with lead nitrate. It was then obtained by acting on commercial aniline with nitrous acid and oxidising the mixture with arsenic acid. The colouring matter prepared in this way was examined by Hofmann and Geyger (*Ber.*, 1872, **5**, 531). They found it to be a base forming crystalline salts, among others a hydrochloride having the composition $C_{21}H_{21}N_4Cl$. As they found that it could not be produced from either aniline or paratoluidine, or a mixture of the two, but from orthotoluidine, they regarded it as a toluidine derivative. They also observed that the formula above given differs from that of mauveine by C_6H_4, making it appear possible that mauveine was phenylsafranine. In the course of an investigation of the safranine, obtained by the oxidation of mauveine, of which I published an account some time after this (*J. Chem. Soc.*, 1879, **35**, 728), this substance was shown to form a hydrochloride represented by the formula $C_{20}H_{18}N_4$, which differs from that of the substance examined by Hofmann and Geyger by CH_2. On examining a commercial product manufactured by Messrs. Guinon and Co., of Lyons, from commercial aniline, both substances were found to be present, showing that two "safranines" existed, and I then also showed that probably a third was formed by the oxidation of pseudo-mauveine.

The formula of the safranine hydrochloride obtained from mauveine will be seen from the above to differ from mauveine by C_7H_6, so that the relationship of these substances is probably not of so simple a character as Hofmann and Geyger supposed, though, of course, C_7H_6 may simply mean displacement of hydrogen by tolyl. No doubt a great similarity exists between them, one proof of which is that their behaviour with sulphuric acid is analogous. This applies both to those referred to above and to the third compound since discovered.

In 1875 Hofmann made an examination of eosin (*Ber.*, **8**, 62), and thus disclosed to the world an important manufacturing secret, proving to demonstration the impossibility in these days of long hiding from chemists the nature of any substance, however complex. Eosin, as is well known, was the first representative of a new class of colouring matters which has since become of great importance.

Chrysoidine, which may fairly be termed the parent of an even more important class of colouring matters, the azo-dyes, the introduction of which marks a new era in this branch of chemistry, was investigated and publicly proclaimed by Hofmann in 1877 (*Ber.*, **10**, 213).

The colouring matter to which he next directed his attention was pittacal, also called euppitonic acid, the interesting compound discovered by Reichenbach, as far back as 1835, produced from wood tar. Hofmann (*Ber.*, 1878, **11**, 1655; 1879, **12**, 1371 and 2216) was led to regard this substance as hexamethoxyrosolic acid, $C_{19}H_8(OCH_3)_6O_3$; on treating it with ammonia, he obtained a beautiful blue dye-stuff, thus,

$$C_{25}H_{26}O_9 + 3H_3N = C_{25}H_{31}N_3O_6O + 2OH_2,$$

which he regarded as hexamethoxypararosaniline,

$$C_{19}H_{13}(OCH_3)_6N_3O.$$

He then made the interesting discovery that the formation of pittacal, or euppitonic acid, from dimethylpyrogallate and dimethylmethylpyrogallate took place in a manner analogous to that in which pararosaniline was formed, thus,

$$\underset{\text{Aniline.}}{2{\cdot}C_6H_7N} + \underset{\text{Toluidine.}}{C_7H_9N} = \underset{\text{Pararosaniline.}}{C_{19}H_{17}N_3} + 3H_2$$

$$\underset{\substack{\text{Dimethyl}\\\text{pyrogallate.}}}{2C_8H_{10}O_3} + \underset{\substack{\text{Dimethyl methyl-}\\\text{pyrogallate.}}}{C_9H_{12}O_3} = \underset{\substack{\text{Pittacol or}\\\text{euppitonic acid.}}}{C_{25}H_{26}O_9} + 3H_2,$$

comparisons which are of considerable interest.

Hofmann's last research in connection with the coal-tar colour industry was made as late as 1887, and related to the quinoline red prepared by Jacobson, in 1882, from coal-tar chinoline, benzotrichloride, and zinc chloride. Hofmann, however, found that a better yield of colouring matter, either identical or isomeric with Jacobson's, is obtained by using a mixture of isoquinoline and quinaldine. Like quinoline blue or cyanine, the colour is not a fast one, which, as previously mentioned, is remarkable, considering the stability of quinoline itself. It is a somewhat remarkable coincidence that this should have been the last research Hofmann made on the coal-tar colours, as chinoline (or leucoline) was one of the two substances he gave an account of in his first investigation published in 1843, when 30 years of age.

Excepting what is said of pittacal, and the brief reference to eosin and chrysoidine, the foregoing account has reference only to what may be termed aniline colours, the great chapter on the history of technical chemistry, with which Hofmann's name is indissolubly linked.

An entirely new chapter in coal-tar chemistry opens in 1868, when Graebe and Liebermann (in connection with their researches on quinones) made their great discovery of the artificial formation of alizarin from anthracene. They patented their process in Germany in October, and in this country on December 18th of that year. Their process, it is well known, consisted in producing dibromanthraquinone, either by brominating anthraquinone in sealed tubes, or by oxidising tetrabromanthracene, and subsequently displacing bromine by hydroxyl, by fusion with alkali.

This discovery for the first time of a method of obtaining a vegetable colouring matter artificially was, however, as it stood, of no practical value, as such a process could not be carried out on a large scale.

But why should this be mentioned here? It may seem that any reference to the alizarin industry is out of place in a notice designed to elucidate Hofmann's influence on the development of our knowledge of products derived from coal-tar, as he apparently never took any part in the investigation of anthracene derivatives. Yet it is to his influence that I can trace back my interest in the subject, for, as mentioned early in this account, the very first subject in research which he suggested to me was to prepare a nitro-compound and a base from anthracene. In the course of this work I not only became thoroughly acquainted with this hydrocarbon, but also prepared anthraquinone and other derivatives of it, and consequently was, perhaps, more fully prepared than any other chemist of the day to appreciate the discovery of the relationship of alizarin to anthracene, and was naturally impelled at once to attempt to adapt it to practical requirements. It is more than probable that I should have paid but ordinary attention to Graebe and Liebermann's work had I not possessed an early attachment to anthracene, and I am glad to recognise that I owe this to the knowledge and insight of my great master.

Being aware of the importance of alizarin as a colouring matter, and having some quantity of anthracene and anthraquinone left over from my experiments at the Royal College of Chemistry, I commenced to experiment on the formation of this substance, with the object of finding a process by which bromine might be dispensed with.

I knew of the remarkable stability of anthraquinone: that it could be crystallised from concentrated sulphuric acid without undergoing change, and that in making a combustion of it, if the operation were at all hurried, part of the anthraquinone would pass through the heated tube, and condense at the cool end unaltered.

Moreover, not long before I commenced to work at the artificial formation of alizarin, namely, in 1867, Wurtz and Kekulé had shown that when benzenesulphonic acid was heated with potassium hydrate, it gave phenate and sulphite; and Dusart had also found that naphthalenedisulphonic acid was in like manner converted into a dihydroxynaphthalene; so that it appeared probable that if a disulphonic acid of anthraquinone could be obtained, it would be possible to convert it by the new reaction into alizarin.

Anthraquinone was therefore heated with oil of vitriol more and more strongly, until the boiling point was nearly reached, as I was determined either to obtain a sulphonic acid or destroy the anthraquinone; and at last it was found that the anthraquinone had disappeared, yielding a product which was soluble in water. After the excess of sulphuric acid had been removed in the usual way with barium carbonate, the product was fused with caustic alkali, and to my delight it changed first to violet, and then became black from the intensity of its colour. On dissolving the melt, a beautiful purple solution was obtained, which gave a yellow precipitate when acidified, and on examination this was found to dye mordanted cloth like garancine.

On the 20th of May (1869) I sent dyed patterns to my friend Mr. Robert Hogg, of Glasgow, who had a very large experience in reference to madder and garancine, and also of the coal-tar colours from the days of the mauve dye, whose opinion I valued very much in all practical matters connected with dye-stuffs, especially from a commercial point of view, and he was very favourably impressed with the results I had obtained. This process, however, was not patented until June 26. (About the same time as I discovered this process, Graebe, Liebermann, and Caro quite independently arrived at the same result in Germany.) This process has proved the most permanently important one yet discovered, and is the one still universally used. I was also fortunate enough to discover a second process, which was of great value in the early days of the industry. but is not in use now so far as I know. It consisted in the use of dichloranthracene as the starting point, instead of anthraquinone. This substance was found to readily afford a sulphonic acid, which could be easily changed into anthraquinonesulphonic acid, either by oxidising its solution with manganese dioxide or more simply by heating it with sulphuric acid. This process was patented in November, 1869.

After discovering processes by which artificial alizarin could be produced, the technical value of the artificially prepared dye-stuff had to be ascertained. Experiments were soon made by the calico printers, as no new processes had to be discovered for the application of this colouring matter, those in use for madder and garancine being suitable. Turkey-red dyers also experimented with it, but some were not so successful as others, for reasons easily understood afterwards, when the properties of anthrapurpurine, which it contained, were better known.

The subject of price, however, was the important question, because this product had to compete with those already in the market, namely, madder and garancine, and therefore high prices could not be obtained as in the case of a new dye.

Before this could be settled, the first thing necessary was to get a supply of anthracene. This substance was not at this date separated by the tar distillers, there being no use for it; many of them, in fact, knew nothing of its existence, and the question as to whether it could be obtained in sufficient quantity and at a sufficiently low price had to be settled.

But experiments I had made on the small scale, on the distillation of soft pitch, at the Royal College of Chemistry, gave me confidence, and my brother and I entered into the matter with great energy.* At first we prepared anthracene by distilling pitch ourselves, and thought of using this as a source of this hydrocarbon on an extensive scale, as we felt it was capable of yielding a considerable supply. We knew, however, that it could also be obtained from the last runnings of the tar stills, from which it crystallised on cooling. My brother, therefore, visited nearly all the tar works in the kingdom, and showed the distillers how to separate the anthracene, promising to take all they could make, and in this way a sufficient and rapidly increasing supply for our requirements was soon obtained of all sorts of qualities, some being not much thicker than pea soup, from the imperfect way in which it was drained. Very few tar distillers in those days had hydraulic presses, such as are now used, with which they could free the solid from the excess of oil. The value of the anthracene was estimated by washing with carbon bisulphide, afterwards alcohol was used, but for our own purposes we all along used an anthraquinone test. This method was afterwards worked out more perfectly on the Continent, and made a practical test for both the buyer and seller; but at the time I am writing of tar distillers were not sufficiently educated in such matters to use any but very simple tests.

The purification of the anthracene sufficiently for our purpose had then to be worked out, and in doing this I found out a curious fact, namely, that when distilled with caustic potash it was much improved in quality—considerably more so than when distilled either alone or with caustic soda. And potash distilled anthracene was especially necessary when dichloranthracene had to be prepared, as it yielded a well-crystallised, easily purified product, whereas anthracene which had been distilled, either alone or with caustic soda, gave a badly-crystallised, sticky product, which was very difficult to purify.

On examining into the action of caustic potash on anthracene, it was

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* My father, to whose great kindness I was so much indebted, died in 1864, so that our firm then consisted only of my brother and myself.

found that if, after the anthracene had been distilled off, the residue was freed from akali by washing, and then distilled, a substance very like anthracene was obtained, which Graebe subsequently found to be the nitrogenous compound now known as *carbazol.* It is by means of caustic potash that this substance is now separated from crude anthracene, and the process is still used to a large extent to improve the quality of anthracene. All the anthracene we used at Greenford Green was treated in this manner.

The purification of the anthraquinone was at first effected by sublimation, followed by crystallisation. A good deal of difficulty was experienced in the conversion of this substance into its sulphonic acid, however, and at the high temperature at which combination took place, the formation of steam from the water produced at the same time led to considerable quantities of the anthraquinone becoming sublimed, which, although not lost, yet was a source of trouble in various ways. The means of overcoming this difficulty was to use fuming sulphuric acid, with which anthraquinone combined at a much lower temperature, but the only acid of the kind then made was the old-fashioned Nordhausen acid. We imported a quantity of this, and, of course, found it to work satisfactorily, but the difficulties and expense connected with the carriage and transport of this substance on account of its dangerous nature—supplied as it then was in large earthenware bottles—made it unsuitable for use in this country.

The artificial alizarin we first made was produced by the anthraquinone process, the method still used for its manufacture, but the difficulty in preparing the sulphonic acid in those early days just referred to caused us to turn our attention to the second process I had discovered, in which dichloranthracene was used. After finding out the best way of preparing the substance, our difficulties in reference to the sulphonic acid vanished, as dichloranthracene dissolves easily in hot ordinary oil of vitriol, producing dichloranthracenedisulphonic acid; on continued heating this acid oxidises, hydrogen chloride and sulphur dioxide being evolved and anthraquinonedisulphonic acid formed. Without this process, the manufacture of artificial alizarin in this country could not have been carried on with much success in the early days of its manufacture.

The conversion of the anthraquinonesulphonic acids into colouring matter by treatment with caustic alkali at a high temperature at first presented many difficulties when carried out on the large scale. Our earliest experiments were made by heating the mixture in iron trays in a large air bath. Mixtures of caustic potash and caustic soda were also experimented with instead of caustic soda alone. Then the mixture was placed in a revolving cylinder, heated in an air bath, small cannon balls being put into the cylinder to mix the product. But all these methods were only partially successful, the percentage of colouring matter produced not being so high as it should have been. At last heating in a very strong iron boiler under pressure was resorted to, and by adopting this method—which is now that universally used—we obtained a satisfactory result.

From the experiments we made in 1869 we felt pretty confident that artificial alizarin could be made at a price to compete with madder and garancine, and before the end of the year we had produced 1 ton of this colouring matter in the form of paste, in 1870 40 tons, and in 1871 220 tons, and so on in increasing quantities year by year.

The colouring matter produced from dichloranthracene was chiefly anthrapurpurin containing a little flavopurpurine. Theoretically it should have consisted of these products only, but owing to the occurrence of a secondary action, which I need not refer to here (see *Lectures Soc. Arts*, May 30th, 1879), it also contained alizarin, which we sometimes separated when required for dyeing purples. This colouring matter yielded a shade of colour which answered most of the requirements of the consumers for some time, as it was chiefly used by the Turkey-red dyers, and the supply being limited, it was often used in combination with garancine, as in this way more brilliant reds could be obtained than when using garancine alone, though, of course, the use of the artificial colouring matter alone yielded still clearer and more fiery shades.

Dichloranthracene was afterwards found to yield a monosulphonic acid when treated with sulphuric acid, provided the temperature were kept low and the amount of acid limited; and when oxidised with manganese peroxide or other oxidising agent, this yielded anthraquinonemonosulphonic acid, from which alizarin alone could be obtained. But the properties of dichloranthracenemonosulphonic acid were such, and the technical difficulties of carrying out the process so considerable, that it was never used very successfully. Moreover, by this time, fuming sulphuric acid had come into use, and anthraquinonemonosulphonic acid could be more readily produced directly from anthraquinone. As we had been successful in producing artificial alizarin, others did not run much risk in following our lead; yet, up to the end of 1870, the Greenford Green Works were the only ones producing artificial alizarin. German manufacturers then began to make it, first in small and then in increasing quantities, but until the end of 1873 there was scarcely any competition with our colouring matter in this country.

From the foregoing, it is seen that, as in the case of the aniline colours, all the pioneering work connected with the foundation and establishment of this branch of the coal-tar colour industry was also done in this country.

For the due development of this industry, it was necessary not only to attend to technical processes, but also to carry on scientific research in connection with it. Early in 1870, I had the honour of bringing before this Society an account of some experiments on the formation of the colouring matter obtained from the sulphonic acids of anthraquinone, showing that it contained alizarin possessed of both the chemical and optical properties of that obtained from madder root. At the same time, attention was directed to the existence of a second colouring matter, yielding reds more scarlet and purples of a bluer shade than alizarin (*J. Chem. Soc.*, 1870, **23**, 133). This second colouring matter was afterwards made the subject of further investigation, and shown to be an isomer of purpurin; it was therefore called *anthrapurpurin* (*J. Chem. Soc.*, 1872, **25**, 659, and 1873, **26**, 425). Dichlor- and dibrom-anthracene and their disulphonic acids, &c., were also investigated. Anthraflavic acid, discovered by Schunck in some secondary products sent to him from my works, was made the subject of two researches; in the first of these, this compound was shown to be an isomer of alizarin, and not to contain C_{15}, as supposed by its discoverer. In the second, the sublimed acid was examined and found to be identical with the unsublimed; it was also shown that when fused with alkali it did not yield alizarin, as stated by Schunck, but a colouring matter yielding orange-red colours with alumina mordants. This, Schunck and Roemer, some time afterwards showed to be another isomer of purpurin which was named by them flavopurpurin.

In this investigation, anthraflavic acid was found to yield a diacetyl and dibenzoyl derivative, which was evidence that it contained two hydroxyl groups like alizarin (*J. Chem. Soc.*, 1873, **26**, 19). Later on, an investigation was made on the formation of anthrapurpurin, proving that, as in the case of flavopurpurin, the formation of the colouring matter from the disulphonic acid of anthraquinone is preceded by that of a dihydroxy-derivative, also an isomer of alizarin, now known as *isoanthraflavic acid*, which, when heated with caustic alkali, is partially oxidised into anthrapurpurin and partially reduced (*J. Chem. Soc.*, 1876, i, **29**, 851). Besides these, the formation of bromalizarin (*J. Chem. Soc.*, 1874, **27**, 401), of β-nitroalizarin (*J. Chem. Soc.*, 1876, ii, **30**, 578), of anthrapurpuramide (*J. Chem. Soc.*, 1878, **33**, 216), and of the dibromanthraquinones discovered by Graebe and Liebermann and the colouring matters obtainable from them, were investigated (*J. Chem. Soc.*, 1880, **37**, 554). Much work has also been done in reference to this industry by Graebe and Liebermann and other investigators.

The manufacture of artificial alizarin in Germany has been almost entirely confined to the anthraquinone process, fuming sulphuric acid being used in the preparation of the sulphonic acids. For this purpose very strong acid, containing about 40 per cent. of anhydride, was made from Nordhausen acid, and used until the process of making sulphuric anhydride by decomposing sulphuric acid into sulphurous oxide, oxygen, and water, and recombining the two former, was introduced.

After being engaged in the coal-tar colour industry for 18 years, my connection with it, technically, came to an end in 1874, when the alizarin industry had been well established and was rapidly extending.

On looking back over the period, it is of interest to see the wonderful progress the industry had made up to that time—a progress which was going on by leaps and bounds. I have no statistics connected with the precise period, but four years afterwards, namely in 1878—with the kind assistance of Dr. Caro—an estimate of the value of the colours produced during that year was obtained, at a time when the industry had just passed its majority and was 22 years old. The sum amounted to £3,150,000. (See *Jour. Soc. Arts.*, May 30, 1879.) Of its present position, it is very difficult to speak. Certainly its progress has been very great since 1878; but chiefly owing to the scientific skill bestowed upon the production of the colouring matters, their cost has been greatly diminished, so that I understand rosaniline hydrochloride, which once was worth about £3 3*s*. per ounce, may now be purchased at 2*s*. 9*d*. per lb., and aniline at less than 6*d*. per lb.

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During the early days of the coal-tar colour industry, the complaint was made that the prosecution of purely scientific chemistry was being injured by its influence, as chemists were everywhere experimenting with aniline and other products, with objects of a more selfish than scientific character. It is probable that there was some truth in this for a time, but it was not long before a welcome change set in, and the work carried on in relation to this industry was soon conducted in a scientific spirit, even when the result sought for was expected to be of technical, as well as where it was expected to be of scientific, value. But the amount of work carried on from the latter point of view increased more and more, as interesting questions connected with the colouring matters and the methods by which they were produced presented themselves to chemists, and now if we look back and consider what has been accomplished, we find that this industry has directly and indirectly had a most marvellous influence on the advancement of chemical science, especially that part of it relating to the aromatic series of compounds. No other industry in existence can at all be compared with it from this point of view. This has arisen from a variety of circumstances, one of which is that it has not been carried on by the rule of thumb method which has been so common in other cases. Again, as it has utilized the discoveries of chemists, it has handed back to them in return new products which they could not have obtained without its aid, and these have served as materials for still more advanced work: this kind of exchange, indeed, has been going on so repeatedly, that products formerly of the rarest and most complex character are now quite common substances in the coal-tar colour works.

We knew that aniline was at first a rare substance, and when it was afterwards proposed to use ethyl and methyl iodides in the preparation of ordinary dye-stuffs, it seemed incredible that such substances could be introduced for such a purpose as already mentioned, substances which were but rarely met with even in chemical laboratories: but what are these compared with the substances now in use? —their names would be too numerous to mention. One of the most striking facts connected with this industry is the remarkably rapid way in which it has utilized new discoveries which have often been no sooner made than they have been practically applied. This no doubt arises from the fact that an ever increasing army of highly trained and highly gifted chemists are engaged in the industry, especially on the Continent, provided with splendid laboratories, libraries of scientific works and all the most advanced appliances required in scientific research; and the members of this army are not only making discoveries themselves and applying them, but are always on the alert to make the discoveries of others subservient to the industry.

As I have already mentioned, when this industry was first instituted, organic chemistry was comparatively in its infancy, especially if we regard it from our present standpoint. Kekulé had not then brought forward his remarkable benzene theory, and after he had done so its bearings required much elucidation before their importance was well understood. Only solid toluidine was known, orthotoluidine not having been discovered, although it was constantly present in the high boiling aniline used in making rosaniline; but now the facts connected with the ortho-, meta-, and para-position in substances containing the benzene nucleus, or of the α- and β-positions in the naphthalene series, are among the most important to be considered in the manufacture of colouring matters; in fact, this industry has done more to accentuate the importance and character of these positions than any other kind of experimental work.

Although at the commencement of the industry a good deal of work of a purely experimental character had to be done, nevertheless, from the first it was carried out on scientific lines, and this characteristic increased very rapidly, as is seen by the early date at which mauve and magenta were obtained in the pure crystallised condition: it was at this period, as previously stated, that Hofmann commenced his researches on rosaniline and its derivatives, and on other colouring matters, and these researches, taken with those of others, bear out the observations which have just been made. In looking over the work of Hofmann in this field, all who have had experience in the investigation of the subjects he undertook must realise that they presented no ordinary difficulties, especially as for some time he had nothing to guide him in his conclusions but the analytical results. In the early days of organic chemistry, it is well known that on finding colouring matters in the products they were examining, chemists usually regarded them as impurities, and the use of animal charcoal and other means were resorted to for the purpose of getting rid of them; and those who undertook the examination of colouring matters themselves were considered as bold men, and not likely to get much result from their labour. Doubtless, there was much truth in this. Hofmann, however, *was a bold man*, and not one to be daunted, but rather inspired, by difficulties; and from his results we see how great his success was in this department of chemistry, some of his work proving to be of direct practical value, whilst other parts possessed important bearings both on the practical and scientific development of this subject. His researches on colouring matters extended over a quarter of a century, commencing in 1862 with rosaniline, and ending in 1887 with quinoline red; and during that period there were but few years in which he did not produce one or more investigations, either related to colouring matters or the products connected with their production.

It will be obvious from what has been said, how Hofmann's early work—after that of Faraday, Unverdorben, Runge, Fritzsche, Mitscherlich, and Zinin—continued to pave the way for the introduction of the coal-tar colour industry, also how the important influence he exercised on the training of his students led in the same direction. I especially refer to Mansfield, who did such valuable work on coal-tar, and Nicholson, whose chemical education under Hofmann was such an important preparation for the work he undertook in after years on rosaniline and its derivatives; and if I may speak for myself, I can only say how much I owe to Hofmann's training, which fitted me to carry out the work which fell to my lot in connection with the introduction and development of this industry. Then if we further consider the importance of the beautiful researches Hofmann made, some of which yielded practical results, throwing fresh light on the nature of the colouring matters and products related to them which were obtained as time went on, some idea may be formed of the contributions made by Hofmann and his school to the coal-tar colour industry.

And yet we must bear in mind that his work in this department of chemistry represents but a small part of all that he accomplished—indeed, the amount of scientific work he did was something marvellous.