Spectroscopy in the Service of Industry*

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IN recent years, standard spectroscopic technique has been adopted by many industrial research laboratories and has proved a most valuable tool for the identification of the form and nature of impurities which have crept into the materials of ordinary technical processes. It frequently happens that when a manufacturing process goes wrong, there are very few outward and visible signs of the nature of the trouble. A lamp, for example, may have a slightly darkened glass bulb which is indicative of trouble to come. This darkening of the bulb may be due to minute traces, a thin film perhaps, of some deposit. It would be difficult, and sometimes impossible, to determine the nature of the deposit by ordinary chemical means. If the whole of it could be removed it might not weigh more than one ten thousandth of a gram. If the spectroscopist can remove the deposit, he is in an ideal position to give the manufacturer further clues as to the nature of his trouble. Technical processes are also frequently dependent on the addition of a small percentage of some foreign material to the bulk. In applied physics we may mention the quantity of thoria or silica in a tungsten filament; in metallurgy the percentage of nickel or tungsten in a steel.

The methods of excitation of the spectra are usually the standard ones of arc and spark; sometimes the technique of absorption spectra may be used. A very useful modification of the spark method consists in 'exploding' a wire and exciting the spectrum of the resultant vapour. This was developed by J. W. Ryde†, and is of great value in the electrical industry where the quality of wire is such an important factor. In order to facilitate the analysis of unknown spectra, Ryde and Jenkins have developed a special powder containing more than fifty elements. The quantities have been so adjusted that the *raies ultimas* of all of these elements appear when the powder is 'arced'. This method and the 'ratio-quantitative' method of Judd Lewis have been of great assistance in the routine applications of spectroscopy to industrial problems.

The applications of the general spectroscopic method are many, and it is impossible to refer to more than a few here. The exploded wire method has been used with great success on small samples of various metallic wires such as tungsten, nickel and molybdenum. The transmission of ultra-violet light through glass is dependent, among other things, on the quantity of iron present. Preparation of a set of standards containing, say, 0·005–0·05 per cent of Fe_2O_3, enables the quantity of iron in various glass-making sands to be estimated. The testing of steels before they leave the works is now carried out by means of the 'steeloscope'. An upright rod of pure iron comes into contact with the test bar at some convenient point and the arc spectrum is observed. Bars which may have got into the consignment by mistake can in this way be readily identified. This is one of the first instances in which the spectroscope has been used in a routine manner by unskilled workers. Spectroscopic technique has been of great value in the development of hot cathode discharge tubes, such as the Osira lamp. In work of this kind new fundamental information is frequently obtained. With the Osira lamp, changes of colour and intensity can be followed as the pressure of mercury vapour increases: similar effects are to be observed with thallium rare gas spectra, as Krefft has shown.

The work of Hevesy and Laby on X-ray spectra is likely to be of use to industry, but has not yet received wide application. On a broad view, the applications of X-ray diffraction principles may be included in this summary. Provided the crystal structure is known, the X-ray crystallographer can indicate the form of any particular substance. For example, the state of the silica in refractory materials has a considerable effect on the expansion properties. The properties of drawn wires, in respect of crystal orientation, can readily be studied by this method. The cause of the red colour of selenium ruby glasses has been shown to be due to the actual composition of a cadmium selenide-cadmium sulphide solid solution. X-ray investigation of commercial glasses and of carbon blacks has also given useful information. Violet phosphorus has been shown to be fundamentally the same as red phosphorus, the only difference being one of crystal size. Very interesting work on the nature of oxide-coated cathodes has been correlated with their thermionic properties.

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Natural Colouring Matters

IN opening a discussion on September 7 in Section B (Chemistry) of the British Association meeting at Leicester, which followed Prof. R. Robinson's address to the Section on "Natural Colouring Matters and their Analogues", Prof. R. Kuhn first reviewed the inter-relationship of the colouring matters of the carotene group. These substances are synthesised in plants and their molecules each contain forty carbon atoms. They undergo two types of degradation: in the animal body they produce vitamin A by hydrolytic fission, whilst in plants they are oxidised to carotenoids containing fewer carbon atoms. Among the natural oxidation products so formed are the pigments bixin, crocetin and azagrin. The other decomposition products formed in these oxidations frequently possess characteristic colour, smell or taste. Similar oxidations of carotene have recently been carried out in the laboratory.

Another widely distributed class of natural dyes is the flavines. Two of these, ovoflavine from egg-albumin and lactoflavine from milk, have recently been obtained as yellow crystalline solids and are probably identical. These substances exhibit high vitamin B_2 activity, which persists after repeated crystallisation and even after acetylation and hydrolysis of the acetyl derivative. The flavines appear to be necessary items in the diet of mammals, like the carotenes. The general properties of the two classes are, however, very different, as the flavines, unlike the carotenes, contain nitrogen, are soluble in water, resist the action of acids and oxidising agents and are labile to alkalis. The flavines can act as enzymes when combined with complex carriers and also as biological hydrogen acceptors.

Dr. R. P. Linstead described the phthalocyanines, a new class of synthetic colouring matters related to the naturally-derived porphyrins. These may be prepared from *ortho*-cyanobenzamide by the action of metals at 250° C., when they are formed as blue pigments containing metal (magnesium, iron, copper). Of these, only the magnesium compound is unstable to cold concentrated sulphuric acid, which removes the metal and yields the parent substance of the group, phthalocyanine. The metal-free, copper and magnesium pigments have the formulæ $(C_8H_4N_2)_4\ H_2$, $(C_8H_4N_2)_4$ Cu and $(C_8H_4N_2)_4$ Mg. $2H_2O$ respectively. They can be purified and the properties determined. They are remarkably stable except to acid oxidising agents; the copper compound may even be sublimed in nitrogen at 580° C.

Phthalocyanine differs from porphin, the structural basis of the porphyrins, in having four *iso*indole (benz-pyrrole) rings in place of four pyrroles. These are joined by nitrogen atoms ($-N=$) in place of the methine groups ($-CH=$) of the porphyrins and the whole forms a large, presumably planar, ring.

It was suggested by Dr. N. V. Sidgwick that the existence of the magnesium compound as a dihydrate is due to the inability of the metal to assume a planar 4-covalent state. If this is so, then beryllium, which can be neither planar 4-covalent nor hexavalent, should form no phthalocyanine pigment. Dr. K. F. Armstrong said that work which he has carried out in the porphyrin series gives somewhat analogous results in that certain zinc compounds appear to exist in a hydrated form.

In reply to a question by Prof. Freudenberg, Prof. R. Robinson stated his opinion that anthocyanins, flavines and substances of the tannin group are not capable of direct interconversion in the living plant but probably have a common natural precursor.

Early Bronze Age Site in the South-Eastern Fens

SPECIAL interest is attached to a report on the investigation of an Early Bronze Age settlement site on Plantation Farm, Shippea Hill, seven miles east-north-east of Ely, which appears in the *Antiquaries Journal*, 13, No. 3. It is the firstfruits of the activities of the Fenland Research Committee, which was founded in 1932 under the presidency of Prof. A. C. Seward with the object of studying the fens, as an area affording opportunities unrivalled in Britain for investigating post-glacial changes of environment in relation to man. An essential feature in the Committee's scheme of research was to secure the co-operation of specialists in the different sciences. How far this has been carried out may be seen in the report under consideration, in which Mr. Grahame Clark is responsible for the account of the site and the archæological data, the investigation of the peat deposits and the analysis of the contained pollens has devolved on Dr. H. and Mrs. M. E. Godwin, Dr. W. A. Macfadyen reports on the foraminifera of the silts and clay, Dr. Wilfrid Jackson on animal remains and Mr. A. S. Kennard on the Mollusca.

The site, a sandhill, lies in flat black peat country reduced to agriculture only by the drainage of the seventeenth century. This country is traversed not only by modern dykes and communications, but also by the meandering 'roddons'—banks of light brown silt. Recent investigation has shown that these roddons are extinct watercourses, of which the silted up beds appear as banks, owing to the shrinkage of the adjacent peat. On Plantation Farm some of them are as much as 7 ft. 3 in. above the surface of the peat. The site under investigation was rather less than three feet above the present surface of the peat, but when the Little Ouse flowed along the course of the roddon, the upper peat, which now blankets all but the extreme top of the sandhills, must have covered the whole to a depth of 12–13 ft.

The results of the archæological investigation may be summarised briefly as follows. The main occupation of the sandhill began in the Early Bronze Age, when a few inches of the upper peat had already formed. A numerically insignificant group of flint instruments of Tardenoisian type, lying loose on the sand, pointed to an earlier occupation of brief duration, for which there is no indication of dating, apart from the fact that in boring through the lower peat a micro-flake was found at the base some 17½ ft. down, which, it may be suspected, belongs to the Tardenoisian group. This would point to a Late Boreal date. The significant pottery of the Early Bronze Age settlement is Beaker, some of it of the best period. An ill-fired buff-coloured ware is difficult to place, but cannot be long after the Beaker, as the occupation of the site was short. The stone implements form an assemblage conforming to what might be expected in the early phases of the bronze age. Scrapers are the predominant implement of the industry, and barbed and tanged arrow heads are the most usual. In the absence of the leaf arrow head, the polished axe and the narrow finely serrated flake, the industry differs essentially from that of neolithic camps.

The majority of the animal remains belong to domestic animals; wild animals are rare. The dog and horse are absent. Dr. Wilfrid Jackson reports that the animal remains closely resemble those from Woodhenge.

Borings were made with the object of ascertaining the history of the site. The basal deposit consists of sand. At one point the sand dips to form a flat-bottomed hollow, 17 ft. below the present surface of the ground. Here the deposits consist of a lower peat with a maximum thickness of 7½ ft., overlaid by a continuous deposit of buttery clay, and overlying this an upper peat, of which the greater part has wasted away.

The pollen analyses by Dr. and Mrs. Godwin point to the lower peat beds being of Late Boreal age, the most noteworthy feature being a marked predominance of alder. Oak, lime, hazel, elm and birch are present, but correspondingly low in amount. In the lowest deposit, however, there is a striking difference. *Pinus* is 68 per cent, alder falls to 22 per cent, and hazel is 42 per cent. In the upper peat, now reduced to 40 inches thick with the lower 24 inches only undisturbed by cultivation, there is a marked change.