

lights easily and does not go out overnight; accordingly, the questions of coke reactivity and size become the pertinent issue and the metallurgical requirement is the direct contrary of the domestic need. There are, however, situations in which hard coke may suffice for the domestic boiler; they may be defined by suitable experiment.

Progress has been made in the Association's contribution to the provision of cheap and effective methods of liquid-effluent treatment and measures to be taken for the reduction of the emission of smoke, dust and grit at coke ovens. With regard to the former, the Association is supporting, both financially and technically, basic research at the University of Leeds into the biological treatment of gas liquors. Considerable strides have been made in the study of the activated sludge process as applied on a coke-oven plant and of the relative merits of percolating filter processes. It is most interesting to know that these microbiological processes can destroy such undesirable constituents of waste liquors as phenols, cyanides and thio-salts, including thiocyanates, substances which by their poisonous activity can persuade even the scientists to describe some of them as 'devil liquor'. Perhaps even more interesting to the layman is the fact that spoil heaps may be brought into service as percolating filters, and where they also have lagoons these may serve as means of aeration. To bring the rejected refuse of the

mine back as an active agent in solving surface effluent problems is indeed to raise slumbering devils to serve mankind. The genus *Thiobacillus* would appear to give much scope for study, since preliminary results indicate that the organisms reported in the literature are only a fraction of those that exist in Nature. In the matter of atmospheric pollution much has been done in the mitigation of air pollution as the result of the training of coke-oven staff and operatives.

In the associated work of the Northern Coke Research Laboratory the tradition of the devotion to fundamental studies has been sustained. They involve methods of adsorption and microwave spectroscopy. The objectives include the unravelling of the mechanism of the adsorption on carbon of oxygen, carbon dioxide and nitrogen under controlled conditions. It is a problem which has challenged the scientific world since the earliest physical chemists applied the methods of chemical kinetics to the basic problems of combustion. The latest methods permit rapid determination of surface area, an essential parameter.

Coke science is not like nuclear science, a subject which makes popular news, but progress which is respected by that section of the scientific world able to appreciate the problems involved is just as worthy of recognition. The Council of the Association, its director, Mr. G. W. Lee, his colleagues and staff are therefore indeed to be congratulated on their achievements. R. J. SARJANT

GEOMETRICAL OPTICS

THE Optical Society of America, at its Rochester meeting in October 1962, awarded the Frederic Ives Medal for distinguished work in optics to Dr. M. J. Herzberger, the head of the geometrical optics department and senior research associate, Research Laboratories, Eastman Kodak Co. The Medal was presented on October 4 by D. L. MacAdam, the president of the Optical Society. A list of some 150 of Dr. Herzberger's publications is given in the June issue of the *Journal of the Optical Society of America* (53, 659; 1963) together with the text of his address entitled "Some Recent Ideas in the Field of Geometrical Optics". Dr. Herzberger discussed three particular optical problems on which he had worked—the analysis of optical images, the improvement of achromatic systems, and the algebraic method of designing optical systems. The use of spot diagrams to describe image formation in optical systems is illustrated by application to the analysis of the so-called 'rim-ray curves' and the four-element air-spaced compound triplet, an $f/5$, 300-mm 'Tessar'-type lens, is taken as a numerical example. The method will appeal to those who prefer to think in pictures rather than numerically. In 1959, Dr. Herzberger discovered that it was possible to design lenses, with or without fluorite, which were corrected for colour over a wide range of wave-lengths. The fundamental idea is to consider the refractive index n , and not its square, as a characteristic physical quantity, and to utilize the dispersion formula:

$$n = A + B\lambda + C/(\lambda^2 - \lambda_0^2) + D/(\lambda^2 - \lambda_0^2)^2$$

where λ_0 is a constant which for the wave-length range 365 m μ to 1.01 μ and 176 glasses and other transparent substances used in optical design has the value 0.168 μ . Four data are therefore required to fix the dispersion of an optical substance in the visible region. The data suggested are discussed, and it is shown that two glasses can be used to design an achromat, and if three lens elements made of different glasses are used a super-achromat can be designed which is corrected for four colours.

The basic mathematical problems associated with the algebraic design of optical systems, that is without ray tracing, have recently been solved by Dr. Herzberger, and the work remaining consists only of the elementary, but tedious, job of the algebraic solution of certain linear equations with algebraic coefficients and the same non-zero determinant for all orders. In his address Dr. Herzberger explained the meaning of the 'characteristic function' or 'eikonal' and posed the two questions, the answers to which would reduce the designing of lenses to pure mathematics. He then outlined the procedure adopted to determine the focal eikonal to any desired order for an image formation given by a single thick lens with two aspheric surfaces. Dr. Herzberger concluded by saying that he felt confident that it would not be long before the brain achieves a decisive advantage over the computer in the design of optical systems.

FLUOROCARBONS

THE origin of the organic fluorochemicals industry lay in the refrigeration industry wherein, following several fatal accidents, there arose an urgent demand for a non-inflammable, non-toxic, low boiling-point refrigerant. The pioneers working for General Motors were Drs. McNary, Midgley and Henne, who carried out research on compounds of carbon, fluorine and chlorine, particularly CCl₂F₂, made by the action of SbF₃ on carbon tetrachloride. Prof. M. Stacey of the University of Birmingham con-

tributes an interesting article on this subject in the Spring 1963 issue of *Catalyst*, the excellently written and illustrated industrial journal of the Shell Chemical Co., London. "Success was immediate and dramatic", says the author, "and, in 1931, in collaboration with Du Pont, General Motors formed the corporation Kinetic Chemicals which began the commercial production of a range of colourless odourless non-toxic and non-inflammable fluorochlorocarbons which were named the Freons".

These compounds derive from the reaction of anhydrous hydrogen fluoride on carbon tetrachloride, chloroform or ethylene. There are five major ones, CCl_2F_2 , CCl_3F , CHClF_2 , $\text{C}_2\text{Cl}_3\text{F}_3$ and $\text{C}_2\text{Cl}_2\text{F}_4$; these together constitute 95 per cent of the fluorochlorocarbons at present being used in industry. To-day they are produced in fourteen different countries and are severally known by titles such as 'Freons', 'Arctons', 'Isecons', 'Genetrons', 'Foranes', 'Eskimons', etc. World annual production is now in the region of 150,000 tons.

Besides refrigerants, however, there are other important applications of and developments from these fluorocarbons. One example is found in certain pressure packaging 'aerosols'. "As aerosol propellants, their production has risen dramatically in ten years from about 40 million units (cans) to 500 million units, and world production is still growing". Another development is a remarkable plastic based on tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$). In its polymerized form, $(\text{CF}_2)_n$, this plastic possesses quite exceptional properties; it is chemically inert to solvents, acids, alkalis, oxidizing agents, steam, lubricants, etc.;

at temperatures up to 300° C only fluorine gas and molten alkali metals attack it. As polymerized tetrafluoroethylene is thermally stable up to 300° C and has a constant and low power factor, it is especially valuable for electrical uses also in highly corrosive environments.

Prof. Stacey states: "... a number of new oils and plastics are now made from trifluoro chloroethylene and co-polymers. Various fluoro alcohols are being developed as monomers for polymers, and the esters of these alcohols are being used as stable lubricants". On a practical laboratory scale, it is found that the life of ground glass joints can be prolonged by covering them with polymerized tetrafluoroethylene sleeves as a protection against action of corrosive liquids. The article also gives details of the biological developments of these compounds and concludes: "Thus it will be seen that potentialities for synthesis are even greater than in the vast area of coal tar chemistry. There are prospects for new dyestuffs . . . new drugs and medicinals, as well as new materials for the study of reaction mechanisms".

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REDUCTION OF OXYGEN AT A CARBON ELECTRODE EMERGING FROM AN ELECTROLYTE

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PHERSCH¹ has described an experiment in which the corrosion of a metal is facilitated by the presence of a three-phase boundary between metal, electrolyte and the atmosphere. Weber² investigated the transport of oxygen to metal cathodes. He found that metal cathodes afforded higher current densities when partially submerged. Will³ examined the oxidation of hydrogen at platinum electrodes. He found that a large increase in current occurs when the electrode is partially immersed in the electrolyte. The entire electrode was wetted by the electrolyte and no three-phase boundary existed; the oxidation occurred almost exclusively in a narrow region at the upper edge of the electrolyte meniscus and the adjacent film close by.

The purpose of this article is to describe similar experiments in which oxygen reduction at porous carbon cathodes is enhanced by raising the electrodes in the electrolyte.

One of the factors which limits the capacity of a fuel cell is mass transport of oxygen to the cathode. It is generally believed that oxygen first dissolves in the electrolyte and then diffuses to the surface of the cathode for reaction. It is desirable to have an electrode of large surface covered with a thin film of electrolyte in which the dissolved oxygen reaches this surface by diffusion along a short path. Establishment of large extents of this electrolyte film of optimum thickness is one of the difficulties encountered in the preparation of fuel cell electrodes.

A porous carbon electrode partially submerged in an electrolyte which wets it should have on it a film of varying thickness. An electrode under these conditions should show a larger current capacity than when it is completely submerged. This increase in current has been observed for porous carbon cathodes at which oxygen is being reduced in an electrolyte of aqueous potassium hydroxide.

The electrolyses were carried out in an H-shaped glass vessel with separate electrode compartments. The electrode assemblies were held in place by rubber stoppers. The anode was a porous block, 2.5 × 2.5 × 7 cm, made of Stackpole No. 139 carbon. The cathodes were made of porous carbon rods, 6-7 cm long, with circular cross-sections. These cathodes were sealed in U-shaped

holders of glass with either epoxy resin cement or Corning 'RTV-731' silicone rubber. The cathode compartment of the electrolysis cell was provided with a tube for entry of oxygen into the catholyte via a fritted glass gas dispersion tube. Another tube permitted oxygen to enter only the vapour space above the electrolyte. A saturated calomel electrode was used as the reference electrode. The electrolyte was aqueous potassium hydroxide of density 1.302 g/cm³ at 25° C (a nominal 40 wt. per cent solution). The potassium hydroxide solutions were prepared with A.C.S. reagent grade potassium hydroxide pellets using water having a specific resistivity of 2.0 - 4.0 × 10⁶ ohm cm. The oxygen was U.S.P. grade twice washed with water before use. Fig. 1 illustrates the principal parts of the electrolysis cell.

After assembly of the cell with the cathode in the submerged position, oxygen, saturated with water vapour, was bubbled through the potassium hydroxide solution for a period of 2-4 h. The oxygen was then arranged

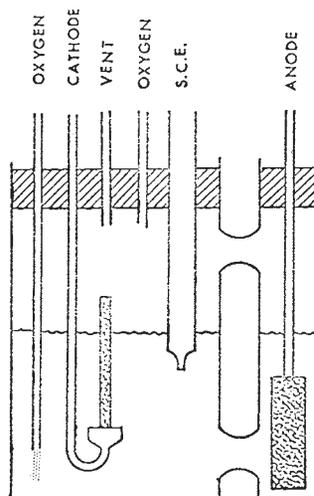


Fig. 1. Electrolysis cell