

## THE CHEMICAL RESEARCH LABORATORY

THE annual open days of the Chemical Research Laboratory (Department of Scientific and Industrial Research) were held during October 1-4.

The Corrosion of Metals Group showed the results of research, on behalf of the British Shipbuilding Research Association, on methods of preventing pitting of mild steel tubes in Scotch marine boilers. Electrically heated model boilers were in operation, and corroded boiler tubes after test were displayed. Results were summarized in the form of curves showing the influence of various factors on the depth of pitting of the tubes. An increase in salinity or in oxygen content of the boiler water increases the rate of pitting. Even in very adverse conditions, however, the danger of serious pitting can be greatly reduced if the boiler water is kept slightly alkaline or the copper content of the mild steel tubes is more than 0.1 per cent.

Fundamental and applied investigations of corrosion inhibition in aqueous solutions were illustrated. The use of radioactive tracers has enabled a quantitative study to be made of the formation of invisible films on iron and steel immersed in solutions of corrosion inhibitors such as sodium chromate, sodium nitrite and sodium benzoate. After a short initial period of rapid adsorption, the film grows logarithmically with time of immersion, with an adsorbed film always present. The steel is passivated only if the concentration of inhibitor is maintained at a value sufficient to maintain the logarithmic growth of an oxide film, and an adsorbed layer of inhibitor on the film.

Examples were shown of the effectiveness of combinations of various inhibitors, such as sodium benzoate/sodium nitrite or triethanolamine phosphate/sodium mercaptobenzothiazole, in protecting a wide range of metals and alloys in ethylene glycol antifreeze solutions.

In chemical engineering researches a light transmission instrument has been developed for measurement of the interfacial area in gas-liquid and liquid-liquid dispersions and this instrument is being applied to the evaluation of this property in agitated vessels.

A parallel beam of light is passed down a tube immersed in the dispersion and by means of prisms is caused to pass through the dispersion and thence upward through another tube similar to the first on to a photocell. The second tube is blackened internally to remove scattered light so that only that portion of the incident light beam which meets no obstruction in the dispersion is recorded by the photocell.

The photocell is connected to an electronic integrating device so that a time-average value of interfacial area may be measured in dynamically maintained dispersions.

The two immersion tubes, light source and photocell are rigidly mounted together on a traversing platform so that interfacial areas may be evaluated near to and at various distances from the impeller in agitated vessels.

An attractive display of pure metals was seen in the Inorganic Group. The process of zone refining has been applied not only to the purification of

metals but also to some non-metals like tellurium and to compounds such as indium iodide. One striking effect that was brought out was how closely many metals resemble each other in appearance when pure and when the surface oxide film has been removed. In connexion with the purity of mercury there was demonstrated the 'brightness' test according to which even traces of certain metallic impurities, of the order of 1 in 5-10 million parts, can cause a visible film to form on the surface of the mercury.

The separation of the rare earths by ion-exchange methods was demonstrated, and laboratory and semi-scale equipment for this purpose was in operation.

In the section dealing with spectrographic analysis the emphasis was on the analysis of rare-earth mixtures. The use of a four-step rotating sector to extend a limited range of standard mixtures for calibration purposes was demonstrated, and an improved water-cooled version of the gas cell, enabling high current arcs to be run in atmospheres other than air, was on view. Of interest to users of grating spectrographs was the tabulation of ultra-violet transmission limits of some sixty materials for use as order filters.

The Microanalytical Section exhibited equipment used in routine microanalysis. The 'empty tube' or rapid combustion method was being used for carbon and hydrogen, but the Carius method was preferred for halogen and sulphur. A modified Unterzacher procedure for oxygen was also shown.

New adsorbents and ion-exchange materials for specific purposes were shown by the Radiochemical Group. A typical example was phosphorylated cellulose obtained by treating cellulose with urea and phosphoric acid. This material exhibits cation-exchange properties. The ion-exchange properties of phosphorylated cellulose differ from those of more conventional resins in that certain metals (particularly  $\text{Th}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{U}^{4+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Fe}^{3+}$  and  $\text{UO}_2^{2+}$ ) are adsorbed from strongly acidic solutions (up to 5 *N*). The adsorbed metal can only be eluted with reagents which strongly complex with it, for example, ammonium carbonate for thorium and acetone-hydrochloric acid for iron. This property of phosphorylated cellulose has been applied to the selective recovery of thorium from monazite. Work has continued on solvent extraction as an alternative to ion-exchange for the selective concentration of uranium and other metals from leach liquors. Solvent extraction offers the advantage of continuous counter-current operation, greater flexibility in coping with changes in feed composition, and freedom from mechanical blockage and chemical poisoning which occur in ion-exchange. Against this must be reckoned the loss of solvent to the aqueous phase which represents the chief factor controlling the operating cost of solvent extraction.

Two main types of solvent are used, namely, acidic and basic; the former may be considered as analogous to cation-exchange resins, the latter as analogous to anion-exchange resins; basic solvents are more selective for uranium. Acidic extractants include the long-chain mono- and di-alkyl phosphates, while basic extractants include the many types of high molecular weight amines.

An apparatus for the measurement of low-pressure deviations from the ideal gas laws in the temperature-range of 50–200° C. was shown by the Organic Group; the apparatus is suitable for the study of those organic compounds which have a vapour pressure of at least 200 mm. in that temperature-range. Also shown was an apparatus, still under construction, which has been designed for the precise determination of the latent heats of vaporization of organic liquids, and for the measurement of the specific heats (at constant pressure) of organic vapours; the working temperature-range for this apparatus is likewise 50–200° C.

Of the new developments shown in organic intermediates, the following were of particular interest: a novel method of carboxylation based on the use of sodium ethyl carbonate; the carboxylation of chrysene and pyridine through their sodio-derivatives; the synthesis of a variety of polymeric materials containing the hydrazino group. Particularly noteworthy was the use of N-amino oxazolid-2-one as a source of N-amino ethyleneimine and its polymer, polyethylene hydrazine; the synthesis of arsenic-containing polymers from arsenic pentoxide and epoxides, and the trimerization of aromatic isocyanates in solution in various epoxides by a trace of pyridine.

There is at present considerable interest in the use of electro dialysis for the removal of salt from sea water, or from brackish waters, which are unfit for drinking or irrigation purposes. Successful application of this process depends on the efficiency of the ion-exchange membranes in multi-compartment electrolytic cells. In the High Polymers Group, methods for the preparation of ion-exchange membranes are being investigated, and a study is being made of their electrochemical properties. Membranes prepared by incorporating particles of an ion-exchange resin in an inert binder may contain void spaces which can lead to inferior electrochemical behaviour. Emphasis has therefore been placed on the preparation of homogeneous ion-exchange membranes, and promising cation- and anion-exchange membranes of this type have been prepared.

The possibilities of paper strip chromatography for the analysis of polymers are also being studied in an attempt to find a simple routine procedure for evaluating molecular weight distributions. A synthetic polypeptide (polysarcosine dimethylamide) served as a convenient model polymer since it can be prepared with very sharp molecular weight distributions. Mixed samples of polysarcosines of molecular weights up to 12,000 have been successfully fractionated on paper strips. The best results were obtained by gradient elution, that is, pumping a good solvent steadily into a reservoir of poor solvent from which ascending development took place. In most cases a polymer labelled with carbon-14 was used for assessing the chromatograms.

The Microbiology Group made a feature of the economic and industrial importance of bacteria taking part in the natural sulphur cycle. Various exhibits explained the activities of these bacteria in polluting aviation fuel oils and coal gas, their function in the disintegration of concrete and in the corrosion of buried metals, and the microbial formation of sulphur in Nature. Of special interest was a process, devised at Teddington and now being developed by the London County Council, for producing sulphur from sewage sludge and gypsum by a semi-continuous

fermentation. Continuous techniques, which may well constitute the next important technological advance in the fermentation industries, were also illustrated, and included a novel adaptation of the conventional bubble-cap distillation column. The National Collection of Industrial Bacteria displayed its comprehensive range of assay organisms, which are extensively used by industrial and other research workers for estimating various amino-acids, vitamins and antibiotics.

## INTERNATIONAL COLLOQUIUM ON INTERFERENCE SPECTROSCOPY

THIS colloquium, organized by the Centre National de la Recherche Scientifique, was held at Bellevue, near Paris, during September 9–13.

Interferometric spectroscopy might appear a rather narrow field for an international conference extending over five days. In fact, the organizer, Prof. P. Jacquinot, proved to be wise in imposing a restriction which went as far as excluding diffraction gratings, when used by themselves, as too conventional: there was ample variety, not only of details but also of fundamentally new and interesting approaches. The number of talks and the size of the audience could be kept in reasonable bounds, allowing worth-while discussions to develop. The proceedings of this most stimulating conference are to be published in the *Journal de Physique* and should well represent the main lines of the recent advances in this field. Methods, rather than results, formed the subject of the conference.

Interferometers have a fundamental advantage compared with gratings or prisms, in a way which has been most clearly expressed by Jacquinot in the form of a coefficient of merit. In the latter instruments the path difference depends strongly on the angle, a fact which necessitates the use of a slit. This restriction of area in the plane of the slit, or of angle in the collimated beam, entails loss of light gathered. In contrast to this, interferometers use interference 'in depth', with path differences depending on the angle only to the second power, as shown in the axial symmetry of interference patterns. By imaging an extended source in the plane of an interference pattern rather than on a narrow slit or slit-image, one can gather more light from it.

Full advantage of this can be taken in recording methods where a circular stop is placed in the centre of the fringe pattern, followed by a detector, such as a photo-multiplier. While the path difference is varied at a uniform rate, for example, by variation of the air pressure, the intensity is recorded. This method has lately been increasingly used, and various ways of changing the path difference were described at the conference (R. Chabbal and M. Soulet, J. H. Jaffe, J. Gobert, J. Roig, R. Dupeyrat); besides an alternative method in which the intensity is recorded directly against the air pressure, without a time base (H. G. Kuhn and J. L. Lucas-Tooth).

The quantum efficiency of photocells is generally higher than that of photographic plates, but while the latter collect energy of all wave-lengths simultaneously during the whole time of the exposure, in the recording technique different wave-lengths act