# Journal of Scientific & Industrial Research

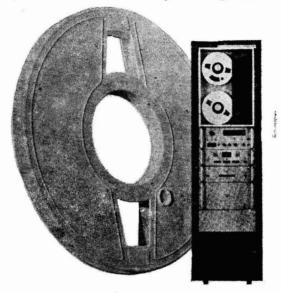


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**VOLUME 23** 

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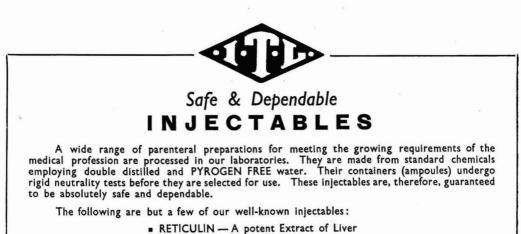
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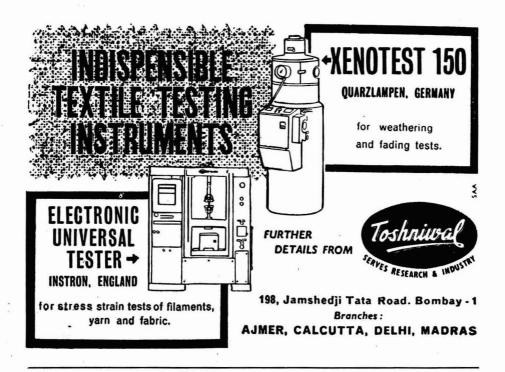
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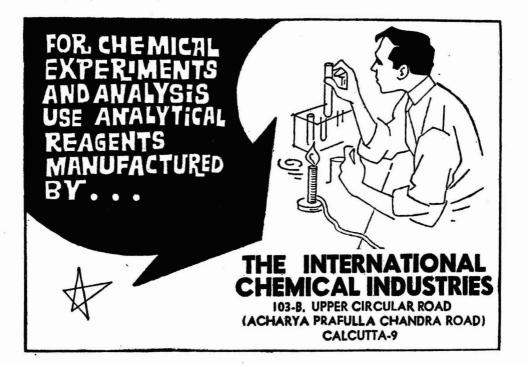
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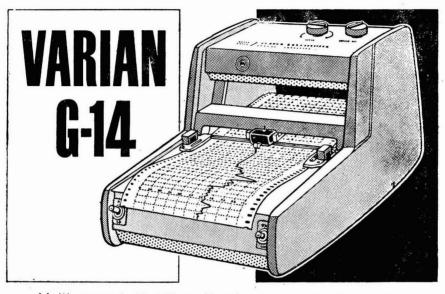
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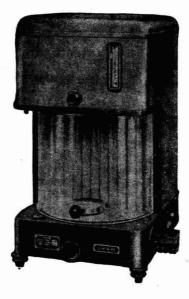
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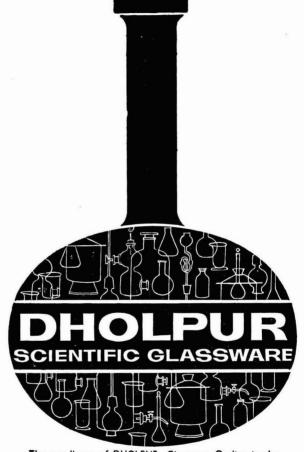


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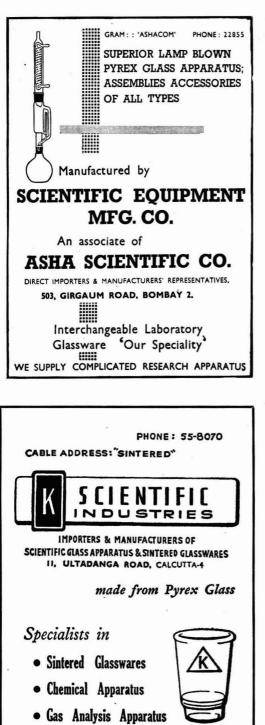
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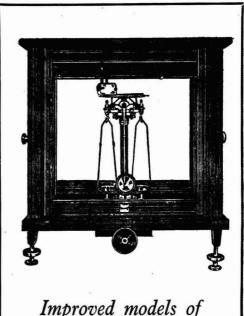


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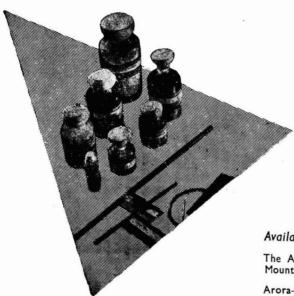
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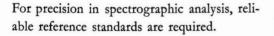
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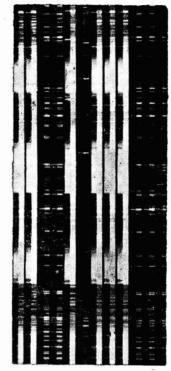
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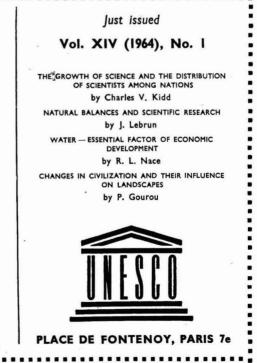
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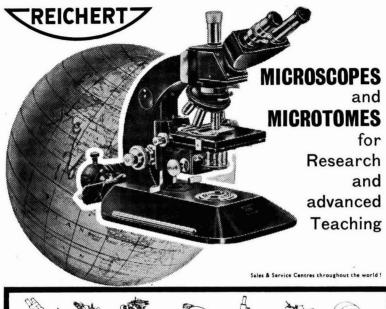
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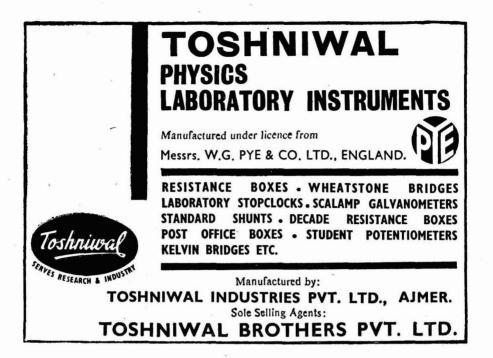
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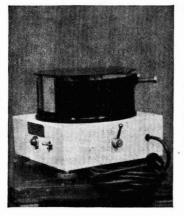
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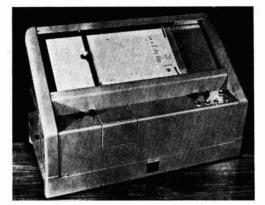
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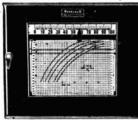
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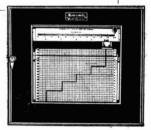
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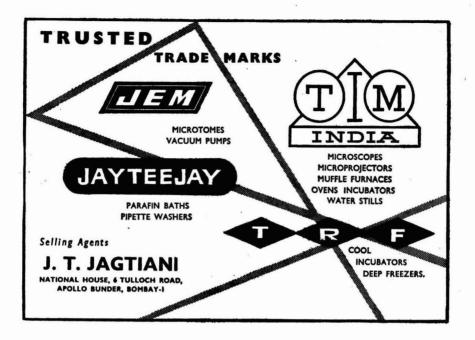
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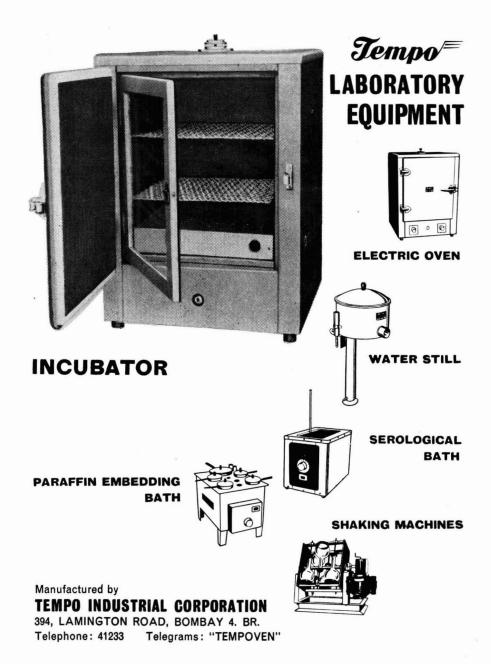
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## Current Topics

### Science & the Nation

THE four-day Symposium on Science and the Nation, organized by the Association of Scientific Workers of India (ASWI) at New Delhi from 27 to 30 July 1964, was a departure from the usual run of symposia and conferences held in recent years. Its implications are many and its impact far reaching. This is perhaps one of the few rare occasions, if not the first, when scientists engaged in different spheres of nation-building activity have sat together side by side with planners, administrators, industrialists and others to deliberate and discuss frankly and freely many vital problems confronting the nation. Also, for the first time, scientist representatives of Afro-Asian nations were invited to participate in a symposium of this kind so that they could have a first-hand knowledge of our country's development plans and programmes, particularly in science and technology. As observed by Dr S. Husain Zaheer, Director-General, Council of Scientific & Industrial Research, the main objective of the symposium at the national level was to help the scientist to take a broader view of science and to evaluate the role of science in national development. At the international level, the purpose of the symposium was to review the position of science and technology in the developing countries and to explore areas in which collaboration could be developed.

Inaugurating the symposium, Dr S. Radhakrishnan, President of India, paid homage to Jawahar Lal Nehru under whose guidance India had accepted the role of science as significant and important in our national life. Dr Radhakrishnan stressed the importance of science and technology in helping emerging nations to raise the living standards of their people. Commending the work done by agricultural scientists, he exorted them to be partners and not patrons in the development of new techniques, so that the results of their researches could be easily available to the farmer.

Dr Zaheer, speaking on the occasion, emphasized the necessity of teamwork among the scientists and the necessity of having an integrated view of science to meet the long-term needs of the country. He suggested to the participating scientists, including those from the Afro-Asian countries, to establish contacts and freely exchange scientific information.

Shri Ashok Mehta, Deputy Chairman, Planning Commission, voiced the viewpoint of the planner. He observed that the size of the Fourth Five Year Plan would perhaps be twice that of the Third Five Year Plan and that the investment of 2·0-2·5 per cent in research during the current plan might be raised to 4-5 per cent of the total investment. He, however, observed that higher investment in research would be possible if immediate results could be assured and that it was for the scientists to show that an investment of the order of Rs 400-500 crores during the next plan period would not be in terms of long-term advantage but of immediate or quick advantage.

In his welcome address, Dr N. P. Gupta, President, ASWI, briefly traced the development of science and technology in the country since independence, particularly of facilities for research and training. He dwelt on the growing disparity in the living standards of the peoples of different nations, and of the problems which confronted the Indian scientists in nation-building activity. He drew pointed attention to the fact that scientific talent and manpower in the country were not fully utilized, that allocations for scientific research were inadequate, and that there was yet no plan to use Indian scientist as a lever for India's industrial development.

Over 300 delegates including some 50 from 25 Afro-Asian countries and representatives from the Soviet Union and the World Federation of Scientific Workers participated in the symposium. Papers numbering 150 were contributed to the following 8 technical sessions: (1) Irrigation and Power; (2) Petroleum and Chemicals; (3) Steel, Mines and Heavy Industries; (4) Food and Agriculture; (5) Transport and Communication; (6) Health, Building and Town Planning; (7) Planning, Finance and Organization of Research; Training of Scientists; and Science and the Government; and (8) Science and International Relations. Since the primary objectives of the symposium were to (i) determine the present state of development in any particular area and (ii) indicate the types of problems to be tackled to achieve the targets set in the Third Five Year Plan, only a few of the papers contributed to the symposium were briefly presented, the coordinator for each session summarizing the salient features of the papers contributed. This allowed more time for discussions. The papers did not discuss technical aspects of manufacturing processes, equipment, methodology or other details but were confined to discussions on (i) techno-economic problems arising during implementation of the Third Five Year Plan, (ii) how and to what extent lack of technical know-how and inadequate application of science and technology were responsible for not achieving the targets, and (iii) the steps that should be taken to find quick solutions to urgent problems. As a result of the discussions, the ASWI has formulated recommendations, numbering about 80, which largely reflect the general sentiments expressed in the papers on the need for effecting improvements in several spheres of economic development and nation-building activity.

During the session on Irrigation and Power, it was generally agreed that greater use should be made of power in agriculture, and that there was need for research for the development of irrigated agriculture, with special reference to end use of irrigation supplies. Scientific study for developing drainage criteria has been recommended. In respect of power development utilizing atomic energy, Dr Bhabha made the suggestion that it was safer to err on the side of overproduction as shortage of power resulted in 10 per cent loss in national income whereas overproduction of power would mean loss of only 1/70th of national income. Standardization of equipment used in power generation and supply was among the other recommendations made.

The sessions on Petroleum and Chemicals, and Steel, Mines and Heavy Industries brought to light some common problems. In all these areas the need for indigenous manufacture of instruments and equipments for survey of natural resources, and for the production of manufactured goods and products was felt. Side by side, there exists a need for training of personnel in various spheres of industry, and for the development of indigenous know-how in process design and engineering. One of the recommendations suggests that the pace of surveys of country's natural resources should be accelerated so that the resources could be more fully exploited.

The session on Food and Agriculture was concerned with ways and means of augmenting food resources. Prevention of losses of foodgrains through insect infestation control, utilization of oilseed proteins, and intensive development of fisheries, poultry and dairy industries were among the recommendations set out. The need for educating people to change their food habits on a scientific basis has been emphasized. Papers on agriculture stressed the need for augmenting fertilizer production and for the introduction of measures such as use of improved seed and resistant strains, application of semi-mechanized farming methods for increasing agricultural production. Crop regulation according to the suitability of soil and climate has been recommended.

The session on Transport and Communication brought out the important point that the railways should be fed with precise information about additional transport needs of trade and industry as much in advance of actual requirements as possible for better economic planning and development of resources.

Papers contributed to the session on Health, Building and Town Planning were concerned with technical manpower problems in health programmes, and the difficulties and lacunae in planning them. Population control also came up for discussion. A national health laboratory service covering rural areas also for controlling communicable diseases and pilot schemes on national health insurance were some of the more important recommendations. The need for scientific method in town planning was emphasized.

Some of the general conclusions arrived at as a result of discussions during the session on 'Planning, Finance and Organization of Research; Training of Scientists; and Science and the Government' were: (i) project orientation of scientific research; (ii) importance of identifying projects for research; (iii) integration of laboratory research with the needs of industry; (iv) participation of scientists at all levels in the formulation of programmes and policies; (v) need for scientific societies to play an increasing and significant role in the organization and decision-making mechinery; (vi) a rigorous system of evaluation of social sciences.

One of the important recommendations of ASWI in respect of international relations is that necessary measures should be taken to promote exchange of scientific information among the developing countries.

In retrospect, the ASWI should be commended for organizing this symposium at a juncture when the country is going through a crucial stage in the execution of the Third Five Year Plan development programmes. Dr Zaheer observed in his address that an integrated view of science and a coordinated picture of scientific research in India has yet to be built. Symposia like these go a long way in achieving this objective. By securing and encouraging informed discussion, the symposium has made a significant contribution towards crystallizing our ideas and finding a basis for a national science policy for the economic uplift of the nation.

## Symposium on Corrosion Research

MOHAN LAL KHANNA National Physical Laboratory, New Delhi 12

THE first Commonwealth Symposium on Corrosion Research, organized by the Research & Development Organization of the Ministry of Defence, was held in New Delhi and Kanpur during 20-23 January 1964 under the auspices of the Commonwealth Defence Science Organization (CDSO), which met for the first time in this country. This enabled the Commonwealth researchers to take stock of the present status of corrosion research in various countries and to formulate the future line of action in this field so as to achieve maximum benefits from a coordinated programme of research. The symposium also provided an occasion to the participating scientists to exchange ideas on current problems of corrosion affecting defence stores and equipment, identify the more important problems of corrosion and evaluate the remedial measures taken in different countries to combat corrosion.

Welcoming the delegates from several Commonwealth countries, viz. Australia, Canada, Ghana, India, Nigeria, UK, etc., Dr S. Bhagavantam, Scientific Adviser to the Ministry of Defence, said that metals are among the non-renewable resources and their judicious use and conservation are of prime importance to mankind. He laid stress on the need for group effort in combating corrosion.

Inaugurating the symposium at Vigyan Bhawan, New Delhi, Shri Y. B. Chavan, Union Defence Minister, emphasized the importance of international cooperation in scientific research so as to prevent unnecessary expenditure and waste of effort. High cost of research and development, which acted as an impediment to the starting of large-scale projects in many developing countries, was also stressed.

The venue of the symposium shifted to the Defence Research Laboratory (DRL), Kanpur, on 21 January where its technical sessions were held under the chairmanship of Dr S. Bhagavantam. In his intro-ductory talk, Major-General B. D. Kapur, Chief Controller of Research & Development, briefly reviewed the research on corrosion being conducted in different institutions in India. He said that under the Metals Committee of the Council of Scientific & Industrial Research (CSIR), ten sub-committees were formed dealing respectively with atmospheric corrosion, underground and sub-soil corrosion, corrosion in the chemical industry, corrosion resistant metals and alloys, marine corrosion, cathodic protection and inhibitors, inorganic and organic coatings, testing procedures, industrial corrosion and service failures, and fundamental studies on corrosion. A Corrosion Advisory Bureau has also been set up so as to help industries faced with corrosion problems by rendering assistance and advice and also for coordinating the work of these different sub-committees. Twentythree research projects are under progress in various institutes in the country and sixty patents on anticorrosion measures have been taken. Major-General Kapur mentioned specifically the panel drawing up a 'Corrosion Map of India', in which the Central Electrochemical Research Institute, Karaikudi, the Defence Research Laboratory, Kanpur, the National Metallurgical Laboratory, Jamshedpur, and other institutions are conducting field studies on atmospheric corrosion testing of iron and other metals. The data collected will provide the basic information for drawing up the map. Information with respect to cathodic protection of underground pipelines, water storage tanks, cables, railway lines, ships, structures, etc., will be provided and engineers planning factories, public utilities, etc., will be helped in the choice of suitable sites and construction materials, paints and other surface coatings and finishes.

Research on basic and applied aspects of corrosion is in progress in the laboratories of the Defence Research & Development Organization, the CSIR, the Indian Railways, the Atomic Energy Establishment, the Indian Institute of Science, Bihar Institute of Technology and various other research laboratories. Among the researches of direct importance to defence, Major-General Kapur referred specially to the development of inhibitors for preventing corrosion in the water jacket and pipes of vehicles, phosphatizing of weapons and protection of underground storage tanks. Preventive measures against specific failures of railway materials and equipment are under study by the Railway Research, Designs & Stan-dards Organization. The Indian Standards Institution, New Delhi, has published four standards on temporary corrosion preventives (IS: 958, 1153, 1154 and 1674).

In the Defence Research Laboratory (Materials), Kanpur, studies are in progress on different aspects of corrosion, besides the collection of data on atmospheric corrosion of different metals. Research on packaging materials in relation to corrosion has also received attention and standardization of various test methods is being attempted. A Commonwealth Corrosion Cell is functioning at the laboratory. He hoped that there would be greater flow and exchange of scientific knowledge among the various Commonwealth countries.

Dr J. N. Nanda, Director, DRL, Kanpur, briefly reviewed the problems of general importance and those of specific interest on corrosion being pursued in his own and other laboratories in the country.

Dr T. Banerjee gave an account of the anticorrosion and corrosion work in progress at the National Metallurgical Laboratory (NML), Jamshedpur. The substitution of scarce metals in alloy compositions by indigenously available metals, aluminizing of steel used for telegraph pole construction, corrosion problems encountered by the industry and their anticorrosion measures and basic research on corrosion of metals and alloys were among the topics discussed.

Lt-Col. V. A. Banjo (Nigeria) said that the corrosion work being undertaken in India was of great interest to his country on account of similarity of problems and weather conditions. Dr R. H. Purcell (UK) suggested short-term courses on corrosion for the benefit of engineers and others employed in industry so as to utilize the existing knowledge. The necessity of teamwork was emphasized. Under CDSO, a cell is being maintained which disseminates information of interest to defence.

Delegates from research laboratories in India, Canada and Australia took part in the discussion that followed.

#### Aircraft Protection

At this session (Chairman, Dr E. E. Longhurst) two papers were presented by H. G. Cole (UK). In the first paper on 'Corrosion and protection of aircraft', the modern methods of protecting aircraft metals, the reasons for their choice and their efficiency in maintaining the static and dynamic strength of metals in service were discussed. With the development of metals possessing higher strength and of aircraft structures operating at elevated temperatures, personnel responsible for aircraft protection against corrosion would be required to solve several new problems. 'Recent developments in aircraft (protection with) paints' were reviewed briefly in the second paper. Particular problems connected with the use of jointing compounds and protection of aluminium and magnesium against environmental conditions were considered. The importance of protective coatings of paints and lacquers with maximum emissivity and maximum reflectance was stressed. The use of ion-exchangers for protection was discussed briefly. Discussions on these papers centred round stress and fatigue corrosion of aluminium alloys and steel components of aircraft. Special requirements of protective coatings for supersonic aircraft, which are subject to surface temperatures of 120-130°C., were emphasized.

#### **Environmental Studies**

At this session (Chairman, Dr V. Ranganathan) four papers from India and two papers from UK were presented. The paper 'Laboratory studies on atmospheric corrosion of metals by sulphur dioxide, dust and nuclei' by B. Sanyal (DRL) presented the results of laboratory studies on the corrosion of metals in synthetic atmospheres containing sulphur dioxide and metallic corrosion initiated by dust and electrolyte nuclei. The behaviour of metallic couples and metals in close proximity in closed atmosphere containing sulphur dioxide has also been examined and the corrosion of steel by electrolyte solution under immersed conditions studied. The extent of corrosion of all metals was found to increase with increase in humidity. Rise in temperature led to further increase in corrosion, which attained a maximum value at a particular temperature; no corrosion occurred above 60°C.

In his paper on 'Corrosion map of India', Dr J. N. Nanda (DRL) presented the results of outdoor exposure trials on metals such as mild steel and zinc conducted at Kanpur, Bombay, Calcutta and Cochin over the last six years. The experimental procedure, apparatus and equipment used were described. Correlation between data obtained and four variables of atmospheric conditions has been attempted using statistical method. A tentative corrosion map of India has been prepared on the basis of corrosion data collected so far. However, more stations are being established in collaboration with other institutions to collect data for the preparation of a broadbased corrosion map of India. N. S. Dempster (Australia) remarked that the duration of wetness is one of the important factors that affect the rate of corrosion wherein many variables are involved. When considering temperature, its degree, variation and rate of variation are important. Each variable is extremely complicated in itself and the effect of one over the other is superimposed. In order to explain the observed trends, all these factors have to be taken into account.

H. G. Cole (UK) presented the paper on ' Corrosion of metals by organic acid vapours' dealing with metallic corrosion in the presence of wood and other organic materials such as adhesives, synthetic resins and paints. Such problems as the release of vapours by these materials and the corrosion caused on metals such as steel, copper, brass, nickel, cadmium and zinc by acetic acid and formic acid vapours have been investigated. Test methods for identifying practical cases of corrosion by organic vapours were described. These include chemical tests, paper and vapour phase chromatography, infrared and X-ray diffrac-tion techniques. N. S. Dempster observed that similar troubles as those reported above have also been experienced in Australia. Contrary to the general belief that painting as well as varnishing of wood reduces the chances of wood corrosion, these experiments indicated that lower molecular weight organic vapours released by paint and varnish cause corrosion of wood surface.

Corrosion of metals in the presence of woods' formed the subject of the second paper. Exposure tests conducted at the Tropical Testing Establishment, Nigeria, have revealed the corrosive effects of a variety of woods on different metals and alloys. The assessment of the effects of fungicides, paint and aluminium cladding applied to woods, of appropriate chemical, electrolytic and organic finishes on the metals, and of the galvanic corrosion arising from fixing bolts of different metals and finishes has revealed that oak and plywoods are the most corrosive woods and magnesium alloys are most easily corroded. Galvanic corrosion is most pronounced in oak boxes and magnesium kept in boxes of different woods and in contact with bolts showed varying degrees of galvanic corrosion. The extent of corrosion was appreciably reduced with aluminium cladding. Paints and fungicides had very little effect, but they increased the corrosion of magnesium alloys in oak boxes.

The corrosion of materials is affected not only by the environmental conditions but also by the physical and mechanical conditions prevailing in the system. Their conjoint action leads to disastrous results; stress corrosion, fatigue corrosion, cavitation corrosion, infringement corrosion, etc., are some of the typical examples of these; impingement corrosion is of considerable importance and usually occurs in condensers, heat exchangers and any other system where high velocities are encountered. This was discussed in a paper by Raj Narain and A. K. Lahiri (NML). Copper and copper-zinc alloys failed when the power and the capacities of sea-going vessels were increased at a rapid rate.

Stress corrosion cracking of hardenable stainless steel was discussed by A. K. Lahiri, T. Banerjee and B. R. Nijhawan (NML, Jamshedpur). The type of heat treatment, corrosive environment, etc., are known to influence profoundly the cracking time of martensitic stainless steel. The effect of tempering temperature and hardness level on the stress corrosion behaviour of 12 per cent chromium stainless steel has been studied by testing in acidic chloride solution containing hydrogen sulphide which promotes the entry of hydrogen into the steel. When tempered above 600°C., steels are immune to cracking. At temperature ranging between 400° and 500°C., maximum susceptibility is observed. The results of this investigation and those of other workers have been explained on the basis of changes in physical properties, the nature of the carbide precipitated and hydrogen embrittlement.

#### Non-ferrous Metals

Five papers were presented at this session (Chairman, Dr T. Banerjee). A paper ' Corrosion of lead, lead-tin and copper-lead alloys by lubricating oils' was presented by Dr N. K. Chakravarty (DRL). The corrosion behaviour of these alloys has been investigated in lubricating oils undergoing liquid phase oxidation in the presence of metal catalysts and under conditions designed to simulate those prevailing in engine bearings. In the case of lead and leadcopper alloys maximum corrosion has been found to correspond more with peroxide formation rather than with acidity, and is associated with the formation of organo-lead compounds as a yellow protective layer on lead and oxidation does not follow the generally accepted course of reaction mechanism. On the other hand, lead-tin alloys undergo insignificant corrosion in oil showing thereby the prevention of corrosion of lead in oils by alloying it with a small amount of tin, for which a tentative explanation has been suggested. Oxidation of gadolinium in the temperature range 500-700°C. has been studied by H. B. Mathur (NCL); this study is of importance to nuclear research. Experiments with radioactive markers showed the oxidation to take place by the oxygen in diffusion through anion vacancies in the oxide layer and to follow a mixed parabolic-linear law.

J. F. Hearne (UK) presented a paper on 'External corrosion of tinned plate containers used for longterm storage of foodstuffs in the United Kingdom'. Storage trials with the commercially available 4 gal. rectangular container variously painted and protected under warehouse climates and building designs were conducted by the Ministry of Agriculture, Fisheries and Food, UK. These containers could be protected against corrosion by providing a polythene drape or tent over the storage stacks. The effect of residual stresses on the stress corrosion properties of the aluminium alloy DTD 5054 were discussed by G. A. Hawkes (Australia). Test specimens were cut in short transverse direction in three different ways so as to obtain three different residual macro stress systems, namely (1) zero residual stress, (2) residual compression, and (3) residual tension in the surface. Curves relating applied stress with time for failure for these three groups showed specimens with zero residual stress to possess the best stress corrosion properties. Failure was due to slow crack initiation and fast propagation in the case of specimen with residual surface compression and due to fast crack initiation coupled with slow propagation, in the case of specimen with residual tension in the surface.

#### Inhibitors

The first paper to this session (Chairman, Dr G. E. Gale, UK), 'Studies on new inhibitors', was presented by K. C. Tripathi (Banaras Hindu University). Inhibitor efficiency of a number of organic compounds containing both nitrogen and sulphur on mild steel in acid and neutral media has been studied by measuring the weight loss. The measurement of open-circuit potential and its shifts towards electropositive or electronegative could not be correlated with inhibitor efficiency. Neither increase in chain length nor attachment of heavier molecular groups increased the inhibitor efficiency unlike what was claimed by earlier workers. The compounds studied were allyl, phenyl and diphenyl thioureas and other substituted thioureas. Some of them exhibited excellent vapour phase inhibition, the mechanism of action being surface adsorption. The protection afforded is enhanced when chemical reaction with surface takes place during adsorption. The theory put forward supports the experimental results.

A paper on 'Corrosion inhibitors for oils used in buffer systems' was presented by B. Sanyal. Dynamic water test as well as immersed corrosion test conducted with straight and inhibited hydraulic buffer oils have shown that steel surfaces do not corrode with oil alone. On oil being contaminated with water, the surface on coming in contact with water is corroded. When 0.1 per cent calcium petroleum sulphonate is incorporated in the oil and the surface is first wetted with oil and then with water. corrosion of steel in aqueous phase is prevented for 9 months. On the other hand, when the surface is first wetted with water and the absorption of the inhibitor by the surface prevented, the inhibitor gives partial protection. A mixture of 0.05 per cent calcium petroleum sulphonate and 0.5 per cent ammonium naphthenate gives complete protection under this condition for 1 year. D. V. Bhadwar (DRL) discussed the 'prevention of corrosion of engine jacket and waterways of vehicles using water or antifreezes as coolant'. Laboratory corrosion tests on metals and alloys commonly employed in engine cooling systems have indicated that mains water, when inhibited with 0.5 per cent soluble cutting oil and 0.5 per cent sodium chromate gives the best protection against corrosion as well as scaling. The corrosion tests were carried out both under dynamic as well as static conditions or under simulated conditions.

V. Ramachandran and H. V. K. Unni (Indian Institute of Science, Bangalore) presented a paper '*n*-Butylamine as an inhibitor for the corrosion of pure aluminium in hydrochloric acid solutions'. It has been found that inhibitor efficiency of n-butylamine is low in the first hour and is thereafter almost independent of time. With increase in concentration the efficiency increases up to a certain limit beyond which it is constant. Similarly, with rise in acid concentration it increases up to 1.25N. For getting optimum efficiency of 63-68 per cent, the inhibitor concentration of 0.5 g./litre of nitrogen and an acid concentration of 1.25N are recommended. Under these conditions di-n- and tri-n-butylamines are also highly efficient. For steel in sulphuric acid, n-butylamine has an efficiency of nearly 45 per cent. With the addition of the inhibitor cathode polarization is increased. With optimum concentration of inhibitor and 1.25N acid, cathode polarization and weight loss measurements show that current density of 1.6 amp./ dm.2 is reduced to 0.48 amp./dm.2, while the other two amines give a higher value for cathode polarization. A curve drawn for the logarithm of the current density with cathode polarization obeyed the Tafel equation. From the exchange current the inhibitor efficiency calculated comes to 51 per cent, which is very close to the observed value.

The last paper to this session entitled 'Electrochemical studies of galvanic couples in the presence of corrosion inhibitors' was presented by S. N. Pandey. For these studies a modified technique was employed for the determination of critical poten-tial for the inhibitor. The proposed mechanism is based on the cathodic processes involving oxygen reduction and oxygen diffusion taking place at different potentials and successfully explains the anomalous behaviour of the failure at exposed edges of galvanized steel in sodium benzoate solution. The proposed mechanism is supported by experimental observations made with oxidizing type inhibitors, such as sodium nitrite and sodium chromate and with non-oxidizing type of inhibitors, such as sodium benzoate. The efficiency, however, depends on the rate of oxidation-reduction brought about by the inhibitor.

#### Cathodic Protection and Underground Corrosion

In this session (President, Dr W. A. S. Butement, Australia) the first paper was on 'Underground corrosion of metals and alloys under Indian conditions'. The corrosivity of soils collected from selected spots on the Durgapur-Calcutta route for cast iron, mild steel, carbon steel and nickel steel and on the Palta-Calcutta, Diamond Harbour-Calcutta and Budge Budge-Calcutta routes for cast iron and mild steel has been determined using modified Denison cell. No correlation between the combined weight losses of electrodes and initial cell current, maximum cell current on maximum pitting could be observed; similarly, no correlation could be observed between weight loss of electrodes and any single physical, chemical or electrochemical soil characteristic. However, a correlation is observed between the combined weight losses of the anodes and cathodes and the ratio of the total anions to the water-holding capacity of the soil. In field experiments in which the weight loss and the extent of pitting in these ferrous alloys buried at a depth of 2 ft were determined, the corrosion was higher than that observed in laboratory tests. Field exposure tests with Chinsura, Saktigarh and Burdwan soils and the ferrous materials painted with red lead showed practically no corrosion. When coated with aluminium, red lead, bituminous and coal-tar paints and field tested in the regions around Calcutta, aluminium paint gives better protection against underground corrosion as compared to bituminous, red lead and coal-tar paints. The corrosivity of four major types of Indian soils, viz. Amraoti black, Bangalore red, Bankura laterite and Berhampore alluvial, for ferrous materials was also studied in the laboratory with modified Denison corrosion cell and no correlation between the properties of soils and the extent of corrosion has been observed. The performance of zinc and aluminium as sacrificial anodes showed reduced corrosion on the basis of weight losses as compared to the unprotected ones in electrolytic cells, in most cases zinc being more effective than aluminium.

In his paper entitled 'The cathodic protection of naval ships', N. S. Dempster outlined the development of cathodic protection in the Royal Australian Navy, with special reference to the design of impressed current cathodic protection installations. However, two major fields, in which further work is necessary, are the study of the process of deterioration of paint films under cathodic protection conditions and development of new paints with an extended service life and assessment of plastic resins for dielectric shields under laboratory and service conditions. For obtaining maximum benefit from cathodic protection, the problems requiring attention are (i) assessment of the value of automatic control, (ii) current distribution in aft-areas, (iii) introduction of grit blasting for the preparation of hull for dielectric shield application, and (iv) further assessment of the flush mounted Ag/AgCl or Zn/ZnCl<sub>2</sub> electrode. An investigation has been undertaken on current distribution in aft-areas aimed at (i) determining whether under-protection of rudders is due to the propellers acting as cathodic sinks, (ii) whether any relationship exists between the incidence of shaft corrosion and cathodic protection, and (iii) the measurement of current distribution between hull and propeller to predict quantitatively the current demand of the propeller.

While discussing 'Corrosion prevention at the stern area of ships', C. P. De described the studies conducted at the Naval Chemical and Metallurgical Laboratory (NCML), Bombay, for evaluating the suitability of some anticorrosive compositions using a high speed rotating disc apparatus simulating the turbulent conditions in the area. Solventless epoxy resins gave the best results with this apparatus and the preliminary service trials currently in progress have given promising results. Dimensions and speed of rotation of the disc and thickness of film applied were the parameters studied.

#### **Research Methods**

The first paper to this session entitled 'Development of a cavitation tunnel for studying the cavitation damage of materials' was presented by G. E. Gale (UK). When cavitation damage becomes troublesome, the best solution is to redesign the system so as to modify, diminish or suppress cavitation.

This is not always practicable and other measures have to be adopted, such as the selection of a more resistant material. Test methods used for evaluating the material are the jet impact slotted disc rotor, magneto-striction oscillator and con-stricted flow type rotor. The 'Factors influencing the corrosion of metals by salt fog ' have been studied by B. Sanyal (DRL, Kanpur). The salt spray test is qualitative and a large number of variables, such as the nature of the protective coatings, angle of exposure, accumulation of fog, etc., are involved. From the point of view of drainage, exposure at an angle of 30° gives better results than exposure in the vertical or horizontal position. The results are affected by the amount of fog collecting, atomization, solubility of oxygen in dilute solution and continuous or intermittent settling of fog on the surface protected. In his paper entitled 'Reliability and corrosion' R. D. Barer (Canada) gave a qualitative definition of reliability of equipment and stores as a long service life with minimum maintenance. With respect to corrosion, the factors to be considered are design of equipment, selection of material and the process of fabrication.

#### **Special Environment**

The first paper to this session (President, B. Sanyal) entitled 'Water side attack on diesel engine cylinder liners' was presented by R. H. Purcell. The origin of the water side attack has been traced to piston-liner relationship wherein impulsive transverse impacts of the piston on the liner wall excite liner vibrations, giving rise to cavitation erosion type damage to the outer surface of the liner. The provision of oil damped piston significantly reduces the connecting rod transverse vibrations initiated by piston 'slap' reaction forces. By doing so the fatigue life of the connecting rod is increased and the incidence of fretting corrosion on big end bearing shells is reduced. The power output of the engine and ring sticking and sludge formation depends on the quantity and quality of the lubricating oil entrapped in between the oppositely phased rings provided.

In the absence of Dr A. A. Krishnan, his paper on ' Liquid metal corrosion ' was presented by Dr Ghosh. Regarding the mechanism of liquid metal corrosion of metals and alloys, a physical approach has been proposed to the problem of corrosion, wherein physical contact between the surfaces of the material and the corrosive medium is necessary to initiate and the driving force is the free energy of the interfaces. Liquid metal corrosion can be inhibited by judicious addition of alloying elements either to the corrosive medium or to the metal being corroded so as to control the 'dihedral angle' of the liquid phase. The angle in the case of the tin-rich phase of aluminium-tin alloys is much lower than that of aluminium-cadmium or aluminium-iridium alloys in similar phases and, therefore, aluminium-tin alloys crack more severely in a patch weld cracking test than the other alloys. Addition of cadmium increases the angle and reduces cracking.

'Protection of very high tensile steels against corrosion, with special reference to hydrogen embrittlement' was the subject of a paper presented by H. G. Cole (UK). The standard methods of protecting steel parts in aircraft by cadmium plating of close tolerance parts, aluminium spraying on wide tolerance parts and chromium plating of bearing surfaces subjected to wear cannot be used because of the difficulty caused by introducing hydrogen with the metal during the aqueous treatments involved in cleaning and plating processes. Susceptibility to hydrogen enbrittlement increases with increasing tensile strength. Earlier work on the subject and the physical factors involved were discussed. A method for measuring embrittlement was described. The influence of environment, cleaning methods, electroplating process and other factors was also discussed. The effect of hydrogen embrittlement on the mechanical properties of metals and the mechanisms of embrittlement were considered.

Corrosion problems on Indian railways and how they are being tackled were discussed by K. C. Chaudhury and S. Ramanajam. Painting of components has been recognized as the simplest and most economical method of preventing corrosion employing different combinations of media and inhibitive pigments. A rough assessment made in 1958 placed the loss due to corrosion of equipment stores in the railways at Rs 200 million. As compared to this, the annual estimated cost in combating corrosion in India, UK, Australia, Canada and USA is 500, 2600, 1950, 1500 and 40,000 millions of rupees respectively. Utilizing indigenously available materials, such as ' red mud ' residue from the aluminium industry, zinc chromate, barium potassium chromate, waste mica, cashewnut shell liquid, linseed oil, bitumen, etc., certain formulations, covered by patents, have been developed, and are now being manufactured in the country for use by railways and other industries. From the point of economy, the aim has been to formulate a minimum number of compositions, which are both inexpensive and versatile in being used with slight modifications as multipurpose materials to meet various needs.

#### **Concluding Session**

In the concluding session held on 23 January, the heads of different delegations summed up the symposium deliberations and made recommendations for short-term and long-term programmes of coordinated research work to be conducted in the Commonwealth countries. It was emphasized that corrosion scientists should make efforts to make those responsible for the execution of the projects cognizant of the problem of corrosion and of anticorrosion methods to be followed in combating corrosion.

In conclusion, the symposium provided a valuable opportunity to research workers in India to understand the wide range of problems encountered in other countries and the manner in which these are being tackled. The ideas exchanged and the personal contacts made would stimulate further research on corrosion.

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## New Route to Higher Sugars\*

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HighER sugars, monosaccharides containing more than six carbon atoms, were only a chemical curiosity until about twenty years ago. It has now become obvious that this class is widely represented in nature and plays an important role in the metabolism of living tissues. As examples may be mentioned sialic acids, isolated from a wide variety of specific biopolymers of animal tissues, and which are responsible for a considerable part of biological activity of higher aldoses from cell wall polysaccharides of a number of patrogenic microorganisms, and sedoheptulose (one of the key intermediates of the photosynthetic cycle) present in green leaves of all the plants.

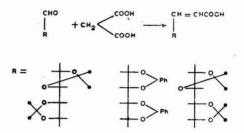
Increasing interest to chemistry and biochemistry of higher sugars makes it desirable to develop new convenient synthetic routes to them. The existing methods for preparation of higher monosaccharides from lower ones are (i) cyanohydrin synthesis1 of Kiliani-Fischer and (ii) nitromethane synthesis<sup>2</sup> of Sowden-Fischer. Although the first of the two methods has found numerous applications, both the two routes have a common limitation as they enable elongation of the sugar chain by only one carbon atom at a time. This limitation becomes especially important with aldoses containing eight and more carbon atoms; the procedure in this case involves a lot of repeating tedious stages. Hence, it seemed desirable to look for novel approaches. Such a novel approach now developed in our laboratory enables elongation of the sugar chain by two carbon atoms at a time<sup>3</sup>:

 $\begin{array}{l} \text{R-CHO} \rightarrow \text{RCH} = \text{CHCOOR'} \rightarrow \text{RCHOH-CHOHCOOR'} \\ \rightarrow \text{RCHOHCHOHCHO} \end{array}$ 

where R = sugar moiety.

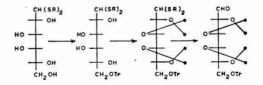
The new route involves transformation of the lower aldose to an unsaturated aldonic acid with two extra carbon atoms. The double bond of this acid is hydroxylated and the higher aldonic acid obtained thereby reduced to its corresponding aldose, containing two carbon atoms more than the starting monosaccharide. Following this route we obtained heptoses from pentoses, octoses from hexoses, etc. The key intermediates of the synthesis were unsaturated aldonic acids, and their availability determined the scope of the new method as well as its convenience. We have elaborated three independent methods for the preparation of this new class of compounds so that now it is probably one of the most readily available one among carbohydrate derivatives.

The first of these methods involves condensation of al-form monosaccharide derivatives with malonic acid under the conditions of Knoevenagel-Doebner reaction<sup>4</sup>, viz. heating at  $100-10^{\circ}$  in dry pyridine in the presence of catalytic amounts of piperidine. Consequently, unstable protecting groups could not be used and protection was best given by isopropylidene or benzylidene groups. The method was applied to the synthesis of three unsaturated aldoheptonic acids from the corresponding pentoses.



The starting al-forms were obtained via ethyl dithioacetals according to a routine scheme, involving condensation of pentoses with mercaptan in acidic medium, subsequent treatment with acetone or benzaldehyde in the presence of acid and treatment of the protected dithioacetal with mercuric chloride and mercuric oxide to give rise to the corresponding derivative with the aldehyde group open to condensation.

One of the serious disadvantages of this method is the formation of isomeric mixtures during introduction of isopropylidene or benzylidene groupings. On the other hand, the synthesis of suitably protected al-form hexoses is considerably complicated by the presence of an 'odd' hydroxyl not covered by alkylidene groups, as can be seen below in the outlined synthesis of al-galactose:

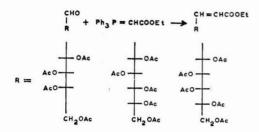


The structure of the unsaturated acids obtained by condensation with malonic acid was proved by the results of potentiometric titration (one open carboxyl), catalytic hydrogenation (double bond) and ultraviolet and infrared spectroscopic data (trans- $\alpha$ , $\beta$ -conjugated double bond). Moreover, the structure proposed explained the formation of fumaric acid by periodate and silver oxide oxidations.

In spite of the above-mentioned disadvantages, the method was of considerable interest. However, the desire to make the new route more general made us look for other approaches.

<sup>\*</sup>Lecture delivered at the University of Delhi under the auspices of the Advanced Centre on the Chemistry of Natural Products on 28 December 1963 and at Osmania University (Hyderabad) on 6 January 1964.

The approaches were directed towards elaboration of the Wittig reaction which was applied to the carbohydrate series for the first time in our laboratory. The first method, affording unsaturated aldonic acids by Wittig reaction, consisted of condensation of al-form acetates with triphenyl carbomethoxymethyl phospharane<sup>6,6</sup>. The compounds were refluxed in dry benzene for 1 hr to give rise to unsaturated aldonic acids in c. 80-90 per cent yield.



Al-form acetates, non-applicable to the Knoevenagel-Doebner condensation due to their lability towards bases, appeared convenient starting compounds in the above reaction. The structures of the resulting unsaturated acids were proved as mentioned above; they also appeared to be *trans*isomers.

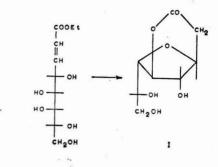
The third, probably the most convenient approach to unsaturated aldonic acids, is based on direct condensation of unprotected monosaccharides with triphenyl carbomethoxymethyl phospharane<sup>7</sup>. This condensation results in a 60-65 per cent yield of unsaturated acids when the starting compounds are heated at 90° in dimethylformamide for 4 hr.

RCHO + Ph P = CHCOOEt ---- RCH = CHCOOEt

		3	+ он	+ он	+ NHAC
н	0+	+ OH	HO	но	но
R ==	- он	- он	+ OM	HO	+ он
R ==	+ он	- OH	- он	-+-OH	+ он
	CH2OH	CN2 OH	CH OH	CH20H	CH2 OH

Wittig condensation is thus a new reaction involving the aldehydic function of monosaccharides, leading to non-cyclic compounds; it comprises a considerable interest for synthetic sugar chemistry. In contrast with al-form acetates, unprotected monosaccharides react with the Wittig reagent with the formation of byproduct saturated derivatives in addition to the desired unsaturated acids. In the case of galactose, this byproduct was isolated in a pure crystalline state and characterized as (I) on the following basis<sup>6</sup>. Elemental analysis and infrared spectroscopic data suggested the presence in this compound of a 8-lactone ring. Consumption of one mole of lead tetraacetate and formation of one mole of formaldehyde during oxidation indicated the presence of a -CHOH-CH<sub>2</sub>OH- grouping. The formation of the compound (I) must proceed by anhydridization of unsaturated aldonic acid

followed by lactonization, as revealed also by a direct experiment.

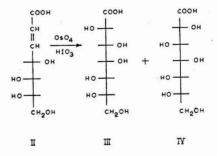


If formation of the byproduct is for some reason to be avoided, Wittig condensation can be accomplished also with readily available 2,3,4,6-tetra-Oacetyl glycopyranoses, affording only the unsaturated aldonic acid in an yield of c. 90 per cent with no byproducts<sup>6</sup>.

The new synthetic methods, and especially the one involving direct condensation of Wittig reagent with monosaccharides, make the unsaturated aldonic acids readily available and suggest the possibility of their wide use in the future monosaccharides synthesis.

In order to go from the unsaturated aldonic acids to higher aldoses according to the scheme outlined in the beginning of the paper it was necessary to hydroxylate the double bond; the stereochemistry of this reaction would determine the configuration of the final higher sugar. We chose *cis*-hydroxylation with osmium tetraoxide, leading from *trans*double bond to threo-glycol grouping.

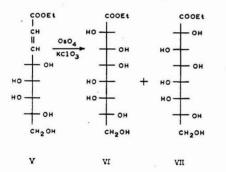
Hence, every unsaturated aldonic acid would give rise, after hydroxylation, to two diastereoisomeric aldonic acids, differing in configurations at  $C_2$  and  $C_3$ . For example, hydroxylation of 2,3-dehydro-2,3-dideoxy-L-araboheptonic acid (II), obtained by one of the above-mentioned methods, should result in a mixture of L-glycero-L-galactoheptonic acid (III) and L-glycero-L-iodoheptonic acid (IV)<sup>7</sup>.



Of the numerous procedures for oxidation with  $OsO_4$  we chose the catalytic one, i.e. the reaction in the presence of minor amounts of  $OsO_4$ , and sufficient amount of oxidizing agent, immediately regenerating  $OsO_4$ . As such agents, potassium chlorate

or iodic acid were taken. The reaction could be effected with unprotected as well as protected unsaturated aldonic acids. The yields of hydroxy-lation are practically the same for all the types of derivatives, so that the starting compounds are chosen only from the viewpoint of their availability and convenience of the synthesis, i.e. individually for every monosaccharide. The reaction mixture after hydroxylation containing diastereoisomeric aldonic acids is purified from minor amount of byproducts using ion-exchange chromatography on Amberlite IR-400 (CH<sub>3</sub>COO<sup>-</sup> form) with acetic acid as eluent buffer. After such purification it is sometimes necessary to subject the preparation to hydrolysis for removal of the remaining protective groupings.

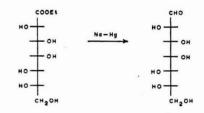
Separation of diastereoisomeric acids is most readily achieved by transforming them to cadmium salts, as cadmium salts of aldonic acids with galactoconfiguration, in comparison with those of iodoconfiguration, are almost insoluble in water. Addition of cadmium hydroxide to an aqueous solution of diastereoisomeric mixture thus results in precipitation of cadmium salt of compound (III) (yield 55 per cent); in order to isolate the second isomer, the supernatant layer is saturated with cadmium bromide, resulting in the precipitation of binary salt - cadmium L-glycero-L-iodogalactonatebromide (IV) (yield 30 per cent). The overall yield of aldonic acids thus makes c. 85 per cent. Hydroxylation of other unsaturated acids was accomplished in an analogous manner. For example, 2,3-dideoxy-2,3-dehydro-galactooctanoic acid (V), obtained from D-galactose<sup>8</sup>, was oxidized to acid, with D-threo-L-galacto- (VI) and D-threo-L-iodo-configurations (VII). In this case potassium chlorate was used as oxidizing agent, as iodic acid brings about partial lactonization of the resulting aldonic acid, which leads to difficulties during isolation.



Separation of the two diastereoisomeric acids was again effected using their cadmium salts; compound (VI) was isolated in a yield of 57 per cent, and compound (VII) in a yield of 26 per cent. It is noteworthy that in this case there also takes place the formation of both the isomers in a ratio of c. 2:1. The reason for the preferred formation of one of the isomers remains obscure; this problem is of considerable interest from both theoretical and preparative viewpoints. Obviously, the rate of formation of the isomer depends upon shielding of the double bond by the aliphatic polyhydroxylic chain of the aldonic acid molecule. However, the absence of any evidence as for the conformation of aliphatic chain of monosaccharides makes it impossible to speculate in this field. However, accumulation of further data concerning hydroxylation of unsaturated aldonic acids will probably enable us to draw some conclusions concerning this important problem.

Evidently, the double bond in unsaturated aldonic acids can be subjected to conversion other than cis-hydroxylation. For example, of considerable interest for the synthesis of higher sugars would be trans-hydroxylation, hydration, aminohydroxylation and a few other reactions, which open new applications of the method developed and are now investigated in our laboratory.

The final step of higher sugars synthesis is transformation of aldonic acids to the corresponding aldoses. This operation encountered no difficulties and was accomplished by standard procedures well known for lower aldoses, as the length of the sugar chain does not practically bear upon the course of the reaction. Lactones or ethyl esters of aldonic acids were subjected to reduction, depending on their availability. Either sodium amalgam or sodium borohydride was used as reducing reagent<sup>7,8</sup>.



High yield of reduction completely depends upon the precise control of the pH of reaction mixture, which must be maintained in the region 3-3.5. The higher aldoses obtained by reduction were isolated by partition chromatography on cellulose and identified as one or another conventional crystalline derivative9.

The data presented in this report reveal widespread potentialities of the new route in carbohydrates synthetic chemistry.

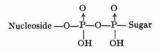
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**N**UCLEOSIDE diphosphate sugars (NDPS) of the general formula



constitute the most numerous group of nucleotide coenzymes considering their central position in metabolism of carbohydrates. The compounds of this class take part in interconversions of monosaccharides, in the biosynthesis of glycosides, polysaccharides and complex carbohydrate containing biopolymers. More than 40 such compounds have been isolated and characterized so far. All five most common nucleosides occur as the corresponding moiety in NDPS, and the class can thus be subdivided into five groups - uridine diphosphate sugars (the major representative being uridine diphosphate glucose, UDPG), guanosine diphosphate sugars, thymidine diphosphate sugars, adenosine diphosphate sugars, and cytidine diphosphate sugars. In spite of the considerable amount of information available, no simple correlation between the structure and biochemical specificity of the compounds of the class has been ever outlined to throw light on the mechanism of enzymic reactions in which they are participants. On the basis of literature evidence concerning chemical structure and biochemical function of NDPS we have recently attempted to make some generalizing conclusion<sup>1</sup>. It appears that within each of the groups of NDPS there exists an intimate relationship between the structure of the heterocyclic nucleus and some structural features of the monosaccharide residue. For example, the monosaccharide residues in all of the uridine diphosphate sugars have identical configurations at  $C_1$ ,  $C_2$  and  $C_3$ .



D-glucose, D-galactose, D-glucuronic acid, D-xylose, L-arabinose, D-N-acetylglucosamine

The sugar moieties in guanosine diphosphate sugars have identical configurations at  $C_1$ ,  $C_2$  and  $C_4$ , the configuration at  $C_2$  being opposite to that occurring in uridine diphosphate sugars.



D-mannose, D-glyceromannoheptose, L-galactose, L-fucose, colitose, L-rhamnose

\*Lecture delivered at the University of Delhi under the auspices of the Advanced Centre on the Chemistry of Natural Products on 3 January 1964.

This regularity which at first seems a merely empirical one becomes more obvious and better understandable if we consider conformations of sugar residues in NDPS. In this consideration we start from the assumption that the sugar moiety in NDPS must occur in the conformation generally adopted to be the preferred one by the free parent monosaccharide. For sugar residues of the uridine group of NDPS this conformation is always CI, and in all of them hydroxyls at C2 and C3 occupy the equatorial position. For guanosine diphosphate sugars this conformation may be CI (for the L-series) and BI (for monosaccharides of the D-series). It appears again that hydroxyls at  $C_2$  and  $C_3$  occupy the equatorial position. This regularity, i.e. the equatorial position of hydroxyls at  $C_2$  and  $C_3$ , was found to be the case for all the other compounds of the NDPS series.

If we now refer to the biological function of various NDPS; we shall see again a rather obvious regularity<sup>1</sup>. Table 1 contains data concerning biochemical transformations characteristic of the three major groups of NDPS — uridine, guanosine and thymidine diphosphate sugars.

As seen in Table 1, each of the three groups is characterized by its own set of biochemical reactions, not covered by the compounds of other groups. For example, compounds of the uridine series take part in such transformations as oxidation at  $C_6$ , epimerization at  $C_4$ , epimerization at  $C_5$ , etc., which do not take place in the guanosine series. On the contrary, guanosine diphosphate sugars are capable of epimerization at  $C_3$  and  $C_4$ , reduction at  $C_6$ , etc., i.e. in reactions not taking place in the uridine series.

The above-outlined general regularities, viz. the dependence of the structure of the sugar moiety

Table 1 — Distribution of Biochemical Reactions between Three Groups of NDPS .

Type of reaction of the sugar moiety	Nucleoside of NDPS		
	Uridine	Guano- sine	Thymi- dine
Oxidation at C.	+	·	-
Epimerization at C <sub>4</sub>	+	-	+
Epimerization at C <sub>5</sub>	÷	-	-
Epimerization at C <sub>3</sub> and C <sub>5</sub>	<u> </u>	+	_
Reduction at C.	-	÷	+
Reduction at C <sub>6</sub> and epimeri- zation at C <sub>4</sub>		÷	+
Reduction at $C_6$ and epimeri- zation at $C_3$ and $C_5$	—	+	-
Reduction at $C_8$ and epimeri- zation at $C_3$ , $C_4$ and $C_5$	-	-	+
Reduction at $C_3$ and $C_6$ with epimerization at $C_5$	-	+	-
Glycosylation of phenols	+	-	+

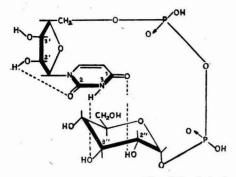


Fig. 1 — Secondary structure of uridine diphosphate glucose (UDPG)

upon that of the nucleoside residue, the equatorial position of hydroxyls at  $C_2$  and  $C_3$  and the distribution of biological functions, cannot be occasional. A reasonable explanation for the phenomenon in our opinion may follow from the assumption that NDPS molecules are capable of forming secondary structures, formed by hydrogen bonding between the heterocyclic nucleus and the sugar residue, as shown schematically in Fig. 1. Molecular models reveal the possibility of such interaction. There have already been brief indications in favour of the existence of this type of secondary structure in metal complexes of adenosine triphosphate and nicotinamide adenosine dinucleotide (DPN). However, the possibility has never been discussed for NDPS. It must be noted that up to date the conformation of enzymic substrate and its effect upon the specificity of biochemical transformation has not been considered properly. It seems obvious that enzyme and substrate are both equal participants of biochemical reaction, and not only the conformation of enzyme but also that of the substrate may strongly bear upon the result of interaction.

As seen in Fig. 1, NDPS are capable of formation of a 'horse-shoe' conformation, fixed by hydrogen bonding between the amide system  $N_3-C_4$  or respectively  $N_1-C_6$  of the heterocyclic nucleus and the two equatorial hydroxyls at  $C_2$  and  $C_3$  of the monosaccharide residue. In this conformation, the heterocyclic nucleus serves as a template for the sugar molety, and thus determines its structure and conformation. The 'horse-shoe' conformation of uridine diphosphate sugars is additionally stabilized by hydrogen bonding between the  $C'_2$ -ribose hydroxyl and carbonyl at  $C_2$  of the uracil residue.

In terms of secondary structure we can explain the general character of the above-mentioned regularities. Fixation of the monosaccharide residue on the base template must sterically limit the scope of possible reactions of the sugar moiety, and may also facilitate conversions if they lead to conformation better fitting the template. To exemplify these statements, I shall consider now reactions of the uridine series. As seen in Table 1, monosaccharide residues of this group of compounds are capable of enzymic oxidation at  $C_6$  to give uronic acids. Consideration of molecular model reveals the centre in the 'horse-shoe' conformation to be open to attack. The other reaction taking place in the uridine series is glycosylation accompanied by inversion of configuration at  $C_1$  to give phenol glycosides. This peculiarity also finds its explanation in the secondary structure, which leaves the glycosidic centre open to attack only from the opposite direction leading to inversion at  $C_1$ , whilst attack from the opposite direction is sterically hindered.

The usefulness of the assumption of secondary structure is demonstrated also by a considerable number of other examples<sup>1</sup>.

Experimental verification of the above-outlined concept is now in progress in our laboratory. For this purpose we synthesized a series of previously unknown analogues of uridine diphosphate glucose (UDPG) with modified uracil nucleus. If the above concepts were valid, modification of the uracil nucleus and, particularly, of its amide system, leading to a change of its capability of hydrogen bonding, should cause changes in the secondary structure. The changes in secondary structure must bear upon physical and chemical properties, and, if our viewpoint is correct, upon activity and specificity of enzymic reactions. Hence, study of the behaviour of analogues of UDPG in various biochemical reactions might help in arriving at a certain conclusion for the validity of the concept.

The most interesting compounds from the above viewpoint seemed to be analogues with the uracil nucleus modified at atoms responsible for hydrogen bonding, i.e. at the system  $C_2-N_3-C_4$ . We have synthesized and investigated the following six analogues of this type: 3-N-methyl-UDPG (I), 4-thio-UDPG (II), 4-amino-UDPG (IV), 2-amino-UDPG (isocytidine diphosphate glucose) and, for comparison, 6-aza-UDPG (VI) with unchanged amide system of uridine nucleus.

The rather complicated synthesis of these six analogues was accomplished (Chart 1) starting with uridine, by modifying its heterocyclic nucleus, subsequent phosphorylation and condensation with glucose-1-phosphate<sup>2</sup>.

This scheme is based on the methods proposed by H. G. Khorana for the synthesis of UDPG; however, marked lability of the analogues made us modify the procedures or even elaborate new methods.

The first step involved the synthesis of 2,3-isopropylidene derivatives of modified uridine. In two cases it was necessary only to make the isopropylidene derivatives from commercially available nucleosides (cytidine and 6-azauridine). 2,3-O-Isopropylidene-3-N-methyluridine was obtained by the methylation of 2,3-O-isopropylidene uridine with diazomethane in ether-methanolic solution<sup>3</sup>. 4-Thiouridine was obtained by modification<sup>4</sup> of the method of Fox *et al.* 2-Thiouridine and isocytidine were obtained via 2,3-O-isopropylidene-2,5-cyclouridine (VII)<sup>5</sup> by treating the compound with hydrogen sulphide or ammonia; in the former case, 5-deoxy-5-thiouridine — the second of the two possible

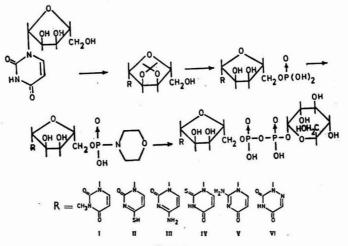
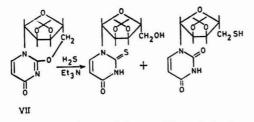
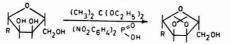


Chart 1

products of the anhydro cycle opening — was also isolated from the reaction mixture.



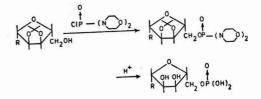
For the synthesis of isopropylidene derivatives of synthetic nucleosides routine methods based on treatment with acetone in the presence of acid and desiccant appeared to bring about destruction of labile analogues. Therefore, it appeared convenient to use the recently proposed method, using 2,2diethoxypropane and di(p-nitrophenyl)-phosphoric acid.



With the new method, good yields of all the modified nucleosides, involving acid-unstable 4- and 2-thiouridine, were obtained. The protected derivatives were purified by crystallization or, if needed, by adsorption chromatography on alumina. Their purity was controlled by conventional spectrophotometric methods, as well as by thin layer chromatography on alumina, which was applied to protected nucleosides for the first time in our laboratory.

The next step of the synthesis of UDPG analogues was phosphorylation. Phosphorylation of nucleosides is effected usually by treating them with suitably protected phosphoric acid and removing subsequently the protective groupings to give nucleoside monophosphates. Among our compounds, there were both acid-unstable (thio derivatives) and alkali-unstable nucleosides (N-methyluridine). Hence, we used two phosphorylating agents. Alkalistable nucleosides were phosphorylated by the method of Tener (condensation of isopropylidene nucleosides with 2-cyanoethyl phosphate in the presence of dicyclohexylcarbodiimide) and subsequent removal of the cyanoethyl grouping by mild treatment with KOH. It proved convenient to react the compounds at elevated but not at room temperature, as originally proposed, so as to reduce the time of reaction from two days to several hours. For removing the isopropylidene protective groupings, the phosphates were hydrolysed by treatment with acetic acid.

Alkali-labile N-methyluridine could not be successfully phosphorylated by the known methods. For the purpose we had to develop a new method of phosphorylation of nucleosides, involving short-term reflux of isopropylidene derivatives with dimorpholinophosphochloridate in pyridine and subsequent removal of protective groupings by mild acid hydrolysis (0·1N HCl; 100°; 2 hr).



The method afforded a high yield of N-methyluridine-5-phosphate and proved applicable to other alkali-unstable nucleosides.

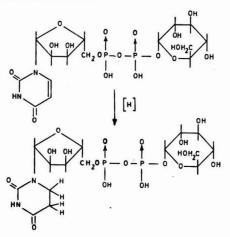
As we intended to use the method of Khorana for transforming nucleotides to the desired pyrophosphates it was necessary to transform nucleotides to their corresponding morpholidates. No difficulties were encountered in this step and morpholidates of modified uridilic acids were obtained under standard conditions, by condensing nucleotides with morpholine in the presence of dicyclohexylcarbodiimide. Complication was observed only with the 4-thio analogue, which partially exchanged its thio group for morpholine residue if long reaction periods were taken.

The final step, pyrophosphate condensation, was outlined according to the method of Khorana via nucleotide morpholidates, treating them with trin-butyl ammonium a-D-glucose-1-phosphate in dry pyridine. The original method was modified by carrying out the condensation at 60° instead of room temperature so as to reduce the time of reaction. The synthetic UDPG analogues from the reaction mixture were isolated by ion-exchange chromatography on Dowex I or DEAE-Sephadex A-25 with triethylammonium acetate (pH 5) as eluent buffer, and the compound subsequently transformed to sodium salts. The yields of pyrophosphates were usually of the order of 40-50 per cent, but with isocytidine-5-phosphomorpholidate the yield was only 15-20 per cent.

At present, we have not obtained complete data concerning biochemical activity of our analogues. However, the results of preliminary biochemical assays now available are in agreement with the concept outlined in the beginning of the present report. For example, of the analogues tested, the N-methyl derivative (I) and cytidine diphosphate glucose (III) appeared completely inactive in the synthesis of sucrose (glucosylation) and in oxidation of glucose residue to glucuronic acid (oxidation at C6). Such behaviour was expected, because all the system of hydrogen bonding is destroyed in these compounds. On the contrary, 4-thio-UDPG (II) and 6-aza-UDPG (VI) entered both the enzymic reactions, though they exhibited a somewhat reduced activity. In this case there must have taken place only partial weakening of hydrogen bonding and of the secondary structure. More detailed investigation of biological activity now in progress will certainly allow making more precise conclusion concerning the validity of the general concept.

Besides this approach, confirmation of the hypothesis will probably be obtained by physical and chemical study of the analogues. The secondary structure of NDPS must in some manner bear upon their reactivity. In other words, there must be reactions proceeding at different rates with NDPS having 'horse-shoe' conformation and with their analogues having no fixed secondary structure. The concept would receive a strong support if such reactions were found. In this connection I shall mention here our very interesting recent observation.

First attempts to obtain 5,6-dihydro-UDPG by catalytic hydrogenation of UDPG were unsuccessful, as this reaction proceeded very slowly. At the same



time, hydrogenation of the double bond of uridine-5-phosphate, leading to 5,6-dihydrouridilic acid, proceeded very readily under identical conditions. The fact is probably accounted for by the shielding of this double bond in UDPG by the 'horse-shoe secondary structure. The explanation seemed even more reasonable after we found that addition of urea to the reaction mixture caused a considerable increase in the rate of hydrogenolysis. It is well known that in concentrated solution of urea hydrogen bonds are weakened, or even completely cleaved. In our case this cleavage has probably resulted in disruption of the 'horse-shoe' conformation, which made the double bond sterically available for hydrogenation. More detailed investigation of this phenomenon is now in progress.

The data presented above covering only the first stage of our investigation of synthetic analogues of UDPG have probably demonstrated the prospects of investigation of molecular mechanism of NDPS activity and of the effect of substrate conformation upon the specificity of enzymic reactions.

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## Chemical Modification of RNA\*

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TRUCTURAL modification of ribonucleic acids by the action of various chemical reagents, affecting only one moiety or type of bonding of these biopolymers, is becoming one of the most important problems of nucleotide chemistry. Modification of the covalent structure must necessarily bring about changes in physical, chemical and biological properties of the macromolecule, and hence can be applied in one or another form to the investigation of (i) physical characteristics and secondary structure of nucleic acids, (ii) their reactivity, and (iii) problem of their biological specificity, including genetical, enzymological studies, etc. The most important application of the important application of the chemical methods for selective modification must become the analysis of the primary structure of RNA, which can be considered an urgent task of the modern nucleic acids chemistry. During the last three years chemical modification of nucleic acids has been extensively studied in our laboratory in connection with the problem of sequence analysis.

One of the most promising approaches to elucidate the sequence of nucleotides in RNA can be based on the principle now widely used in protein chemistry, i.e. selective cleavage of the polymer chain into oligomer blocks and sequence analysis within these blocks, enabling reconstruction of the whole pattern<sup>1</sup>. The problem of isolation of homogeneous preparations is now principally solved for the so-called 'soluble' or 'transfer' RNA, bearing adaptor functions in protein synthesis<sup>2</sup>. The problem of separation of the oligonucleotide mixture has been finally solved by elaboration of two methods - that of Tener and coworkers<sup>3</sup>, who used 7M urea as solvent in ionexchange chromatography, for removing the nondesirable adsorption effects and that of Budowsky and Demushkin<sup>4</sup> from our laboratory, who demonstrated that the best resolution can be achieved by using for rechromatography eluant buffers with pH sharply different from that applied in the first run.

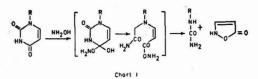
The limiting step of the above-outlined approach to sequence analysis is that of specific cleavage of the polymer chain of RNA. Evidently, complete sequence analysis needs elaboration of several — no less than two — independent methods for selective cleavage. Such completely selective cleavage of the polymer chain can be achieved by (i) isolating completely specific hydrolytic enzymes (up to the date, only one such enzyme  $T_1$  ribonuclease or guanase has been described), (ii) a purely chemical approach, i.e. a reaction, involving only one type of bonding, and (iii) a combined approach, based on selective modification of a given type of moiety of the polymer followed by hydrolysis with a nonspecific enzyme, like pancreatic ribonuclease, which becomes completely selective due to the modification.

The second and third approaches need chemical agents modifying selectively one or another moiety or type of bonding of RNA. Until recently, the chemical methods have been of incomplete selectivity. For example, treatment of RNA with nitrous acid<sup>5</sup>, alkylating agents<sup>6</sup>, halogenation<sup>7</sup>, condensation with formaldehyde<sup>8</sup>, the reaction with mercaptans9, and some other reactions10,11 cannot afford selective modification, at least, when applied in their present form. It must be mentioned, however, that some of them are of potential value for the purpose and need detailed investigation. The above considerations should have led one to the conclusion that the problem of sequence analysis, as well as biological, say genetical, studies would receive a considerable impetus after elaboration of a reaction, modifying selectively one type of the nucleic base residues.

Our investigations are aimed first of all at developing these types of reactions. We have demonstrated that hydroxylamine, a long-known mutagen, is a mild reagent reacting with RNA rather selectively<sup>12</sup>. The selectivity of the reaction with hydroxylamine appeared much greater than that of the related hydrazine. Preliminary investigation of the reaction of hydroxylamine with yeast polymer RNA revealed that under appropriate conditions (pH 9.5-10.5) there takes place almost quantitative destruction of uracil residues, whereas the use of other conditions (pH 6.5) leads to almost complete destruction of cytosine nuclei. The purine bases remained intact in the whole range of conditions investigated. The same selectivity was observed for the reaction of hydroxylamine with individual nucleosides. Analogous results were obtained simultaneously in other laboratories13-15.

The development of a completely selective method on the basis of reaction of RNA with hydroxylamine needed the solution of a number of difficult problems. First of all, it was necessary to exclude non-specific hydrolysis of RNA during hydroxylaminolysis. For example, 2 per cent of the phosphodiester bonds per hour were hydrolysed non-selectively under the conditions employed by Schuster<sup>14</sup> and Zillig and coworkers13. As quantitative hydroxylaminolysis takes some 50-70 hr, this side reaction would annul all the selectivity and the pattern obtained would be of no value for sequence reconstruction. We have succeeded in finding appropriate conditions to bring the non-selective hydrolysis to a minimum. Treatment of RNA with 5M hydroxylamine at 0° during 80-100 hr resulted in quantitative modification, overall spontaneous hydrolysis making no more than 2-3 per cent, which is of no importance for sequence analysis, at least with soluble RNA.

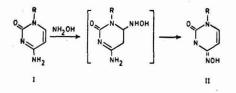
<sup>\*</sup>Lecture delivered at the University of Delhi under the auspices of the Advanced Centre on the Chemistry of Natural Products on 27 December 1963.



The second problem was the development of methods for selective cleavage of the polymer chain of modified ribonucleic acid at the sites of the modified pyrimidine residue. The mechanism of the reaction of hydroxylamine with uridine as shown in Chart 1 accounts for the data obtained in our and other laboratories<sup>1,12,14</sup>.

As seen in Chart 1, the reaction results in the formation of urea residues in place of uracyl mojeties.

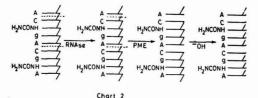
The other pyrimidine nucleoside, cytidine (I), reacts with hydroxylamine to give uridine oxime (II) (ref. 16).



Comparing the two reactions, one comes to a simple idea, i.e. to split the polymer chain at the sites of destructed uracil moieties, achieving this by removal of the urea residues and subsequent mild alkaline hydrolysis to cause elimination of the phosphate groupings, occupying the  $\beta$ -position with respect to the open ribose carbonyl. However, this simple idea as many simpler ideas failed. All attempts to hydrolyse this N-glycosidic bond without nonselective degradation of the polymer were completely unsuccessful. We tried to remove the urea residue by acid hydrolysis, by reglycosidation with large excess of glucose and hydroxylaminolysis with large excess of hydroxylamine. The elimination of urea residues under mild conditions was too slow, whereas drastic conditions, leading to more ready elimination resulted in considerable non-specific hydrolysis of the polymer.

Hence, we were made to look for other approaches. As it is known<sup>17</sup>, ribonuclease hydrolyses polyribose phosphate up to hundred times slower than RNA. It could be anticipated that the presence of urea residue will not increase this rate. If it were the case, ribonuclease would split the hydroxylamine modified RNA only at the sites of intact pyrimidine bases, that is, after cytidine or modified cytidine residues, and would not touch the phosphodiester bonds adjacent prior to uridine. To say it in other words, ribonuclease would become a completely selective enzyme.

Experimental verification of the idea showed its validity. First of all, it appeared that polyuridilic acid, when treated with hydroxylamine under the above conditions and containing no uridine residues, is completely stable under the conditions of ribo-



nuclease hydrolysis. This result was very promising, as it showed the phosphodiester bonds adjacent to the ribosylurea residues to be stable towards ribonuclease action.

On this basis, the first completely selective method for degradation of RNA was developed<sup>18</sup> (Chart 2). RNA was treated with hydroxylamine as usual, and the modified polymer, containing no uracil nuclei, subjected to ribonuclease hydrolysis.

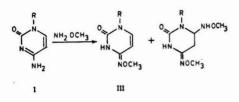
In order to prove the complete selectivity of the method the resulting oligonucleotide mixture was digested with prostatic phosphodiesterase, which removed all the terminal phosphate groupings. After this treatment, the mixture was subjected to alkaline hydrolysis, which leads to the formation of nucleotides from the non-terminal residues and of nucleosides from the terminal residues, containing no phosphate groupings. Analysis of this alkaline hydrolysate revealed the nucleoside fraction to contain only cytidine and modified cytidine. Thus, only cytidine was the terminal nucleotide in all the oligonucleotides obtained by ribonuclease digestion of hydroxylamine-modified RNA. Chemical modification of the substrate made the enzyme completely selective, and it cleaved only the postcytidine phosphodiester bondings. So we had in our hands the first completely selective method useful for sequence analysis.

It has been already mentioned that complete sequence analysis of RNA needs several independent methods for selective cleavage of the polymer chain at the sites of different types of phosphodiester bondings. In this connection parallel investigations of other possible approaches were made.

Comparing the above-presented mechanisms, proposed for the reactions with hydroxylamine of uridine and cytidine (ref. 14 and 16), one notices their essential difference. Really, the rate of the reaction of hydroxylamine with cytidine increases with the protonation of hydroxylamine (pH 6) and decreases with the protonation of cytidine (pH 4·2). On the other hand, uridine is most probably attacked by non-ionized hydroxylamine, as revealed by the drop in the rate in strongly alkaline medium where ionization of -hydroxylamine (ion NH<sub>2</sub>O<sup>-</sup>) takes place. These considerations lead to the conclusion that N- and O-substituted hydroxylamines should exhibit a somewhat greater selectivity.

Investigation of O-methylhydroxylamine<sup>19</sup> as potential highly selective reagent demonstrated validity of the above considerations. Of the four common ribonucleosides, the reagent affected only cytidine and did not attack uridine over the whole range of conditions tested in spite of the very long reaction periods (up to 100 hr). Reaction of cytidine (I) with O-methylhydroxylamine resulted in a

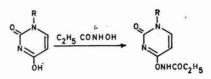
mixture of two products, one of which was uridine O-methyloxime (III), and the other could be readily converted to uridine O-methyloxime, being most probably the intermediate product shown in the above mechanism. Hence, the overall reaction could be presented by the following scheme:



The pH optimum of this reaction lies near 6. It is very slow at pH values 2 and 8 and does not take place at pH 10. The mild conditions necessary for quantitative modification made it possible to apply it directly to ribonucleic acid as they excluded any possibility for non-selective hydrolysis20. Hydrolysis of RNA treated with O-methylhydroxylamine revealed the complete disappearance of cytidine and the retention of the adenosine/guanosine ratio. The reaction of O-methylhydroxylamine with RNA was the first method for completely selective modification of only one of the base residues. The reagent must soon gain importance in biological and genetical studies, as its advantages over the now existing non-specific mutagens (HNO2, hydroxylamine, alkylating agents) are obvious.

In order to apply the reaction with O-methylhydroxylamine to selective cleavage of RNA it was necessary to study the digestion of the modified polymer with ribonuclease. It could be expected that the modification will again increase the selectivity of the enzyme, and it will hydrolyse only the posturidilic phosphodiester bonds. Unfortunately, experimental evidence obtained was not in support of this supposition. Ribonuclease hydrolysis of modified RNA as well as of O-methylhydroxylamine treated polycytidilic acid resulted in cleavage of the polymer chain at the same sites as before modification<sup>20</sup>. Moreover, ribonuclease appeared non-sensitive to modification with O-benzylhydroxylamine. Though the reagent quantitatively modifies the cytosine residues in a manner similar to that of O-methylhydroxylamine, introduction of the bulky benzyl grouping was of no effect upon the specificity of the enzyme. This result being discouraging in view of the development of the new methods for selective cleavage is important for our understanding the mechanism of ribonuclease hydrolysis. Obviously, the purely steric hindrance caused by the presence of the bulky substituents is not essential, and for changing the rate of hydrolysis it is necessary to block some reactive grouping of the pyrimidine residue.

As already mentioned, the mechanism proposed for the reaction of pyrimidine nucleosides with hydroxylamine suggested that not only O- but also N-substituted hydroxylamines may appear more selective reagents than the parent compound. Really, it appeared that hydroxamic acids (which can be regarded as N-acyl hydroxylamines) do not react with cytidine, but, in accordance with the above mechanism, modify uridine<sup>21</sup>. Cytidine and adenosine are completely inert to this reagent. However, not only uridine but also guanosine, pseudo-uridine and thymidine are reactive. The modification consists of acylation of the phenolic hydroxyl by hydroxamic acid, as outlined for uridine in the following equation:



The rates of modification of guanosine and uridine seem to be different enough to enable selective modification of only guanosine (at pH 8) or of both the two nucleosides (pH 9). On the other hand, the reaction seems very promising as an approach to selective cleavage of the transfer RNA chain at the sites of 'minor' nucleotides to give long oligonucleotides of greatest interest for sequence analysis.

The novel approach developed in our laboratory to the problem of sequence analysis of RNA, based on selective chemical modification and subsequent hydrolysis with a non-selective enzyme, seems one of the most promising ones, and we hope that it will be soon tried for elucidating the covalent struc-ture of low molecular 'transfer' ribonucleic acids. On the other hand, O-methylhydroxylamine — the most selective mutagen ever studied - is, as we know; now successfully applied.

Hence, the design of new chemical reagents of complete selectivity and study of the possibilities to increase selectivity of the old ones (e.g. hydrazine) seem of greatest interest to the chemists of our laboratory.

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## Hydraulic Lime

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THE use of lime as a building material dates back to antiquity. Of the various types of lime used for construction work, the first ever known is perhaps hydraulic lime produced by the calcination of limestones containing a large portion of clayey matter; it possesses the property to set and harden under water. Before Portland cement came into prominence as an outstanding construction material, hydraulic lime had been the chief cementitious material. However, by the end of the nineteenth century standard quality Portland cement became easily available, and hydraulic lime was reduced to the position of a secondary material.

There has recently been greater awareness of the beneficial effects of the use of lime in masonry work and it has been recognized that compared to any other building material, lime improves some of the basic requirements of masonry mortars, such as water retention, workability, watertightness, small cyclic volume changes, etc., and it costs less. However, although the manufacture of high calcium lime has improved greatly, the manufacture and use of hydraulic lime has not been standardized and has received much less attention. This appears to be mainly due to the variable nature of limestones from which hydraulic lime is produced. The present article reviews some of the important aspects of the manufacture and use of hydraulic lime, viz. clayey matter in limestones and their effect on the calcination process, specifications, constitution and hydration of hydraulic lime.

#### Impurities in Limestones and Manufacture of Hydraulic Lime

Generally, the impurities in limestones consist of silica, alumina, ferric oxide, titania, etc. These impurities combine with calcium oxide at the usual firing temperature of a limekiln. The combination of calcium oxide with the impurities occurs at the most active surfaces of calcium oxide. Consequently, the reactivity of the lime produced is diminished not only because the impurities render part of the lime unavailable for reaction with water, but also because the portion rendered unavailable would otherwise have been most reactive.

Deforge<sup>1</sup> studied many theoretical and practical aspects of the manufacture of hydraulic lime. The

uses of hydraulic lime in building have been reviewed by Lafuma<sup>2</sup>. Some useful contributions were made by Hoon<sup>3</sup>, Dumas<sup>4</sup> and Alherton<sup>5</sup>. Most of these investigators considered the clayey matter in limestones as merely acting as an admixture of different oxides and the process of manufacturing hydraulic lime to be more or less akin to the manufacture of cement

In the manufacture of hydraulic lime the reactions between calcium oxide and the components of clay minerals are mostly solid state reactions. These reactions depend not only on composition and temperature but also on the duration or rate of heating. The processes are greatly influenced by the physical and chemical conditions of the specific clay minerals and their distribution in limestones. Large particles of quartz or isolated pockets of clay will react at the surface, and even though calcium oxide may be available, complete combination may not occur. Contrary to this, in the manufacture of Portland cement a complete combination of clay components with calcium oxide is invariably aimed at and achieved.

For the manufacture of hydraulic lime it is desirable to produce lime by 'soft burning', i.e. at low temperature so as to obtain maximum porosity and, therefore, large surface available for reaction of lime with water. At the same time, it would be logical to burn limestones at the highest possible temperature to obtain maximum kiln efficiency as well as maximum hydraulic value due to the formation of cementitious constituents. However, in the latter process 'hard burning' or 'sintering' of lime is to be avoided as far as possible. A compromise, therefore, has to be made so that a hydraulic lime retains its beneficial physical characteristics, yet possesses the best possible cementitious properties. This ideal condition is particularly difficult to achieve unless the behaviour of clay matter in a limestone during its calcination is precisely known.

Although knowledge of the products of reaction between calcium oxide and clay is fairly advanced, comparatively little is known about the effects of the dehydration and nucleation characteristics of different clay minerals on the combination of calcium oxide and clay components, and on porosity and reactivity of lime. Hence, whether the reactivity of a lime is based purely on surface available for reactions as pointed by Wührer<sup>6</sup> or whether a chemical factor also affects it is not well understood.

With a view to understanding some of the above factors,  $Azbe^7$ ,  $George^8$  and Ludwig *et al.*<sup>9</sup> studied artificial hydraulic limes as the calcined product of mixtures of calcium carbonate and silica, alumina, iron oxides, etc., or a clay mineral, but the results obtained were of little practical value as they were not corroborated by studies on natural limestones. It is, therefore, of great practical consequence, firstly, to devise suitable methods for the separation, identification and estimation of clay minerals in limestones and, secondly, to study the effect of dehydration characteristics of clay minerals on such physical properties as shrinkage, porosity, reactivity and hydration of hydraulic limes.

#### Specifications on Hydraulic Limes

In practice, hydraulic lime, obtained by burning argillaceous and siliceous limestones at temperature of 950-1200°C., contains free calcium oxide, some cementitious constituents and certain non-cementitious constituents. The relative quantities of these constituents determine the degree of hydraulicity and accordingly hydraulic lime is designated as 'semi-hydraulic' or 'eminently hydraulic'. These classifications are arbitrarily based, for example, on early strength as in the French standard specification (P-15-310) or on the contents of calcium and magnesium oxides as in the British standards (BS 890:1940) or on both as in the ASTM specification (C-141-1961) and Indian standard specification (IS:712-1956). These classifications often result in confusion because two limes of more or less similar chemical composition may show entirely different setting and strength development properties. According to the standard specifications, if soluble silica, alumina and iron oxide together in a lime lie within the range 15-25 per cent, the lime is considered hydraulic. However, these oxides would have combined either in the hydraulic or nonhydraulic constituents or both, which cannot be determined by chemical analysis. Hence, the usual chemical analysis does not indicate the difference in the hydraulic properties of two limes similar in chemical composition but different in constitution.

#### **Constitution of Hydraulic Lime**

The constitution of hydraulic lime is little understood. According to some workers<sup>1,8,10-12</sup>, hydraulic lime consists of a mixture of calcium oxide and a cement almost identical with Portland cement. However, it is not so, because the formation of cement minerals in hydraulic lime is not exactly governed by the equilibrium conditions and phase relations between calcium oxide, alumina, silica, iron oxide, etc., as in the manufacture of Portland cement.

Azbe *et al.*<sup>13</sup> identified the constituents of a few hydraulic limes and reported the presence of calcium oxide, magnesium oxide,  $\beta$ -dicalcium silicate and tricalcium aluminate. No evidence of the presence of tricalcium silicate, the most important constituent of Portland cement, was obtained. Roberts<sup>14</sup> studied the constitution of five commercial hydraulic limes manufactured in the United Kingdom by X-ray diffraction, optical microscopy and chemical methods and identified  $\gamma$ -dicalcium silicate, and  $\alpha$ - and  $\beta$ -calcium silicate, tetracalcium aluminoferrite, dicalcium aluminosilicate and tricalcium disilicate in addition to the minerals identified by Azbe *et al.* However, no explanation was given about the conditions which facilitated the formation or otherwise of a specific constituent. According to Roberts, phase equilibrium data are of little consequence for quantitative determination of various cementitious constituents in hydraulic limes.

Ludwig et al.<sup>9</sup> prepared artificial hydraulic limes from calcium oxide and one of the clay minerals, viz. kaolinite, montmorillonite and illite. On the basis of the compounds estimated by X-ray and electron microscopy they computed the mineralogical compositions of 25 commercial hydraulic limes. In this study it was supposed that the clay minerals in limestones occur in as homogeneous a state as they could be distributed in an artificial mixture. However, the distribution of clay minerals in limestones is far from homogeneous and, therefore, an exact determination of the mineralogical composition on the basis of studies on artificial mixtures is not adequate. The homogeneous state of reactions in the manufacture of hydraulic lime at the best occurs only at some localized positions.

β-Dicalcium silicate is by far the most important constituent of hydraulic lime. In the manufacture of limes, due to slow cooling operation, often the inversion of cementitious β-dicalcium silicate takes place into non-cementitious γ-dicalcium silicate. Sometimes irrespective of slow cooling of hydraulic lime β-dicalcium silicate is present in stabilized form due to excess of calcium oxide or some minor constituents like potassium oxide, phosphorous pentoxide, chromium oxide, etc.<sup>15</sup>, and these constituents sometimes modify the rate of hydration of β-dicalcium silicate<sup>16</sup>. But it is not known exactly under what conditions a hydraulic lime would contain β-dicalcium silicate or γ-dicalcium silicate.

#### Hydration of Hydraulic Lime

During slaking or hydration of hydraulic lime the free calcium oxide must be hydrated completely and the lime putty left for at least 24 hr for maturing. However, during this process the hydraulic constituents of hydraulic lime are likely to lose a part of their cementitious value. As a result there is controversy about the method, time and temperature of hydration of hydraulic lime. Hydration of hydraulic lime for 24 hr is specified, presumably because the loss of hydraulic value is considered negligible, as β-dicalcium silicate, the most predominant constituent, is expected to hydrate very slowly. However, a hydraulic lime may contain some other cementitious minerals like tricalcium aluminate, dicalcium aluminosilicate and tetracalcium aluminoferrite in different amounts and may hydrate very quickly during slaking, with consequent loss of hydraulic value. Hence, there is need to find out a proper method of hydration or slaking of hydraulic lime to satisfy the various requirements resulting from the above controversy.

In conclusion, the problems relating to the manufacture and use of hydraulic lime which need further investigation may be listed as follows:

(1) Physical and petrographic properties of argillaceous and siliceous limestones to determine the nature and distribution of clayey and non-clayey constituents; (2) separation, identification and estimation of clay minerals in limestones; (3) effect of the dehydration and nucleation characteristics of clay minerals in limestones on the calcination process and on the physical properties like porosity and reactivity of hydraulic lime; (4) constitution of hydraulic lime, particularly the method for the quantitative determination of mineralogical composition; and (5) hydration of hydraulic lime with a view to arriving at a suitable method of hydration and determining the compositions of the hydration products.

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#### **Recent Advances in Optics & Their Applications in Defence**

A Seminar on Recent Advances in Optics with Particular Reference to Their Applications in Defence will be held at the Instruments Research & Development Establishment, Ministry of Defence, Dehra Dun, under the auspices of the Defence Research & Development Organization on 30 and 31 October 1964. The main object of the seminar, which is expected to be attended by senior officers from the three Defence Services as well as by top defence and civilian scientists, who are specialists in the field, is to review and discuss some of the recent advances in the fields of optics and applied optics and their possible applications in meeting the futuristic needs of the Defence Services in particular, and of optical instrumentation in general. The

following topics have been included for discussion during the seminar: (1) Fibre optics and its applications; (2) Lasers and their applications; (3) Infrared optics and its application; (4) Modern trends in optical image evaluation; and (5) Recent developments in interferometric techniques and their applications.

As part of the programme of the seminar, a popular lecture by Dr S. Bhagavantam will be delivered on the evening of 30 October.

Those intending to participate or contribute papers for discussion during the seminar should write to the convener, Dr C. S. Rao, Director, Instruments Research & Development Establishment, Dehra Dun, by 10 October 1964.

### Microbiological Corrosion: Sulphate Reducing Bacteria & Their Corrosive Influence on Metals

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CULPHATE reducing bacteria are largely responsible for the corrosion of subterranean metal structures. These bacteria also cause the corrosion of submerged metal structures at favourable sites. In respect of prevalence and severity, bacteria are one of the most important natural corrosive agencies. The problem of bacterial corrosion is particularly serious in the case of subterranean ferrous pipelines. Huge economic losses due to this phenomenon have been reported from several countries. Such corrosion in the United States alone has been estimated to cause a loss between 500 and 2000 million dollars per annum<sup>1</sup>. A corresponding figure for United Kingdom is 5 million pounds<sup>2</sup>. Corrosion loss due to subterranean cables and pipelines in Japan is 0.2 million dollars annually3. Unlike a temperate country, the conditions in a hot humid tropical country like India are more conducive for bacterial corrosion. However, no estimate has been made of the losses due to this agency in India.

With accelerated industrialization of the country, specially the development of petroleum industry and installation of different types of subterranean and submerged pipelines, storage tanks and other metal structures, the problem will become more formidable. A survey of the literature reveals that little research work on the corrosive influence of bacteria and its mitigation has been done in the country. In view of this it was considered of interest to review this aspect of corrosion.

#### Taxonomy and Morphology of Bacteria

Several families of bacteria reduce sulphate, including those which reduce sulphate prior to the synthesis of sulphur containing amino acids. But the dissimilatory bacteria, whose major energy yielding reactions are associated with the reduction of sulphate to sulphide, are designated as the sulphate reducing bacteria<sup>4</sup>. There are several species. Some of the apparently different species have been gradually acclimatized to grow under conditions favourable to others, such as mesophilic strains which can be acclimatized to grow at 50°C. and thermophilic strains at 30°C. Hence, it was suggested that such species should be regarded as the different strains of the same species<sup>5</sup>. But recent studies have provided results contrary to this view<sup>6</sup>. Certain varieties of mesophiles are unable to grow at temperatures higher than 37°C.; the highest temperature to which the mesophiles can be acclimatized is below 50°C.; certain halophiles cannot grow in soft water, some form spores and others do not. A brief account of the taxonomy and the morphology and some other characteristics of the sulphate reducing bacteria would be of importance.

Desulphovibrio desulphuricans — It has been classified' under Schizomycetes and is the most

commonly occurring species. It is a mesophilic, gram-negative vibrio. In actively growing cultures at about  $30^{\circ}$ C., the cells are slightly curved vibrios  $c. 2 \times 10^{-3}$  mm. long, each with a single polar flagellum  $c. 10^{-5}$  mm. thick<sup>8</sup>. Under specific conditions of growth they also appear as coccoid cells, short rods or spirilla<sup>9</sup>. Its cells possess rapid progressive motility.

Desulphovibrio aesturii — It is a halophilic or salt tolerant variant of the species D. desulphuricans, with which it resembles in most of the physical and physiological characteristics.

Desulphovibrio orientis — It is a spore forming mesophilic vibrio which resists heating and drying. It lacks certain pigment characteristics of D. desulphuricans<sup>10</sup>.

*Clostridium nigrificans* — The thermophilic sulphate reducing bacteria were earlier designated as D. thermodesulphuricans. But now it has been unequivocally established that such species are *Clostridium nigrificans*<sup>11,12</sup>. It is spore forming, thermophilic, gram-negative bacteria flourishing best at 55°C. Some strains may be capable of growing<sup>13</sup> at temperatures as high as 60-80°C. Its cells are larger in size and possess several flagella scattered around. Its cells rotate with very little progressive motion<sup>14</sup>.

A barophilic species of peculiar morphology has been reported  $^{15}$ .

Desulphovibrio rubentschickii, capable of utilizing acetate, propionate and butyrate, and Desulphovibrio rubentschickii var. anomalous, capable of utilizing propionate and butyrate but not acetate, have been mentioned as separate species<sup>5</sup>. But these species could not be isolated later<sup>16</sup>. Hence, their existence is doubtful.

Desulphoristella has been mentioned as a different genus<sup>17</sup>. But it is not considered to include a single pure species.

#### Sulphate Metabolism in Bacteria

The mechanism of conversion of  $SO_4^{2-}$  to  $S^{2-}$  has not been completely elucidated, but it is definite that it involves several steps. The potential inorganic intermediates between  $SO_4^{2-}$  and  $S^{2-}$  which are reducible by the bacteria are  $SO_3^{2-}$ ,  $S_2O_3^{2-}$ ,  $S_4O_6^{2-}$ ,  $S_2O_4^{2-}$ ,  $S_2O_5^{2-}$  and colloidal sulphur.  $SO_3^{2-}$  is reduced at a faster rate and all others at much slower rates. The bacteria are not able to reduce  $S_3O_6^{2-}$ ,  $S_5O_6^{2-}$ ,  $S_2O_6^{2-}$  and  $S_2O_8^{2-}$  ions, non-colloidal sulphur and a large number of other sulphur compounds including cysteine. It has been shown that  $SO_3^{2-}$  may be the intermediate<sup>18</sup>. This was supported by the observation that  $SO_3^{2-}$  inhibits the reduction of labelled  $SO_4^{2-}$ while  $S_2O_3^{2-}$  does not<sup>19</sup>. In a mixture,  $SO_3^{2-}$  is preferentially metabolized first and the reduction of  $SO_4^{2-}$  is initiated only after all sulphite has been used up. The attempts to trap  $SO_3^{2-}$  by reducing  $SO_4^{2-}$  in the presence of acetone have not given any indication of  $SO_3^{2-}$  formation. Instead of free  $SO_3^{2-}$  ion, some organic derivative of  $SO_3^{2-}$  inside the cell may be the true intermediate<sup>20</sup>. If bacteria are grown in excess of  $SO_3^{2-}$  containing some isotopically labelled  $SO_4^{2-}$  and the reaction is stopped before completion, some of the isotope is found to be present as sulphite<sup>21,22</sup>. Hence the sulphite or some other derivative in biochemical equilibrium with it may be the intermediate. Recently it has been found that  $SO_4^{2-}$ forms an organic derivative and then it is directly reduced to  $SO_3^{2-}$ . This activity represents a new mechanism<sup>23</sup>.

Selenate, an analogue of sulphate, is not attacked by bacteria, but it completely inhibits  $SO_4^2$  reduction, whereas the reduction of  $SO_3^2$  is not inhibited either by selenite or selenate<sup>24</sup>. Hence selenate inhibits the conversion of  $SO_4^2$  to  $SO_3^2$ .

#### **Ecological Changes**

The sulphate reducing bacteria during their growth utilize hydrogen or other reducing agents to reduce sulphate to sulphide. The free hydrogen gas formed as one of the products of anaerobic microbiological metabolism is used up. The utilization of cathodic hydrogen on metal surfaces is a prominent cause of corrosion in such environments. Because of the reduction of sulphide, the concentration of sulphate ions in the medium gradually decreases, unless there is some mechanism of its replenishment. In natural waters the sulphate content is sometimes low and hence by initial growth of bacteria all sulphate is exhausted and further growth automatically ceases.

The ferrous sulphide formed by the corrosion process blackens the surrounding soil. Usually the sulphide is in porous and finely divided state which gets rapidly oxidized on exposure to air. At pH 7, the sulphide hydrolyses with the evolution of hydrogen sulphide, which is involved in several of the following ecological changes: (1) The growth of bacteria increases the pH of the environment by the escape of hydrogen sulphide, unless there are some compensatory processes such as the formation of metal sulphide or acid fermentation. (2) Heavy metal ions are precipitated as sulphides. (3) Hydrogen sulphide being an active reducing agent greatly depresses the oxygen concentration and hence enhances anaerobiosis. The redox potential goes down and a better condition for the growth of anaerobic bacteria is attained. (4) Hydrogen sulphide exerts a poisonous effect on most of the higher aerobes. After their death, the putrefaction provides the - nutrients required for the sulphate reducing bacteria. (5) Hydrogen sulphide exerts deactivating influence on certain anaerobic bacteria such as methane bacteria. Hence they are rendered inactive during large-scale growth of sulphate reducing bacteria. (6) Hydrogen sulphide helps to enhance the growth of certain microorganisms such as sulphide and sulphur oxidizing bacteria and blue or green algae by favouring their metabolism.

These ecological changes are important from the point of view of corrosion of metals by bacteria.

# Conditions for the Natural Growth of Bacteria

The essential physico-chemical factors for the growth of bacteria are the following:

Anaerobiosis - As the bacteria are anaerobic, their growth occurs only in the environments where anaerobic condition can be established and maintained. Such environments occur mostly under natural or artificial water systems or water saturated soils. Sometimes sufficient degree of anaerobiosis may frequently occur at isolated regions in water or soils with high oxygen content, because of chemical or biochemical reducing reactions such as action of reducing metal ions, cellulose fermentation, etc. Hence such regions can also be the locations of the growth of bacteria. When bacteria are exposed to aerobic environment, their growth stops and they remain dormant and flourish again when they enter anaerobic environments. Thus the bacteria are aeroduric and oxygen exerts only bacteriostatic action25.

Temperature — The sulphate reducing bacteria can exist and grow in suitable locations over a wide range of temperature ( $25-60^{\circ}$ C.). Bacterial activity up to  $80^{\circ}$ C. is also reported<sup>13</sup>. Several strains are capable of acclimatization to new conditions of temperature.

pH — The effect of pH of the environment on sulphate reducing bacteria is characteristic. The bacteria are active only in neutral or slightly alkaline medium. The most favourable pH is 7.5. A pH above 9.0 (ref. 26) and below 5.0 (ref. 27) is detrimental to their growth.

Carbon requirements — Most of the strains are facultative autotrophs<sup>14,28</sup> and only a few do not grow autotrophically<sup>29</sup>. Hence organic materials are not essential for the growth of most of the strains as they can grow with carbonate and bicarbonate as sole carbon source<sup>25</sup>. But the autotrophic growth is slight as compared with heterotrophic growth<sup>26,30–33</sup>. The rates of SO<sub>4</sub><sup>2-</sup> reduction in subterranean waters in summer months greatly exceed the rates in springs. The amount of organic matter dissolved in water is the main factor limiting the growth<sup>34</sup>.

D. desulphuricans derives energy for cell synthesis from inorganic compounds or non-assimilable organic compounds, but the cell carbon is derived from organic compounds which are unable to act as energy sources<sup>35</sup>. D. aesturaii fixes carbon dioxide heterotrophically using organic reducing agents and autotrophically using elementary hydrogen<sup>36</sup>. It has now been established that bacteria are incapable of growth in completely autotrophic, medium<sup>37</sup>. Field conditions are rarely autotrophic, though significant bacterial corrosion may occur under such conditions. A ferrous specimen buried at a depth of 5.5 metres, where the solid does not contain any organic matter in detectable quantity, has been found to suffer severe corrosion<sup>38</sup>.

Reducing agents — A direct or indirect source of hydrogen is required by bacteria for the reduction of  $SO_4$  (ref. 20). Elementary hydrogen is utilized

#### TRIPATHI: SULPHATE REDUCING BACTERIA & THEIR CORROSIVE INFLUENCE ON METALS

in autotrophic growth only<sup>39</sup>. In natural environments, chemical or biochemical processes involving inorganic reducing ions, metal and anaerobic microbiological metabolism, specially cellulose degradation provide hydrogen or organic reducing agents. The organic materials are mostly oxidized to carbon dioxide for providing hydrogen for the bacterial metabolism. A redox potential in the neighbourhood of 200 mV. is necessary for the initiation of growth of bacteria. At lower redox potentials, the rate of growth enhances<sup>40</sup>. Sewage sludge contains much larger number of bacteria than the sewage itself<sup>41</sup>. Apparently their growth takes place only when redox potential falls to a certain limit. In subterranean waters the bacterial activity is initiated only at r<sup>H</sup> value below 17 (ref. 42).

Sulphate requirements — The bacteria require inorganic sulphate for their respiration process. As sulphates are universally present in almost all soils and water systems, the condition is widely fulfilled. Concentration of sulphate required for initiation of growth of bacteria present in marine environments is less than  $2\cdot8 \times 10^{-4}M$  and for supporting maximum growth  $5\cdot6 \times 10^{-3}M$  (ref. 43).

Miscellaneous requirements — Iron is an essential growth factor<sup>25,44</sup>. Some inorganic salts like phosphates and ammonium compounds are also essential for growth. The growth of bacteria is accelerated by magnesium, aluminium, iron sulphide and rust<sup>18</sup>.

# Habitat, Corrosive Locations and Damage

The sulphate reducing bacteria occur in nearly all natural water and soil systems in active or dormant state. Whenever any artificial or natural water or soil system becomes anaerobic and other favourable conditions are also present, the activity of bacteria ensues. Sometimes anaerobiosis is attained biochemically because of the fouling and other organisms. All such locations have been found to be the centres of bacterial corrosion. Densely packed and poorly aerated clays, waterlogged soils<sup>45,46</sup>, bogs, marshes, esturine muds<sup>31,47</sup>, marine muds<sup>48,49</sup>, flood waters<sup>50</sup>, deep well waters<sup>51</sup>, creek waters<sup>52</sup>, stagnant water, polluted waters<sup>53</sup>, lakes and marine waters<sup>52,54-56</sup> are the common locations having adequate growth of bacteria. Subterranean and submerged pipelines1,2, storage tanks57, well casings58-60 and other petroleum equipment parts<sup>61</sup>, steel jetties<sup>62</sup>, various parts of the aquatic vessels<sup>30,63</sup>, industrial cooling systems and heat exchangers<sup>64,65</sup>, internal surfaces of pipes bearing water or civil or industrial wastes<sup>66</sup> and pipes from deep water wells<sup>51</sup> are known to suffer damage due to bacterial corrosion.

Sometimes the ecological materials, especially hydrogen sulphide, formed at a suitable site are responsible for corrosion at other sites. The corrosion of fuel pumps of piston driven and jet aircrafts by the fuel contaminated with hydrogen sulphide produced by bacteria in water bottoms of bulk storage tanks<sup>67</sup> has been reported.

#### **Detection of Corrosive Locations**

As the sulphate reducing bacteria are present nearly in all natural water and soils, demonstration merely

of their presence is not sufficient in deciding their potential corrosive action. It is essential to show that they are present in adequate numbers. Because of their exacting anaerobic character and similarity with some other bacteria which produce hydrogen sulphide from organic sulphur compounds, their enumeration has been difficult. These difficulties have been largely overcome<sup>68</sup>. The media with their redox potential suitably adjusted with cysteine<sup>69</sup>, metal ions<sup>70</sup>, and ascorbates and thioglycollates<sup>71</sup> have provided a valid procedure to obtain the colony counts or dilution counts. Such procedures provide a quantitative assessment of their ecology in relation to corrosion. Ecological surveys of several locations such as marine and esturine environments<sup>56,72</sup>, polluted water73, clays68 and lakes54,55 have been done. A counting procedure using membrane filters has also been described<sup>74</sup>. It seems probable that both the number of bacteria and the suitability of environment for their multiplication may be important factors for evolving a suitable index of corrosive activity75.

The detection and determination of the approximate density of bacterial population at any site can be performed by noting the time that elapses when 1 per cent aqueous soil suspension or diluted solution added to a specified sterilized aqueous medium kept at 30°C. becomes black<sup>76</sup>.

The soil redox potential measures the reducing intensity of the soil and hence provides a good measure of their bacterial corrosiveness<sup>58,77,78</sup>. Very low values of the redox potential indicate the danger of bacterial corrosion. Any neutral soil having redox potential below 200 mV. should be regarded as aggressive and soils having below 100 mV. as severely aggressive. A redox probe suitable for field use has been described<sup>79</sup>. It is an extremely useful tool for detecting the locations where all the conditions necessary for the growth of bacteria are present. Hence it can qualitatively measure the severity of the tendency of bacterial corrosion in soils.

The activity of bacteria with respect to the corrosion of iron can also be measured by iron electrode potential<sup>80</sup>. It has been found that the potential of a ferrous electrode during bacterial growth is -52 mV. with reference to the potential of a similar electrode in a sterile medium. In water systems bacterial corrosiveness can be judged by keeping corrosion coupons. A highly sensitive yet simple technique for measurement of rates of anaerobic corrosion has been described<sup>81</sup>.

#### Mechanism of the Corrosion Reaction

Several mechanisms have been proposed for the corrosion caused by the sulphate reducing bacteria. It is expected that the total corrosion is the net result of the reactions following several mechanisms. The relative importance of each mechanism depends upon several factors depending upon the nature of soil or water, metal and bacterial flora.

Cathodic depolarization — This theory is based on the observation that the cultures of bacteria cause corrosion without hydrogen evolution and that the corrosion products are the mixtures of oxide and sulphide<sup>82</sup>. According to this theory, the initial reaction of iron placed in aqueous environment is as follows:

$$HOH \rightleftharpoons H^+ + OH^-$$
$$Fe + 2H^+ \longrightarrow Fe^{2+} + 2H$$

After an initial attack a protective film of elemental hydrogen surrounds the cathodic regions and further corrosion is stifled normally. But if bacteria are present, they utilize the hydrogen film to reduce sulphate.

$$SO_4^2 + 8H \longrightarrow S^2 + 4H_2O$$

Thus, the cathodic polarization by hydrogen vanishes and the corrosion of iron proceeds on. The final corrosion products are formed as follows:

$$Fe^{2^+} + S^{2^-} \longrightarrow FeS$$
$$Fe^{2^+} + 2OH^- \longrightarrow Fe(OH)_2$$

The overall reaction is represented by

#### $4Fe+2HOH+H_2SO_4 \longrightarrow 3Fe(OH)_2+FeS$

The evidences in favour of this mechanism have been summarized by Starkey<sup>83</sup>.

The analyses of the corrosion products obtained from the field as well as from laboratory experiments confirm this mechanism. The ratio of the oxides and the sulphide in the corrosion products range between  $2\cdot4:1$  and  $3\cdot4:1$ , while theoretically the ratio ought to be 3:1 (ref. 82).

D. desulphuricans possesses a hydrogenase system which is capable of utilizing elemental hydrogen and depolarizing cathodes<sup>18</sup>. The activity of this enzyme system has been measured in terms of hydrogen absorption coefficient expressed in terms of millilitres of hydrogen absorbed per milligram dry weight of a suspension of resting bacterial cells per hour. In the case of fresh water strains of D. sulphuricans -Llanelly, Hiddenborough, Teddington R, America and Benghazi - a linear relationship between the rate of corrosion and hydrogen absorption coefficient has been observed<sup>84</sup>. This indicates that the corrosion due to these strains proceeds principally by the cathodic depolarization mechanism. It has been observed that bacterial depolarization of steel cathodes can result in a 200-fold increase in galvanic current<sup>85</sup>.

The study of the electrode behaviour in contact with bacteria provides a further confirmation of . this mechanism<sup>86</sup>. The potential behaviour of the steel electrodes dipped in a culture solution before, during and after the inoculation and growth of bacteria are practically reproducible. Prior to the inoculation the potential remains constant. This potential is the function of the pH(7.1) of the culture solution. After inoculation, the potential rapidly falls down by about 0.06 V. during a period of about 350 hr or less. In this period the polarizing hydrogen is consumed by the active bacteria and the iron dissolves in the form of ferrous ions. After reaching a minimum, the potential abruptly increases by about 0.16 V. During this period (c. 1000 hr) the bacterial activity is expected to be negligible and polarization due to the corrosion products sets in. Finally the potential constituted by Fe/FeS/electrode is attained. This potential then remains constant.

The participation of bacterial cells in the corrosion reaction during this final phase is doubtful. These observations have been confirmed by a number of workers<sup>87-89</sup>. In the presence of bacterial inhibitors such as proflavine or chromate such a phenomenon of potential variation does not occur<sup>88</sup>.

Anodic stimulation — Wanklyn and Spruit<sup>90</sup> proposed that the acceleration of corrosion due to the sulphate reducing bacteria is due to anodic stimulation rather than cathodic depolarization. The S<sup>2-</sup> formed at the end of bacterial metabolism stimulates the anodic process by combining with the accumulated Fe<sup>2+</sup>. The rate of replenishment of Fe<sup>2+</sup> increases in order to maintain the electrochemical equilibrium. Consequently, the corrosion rate is enhanced.

$$Fe^{2+}+S^{2-} \longrightarrow FeS$$

This mechanism is also supported by several observations.

Under autotrophic conditions, only a part of hydrogen liberated as a result of the corrosion of iron by bacteria is utilized for sulphate reduction. Under such conditions the bacteria exert little influence on the electrode potential. In these experiments of short duration the ratios of the oxide and sulphide have not been found in accordance with the cathodic depolarization mechanism<sup>90,91</sup>. The species *D. orientis* and *Cl. nigrificans* do not contain the hydrogenase enzyme system, hence theoretically both are incapable of acting as a depolarizing cathode. The corrosion due to these species can proceed almost entirely due to anodic stimulation.

By studying the potential behaviour of mild steel electrodes placed in media containing actively growing cultures of different species of bacteria, it has been concluded that both the mechanisms contribute to the corrosion<sup>98</sup> and at any time the relative importance of the two depends upon time,  $\rho$ H, activity and solubilities of corrosion products, bacterial flora and the phase of their growth<sup>92,93</sup>. The corrosion due to *D. desulphuricans* proceeds through both the mechanisms in which cathodic depolarization is more important.

Anodic stimulation by any species of bacteria occurs mainly during early period of the corrosion as the adherent film of ferrous sulphide formed on the metal surface partially protects it from further action by anodic stimulation. In inoculated media, the formation of ferrous sulphide in a compact inhibitory form on the metal surface takes about a week to develop at 30°C. with active cultures of *D. desulphuricans* and *D. orientis*. In the case of *Cl. negrificans* at 55°C. the film formation begins within a day<sup>75</sup>. Hence it has been observed that those species of bacteria participate which in cathodic depolarization are capable of inducing greater rate of corrosion than those participating only in anodic stimulation<sup>84</sup>.

Electrochemical cell action — Oxygen concentration cells having ferrous sulphide and iron electrodes also contribute to the total corrosion by bacteria<sup>84</sup>. Strongly anodic areas are developed by the accumulation of ferrous sulphide which produces low redox potentials. Consequently, the concentration of oxygen in such an environment is much reduced. If such area is coupled with a similar metal without

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ferrous sulphide accumulation and exposed to an environment having greater oxygen concentration, an oxygen concentration cell is established and the corrosion at the anodic areas is enhanced. At the beginning of bacterial corrosion, the oxygen concentration cell action will not be important. It is suggested that the corrosion in partly anaerobic environments may be enhanced by this mechanism<sup>95</sup>. It has been observed that because of the activity of bacteria in natural waters, gun metal may become anodic to steel<sup>96</sup>. This effect is expected to contribute to the corrosion of ship propellers.

Chemical action of ecological materials — The following materials formed as metabolites or their derivatives or corrosion products have been reported to enhance the rate of corrosion.

Hydrogen sulphide: The very first suggestion regarding the mechanism of corrosion by bacteria was that aqueous hydrogen sulphide exerts a major corrosive influence<sup>97</sup>. But the idea was abandoned with the observation that such bacterial corrosion proceeds without evolution of hydrogen and a mixture of oxide and sulphide is obtained as a corrosion product. Moreover, it is expected that aqueous hydrogen sulphide must also be exerting some corrosive action<sup>98</sup>. The electrochemical mechanism<sup>99</sup> of corrosion by hydrogen sulphide is described in terms of iron and hydrogen electrodes, dissociation constant of hydrogen sulphide and the solubility of ferrous sulphide. The driving voltage of the corrosion reaction depends mainly on the activity of hydrogen sulphide in the solution and partial pressure of molecular hydrogen. The corrosive action of hydrogen sulphide sharply drops at pH 7.

One effect of hydrogen sulphide on the corrosion process is the production of strongly reducing anodic areas which result in the establishment of oxygen concentration cell action<sup>49</sup> and better conditions for the growth of bacteria.

Sulphur: Elemental sulphur, formed by the chemical or biochemical oxidation of hydrogen sulphide or metal sulphide, is sometimes found to be present in environments where bacterial corrosion occurs. Hence the possibility of the enhancement of the corrosion of ferrous structures by solid sulphur has been investigated<sup>100,101</sup>. It has been found that the ferrous metals are rapidly corroded by aqueous suspension of sulphur. Elemental sulphur dispersed in a 5 per cent suspension of bentonite is capable of etching steel uniformly at a rate greater than the action by 3 per cent hydrochloric acid. Sulphur stimulates the corrosion process by reducing cathodic polarization and permitting a greater rate of corrosion at a relatively positive potential. Sulphur depolarizes the cathode in a way similar to oxygen. As sulphur is present on the spot in a solid form, the rate of action is not limited by the rate of replenishment. The combined action of bacteria and sulphur has been suggested<sup>100</sup> to be responsible for some of the cases of accelerated corrosion, which occur in intermittently anaerobic conditions102.

Iron compounds: Ferric sulphide, ferrous sulphate and hydrated ferric oxides formed by the oxidation of the corrosion products during anaerobic period may also exert corrosive influence on the metal<sup>100</sup>.

#### Salient Features of Bacterial Corrosion

The relative importance of the species for corrosive action -D. desulphuricans is responsible for the widespread occurrence of bacterial corrosion at various locations. D. aesturii causes corrosion in marine environments and brackish waters. Only a few authentic cases of corrosion by Cl. nigrificans are known<sup>13,103</sup>. Field corrosion by other species including D. orientis has not been reported.

Active period of bacterial life for corrosive action -The activity of D. desulphuricans incubated at 30°C. is reduced after 5 days and almost ceases after 10 days. It has been found that 6-day-old culture of D. desulphuricans possesses corrosive action on zinc, but 25- to 30-day-old one has none<sup>104</sup>. The electrode behaviour of steel in contact with D. desulphuricans shows that the activity declines in c. 15 days<sup>86-88</sup>. Hence, it has been assumed that within c. 30 days all strains of bacteria would cross the period of maximum growth and activity, and reach the inactive stage. This view has been substantiated by the fact that the maximum rate of corrosion found in laboratory is much less than the rate sometimes observed under field conditions. In batch culture conditions, the organism may be highly active only for part of the total period, while in the field a constant supply of nutrients may be available and thus bacteria are continuously maintained in a high state of activity.

Association with other corrosion-causing microorganisms — The sulphate reducing bacteria are mostly and independently responsible for the corrosion at various locations. But under suitable set of conditions they are found to be associated with other corrosion-causing microorganisms. Sometimes under the joint presence of the sulphate reducing bacteria and other corrosion-causing microorganisms, synergism of the corrosion process or symbiosis or parasite-host relationship occurs. The other corrosion-causing microorganisms associated with the sulphate reducing bacteria at suitable locations are:

Sulphide oxidizing bacteria: They are usually found where sulphide is being continuously replenished. The coloured sulphide oxidizing bacteria being phototrophs and anaerobes are invariably found associated with the sulphate reducing bacteria in muds or waters. The colourless sulphide oxidizing bacteria being aerobic are found commonly at sites where hydrogen sulphide formed by the sulphate reducing bacteria is exposed to aerobic conditions<sup>29</sup>.

Sulphur oxidizing bacteria: At locations such as incompletely filled sewers, aerobic conditions are maintained in the vicinity of some anaerobic centre of growth of sulphate reducing bacteria. Hydrogen sulphide produced at the anaerobic centre, on entering the aerobic zone, is utilized by the sulphur oxidizing bacteria to produce sulphuric acid. The end product of the metabolism of one bacteria is the initial required compound for the metabolism of the other. Such locations are responsible for heavy corrosion<sup>29</sup>. Digging and backfilling causes the sulphate reducing bacteria to be distributed throughout the surrounding areas. The lower part of the backfill is usually porous. Hence aerobic microorganisms may develop at such locations<sup>105</sup>. Iron organisms: Tubercles are found inside the water bearing pipe walls and water mains by the action of the iron organisms. The environment between these tubercles and the metal becomes anaerobic and the sulphate reducing bacteria also flourish and the corrosion of metal continues<sup>106</sup>.

Methane bacteria: In the soils near manure heaps and the environments contaminated by offal, sewage and other organic wastes, the sulphate reducing bacteria are associated with the methane bacteria. Such soils are severely corrosive<sup>107</sup>.

Cellulose degrading organisms: In the presence of cellulose materials under anaerobic conditions, heavy corrosion by sulphate reducing bacteria along with the destruction of the cellulosic materials has been observed. It is suggested that the rate of corrosion is promoted by some kind of synergism between the two bacteria<sup>108</sup>. The biological degradation of cellulose provides an important source of nutrients for bacteria.

Miscellaneous microorganisms: A wide variety of microorganisms such as myxobacteria, fungi, algae, protozoa, etc., are capable of establishing a microbiological film on the metals. This induces anaerobiosis on the metal surface and the sulphate reducing bacteria flourish below these films and bacterial corrosion is initiated.

*Corrodible metals* — The corrosion of ferrous metals by bacteria is a widespread phenomenon. But the corrosion of other metals by bacteria is economi-cally much less important. If lead or copper is in contact with a less electronegative material such as carbon; its corrosion is accelerated by bacteria109. The corrosion of brass in laboratory with creek water has been found to be less than in actual creek exposure. This indicates that microbiological factors contribute to the corrosion of brass<sup>52</sup>. Though zinc is somewhat inhibitory to the growth of bacteria, it also suffers corrosion by sulphate reducing bacteria<sup>104,110</sup>. The corrosion of zinc by D. desulphuricans is localized in the zone where air-liquid interface and hydrogen sulphide are in contact with the metal<sup>111</sup>. The bacteria enhance corrosion of zinc but sometimes Zn2+ or some corrosion product induces inhibitory action, when the corrosion is slowed down. Similar tests on other metals confirm the results obtained with zinc and have shown the importance of oligodynamic action of metals in bacterial corrosion<sup>112</sup>. Lead and iron in zinc plates are corroded prior to zinc by D. desulphuricans<sup>9</sup>. The effect of bacteria on aluminium has also been studied. The results, though inconclusive, indicate the absence of a significant influence of the common species of bacteria on the corrosion of aluminium<sup>113</sup>.

Forms of corrosion — Corrosion by bacteria proceeds as pitting rather than in the form of even penetration<sup>25</sup>. Hence buried pipes tend to perforate rather than deteriorate uniformly. The rate of pitting has been found to increase with time. Hence the process appears to be autocatalytic<sup>114</sup>.

The differential aeration cell mechanism is only partly responsible for the pitting action. But the major role for pitting action is played by the microbiological anaerobic corrosion process. Even in very aerobic soils, bacteria are found to be present in pits. In the backfill of the pipes, the organic debris may also get included at several points. The microbial decomposition of cellulosic materials provides the organic nutrients for the sulphate reducing bacteria which in turn suppress the oxygen concentration at such points. Consequently, bacteria develop at these points and localized corrosion ensues. Such a corrosion reaction proceeds by the anodic stimulation mechanism, as under aerobic conditions the bulk of the corrosion reaction proceeds by the maintenance of the anaerobic conditions and low film resistance of the anodic regions. Such a phenomenon commonly occurs in clay and boggy soils where oxygen concentration or some other factors prevent the large-scale growth of bacteria throughout the environment.

In the case of cast iron corrosion by bacteria is less obvious as the high concentration of graphite holds the corrosion products intact. Thus a soft layer of corrosion products containing various iron compounds, unchanged metallic iron and graphite is obtained. This is termed graphitization and usually occurs in the case of corrosion of cast iron by bacteria. The rate of bacterial corrosion of cast iron is generally less than that of steel.

Rate of penetration of corrosion — Because of a variety of conditions controlling the rate of corrosion of iron by bacteria, no standard rate of penetration of corrosion is possible. However, some important examples can be cited. A steel main 1 cm. thick is reported to have been perforated in 9 years<sup>30</sup>; and a piling 1.5 cm. thick immersed in marine mud in 12 years<sup>116</sup>. In the case of pipes, whose walls bear more pressure on one side, perforation will always occur before complete piercing by corrosion. In laboratory experiments maximum corrosion rate of steel coupons by bacteria has been found to be 0.0004 cm. per year<sup>117</sup>.

Optional corrosiveness of bacteria under specific condition — Whenever bacteria are present throughout the surrounding area of a subterranean metal structure, severe corrosion does not necessarily occur<sup>94</sup>. At such regions active bacteria may be present at any part of the soil even in close vicinity of the metal. Very active cultures of bacteria have been isolated from such locations. It is probable that if the ferrous structure is buried in an environment where intense bacterial activity is present, the total surface of the metal reacts superficially and becomes cathodic. Hence, severe corrosion at such locations is occasionally absent.

Alternation of anaerobiosis — Cases of severe corrosion have been found at locations which are alternately anaerobic and aerobic. The alternation is usually caused by a change in the level of water table. The sulphides formed during anaerobic period are chemically or biochemically oxidized to sulphur, sulphuric acid, sulphates or ferric salts. All these are corrosive to ferrous materials<sup>29,100</sup>.

Presence of  $Fe^{2+}$  in the medium — The presence of  $Fe^{2+}$  in the environmental water markedly increases the rate of corrosion of iron by bacteria<sup>118</sup>. In the medium containing no  $Fe^{2+}$ , the corrosion product is found to be hard, crystalline and adherent. But in the presence of  $Fe^{2+}$ , the corrosion product is found to be loose, porous and flocculent. Thus,

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Fe<sup>2+</sup> content in soil or water exerts a pronounced influence on the rate of corrosion of immersed or buried metal structures.

Effect of anchorage — The bacteria are motile, but their growth and activity are limited by their tendency to settle on solid surfaces. They thrive best at solid-liquid interface<sup>84</sup>. Hence the nature of the metal surface may influence the development of the attached bacteria and thus affect the rate of the resulting corrosion<sup>108</sup>. The presence of inert anchorages like bentonite in culture medium does not influence the rate of corrosion of steel<sup>84</sup>. The bacteria have the tendency to concentrate in the corrosion products. It is likely that corrosion causes the bacteria to collect and multiply<sup>119</sup>, hence bacterial corrosion for a certain part of its period may have some autocatalytic tendency.

Effect of galvanic current — The activity of bacteria is doubled if galvanic current flows through the soil in which they propagate. There is a mutual influence between the intensity of bacterial activity and corrosive attack occurring by galvanic currents flowing between the subterranean metals. Hence bacteria present in soil may annul the cathodic protection<sup>120</sup>.

#### Protection against Bacterial Corrosion

A number of methods are available for protecting metals against bacterial corrosion. These methods are based on establishment of a physical barrier between the metal surface and bacteria, introduction of antibacterial physico-chemical conditions around a metal structure, and cathodic protection or the application of antibacterial chemical agents. In the case of permanent subterranean metal structures, a combination of good covering and cathodic protection is the best procedure<sup>57</sup>.

Treatment of the metal surface — Whenever bare metal is exposed to soil or water environments, a potential hazard for corrosion due to bacterial or electrochemical cause always exists. This can be eliminated by a protective covering which will prevent direct contact of the metal surface and the corrosive agency. Such protective coverings have been successfully employed for the simultaneous protection of metals against chemical and bacterial corrosion. Sometimes bacterial inhibitors like strontium selenate<sup>13</sup> and tannin<sup>121</sup> have also been incorporated in the coating materials in order to make them more resistant to bacterial attack.

In the case of the metal structures buried for indefinite periods, sacrificial and cathodic coatings of metals like zinc and lead are of little value. Hence for all such purposes insulating coverings have been employed. The important criteria for the coverings of underground and underwater metal structures are: (i) ease and economy in application, (ii) good adhesion, (iii) good resistance to mechanical damage before and after laying, (iv) good resistance to the environmental chemicals, (v) good resistance against the microbiological flora present in the environment, (vi) good non-ageing property in the present environment, (vii) high electrical resistance, (viii) low absorption of water, (ix) stability in a wide range of temperature, and (x) low cost. In the case of such structures the coatings are based primarily on bituminous materials like tar, pitch, bitumen and asphalt<sup>122-25</sup>. It has been observed that tars possess better qualities like good adhesion but they are more brittle than bitumens<sup>126</sup>. Blown bitumen has enhanced softening point and greater resistance against penetration. Hence it is widely favoured. Natural bitumens or asphalts have very high softening points and very good resistance against penetration<sup>125</sup>. Simple coatings of these materials are not obtained thick and robust. Hence the protection offered by them is of limited value. Addition of fillers like powdered slate, asbestos, pumice, kieselguhr, mica, limestone, talc and other minerals<sup>56,127</sup> improves the qualities of the coating. Their applications in corrosion prevention have been described in detail<sup>128</sup>.

Almost all the criteria of the coating are satisfied to a good extent by the application of bituminous enamels mixed with inert fillers reinforced with inert inner and outer wraps<sup>129</sup>. The inner wrap provides internal reinforcement of the enamel and the outer wrap, resistance against mechanical damage. Unfilled bituminous materials are not recommended. Woven glass cloth, bonded glass fibre mats<sup>130</sup> and asbestos cloth<sup>131</sup> have been employed as inner wraps. Borosilicate glass gives the best performance as it is not affected by wet and alkaline conditions, which may develop through the application of cathodic protection. The inner wrap should have good poro-sity and tensile strength. It should always be well impregnated with the coating material. Phenolformaldehyde resins have been employed as bonding materials for glass fibre mats. The outer wrap of non-woven bonded glass mat or asbestos cloth is preimpregnated with bituminous materials. To resist the bacterial attack a total covering at least 1 cm. thick has been recommended<sup>132,133</sup>. Wraps of hessian or other cellulosic fibres are subject to microbiological degradation which provides the nutrients for the sulphate reducing bacteria. Hence such wraps are not recommended. The application of plastic bandages is becoming increasingly common<sup>134</sup>. Polyvinyl chloride and polyisobutylene on bitumen rubber mastic are good coating materials135.

Several other techniques of protective coverings have been developed<sup>136</sup>. Laboratory tests alone do not yield a correct index of the efficacy of the coverings<sup>137,138</sup>; they have to be supplemented with actual field tests.

Protective tapes have also been employed for protecting the underlying metal structures against corrosion<sup>130-41</sup>. A woven fabric like cotton, jute, nylon or glass fibre cloth is employed as a base. Polythene and polyvinyl chloride, epoxy resins and epoxy bituminous combinations have been found to be the best base materials. The coating compounds are mixtures constituted by (i) petroleum jelly or recovered wool grease, blown bituminous material which may be treated with a synthetic rubber or resin or coal powder, and (ii) natural or synthetic rubber and resins.

In the case of rubber compounds, fillers, stabilizers and antioxidants are also introduced. Special corrosion inhibitors such as phosphates, chromates and tannins are also incorporated in the coating compounds. Self-adhesive polyvinyl chloride tapes have marked resistance against bacterial and electrochemical corrosion.

A novel procedure of electric shock treatment for barges has been developed for reducing corrosion due to bacteria<sup>142</sup>.

Area surrounding a corrosion site and its treatment-Mitigation of bacterial corrosion has been affected by the artificially prepared non-aggressive surrounding area or treatment of the natural environment. In aggressive soils the buried metal structures can be protected by c. 20 cm. surrounding layer of chalk, gravel or sand. Bacterial corrosion of oil well casing is prevented by filling the annulus outside the casing with free silica (180-200 mesh) or some silica-containing mixtures<sup>143</sup>. This ensures aerobiosis in the vicinity of the structure. One essential condition for the success of this procedure is that the system must not become waterlogged. In adopting such a procedure for protection, stabilization of soil should be done, otherwise the structure will always remain in a moisture laden bed, particularly because of the accumulation of water from the surroundings due to electro-osmosis effect in cathodic protection.

Tightly packed heavy clay or loam around underground structures has also been recommended<sup>144</sup>. Such a pack is highly impervious and curtails the movement of water, bacteria and organic nutrients in the immediate neighbourhood of the structure. Consequently, active cultures of bacteria and their metabolites remain out of contact with the metal and bacterial corrosion is avoided. If such area is in contact with an area not so well surrounded by clay, it behaves as anode and the anodic dissolution occurs via differential aeration cell mechanism.

A concrete lining capable of increasing the pH of the surrounding area is also effective in protecting metal structures against bacterial corrosion<sup>146</sup>. Bacterial corrosion of well casings have been prevented by using high pH drilling fluids<sup>58,60</sup>. Pipelines have also been protected by using lime as alkalizer<sup>146</sup>. Backfills consisting of intimate mixtures of alkaline earth oxides and alkali carbonates with bentonite, gypsum, Texas clay or moulding plaster which may contain some sand have been employed as protective coverings<sup>147</sup>.

As decaying organic matter provides the nutrients for the growth of bacteria, precaution should always be taken during burial programme that the organic matter in contact or near the vicinity of the metal structure should be minimum. Though this precaution is not a preventive step, it definitely reduces the hazards of corrosion by bacteria<sup>26,148</sup>.

The control of the growth of bacteria in aqueous systems such as polluted pools, stagnant streams, flood waters of oil wells and flooded clay quarries has been affected by the addition of sulphuric or hydrochloric acid to lower the pH below 5 (ref. 149, 150).

Cathodic protection — As corrosion by bacteria mostly follows the cathodic depolarization or electrochemical mechanism, the cathodic protection should be quite feasible. For economic and technical reasons cathodic protection is always employed in conjunction with protective coverings. One of the mechanisms by which cathodic protection of the underlying structure is effected is by enhancing the pH of the immediate neighbourhood, thereby reducing bacterial growth. Though opinions regarding the effectiveness of cathodic protection differ, it has been recommended by a number of workers<sup>151-54</sup>. Field and laboratory experiments on the effect of bacteria on offshore metal structures in sea-water testify to the efficacy of cathodic protection<sup>117</sup>.

In the presence of bacteria a more negative potential than under sterile conditions is required for cathodic protection. For the protection of ferrous metal in sterile neutral soil or water a potential of -0.80 to -0.85 V. measured with respect to the Cu/CuSO<sub>4</sub>.5H<sub>2</sub>O (saturated) electrode or -0.53 to -0.58 V. on the hydrogen scale is required. In the presence of bacteria further depression of voltage to -0.95 to -1.05 with respect to the 'saturated copper sulphate electrode' is considered to afford good protection<sup>183,155-59</sup>. The current required is of the order of 10-160 ma./sq. m. of the bare surface. Usually, current ranging from 30 to 65 ma./sq. m. is employed. The development and maintenance of high pH around an anodic structure prevents the bacteria coming into contact with the hydrogen charged metal. At some locations, the potential needs to be depressed considerably for complete protection as the usually acceptable potential required for cathodic protection is insufficient when active sulphate reduction is taking place<sup>160</sup>.

In soils of low resistivity, the use of expendable magnesium, zinc and aluminium or their alloys is satisfactory. To protect large bare areas of metals, the application of direct current fed from transformer rectifiers is more economical.

For the protection of steel structures, sometimes swing criterion is employed. Under aerobic conditions, the metal structure is made -300 mV. with reference to its natural potential, but under anaerobic conditions the swing criterion becomes -400 mV. (ref. 161).

Chemical inhibition of bacteria — Several chemicals have been found to exert bacteriostatic or bactericidal activity against bacteria. Some of them have been employed in metal coverings or for inhibition of bacterial growth near metal structures or by some other indirect means to reduce bacterial corrosion. A few of the chemicals have been employed to check up the growth and activity of bacteria involved in some other economic phenomena. The various antibacterial agents are described below:

Halogenated hydrocarbons: Monochlorobutene<sup>162</sup>, trichlorobutane<sup>44</sup> and 1,2-dichlorobenzene<sup>163</sup> have been found to be effective against bacteria.

Aldehyde: Formaldehyde<sup>162,164</sup> is a very effective inhibitor. It inhibits bacterial growth at a concentration of 0-1 g./litre<sup>165</sup>.

Acetone<sup>162</sup> and ethanol<sup>44</sup> are ineffective.

Chlorine: In laboratory experiments a saturated solution of chlorine is found to be ineffective in controlling the growth of bacteria<sup>162</sup>. However, successful application of chlorine for reducing bacterial activity and corrosion in aqueous systems has been reported<sup>166-69</sup>. A minimum concentration of 0·1-1·0 p.p.m. of chlorine must be maintained to inhibit the activity of bacteria. All types of organisms causing aerobic and anaerobic fouling, followed by the corrosion of metals, can be eliminated by chlorination past the breakpoint<sup>170,171</sup>. Hence chlorination can eliminate the possible sites for the development of bacteria.

Sulphur and its derivatives: Free sulphur, rubber containing sulphur and sulphocyanides have been reported to greatly inhibit the growth of bacteria. Their effect is bacteriostatic44.

Some sulphate analogues: Selenate and monofluorophosphate competitively inhibit the growth and sulphate reduction process of bacterial cells<sup>172</sup>. High concentration of perchlorate depresses the sulphate reduction process in a non-competitive way173.

Tellurite and tellurate : Potassium tellurite (1 p.p.m.) inhibits the growth of bacteria in the absence of ferrous salts. But if 60 p.p.m. ferrous ions are present, 100 p.p.m. concentration of tellurite is required. Such adverse effects of ferrous ions on some other inhibitors are also known<sup>13</sup>. This effect has been explained in terms of the requirement of low redox potential<sup>69</sup>. Tellurates are non-competitive inhibitors174.

Chromate: The chromate ion is a powerful inhibitor of the growth of bacteria<sup>88,175,176</sup>. It is effective even at the concentration of 2 p.p.m. It has been successfully employed for the prevention of corrosion and pollution in gas and petroleum storage tanks. Potassium dichromate<sup>13</sup>, sodium dichromate and zinc chromate<sup>177</sup> have been used as inhibitors. A mixture of sodium dichromate and chloramine reduces steel corrosion by 50 per cent and zinc corrosion by 80 per cent and meets the standard for the control of bacteria in water<sup>178</sup>. A mixture of sodium dichromate (50 p.p.m.) and sodium carbonate (400-500 p.p.m.) limits bacterial corrosion<sup>179</sup>. This ion is ineffective against aerobic bacteria associated with pollution.

Metal ions: Zinc chloride in small concentration has been found to be the most economic and effective remedy for checking bacterial corrosion of certain plant coolers<sup>65</sup>. Copper and cadmium salts have also been found to inhibit bacterial growth98.

Mercurials: Phenyl mercuric lactate has been found to be very effective against bacteria<sup>164</sup>. Hydrogen sulphide produced by bacteria reduces the inhibitory action of the mercurials180.

Phenols: A few strains of bacteria have been found to grow even in 1 per cent phenol<sup>13</sup>. But phenol and cresols have been found to inhibit the growth of these bacteria in natural waters162. Chlorophenols such as tri-, tetra- and pentachlorophenols are employed as bacterial inhibitors at a concentration of 50-100 p.p.m.181. 2-Nitrophenol and 2,4dinitrophenol have been found to be promising inhibitors182.

Nitrate and nitro compounds: The activity of bacteria can be controlled by nitrates183,184 and nitro compounds<sup>185</sup>. Nitrates have been employed in the prevention of corrosion in sewage systems<sup>186</sup>.

Quaternary ammonium salts: Such salts of high molecular weights<sup>63,187-89</sup>, specially lauryl pyridinium chloride<sup>162</sup>, cetyl pyridinium bromide<sup>13</sup> and trimethyl alkyl ammonium bromides<sup>190</sup> are effective inhibitors. They are effective at great dilutions and are most effective in air-free waters. The quaternary ammonium compounds of alkyl amines prevent pore plugging<sup>187</sup>. Excellent synergistic effects are obtained when a quaternary amine is used in conjugation with 110 chlorhexidene. Condensed amino substituted alkene oxides are also good inhibitors.

Arsenicals: The growth of bacteria can be checked by the application of arsenicals at a concentration of 50-100 p.p.m.

Tannates: Immunity of some archaeological specimens of ferrous and other metals against bacterial corrosion in soils has been attributed to the tannates present in the soil<sup>158</sup>. The tannates have been considered to be bactericidal agents146, but recent studies indicate that the tannates inhibit the growth of bacteria merely by lowering the pH of the surrounding area<sup>64</sup>. The bacteria are not rendered inactive unless the concentration of tannin is about 5 per cent<sup>191</sup>.

Antibiotics: A natural substance toxic to bacteria has been discovered<sup>192</sup> in the silt of the sites where tannins had remarkably preserved archaeological metal specimens. It is effective even at the concen-tration of 1 p.p.m. Infrared spectroscopy has shown that an antibiotic produced by a specific mold is very similar to this material.

Acridine dyes: A number of dyestuffs have been examined for their inhibitory action on bacteria<sup>193</sup>. Flavine type of dyes, particularly proflavine (2,8diaminoacridine) and acriflavine (1: 2 mixture of acid hydrochloride of proflavine and 2,8-diamino-10methyl acridinium chloride), at a concentration of 4 p.p.m. prevent the growth of bacteria<sup>88,194,195</sup>. Dye '914', a member of the acridine series, has been found to be cheapest effective dye. It has been employed at a concentration of 4 p.p.m. In laboratory experiments it has been observed that the bacteria readily acquire resistance against this dye196, but no such difficulty has been encountered in its field application.

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# REVIEWS

QUANTUM THEORY OF SOLIDS by C. Kittel (John Wiley & Sons Inc., New York, London), 1963. Pp. xi+435. Price \$ 13.50

This book by Prof. C. Kittel is a very welcome and timely addition to the current literature on theory of solids. The rate at which the new experimental facts have been discovered during the past decade or so has been very fast. This has led to greater and greater demand on theory to explain these experimental findings in the various aspects of solid state physics. Most of the recent theoretical work has been either confined to the original articles in various journals or is available in the form of review articles. Prof. Kittel has now made this material available in the form of a text-book meant for advanced students and research workers in theory of solids. The younger generation will have a lot to benefit from this book.

The author has used the quantum field theory to discuss various topics. He has explained in a lucid way the various elementary excitations in solids such as phonons, magnons, plasmons, polarons, excitons and electrons and holes and interactions among them. The Hartree-Fock method of treating electronelectron interaction has been discussed and then the same problem has been discussed using the many-body techniques.

The author has incorporated in the text most of the new theoretical developments in the understanding of the various properties of normal metals, semiconductors, insulators, superconductors, magnetic materials and alloys. The methods of finding the electronic energy states of solids have been given and it has been indicated how a large number of workers, specially at MIT, GE Research Laboratory, University of Chicago and Cambridge University have succeeded in doing very precise energy band calculations. This has led to the possibility of an accurate theoretical determination of the Fermi surface of metals. Such calculations have become very meaningful on account of the possibility of experimental determination of the Fermi surface using the experiments on cyclotron resonance, magnetoresistance, de Haas-van Alphon effect, anomalous skin effect and the magnetoacoustic effect. The energy band structure of semiconductors, the impurity levels in them and the Landau levels have been discussed. The magnetoplasma modes of propagation of electromagnetic waves in metals, called helicons and predicted by Aigrain, have also been discussed.

The use of correlation functions in the study of neutron diffraction and the theory of recoilless Y-emission from radioactive atoms embedded in a solid have been given. The use of Green's function method in the study of various problems in the theory of solids, which is of great interest these days, has also been added. A chapter on the theory of alloys which is still in an early stage of development has been given. The topics which the author did not include due to lack of space have been indicated in the preface. Finally, the book contains a good number of problems, as required by a text-book, at the end of each chapter which the readers can attempt to solve to get a clearer understanding of the subject.

The book is thus well suited to the needs of advanced students and research workers who want to equip themselves with material beyond that available in the introductory text-books on solid state physics. There is, of course, no doubt that for a detailed and deeper understanding of any topic developed in the book one will have to study the review articles and original papers. There is a little more emphasis in this book on new mathematical techniques and so it will be very fruitful if this book is read together with the book with similar title by Peierls or any other book with greater emphasis on physics.

R. P. SINGH

THE BENDING AND STRETCHING OF PLATES by E. H. Mansfield (Pergamon Press Ltd, Oxford), 1964. Pp. xi+148. Price 45s.

This monograph by one of the active workers in the field presents a unified and up-to-date exposition of small and large deflexion plate theory. The book is divided into nine chapters. The first two chapters deal with the derivation of the basic differential equations governing deflexion and vibration of a plate, and the methods of solution of the small deflexion equations for rectangular plates of constant thickness. Chapter 3 deals with the transformation of the differential equation to polar coordinates and the author here discusses plates of constant thickness whose boundaries are circular or sector shaped, elliptical or triangular. One of the most elegant and fruitful methods of analysis of the biharmonic equations, developed and extensively applied by the Russian mathematicians, is concerned with the use of complex coordinates, and in Chapter 4 the author treats plates whose boundaries are amenable to conformal transformation. The sixth chapter gives an account of the variational method, which is a powerful technique for solving problems that refuse to submit to exact analysis.

Part II of the book is a survey of the large deflexion theory. This differs from small deflexion theory by the fact that the middle surface stresses, arising from the straining of the middle surface, are taken into account. The eighth chapter is a review of the large deflexion behaviour of plates of constant thickness, when the loading is either uniform or compressive. While the exact large deflexion analysis of plates generally is formidable mathematically, there are a class of plate problems, known as the asymptotic theories, for which simplified theories are available and the book concludes with an account of the membrane theory and the inextensible theory.

A notable omission which strikes even a casual reader is the absence of any attempt to discuss numerical methods, which are finding ever increasing applications nowadays, thanks to the phenomenal developments in electronic digital computers. While the book is essentially mathematical, the author has striven to present a clear physical picture of the plate behaviour. The book has an aeronautical flavour but that does not diminish its usefulness to mathematicians or to civil, mechanical and marine engineers. K. S. VISWANATHAN

#### HIGH SENSITIVITY COUNTING TECHNIQUES by D. E. Watt & D. Ramsden (Pergamon Press Ltd, Oxford), 1964. Pp. xv+348. Price 80s.

The work under review is a condensed treatise dealing with the techniques of high sensitivity counting, especially with sources of weak activities at low background levels. The work begins with a discussion of the essential counting parameters such as the minimum observable counting rate, including a discussion of the factor of merit. Then, in dealing with the attainment of low background in radiation detectors, the various sources of background are carefully traced, discussed and ways and means of minimizing them suggested. To eliminate the background level of counting systems, the design and construction of laboratories suitable for low background work by the choice of proper construction materials of the building, the counters, the shielding as well as that of the electronic circuitry are suggested.

Then detectors of various types suited for the measurement of weak alpha-counting, low-energy beta-counting such as radiocarbon dating and low-energy gamma-counting as in the case of  $H^3$ ,  $S^{35}$ ,  $Pu^{241}$  as well as soft K- and L-characteristic photons of  $A^{37}$ ,  $Cr^{51}$ , etc., are described. The influences of the geometry of the counting systems and the source are described and suitable methods of eliminating these influences are discussed. Also, the technique of scintillation counters for the measurement of weak gamma activities including the sum-coincidence method are discussed. Finally, the methods of measuring gamma activity in the human body are dealt with in detail.

The subject matter of the work is reliable and dependable inasmuch as the work is the outcome of careful work and study of the authors who are themselves authorities on the subject. The get-up of the book is excellent and illustrations are very clear. The work will be useful as a reference in all the research laboratories where work on nuclear and radiation physics is being carried out. The authors are to be congratulated for bringing out this useful work.

#### SWAMI JNANANANDA

SYSTEM DESIGN FOR COMPUTER APPLICATIONS by H. N. Laden & T. R. Gildersleeve (John Wiley & Sons Inc., New York), 1963. Pp. v+330. Price \$7.50

This publication presents the principles of system design suitable for using an electronic computer as a data processing machine to achieve optimum benefits. The book is divided into three parts. Part 1 deals with the general considerations of system design for computer applications. By system design is meant the critical analysis of the data processing operations and their redesign. It covers (i) fact finding, i.e. documentation, (ii) critical evaluation of the existing business data system, its objective, outputs and inputs, and (iii) creative synthesis of a new system, making thereby a restatement of objectives, a definition of output in terms of these objectives and a reorganization of the input data gathering and processing required to produce the output. The authors have presented in simple and clear language the techniques involved in all these steps. The principles underlying technical problems preceding programming such as block diagram, run organization, file maintenance, process chart and flow chart are fully discussed. In Part 2 are given the source documents consideration covering the design of forms, uses of various systems of coding and output form. Part 3 is an exhaustive description of steps involved in the design and installation of a computer data processing system.

Computer system design is a new subject and the authors have provided a candid description of it. Apart from giving general principles and case histories, the authors have taken pains to quote examples at each stage of discussion. For clarity of terms and definitions used in the book, a useful glossary is given at the end. Though the authors have stated that their book does not deal with programming, perhaps it would have been better if they had included a brief description of it so as to make the book self-contained.

The use of electronic computers in India for data processing in different fields is now gradually increasing, and this book will be helpful to those who are concerned with computer system design.

T. R. SEHGAL

OPERATIONS RESEARCH IN RESEARCH AND DEVELOP-MENT — Proceedings of a Conference at Case Institute of Technology in 1962, edited by Burton V. Dean (John Wiley & Sons Inc., New York), 1963. Pp. xii+289. Price \$ 8.50

This book consists of twelve papers which were presented at a Conference on Research and Development (R. & D.) Management Systems at Case Institute of Technology in 1962, and is the first attempt of its kind that presents applications of scientific methods to the solution of R. & D. management problems.

Because of the complexity of modern business operations and inadequate information processes, management in both the military and industry are faced with the necessity of reducing the time and cost of development programmes. There is a continuing need to identify problems in advance and improve the efficiency of operations through quicker, more responsive and more integrated controls. A company's success or failure depends on its ability to understand quickly and utilize effectively new concepts and techniques like Operations Research, Systems Planning, PERT, etc., in planning and control.

The first chapter is written by Prof. Ellis A. Johnson, Director, Systems Research Centre, Case Institute of Technology, and is a review of the US competitive situation in the application of science to technology. He is concerned with the basic problems of development of US technology and the effectiveness of R. & D. activities with special reference to the optimum utilization and control of technical resources. According to his thinking there is no question about the responsibility of the US Government to enocurage R. & D. activities. The second chapter is devoted to scientific R. & D. and related activities, consisting of dissemination of scientific information, testing, standardization and collection of scientific data. The author discusses the importance of scientific activities in the development of national strength — economical, military and cultural.

In the third chapter, Miles W. Martin deals with the concept of the measurement of value of scientific information and evaluates the usefulness of citation counts as an index of this value. He also feels that the behavioural theory of human communication may be fruitful in the measurement of scientific information.

Chapters 4, 5, 10 and 12 discuss in detail the application of PERT (Programme Evaluation and Review Technique) to R. & D. problems. These chapters make it clear that the combined tools of network analysis, critical-path methods and criticalpath scheduling are highly effective. The network approach offers opportunity to develop integrated planning and control tools to aid in the management of R. & D. processes.

In Chapters 6 and 7 it has been emphasized that the success of a research programme is dependent on the selection, evaluation and control of R. & D. projects.

In the eighth chapter, Prof. Herbert A. Shepard treats an R. & D. organization as an adaptive system and discusses the conditions which will make an R. & D. organization more effective and creative.

Chapters 9 and 11 deal with the importance of scientific models. In Chapter 9 a logical structure has been constructed for the process of getting new business by making proposals against competition. In Chapter 11 it is shown that even simple models play an important role in the studies and improvement of R. & D. management.

On the whole it is a well-presented book and all the phases of planning, model construction, data collection, evaluation, testing and control of the results have been dealt with. The book will serve as an excellent reference book to the managers and a useful guide for those engaged in research in R. & D. management problems.

#### SHIV K. GUPTA

PROBLEMS IN THE DESIGN AND DEVELOPMENT OF 750 MEGAWATT TURBOGENERATORS by V. P. Anempodistov, E. G. Kasharskii & I. D. Urusov; translated by O. M. Blunn (Pergamon Press Ltd, Oxford), 1963. Pp. 76. Price 30s.

At the outset it has been indicated statistically that in most countries electricity consumption increases on the average up to 7 per cent per year, the major share of the demand being met by thermal power stations. Increase in consumption of electricity and fall in available water resources, which can be economically exploited for power generation, has led to a rapid increase in the commissioning of large thermal generating units. In Europe alone there are at present several 250 MW sets in operation and a considerable number of 500 MW units under construction, while the feasibility of 750 and 1000 MW sets is being actively studied.

As regards turbogenerators, it is well known that for many years past, rotor heating has been the main limitation to increasing outputs from single shaft units of a given size. This was partly overcome by the adoption of inner cooling of rotor conductors by hydrogen. Also stator current-carrying capacity registered a great advance by the use of direct water cooling of the conductors. Corresponding improvements in rotor capability are now being sought by resorting to water cooling of the rotor. The authors in the present book have indicated the feasibility of adoption of water cooling of the rotor, while highlighting many of the metallurgical, mechanical and insulation problems associated with it. They have further suggested consideration being given to other aspects of improvements in existing designs, namely (a) use of polyester-resin bonded mica for stator insulation; (b) use of cold rolled grain-oriented sheet steel for stator laminations; (c) utilization of special copper alloys to improve the strength of rotor windings; and (d) use of titanium alloys of low specific weight and high yield stress for rotor end-bell construction.

The present book is mainly devoted to the details of a single shaft generator design study. The authors have taken recourse to liberal use of design and research material in their examination of future trènds of large turbogenerators. By the use of techniques such as ' the variation of characteristics of ideal geometric series', ' series with constant diameter', etc., a theoretical basis for the adoption of a 1250 mm. diam. water-cooled rotor has been laid. The attendant metallurgical, mechanical and thermal problems are yet to be solved before the feasibility of a single shaft design of large output can be firmly established.

Some of the other topics discussed in the book are 'direct cooling and maximum output', 'thermal and hydraulic analysis of direct cooling', 'prospects of new materials' and 'design study of single shaft 750 MW turbogenerators'. The presentation is of a high professional standard executed in a lucid manner with illustrations and useful data. A glossary and a comprehensive bibliography are also included. This volume would be of utmost interest to designers.

S. SWAYAMBU

THE PRINCIPLES OF APPLIED SCIENCE by M. W. Thring (Pergamon Press Ltd, Oxford), 1964. Pr. vii+226. Price 15s.

This publication forms Volume I of the Conferences Division of the National and International Library. The Joint Chairmen of the Honorary Editorial Advisory Board for the Library are Sir Robert Robinson, OM, FRS, and Dean Athelstan Spilhaus, Minnesota. Prof. M. W. Thring is Professor of Fuel Technology and Chemical Engineering, University of Sheffield.

The book is apparently a record of lectures, papers, and studies which formed the programme of a recent conference: the reader is left to infer this from the wording of some of the papers or chapters, of which a list is as follows:

Definitions of Pure and Applied Research by Sir John Cockroft; The Principles of Applied Science by M. W. Thring; Development as a National Problem by J. S. Duckworth; Development in the National Economy by D. C. Hague; The Role of the Research Associations by D. W. Hill; Invention and Innovation by M. Zvegintosov; Some Transatlantic Precedents by W. H. G. Armytage; Higher Education in Applied Science by B. V. Bowden; The Schools and Applied Science by H. S. Lipson; Integration of the Work of Colleges of Advanced Technology and Industry by E. H. Edwards; The Role of Mathematics in Applied Science by D. N. de G. Allen; New Techniques in Steelmaking by J. H. Chesters; The Building Industry - A System of Zero Feedback by J. K. Page; Radar and Microwaves by A. L. Cullen; The Assessment and Development of a New Product in the Petroleum Chemicals Field by R. N. Wheeler; Aircraft and Rocket Propulsion by A. V. Cleaver; Development of Processes for the Production of Industrial Chemicals and Fertilizers by J. B. Harding.

This catalogue promises a rather 'mixed bag', even for a lengthy conference. For some reason or reasons weaknesses had become apparent (in the UK) in the development and improvement of products and processes. The stimulation of such work and the need to foster and encourage new ideas demanded (and demand) serious attention. In the nineteenth century, Britain oftener than not was in the van in putting forward new ideas and in developing them industrially. As examples we need look no further than the Bessemer and Siemens Steelmaking Processes and the Parsons Turbine. In the present century Britain has not been slow in developing industries concerned with atomic energy, aeronautics, radar and microwaves, gas-turbines, petrochemicals and fertilizers. Nevertheless, it remains true that in other fields of recent technical research and development Britain has not occupied the pre-eminent role which she did in former years. The conference referred to above was no doubt called to review the present position, to diagnose the ills, and where possible to suggest remedies.

In the present century, the USA (by contrast) has made great strides in the industrial and technological world. It is true that she has had certain advantages, more especially in wealth and resources, and in the relatively lighter burden which the world wars placed on her shoulders. In Britain the war loads were colossal, both in respect of financial and material demands and losses, and still more in the loss of human potential, a loss whose magnitude cannot be assessed.

In the foreword to this volume attention is drawn to another factor, namely the new circumstances of the present century: "Wealth sufficient to develop a new process against the competition of the highly developed ones already existing is no longer in the hands of men with the enthusiasm to push their inventions through, and we have to find an alternative method of solving this problem. There are many questions to be answered, such as how far committees should control the work, and on what principles one should decide whether it is worth going on with it; what stages the work should go through; how we can educate people to look forward towards quite new processes and at the same time base their ideas on a sound understanding of fundamental science. While this book cannot possibly provide complete answers to these and related questions, it is hoped that it will stimulate the reader at least into thinking out his own answers and realizing the urgency of the problem."

To come to the actual papers, which are given as separate chapters of the book, some of the contributors, notably Sir John Cockroft and Prof. Thring, spend much time in distinguishing between the fields of pure research and applied research and cn the subdivisions arising. No doubt such classification is useful for purposes of organization, but often it is unnecessary, nor is it in general desirable to separate the personnel. It is true that many school-masters seem to be of the opinion that pure science is a more worthy occupation for their scholars than is applied science : To explain how this attitude has come about it is suggested that it is the 'natural child' of those philosophers of old who assumed (a priori) that manual labour and doing anything practical for a living was not the function of a free-man. Such work should be done by slaves. The free-man should devote himself to pure ideas, and presumably the less their useful application, the better. Some modern mathematicians have been credited with the same outlook. It is common in the East.

For some years America has of course taken an almost diametrically opposed view. Is not her progress in science, industry, technology and research, and even in military power due to the more realistic views she has taken? On the other hand, has not the Greek ideal, held by many British pedagogues, helped in deflecting many of the best students to pure research and pure science rather than applied ? This bias may well have deprived industry and technology of men of first class ability, capable of making major contributions and advances in engineering in all its branches. It is high time that such 'fantastic nonsense' (as the late Prime Minister Nehru might have called it) came to an endalong with the prejudices of the pedagogues responsible for the existing state of affairs. Prof. Thring states the position boldly in his paper on 'The Principles of Applied Science'

"While generalizations of this sort are open to particular correction, a great many of the schools are guilty of this national crime. It is a national crime, because it is in applied science that we need the best brains if we are to survive as an exporting nation. Unless we keep ahead in our ideas in industry, we shall be swamped by our competitors, and we shall not be able to export to pay for our imports. Therefore, the national problem is how to raise the status of applied science in the eyes of the school-masters and the schoolboys."

Several authors draw attention to the meagre British financial provision for research, comparing it unfavourably with the position in this respect in the USA. Thus Dr B. V. Bowden in his paper on 'Higher Education in Applied Science' says: "Our universities are very small indeed compared with those of other industrialized countries, and this may have something to do with the fact that our industries are growing *relatively slowly*. Modern science, engineering, and technology are becoming more and more complicated: the number of scientists and engineers in the world doubles every fifteen years. Of all the scientists and engineers who ever lived, three-quarters are alive and working. We need many more today, the demand is growing and it will undoubtedly continue to grow. If our industry has to recruit men who are less educated than the recruits of its competitors, it will never survive in a competitive world." He further states, " In addition to our having too few university places, our universities are much too small to house many of the specialists among the teaching staff that would automatically be present on the staff of large continental engineering schools. It is not very many years ago since most universities seemed to have one Professor of Engineering (Oxford has only one to this day). Few English universities have more than one Professor of Electrical Engineering or one Professor of Mechanical Engineering. It is not unusual to find fifteen Professors of Electrical Engineering in a Continental School, so that among them they can study almost any subject, however specialized it may be. The technical university of Aachen was designed quite deliberately on the assumption that it must have at least 100 professors who could divide the important branches of science and technology among themselves. Each professor has about 100 students, so there are 10,000 students in Aachen. This vast organization is the minimum size, so the Germans believe, for a really efficient school of science and engineering.

In this review one is tempted to give extracts from many of the other papers, notably those on 'Interaction of the Work of Colleges of Advanced Technology and Industry', 'New Techniques in Steelmaking', 'Radar and Microwaves', and 'The Development of Processes for the Production of Industrial Chemicals and Fertilizers'; but there is no substitute for reading the papers individually.

Stepping back, however, from the individual papers and viewing the compilation as a whole, three conclusions seem to stand out. They refer to Britain in the first place, but often also to other countries:

1. There is urgent need for increased national provision for education and training in pure and in applied science, and in research.

2. Applied science and research call for ability and capacity equal to that required for pure science and research: the applied field is frequently more difficult, but often more immediately rewarding.

3. It is important — it is a matter of urgency — to counteract, and if possible eliminate antiquated and false ideas and ideals developed (usually) long before man became aware of the discipline and potentialities of science, pure or applied.

With regard to the last observation, there is not the least suggestion that we should become materialists in the nineteenth century sense of the term. Indeed, modern scientists, pure or applied, tend to occupy the role of mystics, living largely in an esoteric world. But as the world of matter and of related phenomena is the world of matter and of related phenomena is the world 'in which we live and have our being', the humble study of our immediate environment, in its manifold variations, is surely natural to man. In any case the fact and its implications are now being driven home by present economic forces (of no mean order) and by the very urge for survival. 'Sweet are the uses of adversity': sweet, perhaps, but certainly salutary if taken aright.

The paper, printing, and layout of the book are excellent, except for the cover which should be more durable. The subjects discussed are obviously of paramount importance today and their treatment in this volume is such that the book is likely to be used widely for study and reference. At the present stage of development such a collection of essays by eminent authorities on the position and potentialities of applied science is most opportune. Careersmasters, educational advisers and organizers, and the administrators of universities, research institutions, and industry will all naturally be interested; but thoughtful reading of these essays by our legislators and those charged with framing and implementing national policy is also called for - and not only in Britain.

#### J. W. WHITAKER

THE CHEMICAL INDUSTRY — VIEWPOINTS AND PER-SPECTIVES edited by Conrad Berenson (Interscience Publishers Inc., New York), 1963. Pp. x +426. Price \$ 10.00

Books which are timely become significant. For those of us engaged in manufacturing, planning future growth, marketing and management of chemical industry in India, this book is of real value. The author has introduced a fascinating section of case histories and it is here that the practical value of the book lies, as it is both pragmatic in approach and authoritative in its contents.

The book has been divided into four major sec-The first section gives a background of the tions. chemical industry in USA, its problems of overcapacity, lowering profits, intense competition, growth potentialities as well as serious marketing problems. Despite a continued tussle due to squeeze and pressure on profits, on account of rising prices of raw materials, labour, marketing and research, the chemical industry is still holding its own. (The profit picture as of today is very different.) There is not only competition from within the chemical industry, i.e. from similar products, but also a very keen competition from without. On the top of it, chemical industry, like aircraft industry, has a very high rate of obsolescence of products and processes. Surprisingly, this competition has proved refreshingly a boon inasmuch as it has helped to maintain its vigour and dynamism. In no other industry are mergers and vertical expansions known as in the chemical industry. The credit for its vigour should largely go to the glorious role played by research and development.

Some of the statistics mentioned therein are significant. When compared with any other industry, chemical industry in USA grew faster by 25 per cent during 1935-40; 56 per cent during 1940-50, and 119 per cent during 1950-60. This was largely due to the rise of the petrochemicals, which was an outstanding phenomenon of this period. Today, almost 30 per cent of the weight and 60 per cent of the dollar value of the chemical industry is due to petrochemicals. It also signifies that the rate of growth of the organic industries was much faster than that of the inorganic ones. In India, this significant factor has to be clearly understood by us because our growth of the organic and the inorganic industries has similar potentialities.

The second and the most important section deals with the growth, development and trends of chemical industry and has a special treatise on growth cf the caustic soda/chlorine industry, thermoplastics, polypropylene, etc. It gives the mechanisms of growth of various giants of the chemical industry like Du Pont, Union Carbide, Monsanto, Montocatini, etc., and deals with various other medium sized industries with very great growth potential.

The third section brings out the capital intensive nature of the industry and how rationalization of manpower in chemical industry can result in important savings. The general ratio of the profit of the chemical industry to the employee wage bill is 1:3. Hence, a 5 per cent saving in the employee bill will immediately result in an increase in profitability by 15 per cent. This being so, it is incumbent upon management that they utilize the present manpower more effectively and more efficiently. It will also be significant to note that for every three men engaged in the chemical industry, at least two are required to support them in their non-productive activities like sales, stores, accounting, inventory control, etc.

The last section on marketing policies in chemical industry is applicable to the marketing of any other product. For us in India, the strategy is different because we are working under serious shortages and in a protected market. Névertheless, the strategy of marketing in a society with free enterprise is to maximize the profits, keep the competitors on the defensive, confused and uncertain. Thirteen widely different examples have been dealt with in areas such as marketing of new products, pricing the products, consumer service, advertisement, sample surveys, etc.

Chemical market research like any other market research can supply definite identifications and estimates quantitatively. With its help, management hunches can be transferred into calculated risks with odds in favour of the company.

On the whole the book makes a very refreshing reading.

#### J. P. KAPUR

#### ADMINISTRATION OF THE CHEMICAL ENTERPRISE edited by Conrad Berenson (Interscience Publishers Inc., a Division of John Wiley & Sons Inc., New York), 1963. Pp. x+414. Price \$ 11.50

In recent times, the commercial and administrative aspects have been growing in importance as compared to the purely technical aspects in the chemical industry, particularly in the more advanced countries like USA, Germany and UK. With multifold increase in production all round, the accent is shifting to a study of marketing problems, as against methods of increasing production as in the past. In this context, Conrad Berenson's Administration of the chemical enterprise is a welcome publication. It is perhaps the first book which contains interesting information on the commercial aspects of operating a chemical enterprise, including marketing, management, advertising, production, personnel, etc. In his purpose to give the personnel in the chemical process industries a good background to all the information available, the author has correctly taken an illustrative rather than definitive approach. Major factors which affect key commercial areas are expressed clearly to arrive at the basic principles involved. The examples and illustrative material in the book make the book lively and readable. The bibliography at the end of each chapter is useful to the interested reader as a source for obtaining further information.

The book has nine chapters, dealing with marketing, management, mergers and acquisition, advertising and publicity, human resources management. role of patents, sources of business information, accounting and the chemical business and, lastly, financial management in the chemical industry. Marketing is very often considered synonymous with selling. But, in fact, marketing covers a far wider field, which includes buying, selling, transportation, storage, standardization and grading, financing, risk taking and collecting market information. The concept of the role of marketing in finding new uses and creating profitable customers is discussed fully and illustrated by the experiences of some of the leading American chemical producers like Du Pont, Union Carbide, Monsanto and Allied Chemical.

The chapter on 'Management in the chemical industry' discusses the manager's job in the wake of the explosive growth of chemical industry in recent times. Total sales value of chemicals in USA alone has shot up from a mere 3.1 billion dollars (Rs 1500 crores) in 1935 to 34.5 billion dollars (Rs 17,000 crores) in 1963 - a more than tenfold increase in less than three decades. (In comparison, sales value of all chemicals produced in India in 1961 is less than Rs 300 crores only.) The need for setting down clearly the objectives of the firm or the enterprise is rightly stressed as essential for efficient management. The experience of the big companies in USA has resulted in the evolution of different types of management organization, each most suited to a company's own specific purpose. Efficient management involves also the need to establish clear authority relationship, stating one's duty and right to do a job, one's responsibility in relation to the others in the organization, etc. Useful organization charts of some of the big American companies are also given. The role of committees and the fruitful results of group activity are also brought out. The multiple executive system of administration, in other words, the use of an executive team, in administration has proved successful in some cases.

The chapter on 'Mergers and acquisition in chemical industries' reviews the situation in American industry from 1600 to date. The cause and effect concept of the chemical combines are objectively analysed.

The chapter on 'Advertisement and publicity' shows how the sale of ideas, products and services to large number of people is promoted. The importance of research in advertising and publicity and the possible ways of working on an advertising budget are indicated. The chapter on 'Human resources management ' discusses job analysis, merit rating, motivation, employee needs, incentives, etc. The role of patents, their contribution to the industry and the benefits conferred by a patent form the subject of another chapter. The chapter on sources of business information gives the location of important business information centres, information on companies and individuals and handbooks, dictionary, encyclopaedias and other books and journals in USA. The last two chapters discuss accounting methods and financial management in the chemical industry, giving case histories of three large chemical companies in USA. The problem of financing an industry and the need for intelligent planning and control are well discussed.

The chemical industry in the country is still in its early formative years, having had a late start. Only lately, there is better appreciation of the need to integrate production pattern and secure a vertical growth in the industry. To all people associated with the chemical industry in India, this book on *Administration of the chemical enterprise* would provide very useful material for efficient and effective job performance.

S. RAMASWAMY

THERMOCHEMISTRY FOR STEEL MAKING: Vol. II — THERMODYNAMIC AND TRANSPORT PROPERTIES by John F. Elliott, Molly Gleiser & V. Ramakrishna (Addison-Wesley Publishing Co. Inc, Massachusetts), 1963. Pp. xvi+299-846. Price £ 9

The publication *Thermochemistry for steel making*, Vol. II, sponsored by the American Iron & Steel Institute, is probably the only reference book of its kind so far published covering vast technical data on physico-chemical aspects of iron and steel making, such as the thermodynamic properties of important metal and oxide solutions, equilibrium phase diagrams, standard enthalpy increments of selected compounds, kinetics of high temperature reactions and diffusion in alloys and slags, transport properties of important phases, etc.

It is undeniable that although current scientific and technical data on the metallurgy of iron and steel are indeed vast, most of them are too widely. dispersed in published text, technical journals and learned discourses to be of practical use as reference materials to engineers, metallurgists and scientific workers who are directly or indirectly engaged in understanding the physico-chemical properties of iron and steel making and applying it in diverse aspects of ferrous metallurgy. At the same time, it is also true that there indeed are wide gaps in our scientific data on thermochemistry of iron and steel making which tend to become progressively wider with the remarkable rate at which applied technology multiplies in relevant fields; such a growth causes in its wake empirical relationships and practices to mushroom that are often remarkably appropriate and generally applicable even if lacking somewhat in basic theoretical precision. It is in such gaps in scientific knowledge of iron and steel metallurgy that this publication will find a place of honour and universal reference on subjects though widely apart in their intrinsic studies yet aptly fitting in the overall pattern of

basic scientific advancement in iron and steel making.

The publication is remarkable in the scope of its collation, consolidation and summarization of physico-chemical data relevant to ferrous metallurgy. The authors deserve appreciation of many engaged in the art and science of iron and steel making and grateful thanks of scientific research community in making their task of technical reference so much easier and so very interesting.

The wealth of technical and scientific data assembled in this publication has led the authors to adopt a unique method of 'indexing' which in many a brilliant scientific treatise is considered to be of secondary importance since it lies at the end of a publication; in this book, indexing, 'last but not the least', has been organized to make the text readily accessible and as the reader will notice to his delight, a completely different arrangement has been followed in preparing the index.

There is no doubt that this publication, so clearly printed and superbly bound, rich in its wealth of scientific and technical data and knowledge, will be a standard book of reference to the students, research workers, metallurgists, engineers and scientists engaged in somewhat dispersed disciplines of iron and steel technology for many years to come. B. R. NIIHAWAN

BIOCHEMICAL LESIONS AND LETHAL SYNTHESIS by Rudolph A. Peters (Pergamon Press Ltd, Oxford),

1963. Pp. x+321. Price 70s. The first half of this book is a narrative account of the well-known and classical researches carried out by the author and his colleagues over a series of years in various biochemical areas related to pathology and medicine: Reprinted in the second part of the volume is also the text of some lectures by the author dealing essentially with the integration of cell structure with functions. This collection of sesays and lectures brings out the impact of Sir Rudolph's contributions on the emergence of the present-day dynamic biochemistry from the earlier descriptive subject.

That pathological manifestations or other histological abnormalities are invariably preceded by enzymatic disturbances is a concept, now obvious to biochemists, that has stemmed largely from the pioneering researches initiated by Dr Peters on biochemical lesions induced by thiamine deficiency or by poisons like arsenicals, mustard gas, carbonfluorine compounds and thiol group inhibitors. For example, his approach to understand at the enzyme level the action of thiamine by parallel studies *in vivo* and *in vitro* was undoubtedly a novel one at that time. Such logical follow-up of metabolic disturbances to understand the primary biochemical defects has yielded good scientific and practical dividends some of which are reviewed in the first four chapters. It is of interest to recall that although dimercapto-propanel (British Antilewisite, BAL) as an antidote to lewisite gas and other arsenicals was discovered by logical approaches following observations on the marked in vitro effects of arsenicals upon the pyruvate oxidase system of brain brei, it was only some ten years after this work on BAL was completed that the presence of a dithiol component, lipoic acid, in alpha-keto acid oxidase systems was recognized. Again, the discovery of the mutagenic action of mustard gas led to a wide development of synthetic nitrogen mustards several of which have been of value as anticancer agents.

The term lethal synthesis, as contrasted to protective synthesis in detoxification mechanisms, was first used by Peters in his studies on fluoroacetate poisoning which was shown to be due to its conversion enzymatically to fluoro-citrate which inhibited specifically the action of aconitase. Other examples of lethal synthesis and lethal incorporation including the fraudulent nuclootices which could be formed from purine-pyrimidine analogues have been discussed in two chapters. An interesting chapter on research to understand biochemical lesions in burns relates blister formation to the release of a new proteinase from the cell surface, suggesting that an obvious treatment would be with an anti-proteinase.

The four lectures reproduced in the book make instructive reading despite the rapid pace of progress in biochemistry. It is particularly pleasing to find that various ideas on biochemical processes and speculations on cell structure elaborated in the three Harben lectures delivered in 1929 are receiving much support from contemporary studies on intracellular organization. In the illuminating Linaere lecture, 1962, Dr Peters underscores the fact that biochemistry should not content itself by adding essentially to pure chemistry with study of the chemical compounds and of the enzymes present in living matter but rather aim at relating these to the machinery of life and of the organized entities of the cell. In this effort relevance is ensured and progress aided by study of induced biochemical lesions.

The book is of value because classical experiments are presented in a logical sequence and the information has been brought up to date by appending notes on recent developments. The lines suggested to explore further the concepts of biochemical lesions and lethal synthesis are, it may be noted, from an investigator who, with his several years of experience, has paved the way for quicker expansion of knowledge in the field.

A.S.

EXPERIMENTS WITH DRUGS edited by H. J. Eysenck (Pergamon Press Ltd, Oxford), 1963. Pp. xii +421. Price £5

The book is a multi-author (14 contributors) report of a series of experiments designed to test a 'theory' regarding the behavioural effects of certain groups of 'depressant' and 'excitant' (or 'stimulant') drugs. It has been aptly pointed out in the foreword that "the theory contends that these drugs act in such a fashion as to change the level of activity of fundamental psychological mechanisms, which are derived from and defined in terms of modern experimental psychology, particularly modern learning theory". It is the purpose of this book to bring before the reader a number of experiments in the borderland fields of physiology, pharmacology and psychology, together with the theoretical rationale underlying their development. Though the six parts of the book appear to be rather disjointed, there is a central theme pervading the combined presentation which veers round the question of 'Personality and drug effects'. The reviewer being a pharmacologist has found new food for thought in a number of chapters of which Chapter 1 and Chapters 10-15 engaged his attention most. Certain statements and conclusions appear challenging but worthy of attention and further investigation.

The first chapter written by the editor, Dr H. J. Eysenck, critically examines the various theories pertaining to 'personality' and aims at clarifying the concepts of 'excitation' and 'inhibition', with particular reference to such drugs as sodium amytal. alcohol and meprobamate on the one hand, and caffeine, Dexedrine and Meratran on the other. Much of the complexity of this chapter has been simplified by the inclusion of Figure 2 showing the Levels of personality' and Table 1 containing 'Drug studies' on a variety of experiments involving 'conditioning', 'sedation threshold', 'vigilance', 'motor responses', etc., etc. This chapter really has taken up the task of 'setting the stage' for the whole book. The remaining fourteen chapters each deal with a single, clearly demarcated subject such as 'Suppression and masking effects', 'Sedation threshold effects', 'Perceptual after-effects', 'Cons-tancy and apparent movement phenomena', 'Interaction effects of drugs' and ' Physiology and psychopharmacology' and state the logic of the reasoning, as well as the general supporting evidence available for the various steps involved in the argument. Most readers will find areas of disagreement with the theories propounded in some of these chapters, but no uniformity of views need be expected in a presentation of this type where individual contributors have been rightly given the opportunity to develop their arguments based on experimental data and their interpretations.

The last chapter on 'The influence of stimulant and depressant drugs on the central nervous system ' surveys some of the current body of opinion as to the effects of stimulant and depressant drugs on central nervous system and the resultant effects on some of the mechanisms underlying response to stimuli. The reticular formation of the brain has been considered as a mechanism for modulating the functioning of other portions of the central nervous system, under the influence of a multitude of factors including both 'bombardment' by external stimulation and the pressure of internal biological drives. The general depressant drugs have been depicted as altering the balance between the facilitatory and suppressor functions of the reticular formation and indirectly the functioning of the cortex and the peripheral portions of the CNS. The stimulant drugs, on the other hand, have been shown to exert an influence on the tonic or phasic portion of reticular formation so that the effect is one of a general tonic facilitatory influence in opposition to the suppressor mechanisms.

This book deals with an area of investigation in the borderline fields of physiology, pharmacology and psychology which is of paramount importance in present-day drug research - the effects of psychoactive drugs (tranquillizers, energizers, psychotomimetics, etc.) on human behaviour and experience. In view of the social and ethical as well as the medical and psychiatric dimensions of the problem, it is essential that methods be developed for the reliable and accurate assessment of a drug's effects. The approach attempted here to the study of the effects of drugs on behaviour, while utilizing a pharmacological model, has tried to bridge the gap between pharmacology and psychology and to find a parallelism between the two systems of conceptualization. There are several obviously overlapping areas of observation but certain striking analogies are becoming manifest between the general facilitatory and suppressor functions of the reticular formation and the concepts of central 'excitation' and 'inhibition' that are used in the psychological model.

Such books are well worthy of a place in the library of physiologists, pharmacologists and psychclogists and should help in bringing about more collaborative studies between these groups of scientific disciplines in throwing further new light on the intricate functioning mechanisms of the human brain.

B. MUKERJI

#### PUBLICATIONS RECEIVED

- FAST REACTIONS IN SOLUTION by E. F. Caldin (Blackwell Scientific Publication, Oxford), 1964. Pp. x+306. Price 45s.
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# NOTES & NEWS

#### **Inverse fluorescence effect**

Research workers at the Signals Research & Development Establishment (SRDE), Christchurch, England, in collaboration with a research team at the Aberdeen University have recently reported success in demonstrating an effect which is the reverse of fluorescence and was predicted several years ago. Though the effect seems to have been demonstrated earlier in USA, it has only been done using equipment to hold materials at liquid helium temperatures. The present approach uses an extremely simple set-up and an easy procedure.

In ordinary fluorescence, either with ultraviolet, X- or gamma rays, a fluorescent substance absorbs radiation of higher energy and reradiates part of it as less energetic radiation. The SRDE scientists have been able to achieve the reverse phenomenon. They used a crystal of a semiconductor material doped with a rare earth and made it absorb longer wavelength (low energy) infrared light and re-radiate shorter wavelength (high energy) visible light. The effect is accomplished by the crystal's property of adding the energy of two or more quanta of absorbed infrared radiation and re-radiating the total energy. This property depends not only on the electron structure of the atoms of the doping material but also on the structure of the host crystal. To show the effect, the crystal is simply placed in a focused beam of infrared radiation when it will glow. So far, three different types of crystals have been tried which emitted three different colours of light, viz. red, faint green and orange. Though still in exploratory stage, with improvement this development is expected to lead eventually to devices that will show detailed pictures of objects in the dark without the complicated electronics of the image converter — a distinct military advantage. If the sensitivity of the system can be made adequate, the development is also

# Detection of neutrinos from the sun -A new plan

A new plan to detect neutrinos coming from the sun has been envisaged. According to the plan, a tank containing 100,000 gallons of pure perchlorethylene placed 4500 ft deep in a mine would serve as a trap for neutrinos. Although neutrinos react with matter so infrequently that they can, on the average, penetrate 100 trillion miles of lead, the perchlorethylene tank should catch 4-11 interactions each day. The neutrinos would react with the chlorine in the perchlorethylene liquid to produce radioactive argon-37, which is easily detected. A test made with two 500-gallon tanks of perchlorethylene in a mine 2300 ft deep has shown that the proposed plan will be successful in detecting neutrinos from the sun [Sci. Newslett., Wash., 85 (1964), 195].

#### Atomic absorption spectroscopy studies using laser beams

Atomic absorption spectroscopy studies of several substances including the refractory materials has now been made possible by a technique developed at the International Telephone & Telegraph Corporation, Indiana. As a result, it is now possible to detect concentrations of elements as low as one part in a million. In this technique a gigawatt laser pulse is used for evaporating materials for analysis of their composition. In operation, a hollow-cathode lamp generates the spectral lines of the element that it is desired to detect and measure, and this light is directed towards a spectrometer consisting of a prism and an image dissector that measures the intensity of the various spectral lines of the light. The laser beam is focused on a sample of the material under analysis and evaporates a portion of it in the path of the light from the lamp. If the material under analysis contains the element being measured, its vapour will selectively absorb the lamp's spectral lines and the extent of the absorption will be registered by the spectrometer [J. Franklin Inst., 271 (1964), 288].

## Spectrometer for analysis of laser radiations

A versatile and easily operated spectrometer has been designed at the US National Bureau of Standards to study laser frequencies and has the advantages of quick response, high resolving power and intensity, and good reproducibility. The principle of its working is as follows:

The separation between the two mirrors of a Fabry-Perot interferometer is varied periodically by piezoelectric vibrations produced in a ceramic tube. The resulting interference patterns are reproduced on either a strip chart or on oscilloscope screen. Voltages to provide the linear vibrations of the piezoelectric ceramic tube are applied by wires soldered to the inside and outside of the tube from a 60 c/s. power line. A small circular diaphragm placed in the optical path permits only the centre of the circular interference fringe pattern to be viewed by a photomultiplier tube. As the mirror separation of the interferometer was altered by the movements of the piczoelectric tube over a period of time, the light passing through the diaphragm yielded a record of the intensity structure within the fringes. The photomultiplier tube was connected to an automatic recorder or an oscilloscope, so that this structure could be traced on a strip chart or displayed on the oscilloscope screen.

Experiments made so far have shown that the instrument has high resolution and can be used to measure Zeeman splitting frequencies. Because of the high resolution and intensity of the cathode ray oscillograph display, energy shifts back and forth between modes and frequency changes are readily apparent. Further work is in progress to improve the sensitivity of the instrument in order that the fine structures of the frequencies of both visible and infrared lasers may be analysed. Such analysis should provide information for obtaining laser stabilization [*Tech. News Bull. U.S. Bur. Stand.*, **48** (1964), **46**].

#### Confirmation of linear structure of carbon suboxide

The linearity of the structure of the carbon suboxide  $(C_3O_2)$  molecule — a matter of scientific controversy for over 30 years — has now been experimentally confirmed by high-resolution infrared spectroscopic studies conducted at the US National Bureau of Standards Laboratories.

The electronic structure expected for  $C_3O_2$  molecule as well as the valence theory in general indicate that  $C_3O_2$  molecule has a linear symmetrical structure. In 1933, an analysis of the dipole moment value of the molecule indicated a bent structure for this compound. Since then, molecular spectroscopists were divided in their opinion regarding the structure of the molecule. At the US National Bureau of Standards the infrared spectrum of the molecule was investigated in the region 1800-3300 cm.-1 using the NBS-built high-resolution spectremeter operated in the double pass mode after being calibrated using rare gas emission spectra with an interference fringe system. The C<sub>3</sub>O<sub>2</sub> band system centred at 3200 cm.<sup>-1</sup> fortunately falls in the region of peak resolution of the NBS instrument. The first band in the series was found to originate from the ground state. The lines of this band can be accounted for exactly, if the band is assumed to arise from a  $\sum_{u} \sum_{g}$  transition of a linear molecule. The moment of inertia calculated from the observed data is in excellent agreement with that calculated from electron diffraction parameters. Analysis of the second band at 3180 cm.1 showed that it is due to  $\pi_g - \pi_u$ transition originating from the first level of a low frequency bending mode. From the l-type doubling observed in this band, the frequency of the bending mode can be estimated to be 20-70 cm.-1. This observation leads to the conclusions that the molecule is linear in structure and that one of the bending vibrations falls at an unusually low frequency [Tech.

News Bull. U.S. Bur. Stand., 48 (1964), 48].

#### A new automaton

A new automaton having an intelligence level similar to that of an ant has been developed at the Johns Hopkins University Applied Physics Laboratory. The new automaton is mobile and is able to feed itself (by charging its batteries when discharged) and is able to exhibit conditions similar to sleep and panic. The machine which looks like a king-size hatbox has a retractable giraffe-like head having tiny sensors which follow along the wall's surface in search of electrical sockets through which the machine feeds itself until the batteries are fully charged. After feeding the machine wanders at random. However, because of the electronic logic elements stored in the machine, it is able to avoid obstacles. As the machine nears the edge of a step, one of its eight shoes (normally resting on flat surface) drops down, causing the brain to react and the machine draws back. If the machine gets entangled in a railing with its head caught between two poles it wriggles its head back and forth (like a child) and then completely stops and goes into a panic mode before attempting another manoeuvre to get free. When it is time for the machine to go to sleep, it receives a command via a telemetering command system which it stores in its memory. It retains this command for several hours before finally carrying it out. The telemetering system also enables any observer to follow its motion. In addition to the command telemetering system and its touch sensors, the automaton has been recently equipped with two ears to enable it 'coast' freely avoiding obstacles. Efforts are being made to equip the machine with an 'eye' - an optical scanning system so that it could spot electrical sockets for feeding. The new automaton which has been in operation for almost a year has over 400 hr of operating time. The machine is expected to pave the way for the development of automatic electronic devices that could explore the ocean floors, caves, and planetary surfaces. Improved versions of such automatons may thus have a useful role in the preliminary exploration of different planets and some of their features before men could actually land on them [Sci. Newslett., Wash., 85 (1964), 170].

# Linear silicon-nitrogen polymers

The preparation of a series of long-chain, silicon-nitrogen polymers, silazanes, hitherto difficult to make because of the ease of formation and stability of cyclosilazanes, has been reported. The use of bridged monomers, which stereacally prevent cyclization during polymerization has made it possible to make linear polymers with molecular weights up to 8000. The aminosilane monomers have been prepared from chlorosilane intermediates obtained by refluxing allenediamines with diorganodihalosilanes. The bridged chlorosilane is obtained by the reaction of either ethylenediamine 1,3-propylenediamine with or dichlorodimethylsilane, dichloro-methylphenylsilane or dichloro-methylvinylsilane. These bridged compounds are then converted to aminosilane monomers by reacting them with either ammonia or amines. The polymerization of the monomers is effected in reagent grade xylene using ammonium sulphate as catalyst. Ammonia monomers could not be polymerized under these conditions because of the ease with which they lose ammonia. Butylamine and methylamine monomers react more slowly. Monomers with an ethylene bridge react more quickly than do those with a propylene bridge. Substitution of a phenyl group for a methyl group on each silicon atom of the monomer leads to slower polymerization. From intrinsic viscosities, it is concluded that the highest degree of polymerization occurs at 140°. In the infrared spectra of the monomers and polymers, same bands are obtained with an exception of a band at 1180 cm.-1 for some of the polymers. This band can be re-lated to the -SiMe<sub>2</sub>-NHSiMe<sub>2</sub>grouping, which is absent from the monomers. Differences in NH region show the loss of a monomer's free primary group or secondary group on polymerization [Chem. Engng News, 42 (1) (1964), 26].

#### Polypentenamer

Cyclopentene has been successfully homopolymerized to a new polymer, polypentenamer, employing Ziegler-Natta type catalysts. The polymerization takes place exclusively through ring cleavage, and gives a stereoregular polymer in a yield of 98 per cent (trans) or 97 per cent (cis), depending upon the catalyst. With molvbdenum pentachloride and triethylaluminium, cis-polypentenamer (amorphous) is obtained while pentachloride-triethvl - tungsten aluminium catalyst system gives rans-polypentenamer as crystalline material.

The structure of the cis- and trans-polypentenamer has been elucidated on the basis of their infrared spectra. In the cis form. the infrared spectra show an isolated double bond for each monomer unit. The bonds are of cis type with bands at 7.12 and  $13\cdot 8-13\cdot 9$   $\mu$ . The infrared spectra of the crystalline material also reveal one isolated double bond per monomer unit and a band at  $10.35 \mu$  indicative of a linear trans isomer. The spectra of both types do not show bands in 8-8.5  $\mu$  region, which would have indicated cyclic structure. The infrared spectra of both the samples do not show the presence of other types of double bonds, viz. vinyl, vinylidene, conjugated or cumulated bonds. The ozonolysis of the trans polymer indicated that the trans polymer is enchained head-to-tail having three methylene groups between double bonds. The structural investigation on the cis polymer are progressing.

Both the polymers are soluble in aromatic, cycloaliphatic and chlorinated hydrocarbons and are insoluble in alcohols, aliphatic ketones and ethers. They are elastomeric and, like many elastomers, trans-polypentenamer is almost amorphous at room temperature when unstretched. But cooling or stretching produces a crystalline structure. Stretching combined with cooling gives a fibre of even greater crystallinity. With or without reinforcing fillers, vulcanized trans-polypentenamer has good properties mechanical [Chem. Engng News, 42 (14) (1964), 42].

# Hydrogen damage of boiler tubes

According to a theory proposed by A. M. Guy of the Southern Indiana Gas & Electric Co., Evansville, Inc., USA, hydrogen damage can be produced in a pure water boiler even when there is no sodium hydroxide present in the boiler water and no measurable free hydroxyl groups, which have been commonly associated with failure of boiler tubes. The most common cause of hydrogen damage can be the mechanical failure of a baffle tile along the boiler sidewall, which allows an excessive amount of extremely hot gases to flow over a very short section of a water circulator tube that is normally completely out of the heat input area. The hydrogen damage need not necessarily be a result of overheating, but may also be caused indirectly. In the boiler tube a thin layer of iron oxide is supported over steel and the reaction between Fe<sub>3</sub>O<sub>4</sub> and even Fe<sub>2</sub>O<sub>3</sub> and water is a most stable condition. The tube is subject to damage by extreme thermal shock and/or mechanical abrasion. Either or both of these, however, may be accomplished by film boiling, in which case the presence of free hydroxyl ions or caustic soda serves to greatly accelerate the chemical reaction begun by heat. By maintaining proper heat input levels, it is possible to run steam generators for a long time without tube failure of any type in a pure water system [Mech. Engng, 86 (4) (1964), 116].

#### Photochromic glasses

The development of glasses which darken on exposure to light and clear again when the light fades has been reported from Corning Glass glasses Works. Basically, the silicate glasses containing are submicroscopic silver halide crystals. The crystals are precipitated during the manufacturing process and are so minute that they do not affect the transparency of the glass. The photochromatic action can be controlled in an individual glass piece, so that only a part darkens on exposure to light. Ultraviolet light sources cause instant darkening. Under normal indoor lighting the glasses remain clear. The

time required for photochromic glasses to regain original transparency depends upon the glass composition, previous heat treatment and temperature of the material. The rate of clearing on removal of the light source increases with temperature. Fast clearing glasses are more temperature sensitive than the slower clearing glasses [Mech. Engng, **86** (3) (1964), **62**].

#### Human leukaemia virus

The virus associated with the human leukacmia was for the first time isolated by Dr Negroni, working in the Experimental Biology and Virology Division of the Imperial Cancer Research Fund, Mill Hill, UK, from the bone marrow of the patients suffering from leukacmia. He has presented both biological and morphological evidence to show the association of virus-like particles with human leukacmia.

The discovery of the virus causing chicken and mouse leukaemia, and the identification of virus-like particles by electron microscopic studies of the leukaemia bone marrow cells led the way to the isolation and culture of the virus. The virus was isolated in each of the 10 cases of human leukaemia and was maintained by serial passage in tissue cultures. Whole human embryos, made available from women whose pregnancies had to be terminated for medical reasons, and the human foetal kidneys were used for the preparation of tissue cultures. The cultures were made in the same way as for bacteria, with a suitable medium in the form of a jelly put in sterile bottles and dishes containing nutrient sub-stances of organic and inorganic nature. A sample of foetal kidney cells to be cultured was inoculated on to this jelly and kept at constant temperature, so that the cells survive and reproduce to form a mat of tissue on the surface of the jelly. Dr Negroni, taking this type of cell culture, infected it with the bone marrow of the patients suffering from leukaemia. In a few experiments, the cultured kidney cells began to wither and die. The jelly containing such an affected cells was dissolved in salt solution and the solution diluted up to million times was as

infective as the original, indicating that a transmissible living agent had been introduced into the culture line. Electron microscopic observations of the infected cells showed virus-like particles. The control cultures appeared healthy and the affected cells showed varying degrees of cytoplasmic degenerative changes.

In addition to the above discovery, antibodies which neutralize the virus action were found in the blood of seven out of eight leukaemia patients but not in patients suffering from diseases other than leukaemia. Attempts to produce leukaemia in laboratory animals by injecting culture of human leukaemia virus were unsuccessful. Another point of greater significance in Dr Negroni's work is the identification of a naturally occurring ' antiviral factor ' in the blood serum from calves which can inhibit the growth of the virus.

Reports on the discovery of the virus, however, do not mean that the cause of leukaemia has completely been found, excepting that a significant progress has been made in our knowledge of the deadly disease [Brit. med. J., (1964), 927, 929].

#### Selenium cycle in nature

The occurrence of selenium cycle. on the pattern of similar cycles for carbon, nitrogen and sulphur, has been postulated though it still requires to be confirmed on rigorous experimentation. It has earlier been demonstrated that bacteria, fungi and higher plants, particularly species of Astragalus (both those that require selenium and those for which such a need has not been shown), metabolize selenate or selenite, the most oxidized forms of selenium, to the level of selenide. The biological syntheses of various seleno-amino acids and of the seleno-ether, dimethyl selenide, constitute evidence of at least the first half of such a cycle. For the remainder of the cycle, there are indications in literature that some microorganisms are able to oxidize selenium of valence zero to selenium of valence +6.

A selenium cycle can also be inferred indirectly from other information. Selenium accumulator plants always associated with semiarid, seleniferous soils, biosynthe-

size organic selenium compounds and release these compounds when they decay. If there were no way to oxidize these compounds, one would expect a gradual increase of organic selenium, particularly in these drier regions, but surprisingly the selenium in these soils is primarily inorganic. The absence of organic selenium has been attributed variously to absorption by plants, to leaching, and to conversion into inorganic compounds; but of the three possibilities only one, absorption by plants, has been adequately tested. The mounting evidence that selenium is an essential micronutrient also suggests the existence of the cycle [Nature, Lond., 201 (1964), 1304].

#### Indian standard man

The physiological characteristics including body fat content, skeletal weight and pulmonary physiological norms such as breathing capacity, breathing reserve and lung ventilation rate of an average Indian adult are being studied on a comprehensive basis by the Health Physics Division of the Atomic Energy Establishment, Trombay. The object of this study is to evolve radiation protection standards and to evaluate the applicability to Indian population of the safety standards laid down by the International Commission on Radiological Protection (ICRP). The ICRP calculations have been normalized to a 'standard man in USA. As the physiological characteristics of standard man in USA and normal Indian adult differ significantly in several respects, it necessitated the present investigation.

The standards for radiation protection recommended by the ICRP are of two types — primary and secondary. The primary standards are the maximum permissible doses (MPD) for the body as a whole and for individual organs. The secondary standards are the maximum permissible body burden (MPBB, body burden is the quantity in microcuries of radioactive material in the body at a particular time) and the maximum permissible concentration (MPC) of radionuclides in air and water.

Data on total body weight and of 12 different organs including gonads, lungs and thyroid which are sensitive to radioactivity were collected frcm the post-mortem cases from different parts of the country. Studies revealed that the MPBB values of the ICRP may have to be scaled down by 20-44 per cent for a majority of radionuclides while for about 5 radionuclides the values may need an upward revision by 29-30 per cent. These are only tentative conclusions as other factors such as variation in selective localization of radionuclides in body organs, turnover rates, quality and quantity of food consumed by respective people have to be taken into account before any modification of the ICRP values could be attempted. Since food is one of the main media through which radionuclides enter the human system, a countrywide survey of food and feeding habits of various groups of the Indian population has been proposed to be undertaken [Nuclear India, 2 (No. 9) (1964), 1].

#### **Progress Reports**

#### Central Mining Research Station, Dhanbad

The first regular annual report of the station (1961-62) records its diverse activities during the year in the fields of mining operations, safety and health, testing of standard equipment and design of new apparatus for specific and special purposes. The industry and government departments continued to seek assistance from the station for the testing of mine helmets, flameproof equipment, conveyor belts, detonators, safety fuses and in testing and calibrating anemometers and velometers. A number of surveys of interest to the industry have been conducted on subjects such as mine gas analysis, ventilation and lighting in mines, dust sampling, etc. Special mention may be made of the technical assistance given to the management of a big organization in opening a mine closed due to underground fire. This was the first instance that such extensive investigation on scientific lines on underground fire has been undertaken in India. The station extended cooperation to the Indian Standards Institution in the preparation of a draft specification for flameproof enclosures to electrical equipment. An important event in the station's activities during the year was the holding, during 9-12 December 1961, of a symposium on 'The mechanization of mines in India', attended by an international gathering of 500 delegates.

Success has been achieved in preparing a suitable reagent for use in the carbon monoxide detector tube and in the fabrication of the apparatus. During the development of physico-chemical methods for the consolidation of coal dust in underground mines, a salt-cement mixture put on the return-air roadway in the mines has been tried. Cement pastes having higher amounts of cement than that corresponding to a saltcement ratio of 5:1 have been found to sweat and remain moist all the time. As the humidity increases, up to a certain limit an increase in the proportion of cement in the mixture has been found to be helpful. A rapid method based on complexometric titration has been developed for the analysis of manganese ores; the only separation needed in the new method is that of silica and the rest of the elements (mainly Fe, Al, Mn, Mg and Cl) are estimated from the silica-free filtrate. A new method for the determination of the efficiency of fans from wet bulb temperature measurements has been worked out and tested to assess its applicability to mine fans. The method has been found to be satisfactory only if thermistors are used in place of Beckmann thermometers for the measurement of temperature for the drift and evasee of the fan. In the direction of developing a resinbonded mine roof bolt, trials with an alkyd resin mixed with quartz and styrene in the presence of benzoyl peroxide as a catalyst have given satisfactory results. In the field of instrumentation either installed, fabricated or tested, mention may be made of: (1) a fluid network analyser which considerably reduced the time spent on solving network problems of mine ventilation; (2) an X-ray diffraction unit Crystalloflex III; (3) a d.c. amplifier for measuring weak photoelectric currents; and (4) an automatic control for regulating exposure timing in photographic processing work.

Other subjects investigated at the station are: size separation of mine floor dust, wetting characteristics of coal dusts, dust suppression, corrosion of wire rope by pit water, rock temperatures, performance of cap lamps, explosives testing, etc.

# National Science Foundation, USA

The thirteenth annual report of the National Science Foundation for the year ending 30 June 1963 lists the basic research programmes sponsored by it in different scientific disciplines besides presenting a non-technical account of the outstanding achievements in different fields. Details are given of the various fellowship programmes in research and science education supported by the Foundation. A special section is devoted to the programmes in the field of dissemination of scientific information. The funds made available for research activities amounted to \$194 million out of which \$117 were spent towards research grants. Also grants were given to research facilities, to national research centres and for other projects such as Indian Ocean Expedition, Project Mohole, International Year of the Quiet Sun and the US-Japan Cooperation Science Programme.

Important research projects supported in the field of biological and medical sciences were directed towards understanding the life processes in plants and animals organized under 8 different programmes. The fields of study were those which would further the knowledge of the molecular basis of life, nature and action of the genetic material and evolutionary studies, growth and differentiation in all living organisms, mechanism of cell organelle differentiation in a variety of cells and tissues, cell-virus interactions, biochemical reactions involved in the building up and breaking down of the substances of cells and organisms, research on the whole organism and its organ systems, including classical plant and animal physiology, pathology, nutrition and transport of material, investigation into the reactions between the organisms and various features of their environment, research on human and animal behaviour and the survey and collection of data of all forms of life both past and present.

In the field of earth sciences, an electron probe by instruments to determine the chemical composition of individual minerals within a rock makes it possible to elucidate some of the fundamental characteristics of minerals. This is also important in understanding the genesis and evolution not only of individual minerals but also of ore deposits, rock groups and segments of earth crust.

Turbulent fluid flow, gaseous plasma, expansive cements and laser communication are some of the diverse fields of research undertaken in the engineering sciences. Results of fundamental importance have been obtained from the study of the forces that exist when there is turbulent flow around a circular cylinder as of those existing around turbines, blades or airfoils.

In the field of physical sciences, an important progress was achieved with the discovery of a new particle called the 'positive anticascade particle' which was observed in a hydrogen bubble chamber exposed to antiprotons from a 33 billion electron volt accelerator. A major contribution in the field of algebraic geometry related to the demonstration that the singularities of an algebraic variety can always be resolved in a higher dimension thus proving the possibility of resolving singularities of algebraic varieties in the three previously known cases and in all higher dimensions.

Some significant research developments in the fields of biological, astronomical and atmospheric sciences have also been reported during the year. So far it is only known that the specificity of an enzyme is dependent at least in part on its three-dimensional (tertiary) configuration, having an infinite number of possible tertiary structures. The demonstration that tertiary structure of some proteins is self-determined by the primary structure is a basic discovery. The spatial arrangement of the secondary structure of the helix formed from primary sequence and the unique position of amino acids in the primary structure causes a further folding of the helix into the truly unique threedimensional configuration of any particular protein. The prediction of operon theory that a single element coordinates the activities

of adjacent structural genes has been confirmed by the finding that the activities of 8 genes involved in the pathway of histidine biosynthesis constituting an operon are controlled by a single operator, histidine, which is the end product of the biosynthetic pathway.

Investigations into the antibody-antigen interactions have revealed that the structure of the antibody is related to its function of combining and immobilizing the antigen. Chinese hamster embryonal cells have proved to be a suitable medium for investigation of mechanism by which tumourinducing viruses transform normal into malignant cells, as Chinese hamster cells are much more stable in their chromosome numbers than those of other widely studied species. An important investigation undertaken in the field of astronomy has been the first scientific flight of Stratoscope II, a balloon-borne 36 in. telescope, to study the infrared radiation from Mars. Observations were made from a height of 80,000 ft above the earth while pointing and focusing operations were carried on by remote control from the ground. The studies have revealed that Mars is almost completely lacking in water vapour and possesses a sizeable measure of carbon dioxide. A second flight to study the infrared radiation of Jupiter and certain red giant stars has also been carried out.

A new theory has been put forward to explain the origin of sporadic, low frequency emissions from Jupiter while a new device which responds to light polarized only in a particular way has been developed which permits day-time observation of light (air glow) radiating from high atmosphere. Until recently this observation could be made only in the nighttime. Also this development makes use of the fact that light originating from reactions in the high atmosphere is not polarized and the unwanted scattered light is polarized.

#### Mellon Institute

During the year 1963, the Institute celebrated its Golden Jubilee. The fiftieth annual report contains a review highlighting the Institute's progress during the past fifty years in the fields of chemistry, chemical engineering, physics, biology and other related fields. Functionally, the Institute, a centre for both pure and applied research, is also a training school for advanced scientists and a clearing house on specific scientific information.

The fundamental work in biochemistry undertaken during 1963 included structural studies of a plant and a bacterial virus and use of a new combination of immunological and chemical techniques to identify the active sites of enzymes. Carboxypeptidase N and an additional plasma enzyme, possibly aminopeptidase, have been found in blood plasma that inactivate the hypotensive peptides, bradykenin and kallidin.

In the field of polymer chemistry, work has been undertaken to devise methods for expressing and measuring the statistical distribution of chain lengths and of diastereochemical structures characterizing the macromolecules in a given product. An approach to this problem has been suggested which is applicable to the products of homogeneous anionic polymerization of  $\alpha$ -olefins.

In the study of the phosphine complexes the occurrence of a square planar-tetrahedral isomerism in certain nickel complexes has been established and new metal compounds containing four-membered heterocyclic rings have been developed. A unique chemical system capable of carrying molecular oxygen or hydrogen has been discovered as manifested in the synthetic transition metal complex  $[Ir(CO)(Ph_3P)_2]$ which, in solution, takes up one molecule of either gas per metal and releases it under reduced pressure. The adsorbed oxygen or hydrogen can be conveniently stored by isolating the oxygen or hydrogen adduct as crystals that, at ambient temperatures, are stable in air or in vacuum.

The structures of tetraphenyl silicon and tetraphenyl tin have been refined by full-matrix least squares technique using anisotropic temperature parameters for all atoms. In both the compounds the disposition of the phenyl groups about the central atom deviates significantly from a hitherto supposed regular tetrahedral arrangement.

The work on radiation chemistry included electron spin resonance studies of radicals produced by irradiation of liquid hydrocarbons which has provided some interesting structural and kinetic results. Of special interest is the demonstration that the vinyl radical is non-linear and undergoes inversion at a frequency of approximately 108 sec.-1. This geometrical form implies that the electronic configuration of this radical is such that the electron resides for the most part in  $sp^2$  orbital rather than in a p orbital as in most other radicals.

A seven-step synthesis of the pseudo-aromatic hydrocarbon, hexaphenylpentalene, has been accomplished. This represents the first successful synthesis of a pentalene system free of propertyobscuring fused rings. This brown green crystalline hydrocarbon is stable as a solid but air sensitive in solution. It undergoes an unusual two-carbon ring expansion with dimethylacetylene dicarboxylate to form a fully substituted azulene.

In the field of metal physics a low temperature calorimeter for work in the range of liquid helium temperatures has been assembled which permits the measurement of electronic specific heats of alloy systems based on noble metals. A quantitative metallographic study of taemite and kamaeite phases in five octahedrite meteorites resulted in the evaluation of the approximate lowest temperatures at which equilibrium existed in astroidal bodies from which these-metals may have originated.

#### Dr K. Ganapathi

Dr Krishnamurthi Ganapathi has been appointed Director of the Regional Research Laboratory, Jammu. Born on 18 August 1911 in Tanjore dist. (Madras State), Shri Ganapathi received his early education in Madras State and after a brilliant academic record obtained the M.Sc. degree in organic chemistry from the Anna-malai University. During 1934-39, he carried out research on 'Terpenes and the chemotherapy of tuberculosis' at the Indian Institute of Science, Bangalore, leading to the D.Sc. degree of the Madras University. Subsequently, as a Lady Tata research scholar (1936-39) he worked on the chemotherapy of bacterial infections, particularly on the synthetic drugs of the sulpha group.

Dr Ganapathi joined the Haffkine Institute, Bombay, in 1939 and built up the Department of Chemotherapy. His special fields of study in the Institute included the synthesis and testing of sulpha drugs, antimalarials and biochemistry of antibiotics. During 1944-48, Dr Ganapathi worked on the production of penicillin on a laboratory scale and was responsible for the drawing up of plans and proposals for the establishment of a national penicillin production centre which later came up as the penicillin factory at Pimpri. In 1953, he joined, on deputation from the Bombay Government, the Hindustan Antibiotics Ltd, Pimpri, as Director of Research and was responsible for the planning and setting up of its research labora-In 1958, he was Works tory. Manager of the factory. He rejoined the Haffkine Institute as Assistant Director in 1959 and was engaged on chemical-microbiological studies.

Dr Ganapathi has been keenly associated with the scientific workers movement in the country since its inception and has served in various capacities in furthering the movement through the Association of Scientific Workers of India.

Dr Ganapathi was elected a Fellow of the National Institute of Sciences of India in 1946 and of the Indian Academy of Sciences in 1951. He has published over 100 research papers and has 15 patents to his credit.

#### Dr K. N. Sinha

Dr K. N. Sinha has been appointed Director of the Central Mining Research Station, Dhanbad. Shri Sinha (b. 1916) took the B.Sc. degree of the Patna University in 1935 and first class diploma in Mining Engineering of the Indian School of Mines, Dhanbad, in 1939. He obtained the Mine Surveyor's Certificate of Competency in 1940 and First Class Mine Manager's Certificate of Competency in 1942.

In 1940, he served as Secretary of the Coal Industry Reorganization

Committee of Bihar State. He worked as Mining Engineer and First Class Mine Manager in the Jharia coalfield during 1942-46.

He was awarded the Ph.D. degree in Mining by the Leeds University in 1949. During his stay at the University, Dr Sinha visited a large number of European mines to carry out his investigations.

After working as Mining Research Engineer in the mining industry for over ten years, Dr Sinha joined the Central Mining Research Station in 1960 as Officer on Special Duty. He has taken keen interest in initiating research projects of immediate need to the mining industry of the country and providing technical information services to the industry.

Dr Šinha has published over fifty research papers in Indian and foreign journals on various subjects like stowing, mine working, strata control, mine fire, mining research, underground gasification. He has received several awards, medals and prizes in India and abroad for his research work.

He attended the International Conference of Directors of Mining Research Institutes in Poland in 1961 and the Third International Mining Congress in Austria in 1963. He acted as the Chairman of one of the technical sessions of the congress.

Dr Sinha has been the President of the National Association of Colliery Managers (India) and Vice-President of the Mining, Geological and Metallurgical Institute of India and Indian Mine Managers' Association. He is a member of the Institution of Mining Engineers, London.

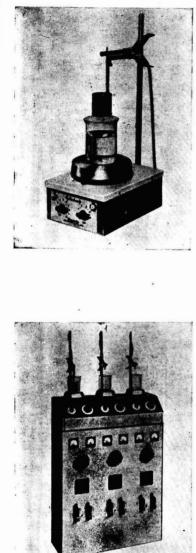
#### Announcements

• A Symposium on the Impact of Mendelism on Agriculture, Biology and Medicine is being organized by the Indian Society of Genetics and Plant Breeding from 15 to 19 February 1965 at the Indian Agricultural Research Institute, New Delhi, to commemorate the Silver Jubilee of the Society and also the centenary year of Mendel's findings. The subjects for discussion at the symposium are: (1) Mendelism and evolution, (2) Gene-

tic recombination, (3) Mutation, (4) Gene function, (5) Genetics and plant breeding, (6) Human genetics. and (7) Teaching of genetics. Distinguished foreign Professors H. J. Muller, G. W. Beadle, J. F. Crow and G. L. Stebbins (USA), A. Gustafsson and A. Muntzing (Sweden), J. B. Hutchinson (UK) and H. Kihara (Japan) are being invited to participate and deliver special lectures at the symposium. Members of the Society who wish to contribute papers may send the abstracts of their papers not exceeding two typed pages in length to the Secretary, Indian Society of Genetics and Plant Breeding, Indian Agricultural Research Institute, New Delhi 12, by 1 October 1964.

The Second International Conference on Lead is being organized by the Lead Development Association of London on behalf of the European Lead Development Committee and will be held in Holland in October 1965. The conference, lasting three days, will have a programme comprising technical sessions and works visits in Holland, Belgium and Germany. The technical sessions and works visits will be divided into three groups dealing with (1) Cable sheating, covering the production and performance of lead and lead alloy cable sheaths; plant and equipment; recent research and development; testing, quality control, standardization, etc.: (2) Batteries, covering the fabrication and properties of grid alloys; development and performance of batteries for specific uses (e.g. aircraft, traction, etc.); and recent developments in commercial applications; and (3) General appli-cations of lead, covering recent developments, special products, established and new uses, e.g. dispersion strengthened lead, lead for sound attenuation, fibre reinforced lead, continuously cast and reinforced lead sheet, water thinnable paints, organo-lead compounds, lead-coated steel, etc.

Brief outlines of papers intended for presentation at the conference should be submitted before the end of October 1964 to the Lead Development Association, 34 Berkeley Square, London W.1, or the Indian Zinc/Lead Information Centre, 5A Lord Sinha Road, Calcutta 16.



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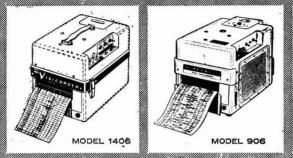


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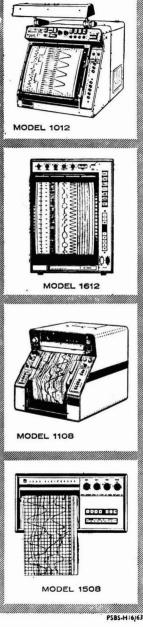
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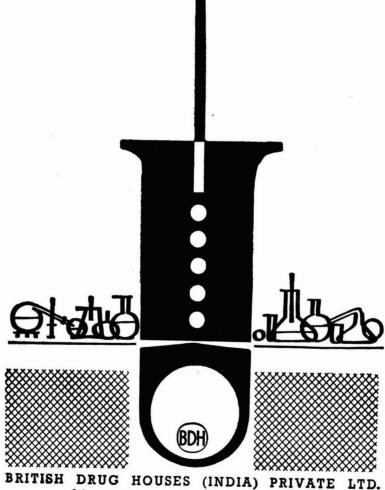
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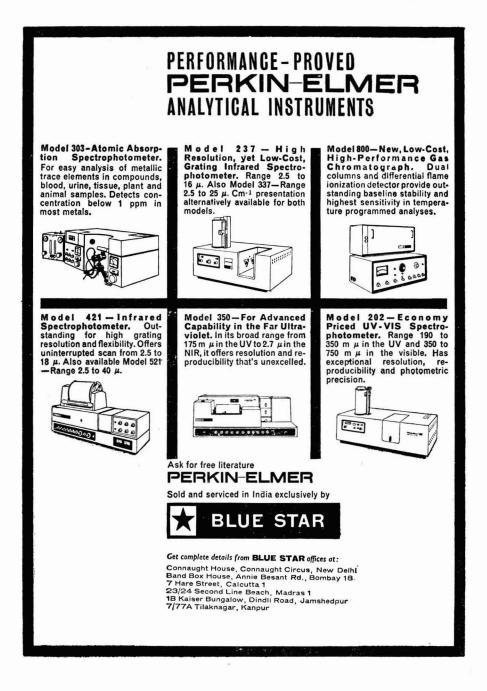
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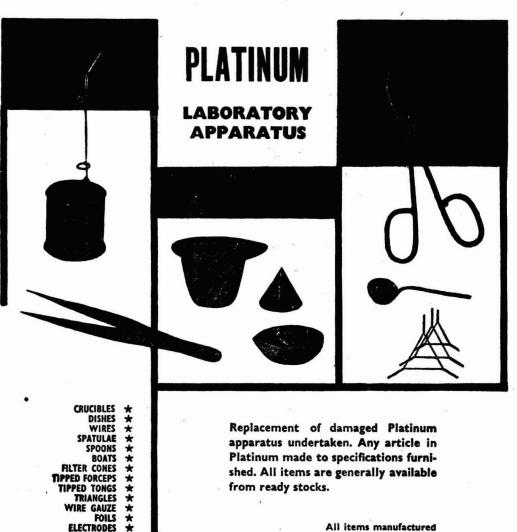
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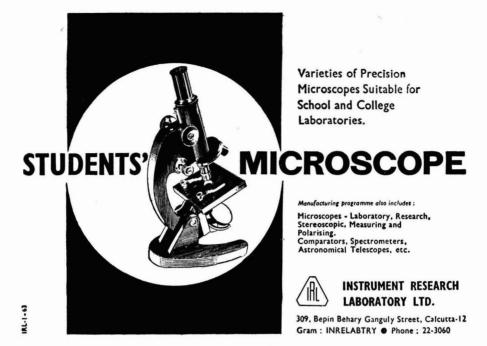
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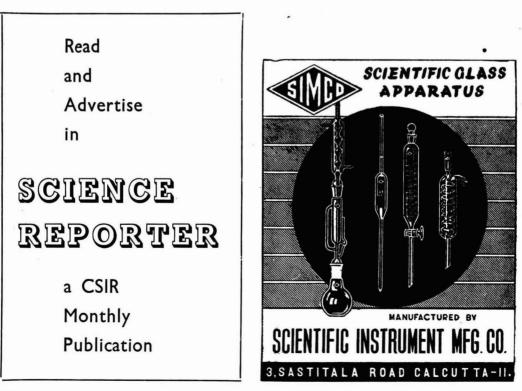
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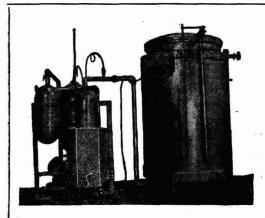
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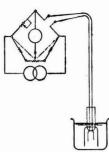
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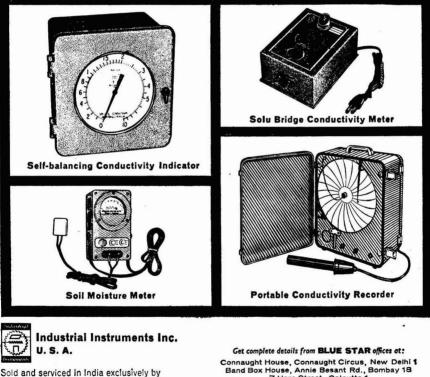
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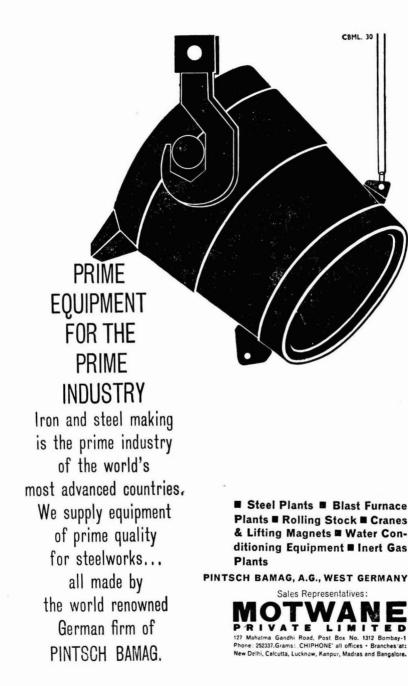
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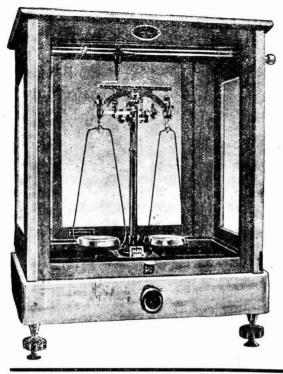
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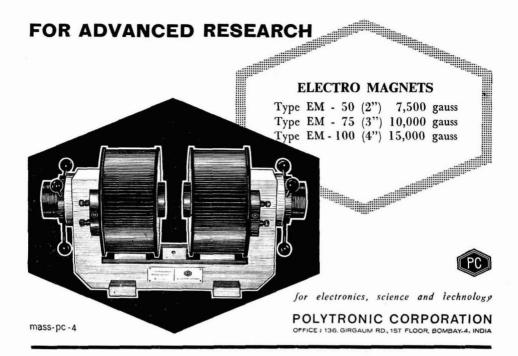
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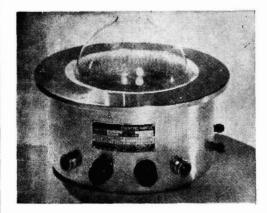
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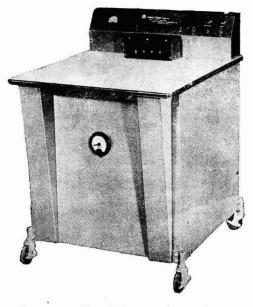
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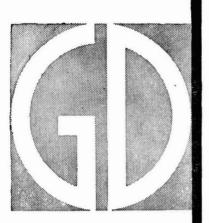
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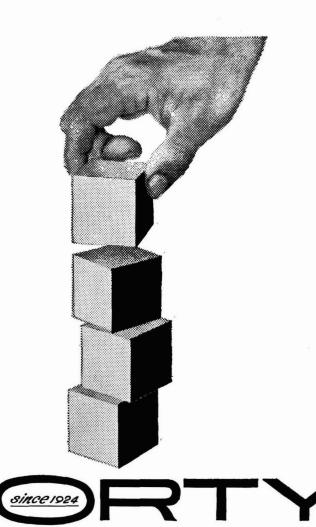
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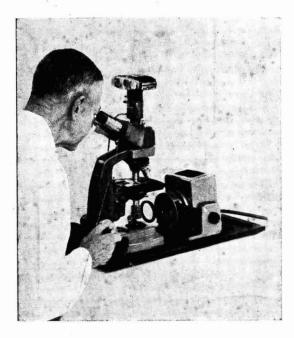
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