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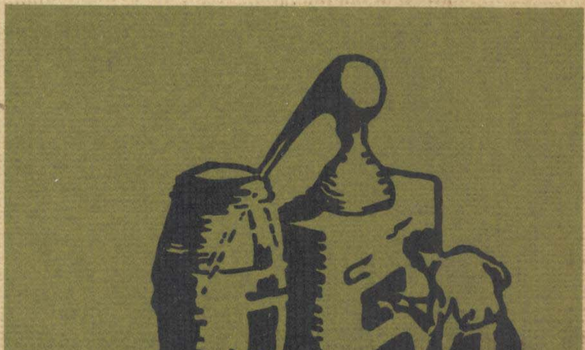

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BY

A. J. GAIT

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Editors' Preface

We were asked by Sir Robert Robinson, O.M., P.P.R.S., to organize the preparation of a series of monographs as teaching manuals for senior students on the chemical industry, having special reference to the United Kingdom, to be published by Pergamon Press as part of the Commonwealth and International Library of Science, Technology and Engineering, of which Sir Robert is a Chairman of the Honorary Editorial Advisory Board. Apart from the proviso that they were not intended to be reference books or dictionaries, the authors were free to develop their subject in the manner which appeared to them to be most appropriate.

The first problem was to define the chemical industry. Any manufacture in which a chemical change takes place in the material treated might well be classed as "chemical". This definition was obviously too broad as it would include, for example, the production of coal gas and the extraction of metals from their ores; these are not generally regarded as part of the chemical industry. We have used a more restricted but still a very wide definition, following broadly the example set in the special report (now out of print), prepared in 1949 by the Association of British Chemical Manufacturers at the request of the Board of Trade. Within this scope, there will be included monographs on subjects such as coal carbonization products, heavy chemicals, dyestuffs, agricultural chemicals, fine chemicals, medicinal products, explosives, surface active agents, paints and pigments, plastics and man-made fibres.

A list of monographs now available and under preparation is appended.

We wish to acknowledge our indebtedness to Sir Robert Robinson for his wise guidance and to express our sincere appreciation of the encouragement and help which we have received from so many individuals and organizations in the industry, particularly The Association of British Chemical Manufacturers.

The lino-cut used for the covers of this series of monographs was designed and cut by Miss N. J. Somerville West, to whom our thanks are due.

J. DAVIDSON PRATT } *Editors*
T. F. WEST

Author's Foreword

THIS book is one of a series on the chemical industry which is, itself, rather a conglomeration of industries than a single industry. It is, moreover, about a part of the industry which is growing rapidly and, at the same time, undergoing great technological changes. From the constantly moving picture the author has tried to describe a "still" for the period about October 1965, together with a description of the developments which led up to the situation at this time and some estimates of the future course of events.

Information on which the book is based has been drawn from many sources; mainly it is based on the author's accumulated experience of some thirty years in the organic chemical industry supplemented by regular reading of scientific publications and technical journals. The author has also received much help from friends and colleagues in the industry and especially from the Directors of Shell Chemical Co., whose approval and encouragement made the work possible, from Mr. E. G. Hancock and many other colleagues in Shell who filled the gaps in the author's knowledge, from Mr. W. A. Dickie and Dr. W. Tyerman of British Celanese Ltd. who helped with information on the early history and current operations of their company and from Mr. H. Bradley and his colleagues at Price's (Bromborough) Ltd. who greatly enlarged the author's meagre knowledge of oleochemicals. To all of these people the author expresses his grateful thanks for their help and interest.

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CHAPTER 1

Historical Introduction

MAN has, perforce, always been interested in natural animal and vegetable materials since he depends on them for his life and well-being; it is in man's efforts to change these materials to meet his growing needs that the roots of the organic chemical industry can be seen to lie. Details of man's first attempts to bring about chemical changes are lost in the mists of antiquity, but it can be inferred with reasonable certainty that they will have been confined to such simple operations as boiling or calcining and, later perhaps, treatment with other materials readily available such as wood ashes or natural earth. It is certain that two processes which have survived to the present day have been known from very early times. These are the fermentation of sugars to produce alcohol—first for potable purposes and later for a host of other uses—and the destructive distillation of wood for production of charcoal in the first instance and later for the recovery of wood tar and other distillation products.

The identity of the human benefactor who first discovered the fermentation process will never be known, but it is fairly certain that, as soon as man had pots in which sugary materials could be left standing, some primitive housewife who could not be bothered to do the washing up will have created the right conditions for the discovery. After this it would only be a matter of time before the changes taking place were noticed, the beneficent effects of imbibing the resultant liquid brought to light and the foundations of one of our most ancient industries firmly laid. After this the discovery of the concentrating effects of distillation may have had to wait for many centuries; it is certain that the process was known to the ancient Greeks, but it is thought that reasonably pure alcohol did not become available until the twelfth century A.D. As the discoverer of fermentation is unknown so, likewise, is the identity of the less beneficent individual who first thought of putting a tax on the products of the industry; this must have happened quite early in the existence of organized societies and the fermentation industries have been a fruitful source of revenue to various rulers and governments ever since. In spite of its long history as a beverage, alcohol did not begin to assume importance as a chemical until the time of the Industrial Revolution in the late eighteenth and early nineteenth centuries. The art of fermentation was given a great boost by the work of Louis Pasteur (1822–95) who showed that the reactions were brought about by the action of microscopic living organisms. Improvements in distillation methods kept pace with improvements in knowledge of the fermentation process and culminated, in 1830, in the introduction of the still designed by Coffey which remained virtually unchanged as a standard piece of equipment in distilleries until well into the twentieth century. In the early nineteenth century pure alcohol was still very expensive due to the high excise duties levied on it. It was quickly realized that this high cost was not only retarding the growth of the industrial alcohol industry, but was also hindering the development of other industries which needed alcohol as a raw material or solvent. In 1855 the Board of Customs and Excise made an order sanctioning the sale of duty-free alcohol for industrial purposes, provided it was first mixed with a small proportion of wood naphtha (methanol) and other materials to make it unpalatable as a potable spirit, and so methylated spirit was born; most other European countries enacted similar legislation at about the same time. This provision has since been broadened and extended by various legal enactments and by regulations issued by H.M. Customs and Excise so that, today, duty-free alcohol can be made available, subject to the appropriate physical controls, in a sufficient state of purity for any chemical process carried out on a substantial scale.

The origins of the wood distillation process, like those of fermentation, are lost in prehistory, but the early Iron Age smelters are known to have used large quantities of charcoal in their operations. Wood tar, also, has been used for caulking the seams of boats and for similar purposes from very early times. Wood distillation has never attained the same importance as an industrial process as fermentation, probably because the yield of chemicals is relatively small, and because developing technology permitted the same products to be made by other means from different raw materials as the demand for them increased.

Already in 1709 Abraham Derby (1677–1717) had substituted coal for wood in iron smelting and in 1796 it is recorded that von Reden in Germany used coke in a blast furnace for the production of iron. However, during the late eighteenth and early nineteenth centuries, the pyroligneous acid from wood distillation was the only source of methanol and was a convenient source of acetic acid and, by calcination of calcium acetate, of acetone. It is interesting to note that in Germany, where the alcohol duties were not as high as in Britain, acetic acid was made by the oxidation of alcohol in the late eighteenth century; this was clearly the most practicable method by which the growing demands for acetic acid could be met, but it appears to have been some time after the introduction of duty free methylated spirit before the process became widely adopted. Although charcoal has been entirely replaced by other forms of carbon for most applications, certain specialized uses for it remain and wood distillation is still carried out on a small scale in Britain today.

It has been shown above how the fermentation industry changed through the period of the Industrial Revolution, roughly from 1750 to 1850. During this period the whole chemical industry, organic and inorganic, experienced a similar growth and development—in fact without it the Industrial Revolution would have been greatly slowed down. In the 1780's Berthollet investigated the nature of oils and fats and Scheele showed that glycerol is a by-product of the saponification reaction.

Shortly afterwards the classic work of Chevreul (1786–1889) demonstrated the nature of the raw materials and the reactions used in soap making. During this period also the process of coal carbonization developed rapidly, the emphasis being more and more on the chemical products rather than the coke; for example, the Earl of Dundonald was granted a patent in 1781 for the production of a substitute for wood tar by the destructive distillation of coal. The by-product gas had already been the subject of investigations since the time of van Helmont in the late sixteenth century and its adaptation for industrial and domestic use by Murdock and by Winsor and Clegg led to greatly increased production of coal tar. Elucidation of the composition of coal tar by such workers as Kekule, Runge and, especially, Hofmann facilitated the development of the dyestuffs industry which was complementary to the enormous growth of the textile industry in the nineteenth century. It is to the pressure put on these early processes by the immense industrial growth of the first half of the twentieth century that the modern heavy organic chemical industry owes its development.

These great developments in technology were only made possible by parallel developments in knowledge. The early chemists believed that organic compounds differed from inorganic in containing some mystic life force derived from their origin in living matter and, even though Berzelius showed in 1814 that organic compounds obeyed the same laws of multiple proportions in their molecular composition as inorganic, he held that they could only be made by living organisms. This belief began to be more and more assailed by chemists until, in 1828, Frederick Wohler produced an undeniably organic compound—urea—from an undeniably inorganic compound—ammonium cyanate. Even then the belief persisted and was finally dispelled in 1862 when Berhelot showed that carbon and hydrogen will react in the electric arc to produce acetylene.

The simple unsaturated hydrocarbons had been discovered quite early—ethylene by Deiman in 1795 and acetylene by Edmund Davy in 1836. Their reactivity made them of great interest to the early chemists and the study of their reactions played a large part in developing an understanding of organic compounds. After 1855 ethylene could be easily and cheaply made from methylated spirit and, after calcium carbide, which had been discovered by Wohler in 1862, became commercially available when Willson established its manufacture in the electric furnace in 1892, acetylene too could be made cheaply on a large scale. Thus, by the end of the nineteenth century, commercial manufacture of two of the most important raw materials of the modern heavy organic chemicals industry was already established.

The nineteenth century was a period of exploitation of natural products; resources in many parts of the world were mobilized to provide for the ever-growing needs of industry in Europe and North America, and the chemical industry grew to provide the means of processing and transforming these materials into finished products. So far, the age of substitution had not arrived and wood, coal, wool and cotton were staple raw materials for many processes. Rubber also became important during this period although it was not until the East Indian plantations, established in the 1870's, began to come into full production about 1895 that the industry could rely on a firmly based supply of raw material. However, this coincided well with the establishment of the motor car industry which is, today, the largest user of rubber and absorbs some 50% of total world production.

Mention of the motor car industry brings us to the exploitation of petroleum and to the development of the great oil industry which has done so much to supply the energy and transport needs of the twentieth century and which has, almost as an afterthought, provided the basic raw materials needed for the growth of the organic chemicals industry.

The existence of petroleum has been known from very early times, but the industry is generally considered to have begun with the completion of Drake's well in Pennsylvania in 1859. As with other naturally occurring materials, the establishment of supplies was only the first stage; finding out how best to use the material is a continuing process and, even today, more than 100 years after the completion of Drake's well, there is still much that is not known about this astonishing material. For an account of the early searches for oil in many parts of the world, the establishment of refining methods and the gradual extension of knowledge on the composition of various crude oils the student is referred to the many excellent books on the subject, of which a selection is given in the reading list at the end of this chapter.

It was quickly found that, in spite of the varied composition of different crude oils, fitting the pattern of products which could be produced to the pattern of demand for them in the market was an ever-present and ever-changing problem. It is to the oil industry's efforts to solve this problem by changing the unwanted oil fractions into useful products that we owe great advances in chemical and engineering technology, especially in the handling and treatment of hydrocarbon gases and liquids in vast quantities, which have found applications in other industries, and especially in the chemical industry.

At first the major demand was for kerosine for lighting and the light petrol fractions were a waste product which was regarded as dangerous and difficult to dispose of. The motor car, which may be said to have been established with the construction of usable vehicles by Daimler and Benz in 1885, was at first seen as providing a God given outlet for the unwanted petrol. The internal combustion engine developed, however, and became more demanding in the quality of its fuel and, by the second decade of the twentieth century, the demands for motor fuel were already creating problems in product pattern for the oil refining industry. These problems were intensified by increasing demands for fuel for aircraft and, to-day, the major part of the industry's technical effort is directed to satisfying the vast but fastidious appetities of these two consumers.

Changes in product pattern from crude oil are usually brought about by breaking down, or "cracking", the long chain hydrocarbons in the high boiling fractions into shorter chain hydrocarbons of lower boiling point and many ingenious methods of carrying out this process have been devised. The importance of these developments from the chemical industry point of view was that, in addition to the desired low boiling petrol fractions, substantial yields of by-product gases were obtained which, unlike natural gas, contained significant proportions of the lower olefins ethylene, propylene and the isomeric butylenes.

It has already been noted that the reactions of these gases had been extensively studied by chemists and it was quickly realized that these by-product streams offered a raw material from which commercially important chemicals might be made on a large scale. Further, the oil refining industry had started by borrowing the techniques and equipment of the chemical industry and had developed them for continuous operation on a vast scale. Construction of the necessary plant, therefore, presented no insurmountable difficulty and the first plant for the production of isopropyl alcohol from a propylene rich refinery gas stream was built by the Standard Oil Co. at Bayway, New Jersey in 1920. Other plants and products soon followed, encouraged by the ready availability of refinery gases and the increasing cost of the traditional raw materials so that, by the outbreak of the Second World War in 1939, the U.S.A. had a large and well-established organic chemical industry based on petroleum and natural gas, which was of vital importance to the Allies during the struggle.

In Great Britain development proceeded along different lines. As a great maritime and colonial power in the late nineteenth and early twentieth centuries, Britain had access to all the natural raw materials of the world and had established vast interests overseas. At home, she had emerged from the Industrial Revolution with great industries based on these raw materials, but with coal as her main indigenous natural resource. Her organic chemical industry consisted chiefly of the manufacture of dyestuffs from the by-products of coal carbonization and of a few simple aliphatic chemicals from the products of fermentation and wood distillation; even in this limited field the initiative was lost to Germany, which had become a great centre of organic chemical research and of industry. Thus, the outbreak of war in 1914 found Great Britain with a small, rather inefficient, organic chemical industry, quite unable to meet the additional demands of the war and not well suited for rapid expansion. The most immediate shortage was of acetone, essential for the manufacture of cordite, which had been mainly imported from Germany. The existing method of manufacture was cumbersome and expensive but, fortunately, in 1912 Dr. Chaim Weizmann had discovered that certain strains of bacteria—the Clostridia—could convert sugars and starches into alcohols, ketones and acids and that one strain—*Clostridium acetobutylicum*—produced mainly acetone and butanol. This process had been set up on a commercial scale by Messrs. Strange and Graham in 1913/14 and clearly offered the best prospects for rapid expansion. It attracted the attention of Mr. Lloyd George, at that time responsible for expanding the production of military supplies, who is reported to have waved a test tube of acetone during a speech in the House of Commons —surely one of the earliest instances of a governmental interest in science. Although a plant was built at the Royal Naval cordite factory at Holton Heath, the greater availability of raw materials in North America, as in the 1939 war, made it advantageous to carry out the process there and plants were built in Canada and, later, in the U.S.A. at Terre Haute, Indiana. The latter plant was erected by the U.S. Government and, when it was offered for sale at the end of the war, a company named Commercial Solvents Corporation was formed to buy and operate it.

Another pioneering effort at this time was the establishment by H. A. Dreyfus in 1916 of the British Cellulose and Chemical Co., later to become British Celanese, at Spondon, near Derby. This company produced cellulose acetate lacquers for doping the fabric used for covering the aircraft of that day. The acetate had the advantage of being less inflammable than the nitrocellulose used up to that time; it is for its work in the development and manufacture of cellulose acetate fabrics and plastics that the company has continued to be best known up to the present day. In order to supply the acetic anhydride required for cellulose acetate manufacture, the company built a plant for production of calcium carbide and it was, in fact, the availability of coal for power production and of coke and lime as raw materials for the carbide which caused the company to choose the Spondon site. The processes by which the acetylene was converted to acetic anhydride will be referred to later; their use by this company at such an early date represents a considerable achievement. Indeed this company has never been a major factor in the marketing of chemicals but the development work which it has carried out in its efforts to manufacture its own requirements of organic chemicals has undoubtedly stimulated the British chemical industry as a whole.

After 1918, as the country began to recover from the war, the great upsurge of industrial activity engendered by it spilled over into civil life as manufacturers tried to develop peacetime applications for plant and products designed to meet war needs. It was found, of course, that other countries had similar problems and British industry, struggling to adapt itself to peacetime conditions, became subjected to severe competition from imports, especially from Germany and the U.S.A. Britain had, up to this time, been essentially a free trade country, but the memory of the shortages of vital materials in the early stages of the war now persuaded the Government to introduce protective legislation, and the Safeguarding of Industries Act, 1921, imposed a $33\frac{1}{3}\%$ *ad valorem* duty—the Key Industries Duty or K.I.D.—on many industrial products including most organic chemicals. This was followed in 1928 by the Import Duties Act which imposed a 10% *ad valorem* duty on virtually all imports, including most chemicals not already covered by K.I.D., except foodstuffs and basic raw materials not indigenous to Britain. The Act imposing K.I.D. also included provisions for dealing with appeals against the inclusion or exclusion of particular materials in the schedules of products subject to the duty. There were also arrangements for temporary exemption from the duty where a material was not made in the U.K. or where home production was inadequate Applications and appeals under this procedure have been a feature of the chemical business for nearly forty years. One of the first was the plea by the British Cellulose and Chemical Co.

in December 1921 that calcium carbide had been improperly excluded from the list of organic chemicals covered by the Act, and one of the last that by I.C.I. and others, just before the Act was repealed in 1958, that polyethylene had been similarly treated. In both cases it was decided that the materials were not organic chemicals as defined by the Act. Although much of the earlier legislation dealing with import duties was consolidated in the new Import Duties Act in 1958, this did not alter the incidence of duties at that time, but provided a somewhat different and more uniform procedure for dealing with changes in, and exemption from, duty.

Behind the protective tariffs industry began to develop; American production line methods were introduced into the motor car industry and the growing output of cars and lorries made demands on other industries, especially for steel sheet, rubber and paint. Nitro-cellulose lacquers became the standard finish for vehicles and these, in turn, needed ketone and ester solvents unknown to the conventional paint industry. It was found that these new finishes tended to be brittle, but could be made more flexible by having "plasticizers" incorporated in them and so another important branch of the organic chemical industry became established.

Companies with "know how" in the aliphatic chemical field were quick to take advantage of this growing market and the names of A. Boake Roberts & Co. and Howards of Ilford appear often in the advertisements for lacquer solvents of that period. The Distillers Co. Ltd. erected a factory at King's Lynn for the production of n-butanol and acetone by the Weizmann fermentation process; this plant was unfortunately wrecked by an explosion and fire almost before it had attained full output. Instead of rebuilding it, the company pursued its efforts to gain a share of the solvents market by the formation, jointly with the German H.I.A.G. company, of a new company, British Industrial Solvents Ltd. A factory was built near Hull in 1929 for the production of acetone, acetic acid and n-butanol, using ethanol drawn from the adjacent D.C.L. owned Hull Distillery Co. and