OBITUARY NOTICES.

SATYENDRANATH CHAKRAVARTI.

1903—1945.

DR. SATYENDRANATH CHAKRAVARTI was born in Calcutta in 1903. After a brilliant school and college career he took the M.Sc. degree of Lucknow University and then proceeded to Oxford in 1926 to work under (the late) Professor Willaim Henry Perkin, Jr., in the Dyson Perrins Laboratory. After taking the D.Phil. degree, he returned to India in 1929 to accept the post of Reader and Head of the Chemistry Department of the newly started Annamalai University in South India. Here he had to organise the honours and M.Sc. degree courses for the first time. Being a man of great enthusiasm, he succeeded in creating a fine department which earned a good reputation. He served as Dean of the Science Faculty and member of the Syndicate of the University; he was also elected by the members of the Syndicate to act as Vice-Chancellor of the University when there occurred a short-time vacancy. After serving the University for about seven years, Chakravarti resigned his post to the regret of all his students and colleagues and accepted the post of Chemical Examiner to the Governments of the United and Central Provinces with his headquarters at Agra. This post he held till the time of his premature death on the 28th August, 1945, in tragic circumstances.

Chakravarti is the author of forty-two original scientific publications. Through Perkin he became interested in alkaloids, and, working for his D.Phil. degree at Oxford, he successfully synthesised tetrahydroprotoberberine and some of its derivatives. Chakravarti's other work in India includes the synthesis of many more derivatives of tetrahydroprotoberberine, paraberine, ψ-opianic acid, hydrindones, homophthalic acids, and hydroxynaphthalene derivatives, and the chemical investigation of Indian medicinal plants. After his appointment as Chemical Examiner, he published papers of medico-legal and forensic interest such as methods of distinguishing various samples of opium preparations, and the detection of arsenic in burnt human bones, ashes, etc.

Chakravarti was a born teacher and commanded the admiration and respect of all his students and colleagues. He had high ideals and always tried, even at the cost of personal sacrifice, to live up to his convictions. He was greatly attached to his students. His lectures were well known for their exhaustive treatment and fine presentation and he took pains to train his students to become good chemists and not merely to pass examinations. He was a perfect gentleman and a man of sterling character.

He obtained the D.Sc. degree of Oxford University, and was elected a Fellow of the Royal Institute of Chemistry of Great Britain and Ireland, the Indian Academy of Sciences, and the National Institute of Sciences of India.

He leaves his wife and four children and a large circle of students and friends to mourn his loss.

K. GANAPATHI.

AUGUSTUS EDWARD DIXON

1860—1946

AUGUSTUS EDWARD DIXON was born on June 2nd, 1860, in Belfast.* He was the eldest son of Wakefield H. Dixon, an alderman of that city. At the Royal Belfast Academical Institute he showed early promise in scientific studies and subsequently in Trinity College, Dublin, at the age of twenty-one he obtained the Senior Moderatorship in Experimental Science with high distinction. He obtained the Gold Medal in Experimental Science and the Ekenhead Scholarship. Under the influence of Professor Emerson Reynolds he decided to make chemistry his profession but, following the usual practice of those days, he first read for a medical degree. Emerson's influence was also evident from his subsequent line of research. The greater part of Dixon's work for over thirty years was directed towards a study of the thioureas and related substances. During the qualifying stages for his medical degree he was for some time engaged as Science teacher at Clongowes Wood College, Kildare (1882—1884). He also found time for research, and in the *Proceedings of the Experimental Society of Trinity College* there are records of early papers by him, for example " The Action of Carbon on Ozone " (1882) and " A New Test for Gallic Acid " (1884); there is also a paper, " An improved Apparatus for drying Combustion Tubes," in the *Chemical News* (1888, **57**, 308).

Dixon obtained the M.D. degree in 1885 and was appointed a Demonstrator in Chemistry in Trinity College for the session 1885—1886. He went to Berlin in October 1886 where he worked under Professor A. W. von Hofmann for some time. On his return to Dublin, in April 1887, he was appointed assistant Lecturer in Chemistry in Trinity College, and in October 1889 was appointed Professor of Chemistry in Queen's College, Galway. Two years later, in October 1891, he succeeded Professor Maxwell Simpson at Queen's College, Cork. The only record of this in the Council Book of University College, Cork, is that he appeared before the Council and produced Her Majesty's warrant appointing him Professor and his declaration made before a magistrate in compliance with the provisions of the Colleges Act of 1845.

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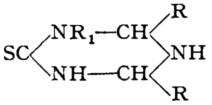
* See also *Nature*, 1941, **157**, 505.

For a very long period the South of Ireland has been fortunate in having good facilities for Chemical research. At the opening of the 19th Century the Royal Academical Institute was established in Cork, and it was here that Professor Edmund Davy first discovered acetylene. In 1849, with the foundation of a Queen's College in Cork, John Blyth, M.D., was appointed first professor of chemistry and was succeeded in 1873 by Professor Maxwell Simpson, M.D. On Simpson's retirement in 1891, Dixon succeeded to the chair which he held, first in the Queen's College and later in the National University of Ireland, until his retirement thirty-three years later in 1924. He was Emeritus Professor until his death on March 3rd, 1946, in his eighty-sixth year. A period of practically one hundred and fifty years is covered by these four prominent chemists.

Dixon's output of over fifty papers deals largely with (1) reactions of *iso*thiocyanates, and (2) reactions of thiourea and its derivatives. The following abstract of these papers has been prepared by Dr. J. Wilson.

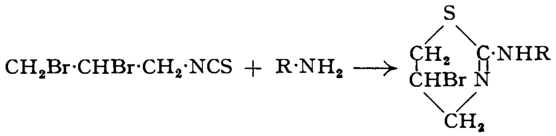
" His first publication (*J.*, 1880, **50**, 411) describes the action of acetaldehyde-ammonia and valeraldehyde-ammonia on some *iso*thiocyanates. Schiff (*Ber.*, 1876, **9**, 565) had described earlier compounds obtained by the same reaction. Dixon extended Schiff's work and assigned provisionally the following structure to the product of the reaction :



Later (*J.*, 1892, **61**, 509) Dixon examined the reaction of thiourea with aldehyde-ammonias and proved that the compounds obtained from this reaction are of the same type as those obtained from *iso*thiocyanates and aldehyde-ammonias.

" While this work was progressing he prepared a number of new substituted thioureas (*J.*, 1889, **55**, 300, 618; 1891, **59**, 561). A logical extension of this investigation was his work on the thiosemicarbazides, and he published several papers on their preparation and the phenomenon of isomerism in that series (*J.*, 1890, **57**, 257; 1892, **61**, 1012).

" Aschoff (*J. pr. Chem.* 1871, **4**, 314) had examined the action of bromine on allyl *iso*thiocyanate but failed to identify any of the products. Dixon (*J.*, 1892, **61**, 545) repeated this work and isolated dibromopropyl *iso*thiocyanate in good yield. He examined its properties and in later papers (*J.*, 1896, **69**, 17; 1901, **79**, 553) reported its reaction with several amines. The thiourea derivative was not produced but lost the elements of hydrogen bromide to give a cyclic product. He explained this reaction as follows :



" Another reaction examined carefully was that between metallic thiocyanates and acid chlorides. Miguel (*Ann. Chim. Phys.*, 1877, **11**, 289) had prepared acetyl and benzoyl thiocyanates by the interaction of the respective acid chlorides with lead thiocyanate. Though on mixing the product with aniline the substance obtained was a substituted thiourea, *e.g.*, $CH_3{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5$ from acetyl thiocyanate and aniline, Miguel did not grasp the fact that the acyl thiocyanates show the reactions of thiocyanates and *iso*thiocyanates. Dixon re-examined this reaction, extended it to the preparation of di*iso*thiocyanates and prepared many substituted thioureas [*J.*, 1895, **67**, 565 (with Doran), 1040; 1896, **69**, 855, 1593; 1897, **71**, 617; 1899, **75**, 388]. The results (*J.*, 1901, **79**, 541) of these investigations showed conclusively that under certain conditions acyl thiocyanates sometimes exhibited the properties of thiocyanates but usually (especially with amines and alcohols) react like *iso*thiocyanates. These compounds continued to provoke his interest and in 1903 (*J.*, **83**, 84) he prepared carbonyl di*iso*thiocyanate in solution and found that it reacted with aniline to give the substituted thiourea, $CO(NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5)_2$. He discovered later, with Hawthorne (*J.*, 1906, **89**, 468), that the reaction of acetyl thiocyanate with aniline at low temperature resulted in the formation of acetanilide and thiocyanic acid. At higher temperatures the acetylphenylthiourea was formed. (See also *J.*, 1906, **89**, 892.)

" An observation in 1903 (*J.*, **83**, 550) that methyl chloroformate unites spontaneously with phenylthiourea led Dixon to examine the reaction of acid chlorides on thioureas. Claus (*Ber.*, 1875, **8**, 42) had reported that a highly unstable compound was produced by adding acetyl chloride to thiourea. A re-examination of the reaction by Dixon, with Hawthorne and Taylor (*J.*, 1907, **91**, 122, 912), showed that in the case of thiourea and mono-substituted thioureas the hydrochloride of the base, $CH_3{\cdot}CO{\cdot}S{\cdot}C{\left\langle{}^{NR}_{NH_2}\right.}$, was first formed which on removal of hydrogen chloride and warming rearranged and gave a di-substituted thiourea. When the α-chloro-acyl chlorides reacted with thioureas, *iso*thiohydantoins were formed (Dixon and Taylor, *J.*, 1908, **93**, 21; 1912, **101**, 558). A later communication (with Kennedy, *J.*, 1920, **117**, 74) describes the preparation of acyl *iso*thiohydantoins.

" Dixon did not confine his attention to thiourea derivatives. Manuelli and Comanducci (*Gazzetta*, 1899, **29**, 142) claimed that α-phenyl-β-*p*-tolylurea was formed by heating phenylurethane with *p*-toluidine. Dixon noted the discrepancy between the melting points reported by them for the substance and the melting point which he himself had observed in a previous experiment (*J.*, 1895, **67**, 562), and he repeated the work of these authors. By detecting aniline in the reaction mixture he showed that the compound reported by the Italian authors was di-*p*-tolylurea. In general he found that when phenylurethane was heated with an equivalent amount of *o*- or *p*-toluidine or with naphthylamine the symmetrical di-substituted urea from the base always accompanied the mixed urea (*J.*, 1923, **123**, 895)."

On a few occasions, Dixon, to confirm certain theories of his, had recourse to physico-chemical methods. He was an expert at mechanical operations and a first-rate glass manipulator. Further, he collaborated with Professor Hartog on the chemical aspect of certain biological problems. In these activities also he was a master of his subject. Apart from his research ability, he was an excellent and stimulating lecturer; he followed the Hofmann tradition of showing many elaborate experiments in his undergraduate classes. He also took a keen interest in the erection of new chemical laboratories in University College, Cork, and was responsible for many novel ideas in their planning and equipment. He designed with Taylor (*J.*, 1910, **97**, 374) an apparatus for demonstrating the electrolysis of hydrochloric acid solution, and with McKee (*J.*, 1923, **123**, 895) a simple apparatus for purifying mercury by air agitation with or without the usual cleansing solutions.

Dixon was of a retiring disposition and only his intimate friends were aware of his very active scientific life. He served on the Council of the Chemical Society from 1900 to 1902. He was a member in 1903 of the grants committee of the Royal Society. He became a Fellow of the Royal University of Ireland in 1908. His hobby was photography, in which he was an expert, and he was one of the founders of the Cork Photographic Society. He was President of the Society until his departure to Sidcup, Kent, on retirement in 1924.

Dixon married Miss Nina Haughton of Dublin in 1888 and his two sons graduated at University College, Cork; Wilfred (who died soon after graduation) in medicine, and Emerson in engineering. He is survived by his widow, one son, and a married daughter.

JOSEPH REILLY.

ARTHUR GEORGE GREEN.*

1864—1941.

> " Life is a pure flame and we live
> by an invisible fire within us."

ARTHUR GEORGE GREEN died peacefully in his sleep on September 12th, 1941, in the seventy-eighth year of his life. From leaving college in 1885 until the day of his death Green was continuously and actively engaged in the practice of chemistry. He was pre-eminently a chemist; all his enthusiasm, and it abounded in him, was for chemistry or for causes which had chemistry at the heart of them. The synthetic dyestuff industry was his foremost passion and practically all the energy of his long life was devoted to it, not merely because he had fertilised it by his early genius as an inventor, or because it furnished an outlet for his talent as an experimenter, but because he believed in it fervently as a matter of major significance in the industrial and scientific development of the nation. The dyestuff industry was a " cause " to Green. He was a servant to science, and a passionate preacher of science in industry. He was properly honoured for his work and for his devotion by his colleagues, becoming a Fellow of the Royal Society and the recipient of many honours, medals, etc., from other learned bodies. From the politician and the general public, however, Green received no recognition. On this account, and because of the intensity of his belief in the urgency of his cause, Green must have experienced many times the pangs of disappointment and frustration, but in spite of it, and of the many changes in his career, his life was happy and uninterrupted in the steady and fruitful practice of the branch of chemistry of which he was a master. To have been able to do this up to the very day of his death was his greatest reward.

Green commenced his life work in dyestuff chemistry while it was still comparatively young, both as a branch of science and as an industry. Very early in his career, he blossomed out as an inventor and ranks amongst the select band whose discoveries ensured the establishment of the great industry of synthetic organic chemicals of which the artificial colouring matters have always been the pivot and the inspiration. He suffered the chagrin of seeing the industry which had been born in this country come to its fullest fruition in another land, then in the last period of his life he saw it flourishing once more in the land of its birth.† At the end of his life Green passed his happiest days amongst the new generation of colour chemists who have arrived on the British scene with the renaissance of the industry on which he had set his heart.

Green was born a Londoner, the son of an architect, and was educated at Lancing College, Sussex. He confessed himself to have been an indifferent pupil until he was allowed to work in the almost unused chemical laboratory of the school during play hours. After matriculating, in 1880, he entered University College, London, where he studied chemistry under Williamson, physics under Oliver Lodge, and biology under Ray Lankester. At the end of his first year, he gained a gold medal and a Clothworkers' Exhibition in chemistry, and the seal was set on his career. More medals, a Tuffnell Scholarship and research work with Dr. H. F.

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† Compare the two lectures: (*a*) The Relative Progress of the Coal Tar Industry in England and Germany during the past Fifteen Years (*J. Soc. Dyers and Col.*, 1901, **17**, 285); (*b*) The Renaissance of the British Dyestuff Industry (*ibid.*, 1930, **46**, 341).

Morley followed. During college vacations Green had worked as a volunteer in the laboratory of Messrs. Williams Bros., aniline dye manufacturers of Hounslow. He introduced to the firm the " baking " process for the manufacture of sulphanilic acid, and throughout his career, with breaks from time to time, he maintained his old connexion with this ancient firm.

Green was by this time completely committed to dyestuff chemistry, and when he left College in 1885 obtained his first post as research chemist to the firm of Messrs. Brooke, Simpson & Spiller, Ltd., Atlas Works, Hackney Wick, where, incidentally, he succeeded Meldola, who was leaving to become professor of chemistry at Finsbury Technical College. While in the service of this firm Green made his first dyestuff inventions. These were of outstanding merit and included primuline, which was not only a new dyestuff but led Green to uncover an entirely new technique in the application of dyestuffs on cotton. In the light of later knowledge it is easy to see that Green's inventions at this early stage of his career could and should have built up the fortunes of a dyestuff business in this country comparable with the powerful firms which were developing in Germany. This was not to be, however, and Green, mortified at the want of appreciation of these wonderful possibilities, transferred his services in 1894 to the Clayton Aniline Company, in Manchester.

From 1894 to 1901, Green laboured at Clayton as research chemist and works manager. His earlier inventions in the primuline field were developed and greatly improved, and progress was made in other classes of dyestuffs, notably the derivatives of stilbene. Under Green's regime the Clayton works was greatly enlarged, and in addition to his many patented inventions during this period, and some publications in scientific journals, Green participated in the development of a modern modern manufacturing technique. A case in point was the establishment on a large scale of the manufacture of *p*-nitroaniline by the acetanilide route, using an aluminium reaction vessel with a silver condenser, great innovations in their day.

At the turn of the century the position of the dyestuff industry in England was critical. Green's inventions and the position he occupied augured possibilities which could be compared with what Caro, for example, had done for German industry. The manufacture of dyestuffs was already emerging from its earliest, or " rosaniline " period when Green commenced his career. In those early days it could only be reckoned as a small sundries type of industry. Now, however, owing to the progress of the azo dyes under Caro's presiding genius, and the consequent demand for intermediates on a bulk scale, a complete change had come about. The improvised technique and the elementary conceptions of plant, borrowed for the most part from other trades, which had characterised the early phase of the industry now no longer sufficed. The manufacture as well as the chemistry of dyestuffs had become scientific, and a new phase was inaugurated by the production of synthetic indigo on the large scale. The latter event saw even inorganic processes such as electrolytic alkali and chlorine, as well as contact sulphuric acid, invented and developed solely in order to meet the need of the dyestuff industry to obtain its primary products on a bigger and more economic scale. With these developments the German dyestuff firms progressed from strength to strength, a fact of which Green was keenly aware, and which caused him to despair as he came to realise his failure to arouse interest among the industrial and political leaders of this country. It is not surprising, therefore, that at this stage Green severed his connexion with industry. He left the Clayton Aniline Company in 1901.

Green's next venture was to open a private laboratory in London in order to sell his ideas and to act as a chemical consultant. Within a short time, however, he was invited to accept the chair of Colour Chemistry and Dyeing at the University of Leeds (at that time the Yorkshire College, a constituent of the Victoria University).

Green's appointment as professor, direct from industry and without any academic experience or standing, reflects considerable credit on the enterprise and judgment of those responsible at Leeds. He was, however, well fitted for the post and, although he had a most distinguished predecessor in the late Professor Hummel, Green, during the period 1903—1916, in which he occupied the chair, greatly enhanced the reputation of his department, both in teaching and in research.

Liberally endowed by the Clothworkers' Company, according to the standards of the day, Green's department at Leeds became not only an outstanding example of the teaching of applied science, but it acquired an international reputation for its research work. Graduates of universities, both in this country and abroad, came to work under Green, and the students of the department were eagerly sought after, even by the great German dyestuff firms.

The nature and the success of Green's work while in the chair at Leeds are well indicated in his original publications during this period. These are almost exclusively of a scientific character, but he never entirely lost his contact with the dyestuff industry at home and abroad, with which he had many consulting connexions. As the discoverer of a new method of dyeing Aniline Black he also had a very intimate practical contact with the dyeing trade through the grant of patent licences in many countries.

By a coincidence, one of Green's contemporaries at Leeds was Procter, head of the Department of Leather Technology. Procter too had been recruited from industry and had an international reputation, not only for the training of students in the scientific aspects of industry, but also for his pioneer work in colloid science. The importance of the teaching and the original work done by men of the type of Green and Procter in the interest of the scientific development of industry is usually insufficiently appreciated by those in authority over matters educational. The faintly acidulous attitude too often shown by the academic world towards the more " applied " aspects of advanced scientific education was not absent at Leeds; perhaps the lessons now brought home so painfully by a technical war were not so obvious in **1914**. Whatever the reasons Green was restless at the time and when war broke out was probably feeling a strong urge to get back into industry.

The war in 1914 brought new ideas and responsibilities to Green. All his forebodings and warnings about the decadence of organic chemical industry in England proved to be only too well founded when, out of our unpreparedness, we had to improvise the means to deal with a scientifically well-equipped foe. Like other academic leaders in chemistry Green was faced with the need of finding men for the understaffed factories and of assisting the Government with advice and hurriedly improvised research work. Green's experience in the dyestuffs field led him to useful contributions in many directions, for example, in the explosives field he pioneered the chlorodinitrobenzene route to picric acid (B.P. 16,607, 1915).

The dyestuff crisis was one of the most acute of the many technical problems with which the country was faced at this time. Not only was there an insufficiency of plant and experience to meet more than a small fraction of the urgent demand, but, owing to the comparative neglect of scientific research and advanced teaching in organic chemistry at the universities, there was an insufficiency of the type of men required for the hurried improvisation of an entire industry, which was what the situation called for. In this chaos Green resigned his chair at Leeds early in 1916, and took on the double responsibility of establishing the Dyestuffs Research Laboratory at the Manchester College of Technology, and at the same time acting as advisor to the firm of Levinstein, Ltd., who were at that time bearing the brunt of the increased dyestuffs production. An outstanding event of Green's connexion with this firm was his collaboration in the working out and establishment of the technical production of mustard gas on the large scale, an event which aroused much enthusiasm amongst our American allies but was attended by some academic controversy in this country (*J. Soc. Chem. Ind.*, 1919, **38**, 363r, 469r).

Green's interest did not wander from dyestuffs for very long, and the end of the war found him working whole time with Levinstein, Ltd., as director of a new research laboratory staffed very largely from the pick of the chemists released from other fields of the war effort. Green held this appointment through the troubled times which fell upon the dyestuff industry in the early years of peace. The struggling industry was the subject of much political controversy as well as many changes in management resulting from the " rationalisation " which was part of the post-war economy, on top of which it was all but ruined by the effects of the Sankey judgment.

In 1923, Green's firm, having in the meantime become the British Dyestuffs Corporation, Ltd., lost his services on account of a disagreement on policy. Green held the view that an industry dependent on scientific development should be in the hands of men having the fullest appreciation of science, that is to say, of scientists. This view was not commonly held by his contemporaries, but Green knew only too well from personal experience the disaster which the industry had suffered in this country through falling into the hands of men who lacked knowledge, and he was anxious that the mistake should not be repeated. Unfortunately he chose the wrong moment to attack, pressed his point, and lost; had he waited, he would have been successful, judging in the light of subsequent events in the industry. It is safe to say, however, that in the period during which Green directed his laboratory at Blackley the seed was sown for the great revival of the dyestuff industry which followed there later. The reason for this was the fact that wherever Green established himself his efforts were always directed along the path of originality and discovery, as the true object of research. When his old firm found itself in circumstances of greater security under the aegis of Imperial Chemical Industries, Limited, it blossomed out in an ambitious and successful research effort which commanded the respect of the world of chemical industry and secured it many commercial advantages. This success can safely be attributed to the inspiration gained in many ways, direct and indirect, from the inventive spirit of A. G. Green.

During his period at Blackley, Green's interests covered a wide field of dyestuffs invention and he revived an old attachment he had always had for the chemistry of synthetic drugs. The close connexion between drugs and dyes is well known, and it is significant that the continental dyestuff manufacturers have been responsible for the world's greatest advances in chemotherapy. It was natural, then, that Green should concern himself with this off-shoot of the dyestuff industry and in his later years his " retirement " was largely devoted to experimental work on the subject in his private laboratory. This work bore fruit in the issue on the market of sulphanilamide EOS, a useful contribution to chemotherapy, shortly after Green's death (Green and Coplans, B.P. 524,011; *idem*, *Chem. and Ind.*, 1940, **59**, 793).

Green resumed his connexion with his old colleagues in the dyestuffs industry at Blackley during the last six years of his life, when he became a consultant to Imperial Chemical Industries, Ltd., and, by his regular visits to the great laboratories which the firm had built at Blackley, was able to participate in and inspire the work of the new generation of dyestuff chemists. It was a unique opportunity for these younger men to learn from one of the early pioneers of the industry that in spite of the enormous strides which had been made on the theoretical side of chemistry in the intervening generations, and the colossal amount of publishing and patenting which had filled in the years, old Nature's lap is still full of prizes for those who will acquire the knack of putting the right kind of questions to her. To quote a Chinese proverb, " To ask well is to know much." Green was very successful in imparting the art of " asking," and his pupils have played a considerable part in the restoration of the dyestuffs industry in this country.

In personal disposition Green's character was of the mildest and gentlest. His fervent belief in science as a keynote in modern life, and in the dyestuffs industry as a keystone in modern industrial development, was never expressed in mere pugnacity, but rather as a quest, a persistent crusade for that in which he believed with all his heart. Nevertheless there was plenty of toughness of moral fibre in Green, and through the varying phases of his career, he never once surrendered the ideals for which he had battled all his life.

Green's work earned him many honours in the worlds of science and technology. These included election to the Royal Society (1915) and the honorary degree of M.Sc. of the University of Leeds (1905). He was the recipient of the Perkin Medal in 1917. He was very proud to be made a Liveryman of the Worshipful Company of Dyers (1918) and on three occasions he was awarded the Company's Gold Medal He was an Honorary Member of the Society of Dyers and Colourists, and President in its Jubilee Year. He was elected a Fellow of the Chemical Society in 1885.

Apart from chemistry Green had few interests. He liked foreign languages and travel, and in his early days tramped and cycled extensively in continental countries. He had a happy family life and his character was seen best in this setting—a simple man whose ambition was all for his science.

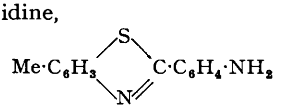
Green's domestic life was one of unclouded happiness until he lost his wife early in 1941. She was the daughter of Henry Charles Heath, a well-known miniature painter. For fifty-two years she supported him in his many struggles and vicissitudes and nursed him through several serious illnesses, for, though apparently as wiry in body as in spirit, Green's health was on the frail side. She gave him two daughters and amongst his private papers he left a most touching tribute to her brave spirit. There is no doubt that the shock of her death hastened his own end, for he followed her within a few months.

In attempting to appraise Green's life-work, one must place his merit as an inventor to the forefront. The outset of his career was signalled by a dyestuff invention which stands out in the history of that industry. Green was also a successful teacher, and, during his academic period, he turned out a great volume of original scientific papers in collaboration with the numerous research students who were attracted to his Leeds laboratory. From the beginning to the very end of his career, however, Green never ceased to give his thoughts to industrial problems and inventions.

Green's career may be divided into three periods : the early-industrial up to about 1900, the middle-academic, interrupted by the war in 1916, and the post-war industrial and consulting period. Green's war-work was an interruption which deserves special mention. Comparison of these phases is not really possible, but, in my view, the first period was the most pregnant, and it was Green's tragedy (and ours) that its potentiality was not recognised and exploited effectively for the benefit of British industry. Green " arrived " just about the end of the early, or " rosaniline " period of the dyestuffs industry. He missed, therefore, being one of that band of the earliest pioneers who in the twenty years following the discovery of mauve made fortunes and retired young.* Instead Green found employers for his young talent who were completely lacking in knowledge of the science on which the industry rested and indeed without ordinary vision, since, apparently, they thought the industry was past its hey-day, an attitude which is almost unimaginable in the light of events and is, perhaps, another example of the curious kinks in Victorian mentality.

It is a matter of history that when Green came on the scene the dyestuff industry was just entering a new phase, when its real economic possibilities were to be clearly indicated by the rise of the azo dyes and eventually confirmed by the large-scale production of synthetic indigo. This was the psychological moment for " big business " to step in. Unfortunately for this country, however, organic chemistry lay beyond the vision of its business leaders; had it been otherwise Green would undoubtedly have given the impetus in this country which men like his contemporaries René Bohn, T. Sandmeyer, and R. E. Schmidt gave on the continent, resulting in the establishment of dyestuff technology in the front rank as an industrial power-centre from which radiated eventually many other branches of organic chemical industry, *e.g.*, drugs, artificial fibres, new photographic technique, and synthetic polymers, to say nothing of the consequent developments in inorganic chemicals which the new organic industry consumed in large quantities. The fruits of Green's inventions up to about 1900 could, if properly developed, and the profits " ploughed in " to produce an ever expanding research, have established an industry in the country comparable at least with that which grew up in Germany and Switzerland. British inventiveness had proved itself in the pioneer period of the dyestuffs industry following Perkin's discoveries; it has proved itself again in the renaissance which followed after the Great War. Green's tragedy was that his talent was not exploited in his hey-day, and it took a war to prove that his views on the importance of the dyestuff industry to this country were not over-stated. In the dangerous time ahead of us we must see to it that the lessons provided by Green's career are not forgotten.

Green's earliest invention was, it so happened, his most outstanding one, the discovery of primuline in 1887 (*J. Soc. Dyers and Col.*, 1888, **4**, 39; 1917, **33**, 137; *J.*, 1889, **55**, 227). By the action of sulphur on *p*-toluidine, the thiazole, dehydrothiotoluidine,



$$Me{\cdot}C_6H_3\overset{S}{\underset{N}{\lessgtr}}C{\cdot}C_6H_4{\cdot}NH_2$$

is formed; this substance is not a dyestuff. Green, studying this reaction, discovered that a more complex

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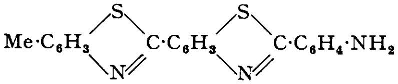
* Cronshaw," In Quest of Colour," Society of Chemical Industry Memorial Lecture (*Chem. and Ind.*, 1935, **54**, 515, 547).

base can be obtained by the use of more sulphur and a higher temperature. The new base when sulphonated gave a dyestuff having affinity for cotton, which is dyed a bright pure yellow without the aid of a mordant. The new dyestuff has been shown to consist substantially of a sulphonic acid of the base :



The derivation from *p*-toluidine is obvious; the position of the sulphonic group has not yet been proved.

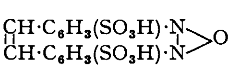
The new dyestuff, although fugitive to light, was an attractive addition to the, at that time, very limited range of direct dyeing cotton colours (Congo red, the first of the benzidine dyes, was less than three years old), but Green had still further work to do before primuline achieved the position it was later to assume as a major dye. Green applied his mind to the technique of dyeing and discovered the process of diazotising and developing on the fibre those substantive dyes which contain a reactive amino group. Primuline in this way gave a red with β-naphthol which achieved great industrial importance, and is still largely used though now past its hey-day on account of the discovery of faster modern " azoic " colours and other developed reds. Green's new dyeing process was as remarkable a piece of pioneering as the discovery of primuline itself (*J. Soc. Chem. Ind.*, 1888, **7**, 179). Many inventors have over the years devoted their minds to the elaboration of direct cotton dyes suitable for diazotisation and development on the fibre, and the range of such dyes is to-day a large one. Invention in the series still goes on because, although every shade is now represented in the range, the production of certain developed shades, *i.e.*, yellows and greens, presents a problem which has a special challenge for the dyestuff chemist.

Besides the red obtained by diazotising and developing with β-naphthol, primuline gives other shades with other coupling components, *e.g.*, a bordeaux with ethyl-β-naphthylamine, a brown with *m*-phenylenediamine, etc. The diazo-compound is light-sensitive and has been employed in photographic reproduction, thus being the forerunner of the modern diazotype process which is now almost universally used for engineers' drawings (*J. Soc. Chem. Ind.*, 1890, **9**, 1001).

The " ingrain " process, as Green called it, of azo formation on the fibre not only had outstanding industrial importance but was a great piece of pioneering. The effect of increasing the molecular complexity of a substantive dyestuff on the fibre is not merely to modify the shade, but to increase the fastness of the dye. To-day this result is achieved in a number of analogous ways, and Green's invention must be regarded as the parent of the great range of " developed " colours, and in part at least, of the modern " azoic " colours. In the latter the process employed by Green is reversed, a coupling component which has a degree of affinity for cellulose, *e.g.*, β-hydroxynaphthoic anilide, being applied first and the diazo component afterwards. The fastness thus obtained is conditioned by the affinity of one of the components, a feature which is shared by the original " ingrain " process of Green, and which distinguishes it from the older " para-red " process of Holliday. This development is mentioned here in order to emphasize the far-reaching effects of Green's early stroke of genius. Green's employers made the fatal mistake of not patenting primuline, and within a very short time it was successfully imitated by the Swiss firm of Geigy and later by every other dyestuff maker in the world.

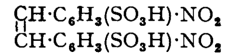
The discovery of primuline led to many other new dyestuffs. A study of the action of ammonia on the diazo compound led to the discovery of a method of conferring cotton dyeing properties on the lower thiazoles derived from *p*-toluidine. These ideas were not patented or developed by Green's firm and dyestuffs arising from them were later manufactured by several other firms under the names of thiazol yellow, Clayton yellow, etc. A similar fate befell the valuable basic dyes discovered by Green when the bases obtained by the reaction of sulphur on *p*-toluidine are fully alkylated. A simultaneous discovery by the firm of Cassella led to the introduction of thioflavin T. Green's employers never took up the manufacture of this valuable dyestuff (*J. Soc. Dyers and Col.*, 1917, **33**, 139, 140). The discovery of primuline and its development created a whole chapter of dyestuff chemistry, competent exploitation of which could, in the judgment of well-placed observers in the German industry, have put the English firm in the front rank of the world's chemical manufacturers (*J. Soc. Dyers and Col.*, 1930, **46**, 341).

From now on, until he left industry in disgust, Green was occupied in a series of useful dyestuff inventions and their industrial development. Azo dyes and derivatives of dehydrothiotoluidine occupied most of his attention. This very substantial contribution to industry is, as usual, only sketchily described in the patents and occasional papers appearing in Green's name about this time. Some time after he became chief chemist and manager to the Clayton Aniline Company he took up the study of the stilbene dyes which was to occupy his interest, on and off, for a number of years. This class of dyestuffs is derived from *p*-nitrotoluene-*o*-sulphonic acid by treating it with alkali under various conditions. The first of the dyes which had been obtained by this reaction, known as sun yellow, or direct yellow A, was thought (Bender and Schultz) to be azoxystilbene-disulphonic acid :



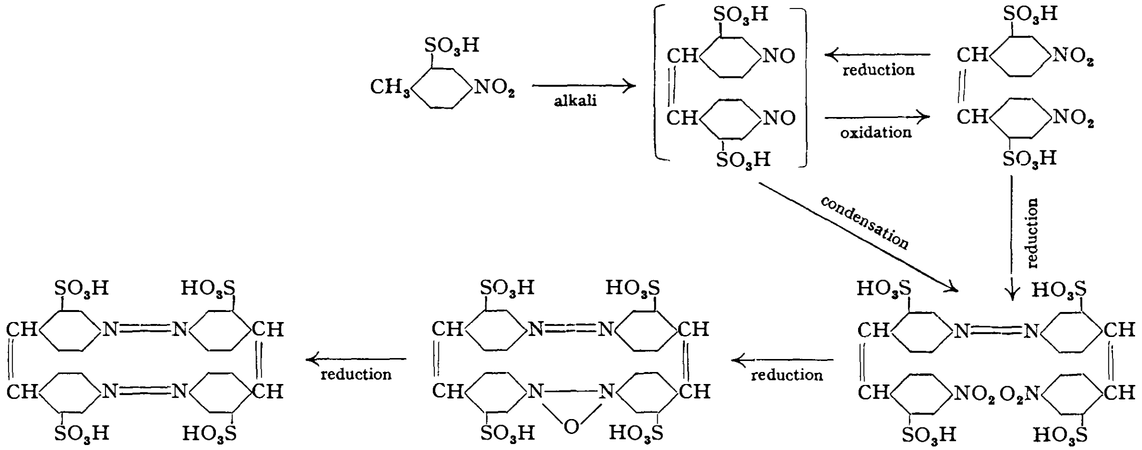
$$\begin{array}{l} \mathrm{CH\cdot C_6H_3(SO_3H)\cdot N} \\ \| \qquad\qquad\qquad\quad | \\ \mathrm{CH\cdot C_6H_3(SO_3H)\cdot N} \end{array} \!\!> \mathrm{O}$$

This formula implies reducing conditions in the condensation. On further reduction a redder shade was obtained in which the azoxy group was supposed to be replaced by an azo group (Mikado orange), whereas under mildly oxidising conditions a greener shade of yellow was obtained (Mikado golden yellow). Green studying these obscure reactions discovered dinitrostilbenedisulphonic acid :



$$\begin{array}{l}\mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}NO_2}\\ \Vert\\ \mathrm{CH{\cdot}C_6H_3(SO_3H){\cdot}NO_2}\end{array}$$

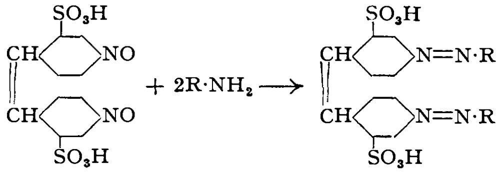
to be the end product of oxidative condensation and from this starting-point he rationalised the preparation of the stilbene dyes. He manufactured them all from one starting-point, dinitrostilbenedisulphonic acid, by alkaline condensation under increasingly strong reducing conditions. In this way he obtained a series of dyestuffs, starting from a greenish yellow and gradually reddening to an orange, which issued under the trade name of stilbene yellows and oranges of various brands. This systematic procedure gave dyestuffs of improved brightness and purity and resulted in valuable business. The stilbenes, together with the thiazoles, still constitute the main bulk of the yellow direct cotton dyes. Remembering that Green had developed the thiazole series also at Clayton, it is not surprising that his company held an important position in this section of the dyestuffs field, a fact recognised jocularly at the time by references to Clayton's " Gelbsucht " (jaundice).



Green's interest in the stilbene class of dyes did not cease with the elaboration of manufacturing methods. He was not satisfied with earlier views on their constitution and began to work on the problem. This work was not completed, however, until ten years later, and is described as a series of papers * published from the Clothworkers' Research Laboratory at Leeds, in which it was finally established that the dyes obtained from *p*-nitrotoluenesulphonic acid were azo compounds, the azo group joining two stilbene residues in their *pp* positions; the *p'p'* positions being occupied by an azo, an azoxy, or nitro groups, according to the degree of oxidation or reduction which had taken place during the alkaline condensation. The mechanism is shown on the scheme above, which postulates the transition formation of a nitrosostilbene, this being the cause of the intense red to blue colouration observed initially when *p*-nitrotoluene derivatives are acted upon by alkali.

Further action of reducing agents results in the formation, first, of a leuco (hydrazo) compound, and, finally, of diaminostilbenedisulphonic acid. The above scheme over-simplifies the actual commercial processes, of course, since a mixture of products is usually obtained consisting not only of stilbene dyes containing a varying ratio of azo, azoxy and nitro groups, but also dinitrodibenzyl derivatives (generally tending to be formed under conditions of milder alkalinity) and traces of azomethine derivatives and aldehydes.

By his work on the constitution and mechanism of the formation of the stilbene dyes, Green paved the way to a further extension of the series. He knew already in his Clayton days that dinitrostilbenedisulphonic acid could be condensed in alkaline solution with various amines to produce stilbeneazo dyes, the formation of which he later attributed to the reactive intermediate nitroso compounds, *e.g.* :



In all probability the products are mixtures, as in the case of the stilbene yellows.

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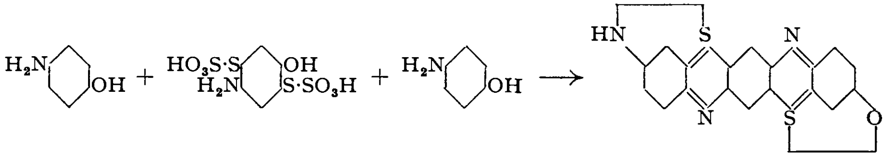
* Green (*J.*, 1904, **85**, 1424); Green, Marsden, and Scholefield (*J.*, 1904, **85**, 1433); Green and Crosland (*J.*, 1906 **89**, 1602); Green, Davis and Horsfall (*J.*, 1907, **91**, 2076); Green and Baddiley (*J.*, 1908, **93**, 1721).

The reaction was later extended by dyestuff manufacturers in several countries to include a wide variety of aminoazo compounds as reactive amines. This has resulted in a considerable number of valuable dyestuffs, chiefly browns, which constitute a major slice of that section of the direct cotton colour range.

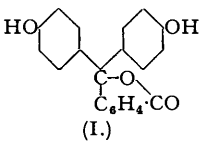
Although developments in the thiazole and stilbene group of dyestuffs represent Green's main achievement in his Clayton period, he introduced a number of miscellaneous azo dyes, chiefly of the direct cotton series, *e.g.*, various rosophenine brands. There is, however, one other main topic to which he gave much attention, though without achieving the degree of success which attended his efforts in other fields.

The sulphide dyes which had already attained some importance, during the last years of Green's stay at Clayton, reached the climax of their development with the arrival of the most important of them all, the famous black obtained by the thionation of 2 : 4-dinitrophenol. The chemistry of the sulphide dyes was unknown and their manufacture was (and still is) based on pure empiricism. Green thought that greater progress could be made if the constitution of the sulphide dyes could be ascertained and their synthesis thereby systematised. He attacked this formidable task, starting from Vidal's view that the sulphide blacks are polythiazines. He attempted a synthesis by making a dithiosulphonic acid of a *p*-phenylenediamine or of a *p*-aminophenol and oxidizing these together with amines, a scheme illustrated by the following example, in which the dithiosulphonic acid obtained by reacting nitrosophenol with sodium thiosulphate in acid solution is reacted first with two molecules of *p*-aminophenol :

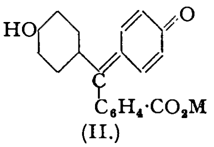


This compound in the third phase of the reaction gave a sulphide dye (Green and Perkin, *J.*, 1903, **83**, 1201; Green and Meyenberg, B.PP. 21,832, 1898; 22,460, 1898; 22,847, 1898; 5039, 1899; 18,658, 1899; 4792, 1900). Along such lines several brands of Clayton fast blacks were made, which, on account of their freedom from the by-products of the usual sulphide " melt," were recommended as non-tendering and capable of use in calico printing (Green, *J. Soc. Dyers and Col.*, 1901, **17**, 89; Green and Meyenberg, B.PP. 15,413, 1900; 15,414, 1900). These blacks were lacking in some other respects, however, and Green concluded, too, that the thiazine hypothesis did not apply to them, but that they were more analogous to aniline black in constitution, *i.e.*, were probably polyazines. The molecule is certainly complex, and depends for its dyeing properties not on its nuclear structure, but on the presence of –S–S– groups which, in the sulphide dye-bath, are reduced to –SH groups, which confer solubility. The soluble leuco compound is absorbed by cellulose fibres, on which it reoxidizes to the insoluble –S–S– form and is then resistant to weak alkalis, acids, and to washing. No substantial advance has been made on these views of the chemistry of the sulphide blacks.

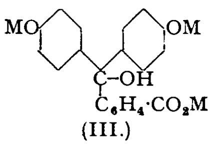
The only aspect of theoretical chemistry which interested Green to any extent was the quinonoid hypothesis as a convenient logical means of explaining the tinctorial properties and the chemical behaviour of dyestuffs, as well as many of the steps in their synthesis. He had been immensely attracted by Thiele's explanation of quinonoid addition and his theory of unsaturation and conjugation. Green became a great advocate of these ideas in their application to dyestuffs, and they made his teaching lucid in a high degree (for an example of this see his paper on " Quinonoid addition as the mechanism of dyestuff formation," to the Eighth International Conference of Applied Chemistry). Various studies bearing on this topic are reported in several of his papers [*] extending over many years. His most challenging contribution was an attack on the textbook explanation [†] of the well known behaviour of phenolphthalein with alkalis (with A. G. Perkin, *J.*, 1904, **85**, 398). The physical chemists were inclined to the view, first advanced by Ostwald, that colour was the result of ionization, *i.e.*, the colourless acid of phenolphthalein forms salts, the ions of which are coloured. Green made the elucidation of the behaviour of the phthaleins a test case and the evidence of his experiments was accepted by Hantzsch as absolutely disproving the physical theory. Green's contention may be summarized thus : in phenolphthalein the coloured form has the quinonoid configuration (II), the original colourless acid and the colourless salt resulting from the action of excess alkali being represented by (I) and (III) respectively :



(I.)



(II.)



(III.)

This view of the *p*-quinonoid structure of phenolphthalein (coloured form) follows, of course, the ideas put

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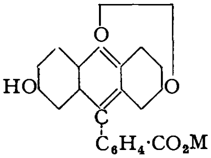
[*] *Proc.*, 1892, 195; *Proc.*, 1896, 226; *Ber.*, 1899, **32**, 3155; *Z. Farb. u. Textilchem.*, 1902, **1**, 413 ; (with F. M. Rowe) *J.*, 1913, **103**, 508.

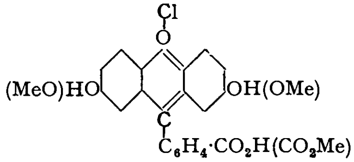
[†] Ostwald, " Wissenschaftliche Grundlagen der Analytische Chemie."

forward to explain the structure of the triphenylmethane dyes by E. and O. Fischer and by Nietzki, *i.e.*, that they are *p*-quinonoid. In the case of quinolphthalein, for which a *p*-quinonoid formula cannot be written, Green postulated an *o*-quinonoid, oxonium, structure, *i.e.* :

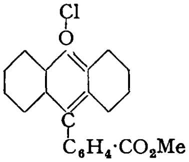


(coloured form)

These views found confirmation in the preparation and study of the ethers and esters of the phthaleins, and in the case of the quinolphthalein the oxonium idea found striking support in the discovery of the series of coloured chlorides (Green and King, *Ber.*, 1906, **39**, 2365; 1907, **40**, 3724. See also *J. Soc. Chem. Ind.*, 1908, **27**, 4; 1909, **28**, 638) :



Analogous oxonium chlorides (Green and King, *Ber.*, 1908, **41**, 3434) of the methyl esters of fluoran were also prepared in order to strengthen the case still further, *e.g.* :



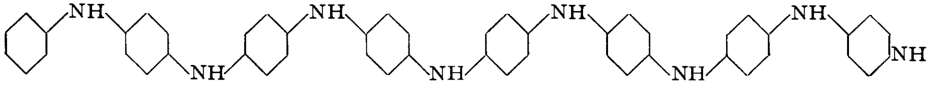
Green made important contributions on the subject of aniline black, on both the chemical and technological sides. Although one of the oldest of dyestuffs, having been observed by Runge in 1834, and having been in industrial use since 1862, its constitution and the mechanism of its formation were unknown. There had, moreover, been no substantial change in the commercial production of aniline black, which takes place on the fibre through the oxidation of aniline hydrochloride, generally with sodium chlorate and a copper salt in the presence of heat and moisture (" ageing "), finishing off with a sodium dichromate bath. Variations of the process consist in the replacement of the copper salt by a ferrocyanide or by a vanadium salt. All these methods require great care to avoid damage to the cotton fibre, which could arise from the presence of hydrochloric acid or oxides of chlorine which could be formed under the conditions of the process. Green endeavoured to mitigate these defects by replacing chlorate oxidation by air oxidation, using a small quantity of *p*-phenylenediamine in the presence of a copper salt as the oxygen carrying system. This process was patented (B.PP. 16,189, 1907; 19,129, 1912) and was successfully reduced to practice by Green and P. F. Crosland in several well-known Continental dye works.

Green speculated, of course, on the rôle of the *p*-phenylenediamine in the new process (*J. Soc. Dyers and Col.*, 1909, **25**, 188) and was led to study the mechanism of the formation of aniline black. He differentiated between " ungreenable " aniline black, which is the end stage of the dyeing process, and products then undergoing investigation at the hands of Willstätter and his school which these workers thought to be aniline black (*Ber.*, 1909, **42**, 2147, 4118; 1910, **43**, 2976; 1911, **44**, 2162), but which in Green's view, merely represented intermediate stages to the formation of the true black. This led to controversy (Green and Woodhead, *J.*, 1910, **97**, 2388; 1912, **101**, 1117; *Ber.*, 1912, **45**, 1955; Green and Wolff, *Proc.*, 1912, **28**, 250; *Ber.*, 1911, **44**, 2570; 1913, **46**, 33; Green and Johnson, *Proc.*, 1913, **29**, 276; *Ber.*, 1912, **45**, 33; 1913, **46**, 3769), but eventually the work of Green's school substantiated his views by identifying the products of the stepwise, *in vitro*, oxidation of aniline with the successive stages in the production of the commercial black and thus establishing a plausible rationale of the process.

According to Green the first stage of the formation of aniline black consists in a series of oxidative additions of aniline to aniline in the manner of indamine formation (*i.e.*, linear) until eight aniline residues have been condensed.

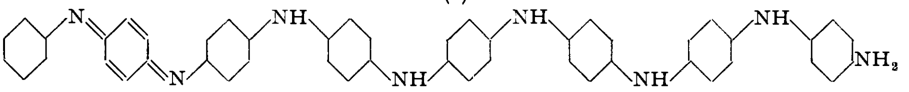
Under carefully controlled conditions in the laboratory the products obtained from the oxidation of aniline salt by any of the commercial aniline black oxidation methods is either emeraldine or nigraniline, which substances are identical with the products well known to the aniline black dyer under these names. Emeraldine and nigraniline are merely oxidation stages of the same leuco compound which is the parent of all these substances, and also of two other oxidation stages which were discovered and named protoemeraldine and pernigraniline. The series is represented thus :

(1)



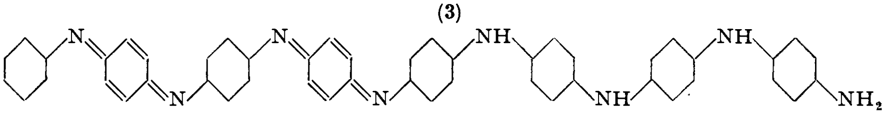
Leucoemeraldine

(2)



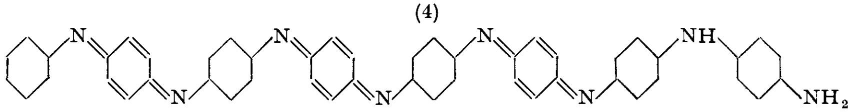
Protoemeraldine (monoquinonoid)

(3)



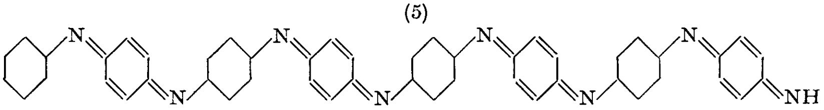
Emeraldine (diquinonoid)

(4)



Nigraniline (triquinonoid)

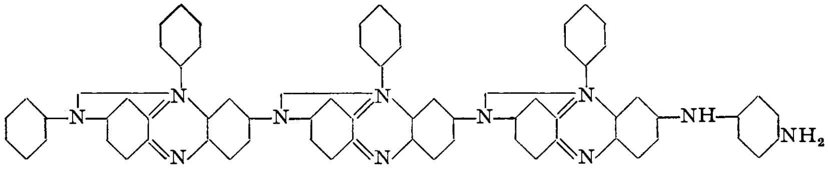
(5)



Pernigraniline (tetraquinonoid)

Degradation results from more drastic action and the molecule breaks down to quinone as would be expected from its linear structure.

From his chemical work and technological observations Green was able to demonstrate that the final stage in the formation of aniline black is of an entirely different type from those which precede it, which are pictured above. Free aniline is involved and without it the reaction cannot get beyond the nigraniline stage, *i.e.*, the ungreenable black cannot be formed. Neutral conditions are also necessary, such as in fact prevail in the last stage of the commercial process, the bichromate treatment. In the laboratory such conditions give a product identical with the true aniline black and Green explained the formation of the latter in practice as being due to residual free aniline, still present on the cloth when it emerges from the ager and before it enters the dichromate bath. From these observations Green felt justified in concluding that the last phase in the aniline black process is an oxidative addition of further aniline with ring closure of the safranine type to give a salt (usually the chromate) of the triphenylazoniumoctaphenazine :

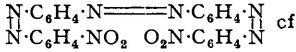


The conditions of the aniline black process are varied for commercial reasons and the degree of " ungreenability " attained depends on the completeness or otherwise of formation of the azine rings (Green and Wolff, *J. Soc. Dyers and Col.*, 1913, **29**, 105; see also Green and Johnson, *ibid.*, p. 338).

The similarity between the colour reactions of dinitrostilbene and of dinitroazobenzene, and the parallelism suggested by the formation of both substances by hypochlorite oxidations, thus :

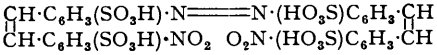
$$CH_3{\cdot}C_6H_4{\cdot}NO_2 \longrightarrow \begin{array}{l} CH{\cdot}C_6H_4{\cdot}NO_2 \\ \| \\ CH{\cdot}C_6H_4{\cdot}NO_2 \end{array} \qquad NH_2{\cdot}C_6H_4{\cdot}NO_2 \longrightarrow \begin{array}{l} N{\cdot}C_6H_4{\cdot}NO_2 \\ \| \\ N{\cdot}C_6H_4{\cdot}NO_2 \end{array}$$

led Green to study the alkaline condensation of nitro-hydrazo compounds (Green and Bearder, *J.*, 1911, **99**, 1960; Green and Rowe, *J.*, 1912, **101**, 2003, 2443), with the object of finding further support for his views on the mechanism of the formation of stilbene dyes. Just as the unstable intermediate products (4 : 4′-dinitrosostilbenes) in the formation of stilbene dyes show a deep bluish-red to blue colour in alkaline solution, so also does the partial reduction product of 4 : 4′-dinitroazobenzene. In both cases the alkaline solutions are readily decolourised by air oxidation, the former yielding dinitrostilbene, the latter dinitroazobenzene. Green's work confirmed the product obtained by reducing 4 : 4′-dinitroazobenzene with ammonium sulphide to be dinitrohydrazobenzene. This dissolves in strong alkali with an intense blue colour and in weak alkali with a violet blue colour. By acidifying the latter solution a compound was precipitated which, from analysis, appeared to be 4-nitro-4′-nitrosohydrazobenzene, $O_2N\cdot C_6H_4\cdot NH\cdot NH\cdot C_6H_4\cdot NO$, the coloured salts of which would have the quinonoid structure, $MO\cdot ON{:}C_6H_4{:}N\cdot N{:}C_6H_4{:}NOH$. While, therefore, the resemblance between the intermediate stages in the action of alkali on dinitrostilbene and on dinitroazobenzene is not complete, there is a striking analogy in the final product in the case of the dinitroazo compound, which yields bisnitrobenzeneazoazobenzene (dinitrotrisazobenzene) :



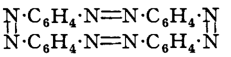
$$\begin{array}{l}N\cdot C_6H_4\cdot N{=\!=\!=}N\cdot C_6H_4\cdot N\\ N\cdot C_6H_4\cdot NO_2\quad O_2N\cdot C_6H_4\cdot N\end{array}$$

cf. Stilbene yellow,



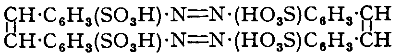
$$\begin{array}{l}CH\cdot C_6H_3(SO_3H)\cdot N{=\!=\!=}N\cdot (HO_3S)C_6H_3\cdot CH\\ CH\cdot C_6H_3(SO_3H)\cdot NO_2\quad O_2N\cdot (HO_3S)C_6H_3\cdot CH\end{array}$$

On alkaline reduction tetrakisazobenzene was obtained,



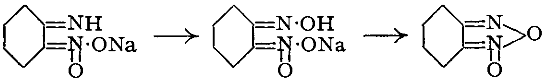
$$\begin{array}{l}N\cdot C_6H_4\cdot N{=}N\cdot C_6H_4\cdot N\\ N\cdot C_6H_4\cdot N{=}N\cdot C_6H_4\cdot N\end{array}$$

cf. Mikado orange,

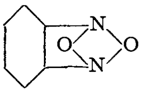


$$\begin{array}{l}CH\cdot C_6H_3(SO_3H)\cdot N{=}N\cdot (HO_3S)C_6H_3\cdot CH\\ CH\cdot C_6H_3(SO_3H)\cdot N{=}N\cdot (HO_3S)C_6H_3\cdot CH\end{array}$$

As the result of observations made during the course of the above work Green was led to investigate the oxidation products of *o*-nitroamines, the result of which are reported in a series of papers in collaboration with F. M. Rowe (Green and Rowe, *J.*, 1912, **101**, 2452; 1913, **103**, 508, 897; 1917, **111**, 613; 1918, **113**, 67, 2023; Green, B.P. 25,205, 1912). The behaviour of the nitroanilines with alkaline hypochlorite led Green to postulate the existence of quinonoid salts, of the nitronic acid type, *e.g.*, $C_6H_4{<}^{NH}_{NO_2Na}$, the reaction proceeding thus in the case of *o*-nitroaniline :



The resulting benz*iso*oxadiazole oxide (or benzfuroxan) was identical with the " dinitrosobenzene " of earlier literature. The constitution finally attributed was the symmetrical one :



because identical products were obtained from the pair of nitrotoluidines: $NH_2 : NO_2 : CH_3 = 1 : 2 : 5$ and $1 : 2 : 4$, and because of other supporting evidence.

Green's last published work in the dyestuffs field related to the so-called " sulphato dyes " and the " ionamines." The major bulk of textile dyeing is carried out in aqueous solution by means of dyestuffs which owe their solubility to the sulphonic acid group attached to an aromatic nucleus. (The sulphonation of rosaniline blue in 1862 by Nicholson was a crucial event in dyestuff history.) Green conceived the idea of solubilisation by means of an extra-nuclear sulphuric ester group and, in collaboration with Saunders, Adams, and Bate, made a series of new dyestuffs of the type $R\cdot NH\cdot CH_2\cdot CH_2\cdot O\cdot SO_3H$ (R represents the rest of the chromophoric nucleus) which are conveniently and economically prepared by introducing the β-hydroxyethyl group into the dyestuff molecule (generally by reaction between an amino group and ethylene chlorohydrin), and then converting it to the sulphato compound by means of sulphuric acid (B.PP. 181,750, 182,031, 185,612, 186,878; Saunders, *J.*, 1922, **121**, 2667; Green and Saunders, *J. Soc. Dyers and Col.*, 1923, **39**, 39). This invention put a useful new weapon into the hands of the dyestuff chemist.

The sulphonic acid group, which plays such a useful rôle in conferring solubility on dyestuffs, has the drawback of enabling the dyeing process to be reversed under certain conditions, *e.g.*, washing with soap or alkali. A further complication arises from the behaviour of the rayon made from acetylcellulose, which has no affinity for dyes containing the SO_3H group, and thus presented a formidable problem to the dyer when it first appeared on the market. Green overcame these difficulties by attaching to a dyestuff devoid of solubilising groups a methyl-ω-sulphonic acid group, a process easily brought about by condensing formaldehyde-bisulphite with an amino group attached to the dyestuff nucleus. Dyes of this type, *i.e.*, $R\cdot NH\cdot CH_2\cdot SO_3H$, are easily soluble in water in the form of their salts, but, on penetrating the fibre, dissociate with loss of formaldehyde and bisulphite, the residual dyestuff, now no longer soluble in water, being left firmly attached to the fibre. When the dyestuff residue indicated by R in the above formula is suitably chosen, useful products for the dyeing of cellulose acetate rayon are obtained which appeared on the market under the name of " ionamines " (Green and Saunders, B.PP. 197,809, 200,873; Green, Saunders, and Frank, B.PP. 212,029, 212,030; Green and Saunders, *J. Soc. Dyers and Col.*, 1924, **40**, 138).

The above account of Green's experimental work covers the main topics which engaged his attention. Isolated researches * and the numerous lectures which he gave cannot be dealt with here, but the service he rendered to the dye technologist by his work on the identification of dyestuffs in substance and on the fibre should be recorded (Green, *J. Soc. Chem. Ind.*, 1893, **12**, 3; Green, Yeoman, and Jones, *J. Soc. Dyers and Col.*, 1905, **21**, 236; Green and Stephens, *ibid.*, 1907, **23**, 118; Green, Yeoman, Jones, Stephens, and Haley, *ibid.*, p. 252; Green and Frank, *ibid.*, 1910, **27**, 83). This work, extending over a number of years, was eventually published in book form. In spite of the volume of his writing on scientific, technological and economic matters, Green was only responsible for one other book, the *Systematic Survey of the Organic Colouring Matters*, adapted from Schultz and Julius's *Farbstofftabellen*, and incorporating a useful synopsis of information on the principal intermediates (published 1894).

The words of Thomas Browne, quoted at the beginning of this notice, are particularly appropriate to our subject. Green's "pure flame" was his creative genius; his "invisible fire" was his extraordinary faith in the urgency of his cause. They sustained a comparatively frail body through a long life, full to the last of fruitful activity. He saw his cause triumphant in the end, though it required the ordeal of war to bring it home reluctantly to his countrymen.

J. BADDILEY.

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* Examples are found in the following references: *Ber.*, 1893, **26**, 2772; (with A. G. Perkin) *J.*, 1906, **89**, 1811; (with R. N. Sen) *J.*, 1910, **97**, 2242; *J.*, 1912, **101**, 1113; (with K. H. Vakil) *J.*, 1918, **113**, 35; (with F. M. Rowe) *J.*, 1918, **113**, 955.