Journal of Scientific & Industrial Research

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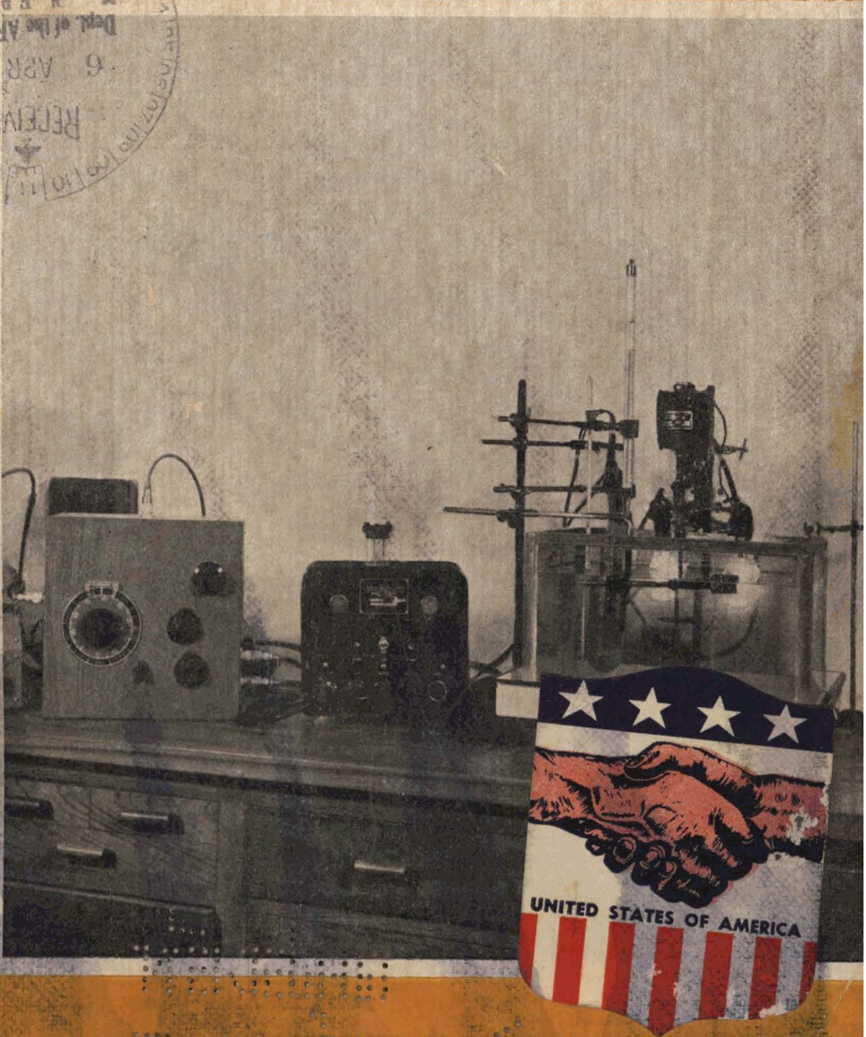
Vol. 13, No. 2, FEBRUARY 1954



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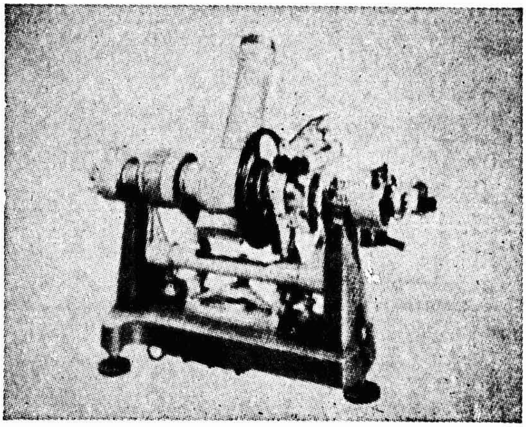

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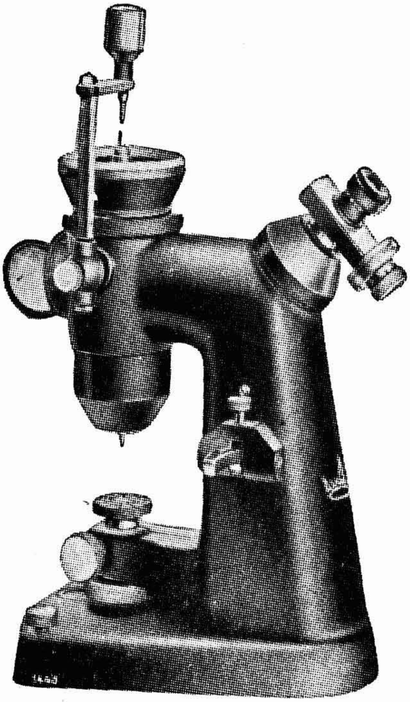

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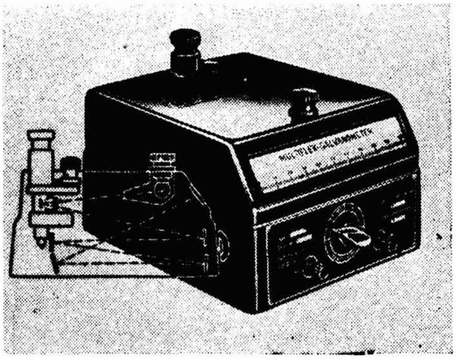
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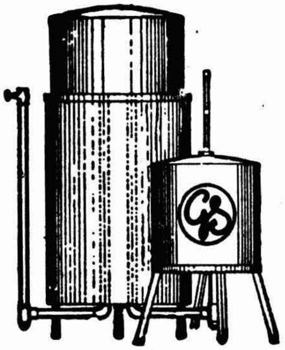

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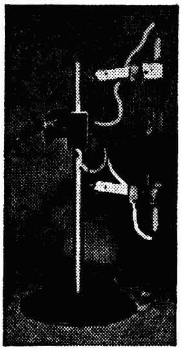

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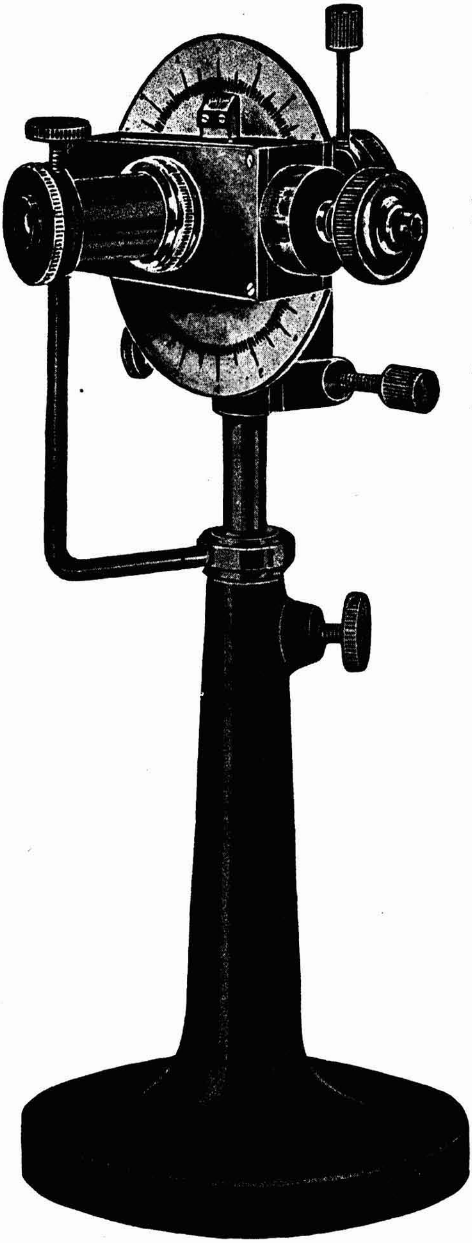

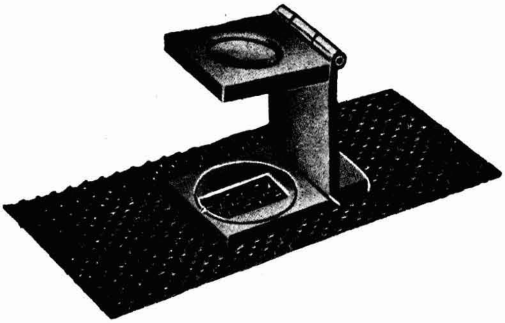

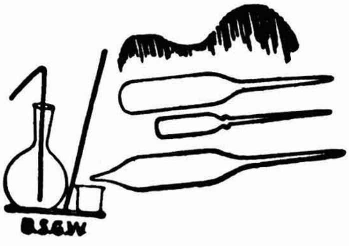
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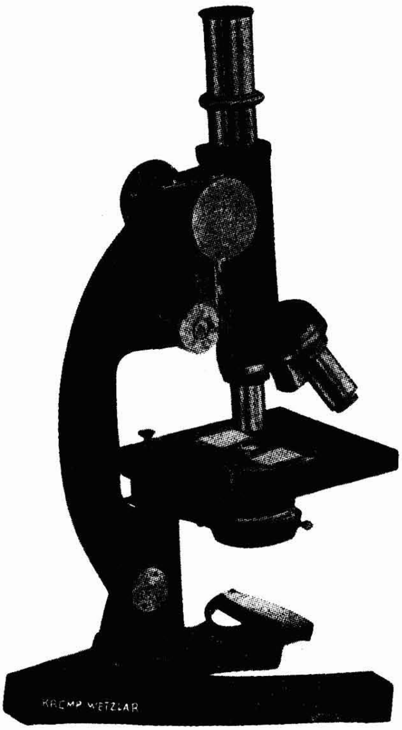
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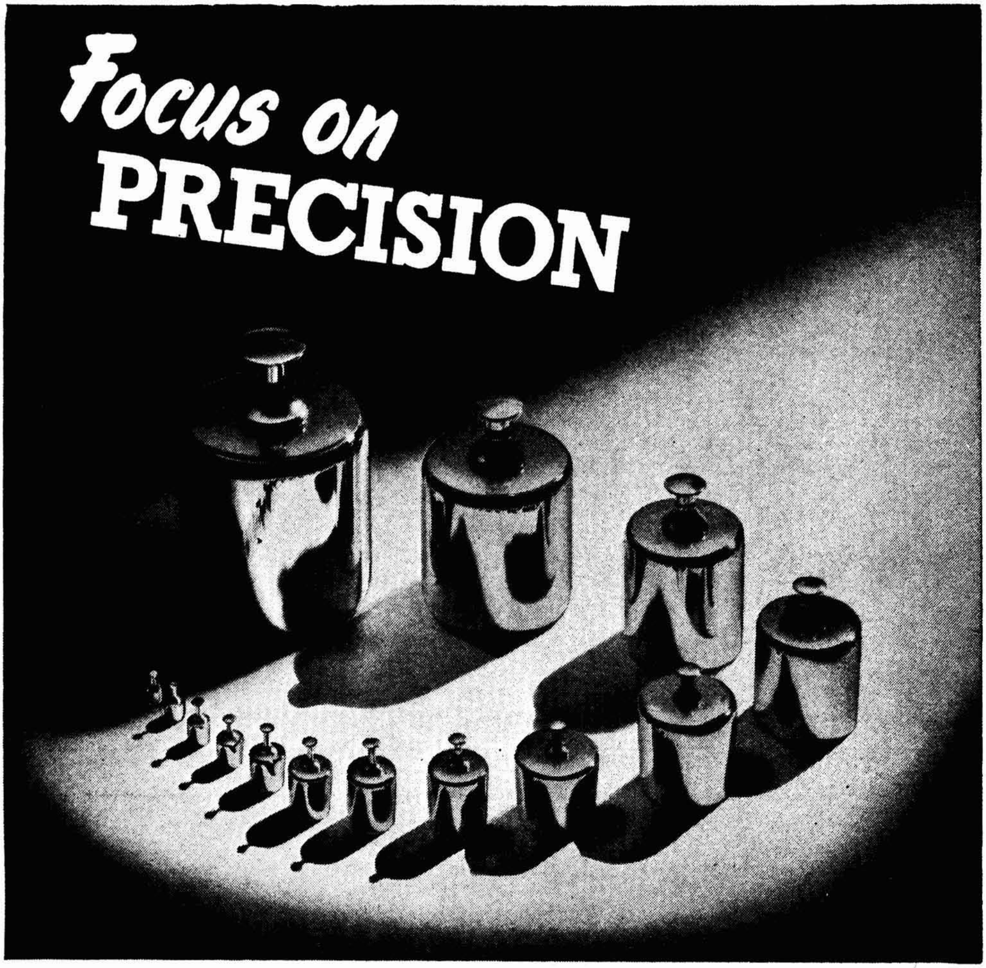
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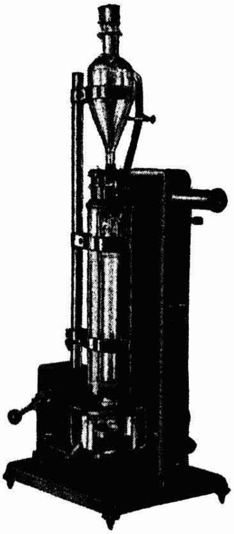

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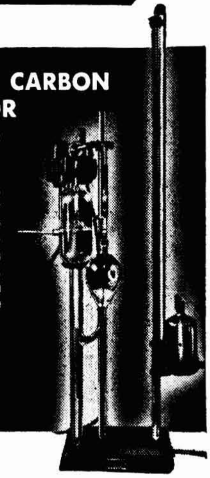

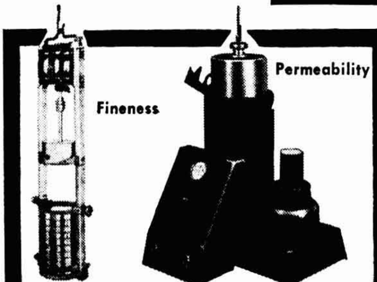
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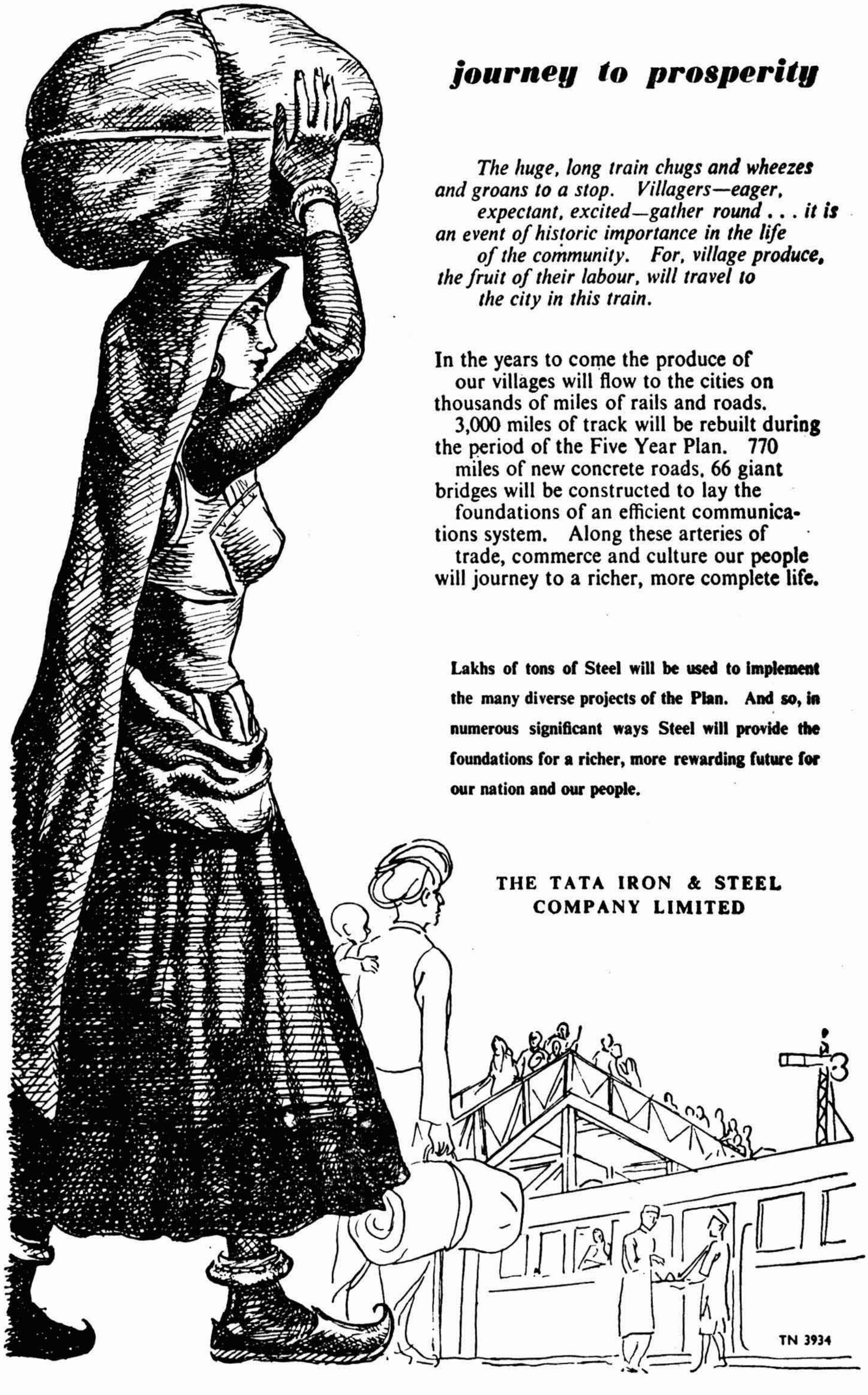

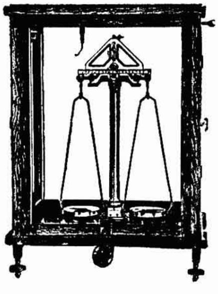

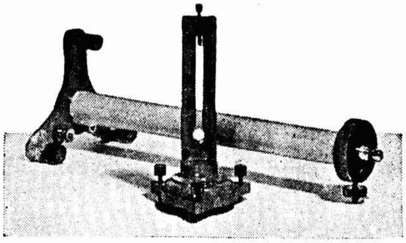

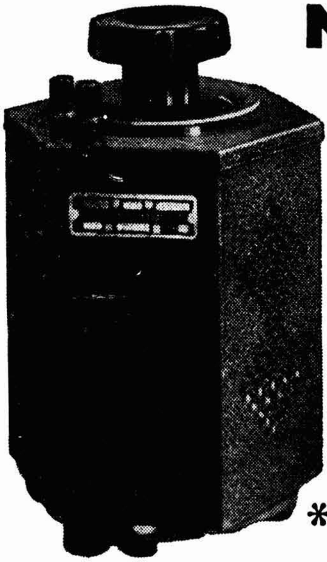

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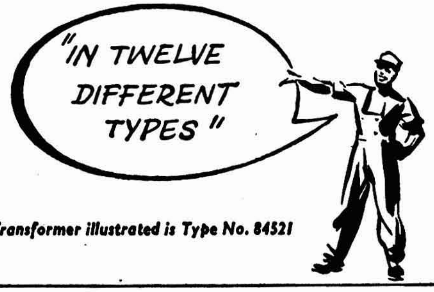

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350	0-150	2.3	6.8	84506	84507
690	0-150	4.6	9	84508	84509
1380	0-150	9.2	17	84510	84511
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260	0-260	1	6.8	84514	84515
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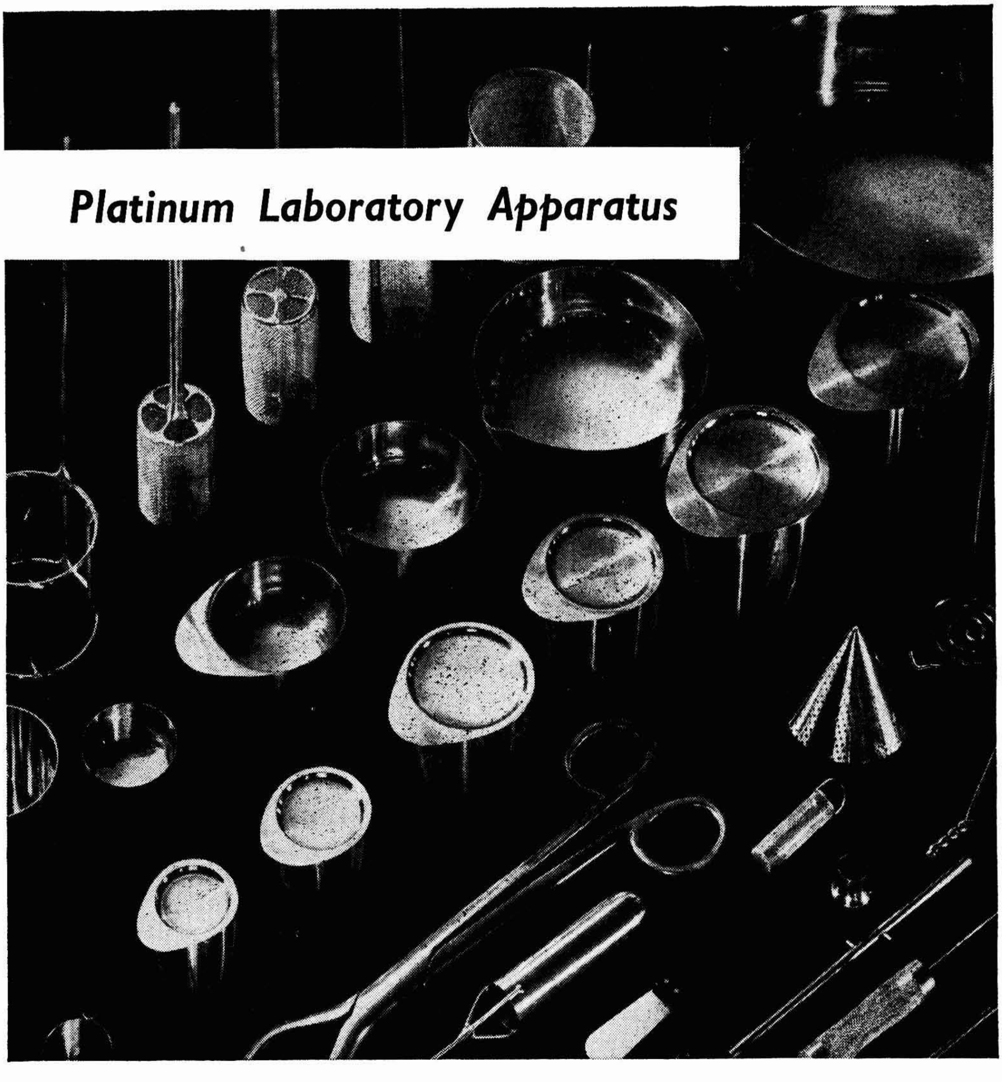

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Patent Law Amendment

THE Patents Bill 1953, introduced during the last session of the House of the People, seeks to give effect to a number of changes recommended by the Patents Enquiry Committee and also includes certain other new provisions. The Bill, when enacted, will result in the separation of patent legislation from the law of designs.

An important clause of the Bill would make it obligatory for the Patent Office to carry out searches for ascertaining the novelty of inventions before patents are granted. Such a measure would no doubt reduce the number of spurious patents and enhance the commercial value attached to patents granted in India.

The definitions of " invention " and "manufacture" have been revised and amplified. Inventions which can be patented must consist of new and useful manufactures or compositions of matter or new and useful improvements of these, must not be previously known or used in India and must be capable of being used or applied in trade or industry. Further, there can be no novelty unless an inventive step is involved and there must be a definite contribution to the existing technical knowledge. A mere discovery of new properties of a known substance will not be patentable. In relation to food and medicines, a mere admixture resulting only in the aggregation of the known properties of the ingredients will not be deemed to be a method or process of manufacture. Methods or processes of testing applicable to the improvement or control of manufacture are also brought under the scope of patentable subject-matter.

The procedure for obtaining a patent has been simplified by omitting formal opposition proceedings before the grant as these proceedings in the past have proved obstructive. But it will still be open for a person to lodge a statement of objections with the Controller of Patents within the prescribed period and the Controller would consider the objections before sealing the patent.

The Controller will have considerably enlarged powers of trying suits relating to patents. Thus he will be empowered to entertain applications for revocation of patents which power at present vests in the High Courts only. An order of the Controller under this clause will, however, be subject to an appeal to the High Court.

Under the existing Act appeals in a large majority of cases lie to the Central Government. Under the Bill, all appeals will lie to a High Court.

A clause in the Bill enables the filing of declaratory suits for the benefit of persons who have a reasonable doubt whether the intended manufacture or use of an article would constitute an infringement of an existing patent. It is hoped that the provision would be beneficial to industrialists and would help in promoting the industrialization of the country. Another clause confers upon an " exclusive licensee " the right to institute a suit for infringement of a patent; at present the right is enjoyed by a patentee only.

The right of the inventor to be associated with his invention is recognized. Each claim in the complete specification is to have the priority date determined on the basis of the disclosure of the corresponding subject-matter.

The Controller is to have wider powers to enforce secrecy in respect of patent applications which may be relevant for defence purposes.

Powers which are now enjoyed by the Central Government for the use of patents for the purposes of the Union are now to be extended to the State Governments.

The Controller is given powers to keep a close watch over the commercial exploitation of patents. Patentees and exclusive licensees should hereafter be prepared to furnish to the Controller, if he so requires, information and periodical statements as to the extent to which their patents have been commercially worked in India. Refusal or failure to supply the required information is made a penal offence.

The Bill for the first time introduces provisions for statutory control over the profession of Patent Agents. A Patent Agent will be required to register himself under the Act. The participation of legal practitioners in patent proceedings is, however, not prohibited.

Provisions are made for broadening the scope of international arrangements for protection of inventions on a mutual basis. At present India has reciprocal arrangements with the United Kingdom and other British Commonwealth countries only.

Among other provisions may be mentioned those intended to avoid certain malpractices regarding transactions connected with patents which seek to impose undue restrictions on the purchase of articles other than patented articles; extension to twelve months of the maximum period available for filing a complete specification after the provisional specification; amendment of the procedure for petitions for extension of the term of patents; such petitions will hereafter lie to the Controller of Patents and not with the Central Government, as at present; restoration of applications for patents which might lapse due to unintentional delay or omission to seal the patent in time; revision of the rules of law applicable to ownership and devolution of patents; strict provisions to enjoin secrecy upon employees of the Patent Office in respect of confidential information and documents; and provisions to permit the Controller to disclose the results of statutory searches made in respect of patent applications.

A financial memorandum has been attached to the Bill to obtain parliamentary sanction for the additional expenditure required for administering the new functions contemplated under the Bill. The memorandum states that the extra expense is expected to be more than balanced by increased recoveries from enhanced rates of fees which are to be imposed.

Summaries of Addresses of Presidents of Sections, Forty-first Session, Indian Science Congress

DEVELOPMENT OF LANDFORMS IN THE HIMALAYAS*

THE second part* of Dr. H. L. Chhibber's address to the Section of Geology and Geography deals with the development of landforms in the Himalayas. Dr. Chhibber discusses in detail the five factors, viz. structure, process, stage, geology and relief, which have influenced the formation of the Himalayan landscape. The landforms developed in the granite and the quartzites are, however, altogether different from those developed in the schists, phyllites and slates.

For purposes of study, Dr. Chhibber classifies the landforms as under:

(i) The Siwalik Range with a maximum elevation of 4,000 ft. above sea level.
(ii) The Middle or the Lesser Himalayas having a maximum elevation of about 12,000-15,000 ft. above sea level.
(iii) The Great Himalayas with an average elevation exceeding 20,000 ft. above sea level.

Structure — The structure of the Himalayas is very complicated. The Himalayan nappes have been pushed forward to considerable distances and thrust over other rocks, but the dip-slope and escarpment feature, so characteristically observed in the

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*The first part has been reported earlier in this *Journal*, **13A** (1954), 13-14.

Siwalik Range, is also to be observed in the Middle as well as in the Great Himalaya. Dr. Chhibber observed this feature in the Tehri Garhwal Himalaya. The same feature is observed in the Pir Panjal Range and also in the Great Himalaya including Mount Everest, etc.

Process — In the Siwalik Range the action of rain and running water are the dominant agents of denudation, especially in carving out the ravines on the scarp side. In the Middle or the Lesser Himalayas the action of frost also is responsible for developing talus and talus streams. As a result of jointing and gravity, rockfalls also occur, but they are more characteristic of the Great Himalaya.

Stage — The study of river terraces of the Bhagirathi, the Yamuna and other rivers has revealed that the base level conditions are reached when the region undergoes rejuvenation and another subcycle is initiated and vertical corrasion commences again. In some places 6-7 such terraces were counted, but 3-4 are common. Dr. Chhibber concludes that the Himalayas underwent intermittent uplift during the Recent Period.

Landforms of the Siwalik Range — A detailed study of the development of the landforms in the Siwalik Range adjoining the Doon Valley reveals in a characteristic manner the dip-slope and escarpment feature. The former is covered with dense sal (*Shorea robusta*) forest, while the much steeper scarp face is highly ravined. The highest point, Amsot, is 3,140 ft. above sea level. The maximum width of the Siwalik Range in this region is about 10 miles. Its trend varies from W.N.W.-E.S.E. to N.W.-S.E. In places the range is traversed by longitudinal valleys.

The Siwaliks on the escarpment side form high cliffs with sharp peaks. From the peaks descend spurs which are really knife-edged. In places the form of the peaks is pyramidal, conical and almost needle-like. The Siwalik Range shows a beautiful serrated crest.

Landforms in the Middle Himalayas — As a result of normal erosion, deep gorges have developed in this region in hard rocks like the granite and the quartzites, while in the schists and phyllites broad open valleys are formed. The rivers descend through transverse and longitudinal valleys. In the region of the softer rocks river terraces commonly occur. The hanging valleys and waterfalls are also formed, but they are even more characteristic of the Great Himalaya. Interesting incised meanders have also developed. They are V-shaped, U-shaped and inverted U-shaped which may be narrow or acute or may be broad. The talus and talus streams commonly occur which tend to grade themselves. Landslips, landslides and rockfalls commonly occur in this region as also in the Siwalik Range. The small tributary streams of the Bhagirathi, etc., especially those which have steep courses, have well-marked alluvial fans.

Landforms in the Great Himalaya — The elevation being greater in this region, precipitation in the form of snow is much greater and consequently the action of snow and ice is very characteristic. Glaciers, both longitudinal and transverse, carve out typical glaciated topography. In this region glacial lakes are common. Rock basins, originally carved out by former glaciers, may occur at lower levels than where glaciers descend today. This indicates the extent of recession of the former glaciers. The hanging valleys and waterfalls are more common in this region and some of the waterfalls may be 200 ft. or even more in elevation. The action of frost is very severe and where the rock is jointed and the joints dip with gravity, rockfalls, sometimes huge in size, are very common.

This region comprises an endless vista of mountains or a chain of peaks, about 20,000 ft. or more in elevation above sea level and not infrequently culminating in a majestic summit. The peaks comprise massifs, great rock-peaks, pyramidal peaks, white domes or beautifully shaped snow-cone summits. There may be twin peaks or the main peak may have its satellites. The peaks are connected by sharp or knife-edged ridges with cols, 18,000 ft. or more in elevation. At some places occur the overhanging rock with snow-fluted precipices dropping several thousands of feet. The Nanga Parbat rises more than 20,000 ft. above the Indus Valley. The slopes are not only precipitous in places with crevices and chasms, but ice walls, ice falls, rock walls, etc., are common.

The lower regions represent a land of glaciers with their crevasses, a series of surface moraines, etc. In places an incredible quantity of rock may cover the ice giving it an appearance of a glacier of rocks. From their snouts issue forth streams which may follow a longitudinal trend for some distance but then pierce the Great Himalaya and carve out deep and constricted gorges. Thus, the action of frost and the work of snow and ice are seen at thier best in this region.

CONTROL & TREATMENT OF TROPICAL DISEASES

THE presidential address of Dr. R. N. Chaudhuri to the Section of Medical and Veterinary Sciences is devoted to a review of the advances made in the control and treatment of tropical diseases. These include malaria, kala-azar, dysentery, cholera, typhus fever, plague, leprosy, filariasis, etc. Diseases of nutritional origin such as those arising from under-nutrition, vitamin B and protein deficiencies and those caused by adulteration of foodstuffs have also been dealt with briefly.

Most " tropical diseases ", once prevalent almost all over the world, have now become rare in colder climates. The change came over about a century ago as a result of the discovery of micro-organisms as causative agents and of the discovery of vectors, e.g. mosquitoes, which act as intermediate hosts and transmit the parasites to man in diseases like malaria and filariasis. These discoveries led to the adoption of suitable preventive measures.

On the curative side, the present century has witnessed phenomenal progress in the discovery of specific drugs for treatment of various diseases. An outstanding event in the history of malaria is the finding that the sporozoite injected by the mosquito into man first undergoes development in the liver cells before invading the red blood cells. This discovery is closely linked to the problem of *P. vivax* relapses and their prevention, for the liver appears to act as a reservoir of infection in the human body. By the use of DDT and gammexane it has been possible to exterminate, or at least effect a reduction in the number of mosquitoes sufficient to influence malaria incidence. Where this is not practicable, the infection can be suppressed by the use of certain drugs taken once a week or fortnight. During the past twenty-five years a number of valuable antimalarial drugs have been synthesized. Of these chloroquine and camoquin are very potent. But quinine still holds a place as a schizonticide and is the drug of choice when given parenterally for the treatment of pernicious malaria. For this reason and also because quinine is an indigenous drug, it is important that cinchona cultivation in India should continue. For the prevention of malaria relapses, pamaquine or, better still, primaquine can be used, this being active against the tissue forms of *P. vivax*. Given with quinine, camoquin or chloroquine, it significantly reduces the relapse rate.

The discovery of the causative parasite in kala-azar in 1903 was followed by a prolonged search for the vector which was ultimately traced 40 years later to one species of sandfly. Antimony has been found to have a powerful action on the leishmania parasite, the pentavalent compounds giving better results than tartar emetic, with a high percentage of cures. Different methods of diagnosis are now available in kala-azar.

With the advent of sulphonamides the treatment of bacillary dysentery has radically changed. With emetine it is possible to relieve most cases of amoebic dysentery, but better results are obtained by using a combination of amoebicides. In chronic cases with much secondary bacterial invasion and pathological changes the response is rather poor, but the newer antibiotics are helpful. Other forms of amoebiasis (e.g. pulmonary) have been recognized, and the successful treatment of hepatitis and hepatic abscess with emetine and chloroquine, seldom requiring operation, is a noteworthy advance.

In cholera the replacement of body fluid lost by vomiting and diarrhoea is a life-saving measure. The extent of fluid loss, electrolyte changes and their bearing on prognosis and treatment are some of the important considerations discussed in the note. No specific chemotherapeutic agent has, however, been found to control the disease.

Typhus fever now includes a large group of fevers caused by rickettsias. Some of these fevers are found only in tropical countries including India. Of these the most important is scrub typhus. Chloromycetin and aureomycin have specific action on the disease, bringing about a dramatic improvement of the symptoms. The vectors and reservoirs of infection being now known in most typhus fevers, prevention has also become easier.

Chloromycetin is also a specific in typhoid fever. In this disease diet is given much more liberally than before; this conserves the patient's strength. The value of prophylactic vaccine has been established.

In the treatment of plague streptomycin and sulphonamides are beneficial even in severe cases, and in recent years more attention is being paid to flea destruction with DDT.

There are a few important diseases like leprosy and filariasis in which progress has been slow. For the former, the sulphone treatment has proved more effective than chaulmoogra oil. In the control of leprosy it is necessary not only to treat individual patients, but also to segregate the infected cases and rehabilitate those who are cured. These involve large social and economical problems, which must be tackled before success can be obtained. Attempts are being made to control filariasis by anti-mosquito measures and with " hetrazan " or " banocide " which can render human carriers free from microfilariae for months.

There is another group of diseases which abound in the tropics; these are of nutritional origin and are due to inadequate diet. Some of these including under-nutrition, vitamin B deficiencies (beri-beri, pellagra) and protein deficiencies (Kwashior-kor, macrocytic anaemia, nutritional oedema) have been discussed briefly. Adulteration of edible oils with argemone (*sial-kanta*) and mineral oils is discussed. Argemone oil is the cause of epidemic dropsy and rice diet appears to favour the appearance of oedema. The oil can be toxic in very low concentration. A simple sensitive test is now available to detect the adulteration. Work is in progress with the alkaloids so far extracted from the oil. Mineral oil is also toxic to animal tissues, moreover it interferes seriously with absorption of fat soluble vitamins and of calcium and phosphorus. Dr. Chaudhuri has, therefore, urged that the use of these oils in food be prohibited.

Dr. Chaudhuri concludes that the major problems of tropical medicine have their roots not so much in the climate of the tropics but essentially in the poverty and general backwardness of these countries. Better and abundant food, and instituion of public health measures by way of better housing, environmental and personal sanitation and hygiene, improved drainage and sewerage and good water supply are some of the essential conditions which must be satisfied. Our knowledge of tropical diseases, their prevention and cure has advanced to a remarkable degree and with wider practical application of this knowledge and with parallel improvement in social and economic conditions there is little doubt that our efforts will be crowned with success.

The Indian Science Congress, Hyderabad

THE INDIAN SCIENCE CONGRESS ASSOCIATION held its forty-first annual session during 2-8 January 1954 in Hyderabad. Representatives of scientific organizations in Burma, Italy, Japan, Norway, Pakistan, U.S.S.R., Switzerland, U.K., U.S.A. and Viet Nam attended the session. The proceedings were opened by the Prime Minister, Shri Jawaharlal Nehru.

Nine hundred and twenty-nine research papers were submitted for discussion as under: Chemistry, 280; Botany, 129; Medical and Veterinary Sciences, 124; Agricultural Sciences, 73; Geology and Geography, 58; Zoology and Entomology, 57; Engineering and Metallurgy, 51; Physiology, 38; Physics, 35; Mathematics, 26; Anthropology and Archaeology, 24; Statistics, 21; and Psychology and Educational Sciences, 13. Eleven technical discussions, in which two or more sections participated, were organized during the session. Seven special lectures were arranged under two or more sections. They were: (1) *Mathematics of time series* — Prof. Norbert Wiener (U.S.A.); (2) *Polymorphism and evolution* — Prof. Julian Huxley (U.K.); (3) *Development of knowledge on plant viruses and virus diseases* — Prof. F. C. Bawden (U.K.); (4) *Basis of quantum theory* — Prof. Norbert Wiener (U.S.A.); (5) *Origin of magnetic oxide ores* — Prof. Alan Mara Bateman (U.S.A.); (6) *Problems on the spectre of Novas* — Prof. F. J. M. Stratton (U.K.); (7) *Chemistry of viruses* — Prof. F. C. Bawden (U.K.); (8) *Chemistry of Rauwolfia serpentina alkaloids* — Prof. E. B. Chain (France).

The Association of Scientific Workers of India organized a symposium on the Five-Year Plan. Besides, 20 other symposia on technical subjects were held.

The evening lectures on subjects of popular interest attracted large audiences. Among the lectures were: (1) *International implications of mineral resources* — Prof. Alan Mara Bateman (U.S.A.); (2) *Plant viruses: what they are and what they do* — Prof. F. C. Bawden (U.K.); (3) *Evolution and modern thought*—Prof. Julian Huxley (U.K.); (4) *The structure of the universe* — Prof. F. J. M. Stratton (U.K.); (5) *The main features of Soviet science* — Academician G. F. Alexandrov (U.S.S.R.).

The exhibits displayed at the Science Exhibition by about 50 firms covered a wide range of apparatus and precision instruments made in India and foreign countries.

Honorary Members — Shri Jawaharlal Nehru, Prime Minister, and Dr. Shanti Swarup Bhatnagar, Secretary to the Government of India, Ministry of Natural Resources and Scientific Research, were admitted as Honorary Members of the Indian Science Congress Association at the inaugural session. The citations read as follows: " Shri Jawaharlal Nehru has rendered conspicuous service to the development and welfare of science in India by his keen interest in the application of science to the needs of the country. His encouragement of scientific enterprises, both pure and applied, has been a source of inspiration to all of us." " Dr. Bhatnagar is an eminent scientist and has made many important contributions to science. As a teacher, an organizer and an administrator, he has rendered conspicuous service to science, specially in harnessing science to the needs of the expanding industries in India."

Office-bearers, 1955 — The following office-bearers were elected for the 1955 session to be held at Baroda: *President* — Dr. S. K. Mitra; *General Secretaries* — Dr. U. P. Basu and Dr. B. N. Prasad; *Treasurer* — Prof. P. C. Mahalanobis.

Prof. R. A. Millikan (Obituary)

MANY READERS WOULD HAVE LEARNT WITH deep regret the demise of Professor R. A. Millikan, Nobel Laureate, on 19 December 1953 at his residence in California.

Robert A. Millikan was born on 22 March 1868 at Morrison (Illinois) and was the second child of Rev. Silas Franklin Millikan and his wife Mary Jane. He grew up in an atmosphere marked for its simplicity and biblical virtuosity. Under its influence he acquired a keen sense of duty, intellectual honesty and an immense capacity for taking pains. He had his early education in Maquoketa (Iowa) and graduated from Oberlin College, Ohio, in 1891. His appointment as a tutor in physics in the same college soon after graduation was largely responsible for the development of his inherent interest in physics, although before that his subjects of study were mainly classics. Subsequently, in 1893, he joined the Columbia University as a graduate student and took the Ph.D. degree in the year 1895. Later he went to Germany to work under Prof. Nernst at Gottingen in 1895-96. On his return from Europe he was appointed as an Assistant under Prof. Michelson at the University of Chicago, and was later promoted successively as Instructor in 1899, Assistant Professor in 1902, Associate Professor in 1907 and finally Professor in 1910. During this period, his activities were mostly directed towards writing of text-books of physics. In collaboration with Mann he translated the *Theory of Optics* by Drude and thereby made this great masterpiece available to the English-speaking world.

In the year 1910, Dr. Millikan started an intense programme of research which led to his famous experiments for the determination of the electronic charge and the verification of Einstein's equation for the photoelectric effect. During World War I Prof. Millikan's time was mostly taken up in solving military problems of a scientific nature. He was partly responsible for the establishment of the National Research Council of which he became the Vice-Chairman in 1917.

In 1919, Dr. Millikan was invited by the California Institute of Technology at Pasadena for developing a Research Laboratory in Physics. During the next two years he carried on part-time work at the Institute. In 1921, he was offered the post of President of the California Institute of Technology and Director of the Norman Bridge Laboratory for Physics. While accepting the latter, he agreed to become the Chairman of the Executive Council to be formed to take charge of the administrative responsibility of the Institute. Under his leadership, the Institute rapidly changed from an obscure polytechnic into one of America's leading educational and research centres in pure and applied sciences. Millikan believed that educating a creative scientist should be carried out only in an atmosphere of research and to this end it was essential that research activities be given primary rather than secondary importance. In 1946, he retired as the Chief Executive and Director of the California Institute of Technology, but continued to serve the Institute as Vice-President of the Board of Trustees and carried on his research activities.

Dr. Millikan had well over a hundred publications to his credit and a glance at their titles will indicate the catholicity of his scientific interests. By far the best known work of Millikan is the experimental measurement of electronic charge to within one thousandth degree of exactitude using a method marked for its elegance and simplicity. His experiments on the photoelectric effect, especially with the " Workshop in Vacuum ", enabled him to arrive at a very precise value of the elemental quantum of action and to verify Einstein's equation. By his investigations in the extreme ultraviolet region of the spectrum, he was able to bridge the gap between X-rays and the optical region. This line of research led to his discovery of the theoretically important spectra of the so-called " stripped atoms ". His work in connection with the Anti-submarine Board during World War I led to the new technique of supersonic detection. His contribution to the problem of accurate determination of viscosity of gases and his work on the cold emission of metals are worthy of mention. Later at Pasadena, he became actively interested in cosmic rays. With the help of a new technique of sending self-recording instruments high up into the atmosphere by means of sounding balloons, he made outstanding contributions to the subject of cosmic rays and the mechanism of their absorptions, and propounded the theory of annihilation of atoms in the interstellar space. In connection with his researches on cosmic rays, he visited various countries, including India, in the year 1940. The award of the Nobel Prize in 1923 only marked the beginning of a period of intense activity and fruitful career. Even a casual perusal of his scientific publications will reveal at once his great experimental skill, his characteristic intuition and imagination and the originality of his researches. He found immense pleasure in entering new and unexplored fields. It may be said without exaggeration that a good deal of the current educational thought of physicists in America today has been strongly influenced by Millikan.

Millikan was not only a great investigator but also a great teacher. He was interested in young scientists and liked to have them about him. Millikan's relations with his former pupils were always cordial and in most cases they developed into life-long friendship. He not only imparted to them a sound knowledge of the physical methods of research but, by his own shining example of enthusiasm and perseverance, he made them realize the necessity of endurance, steadiness and hard work in the pursuit of knowledge. Because of his far-sighted grasp of physics, he was able to start his pupils off on important problems. He was never satisfied with the results which could be improved upon. Millikan possessed the ability for team work to a high degree. Indeed, he had all the qualifications of an exceptional teacher and he must be classed as one of the most successful teachers in the history of science.

The world was not slow to recognize the importance of the achievements of Prof. Millikan as an investigator and as a leader of scientific research. He received his first Honorary D.Sc. degree in 1911, from his Alma Mater, Oberlin College. In 1913, he was awarded the Comstock Prize of the National Academy of Sciences. These were just the beginning of an avalanche of honours showered on him in the form of medals and

(*Continued on page* 60)

Ionospheric Data—November 1953

CHARACTERISTICS OF THE IONOSPHERE OVER CALCUTTA

S. S. BARAL, R. K. MITRA, A. K. SAHA, B. CHATTERJEE & M. R. KUNDU

Ionosphere Laboratory, Institute of Radio Physics & Electronics, University College of Science, Calcutta

FIG. 1 shows the monthly average diurnal variations of the ordinary ray critical frequencies of regions E and F_2 (f°E and $f°F_2$) and also similar variations of the heights of maximum ionization (hpF_2) and the bottom ($h'F_2$) of the F_2 layer during November 1953. The $f°F_2$ variation curve has been compared to that predicted three months before. The percentage of the total number of occasions during routine observations when the critical frequency for the sporadic E layer (fE_s) was greater than 3, 5 and 7 Mc./s. have been plotted for the different hours in Fig. 2. Table 1 gives the median values for the different ionospheric parameters for November 1953.

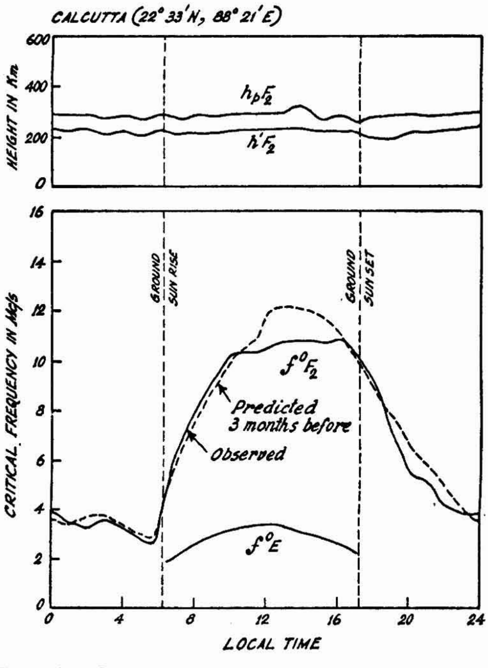

FIG. 1 — MONTHLY MEAN IONOSPHERIC CHARACTERISTICS

Fig. 3 gives the mean M.U.F. predictions for transmissions to different distances via F_2 region over Calcutta during February 1954.

In conformity with previous years' observations, sporadic E was of very infrequent occurrence during November 1953. The behaviour of F_2 region was normal. The midday values of $f°F_2$ were, however, somewhat lower than those predicted three months earlier.

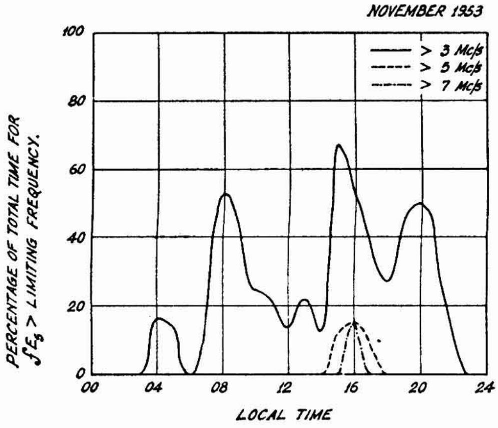

FIG. 2 — PERCENTAGE OF TOTAL NUMBER OF OCCASIONS WHEN fE_S WAS GREATER THAN 3, 5 AND 7 Mc./s.

TABLE 1 — MONTHLY MEDIAN VALUES

(*November* 1953)

TIME*	$f°F_2$ Mc./s.	hpF_2 km.	$h'F_2$ km.	f°E Mc./s.	fE_S Mc./s.	$(M3000)F_2$
00	3·60	292	240			3·20
01	3·65	270	210			
02	3·20	285	225			
03	3·65	270	210			3·30
04	3·25	270	210			
05	2·70	270	210			
06	3·30	292	217			3·15

* Time: 90° East Meridian Time (U.T. + 6 hr.)

TABLE 1 — MONTHLY MEDIAN VALUES — *contd.*

(*November* 1953)

TIME*	f^oF_2 Mc./s.	hpF_2 km.	$h'F_2$ km.	f^oE Mc./s.	fE_S Mc./s.	$M(3000)F_2$
07	6·75	270	210	2·05		
08	7·85	270	210	2·50	3·10	
09	8·70	270	210	2·80		3·30
10	10·60	270	225	3·20		
11	10·60	285	210	3·35		
12	10·95	300	210	3·35		3·10
13	10·95	277	210	3·30		
14	11·00	300	210	3·10		
15	11·00	255	210	3·20	3·50	3·40
16	11·00	270	210	2·60	3·00	
17	10·80	240	202	2·20		
18	9·40	270	180			3·30
19	7·10	270	188			
20	5·50	270	210		2·95	
21	5·15	270	210		(2·70)	3·25
22	4·20	270	210			
23	3·60	270	217			

* Time: 90° East Meridian Time (U.T. + 6 hr.)

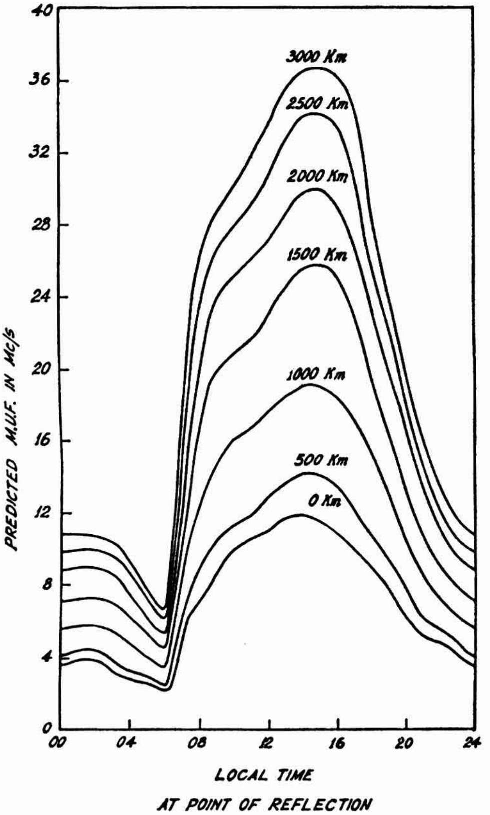

FIG. 3 — PREDICTED M.U.F. FOR TRANSMISSION VIA F_2 LAYER OVER CALCUTTA DURING FEBRUARY 1954

CHARACTERISTICS OF THE IONOSPHERE OVER AHMEDABAD

K. M. KOTADIA & R. G. RASTOGI

Ionospheric Research Station, Physical Research Laboratory, Ahmedabad

FIG. 1 shows the variations of the critical frequencies of the ordinary waves reflected from E, F_1 and F_2. Fig. 2 shows the variations of the height of maximum electron density and of the minimum virtual height of the different regions. Table 1 gives the monthly median values of the various parameters for E, E_s, F_1 and F_2 regions and the frequencies of occurrences of E_s during

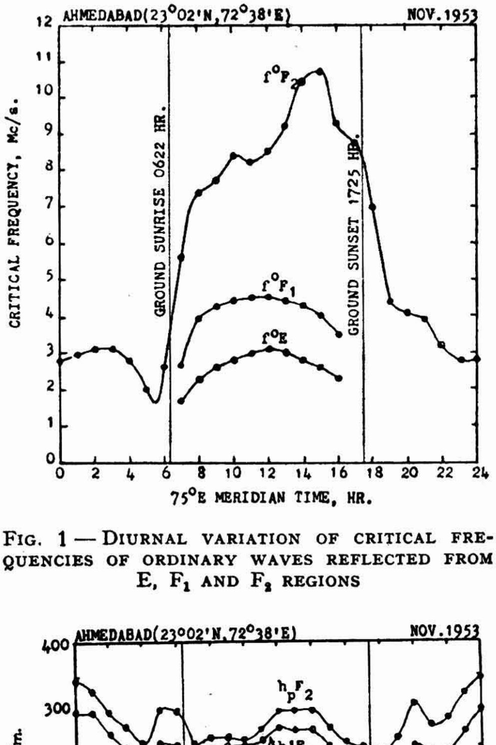

FIG. 1 — DIURNAL VARIATION OF CRITICAL FREQUENCIES OF ORDINARY WAVES REFLECTED FROM E, F_1 AND F_2 REGIONS

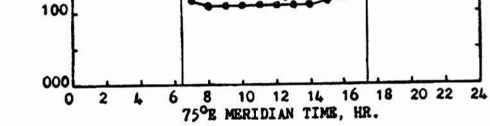

FIG. 2 — DIURNAL VARIATION OF VIRTUAL HEIGHTS OF E, F_1 AND F_2 REGIONS

routine observations when fE_s was higher than 3, 5 and 7 Mc./s.

The median critical frequencies of F_2 in this month were lower than in the previous month practically for all hours. The maximum separation between the lowest levels of F_1 and F_2 has come down to 43 km. as against the high value of 180 km. in June. The frequency and intensity of E_s occurrences showed an overall decrease from that in previous month except near sunset hours when E_s occurrences were more frequent and intense.

TABLE 1 — IONOSPHERIC DATA, AHMEDABAD, NOVEMBER 1953

Tabulated hours, 75°E. Meridian Time)

Time hr.	Median values								No. of occurrences of sporadic E with			No. of days for which E_s data are available
	$f^{\circ}F_2$ Mc./s.	h_pF_2 km.	$h'F_2$ km.	$f^{\circ}F_1$ Mc./s.	$h'F_1$ km.	$f^{\circ}E$ Mc./s.	h_pE km.	fE_s Mc./s.	$fE_s >$ 3 Mc./s.	$fE_s >$ 5 Mc./s.	$fE_s >$ 7 Mc./s.	
0	2·8	345	300	—	—	—	—	3·7*	4	—	—	26
1	2·9	330	300	—	—	—	—	2·3*	1	—	—	26
2	3·1	300	270	—	—	—	—	2·5*	3	—	—	26
3	3·1	280	250	—	—	—	—	3·0*	2	—	—	26
4	2·8	255	235	—	—	—	—	2·7*	2	—	—	26
5	2·0	305	257	—	—	—	—	3·6	12	—	—	26
6	2·6	303	255	—	—	—	—	3·5*	5	—	—	26
7	5·6	255	240	2·6*	230	1·7	117	3·7	12	1	—	26
8	7·4	265	250	3·9	230	2·3	110	3·6	11	—	—	26
9	7·7	263	255	4·2	233	2·6	110	3·7*	8	—	—	25
10	8·4	260	255	4·4	225	2·8	110	3·9*	6	—	—	28
11	8·2	275	260	4·5	220	3·0	110	3·8*	4	—	—	28
12	8·5	300	277	4·5	235	3·1	110	3·9	4	—	—	26
13	9·2	300	273	4·4	230	3·0	110	3·8*	8	2	1	26
14	10·4	300	273	4·3	230	2·8	110	3·9*	7	—	—	25
15	10·7	275	250	4·0	240	2·6	115	3·7	11	3	2	25
16	9·3	255	233	3·5	237	2·3	120	3·8	11	3	2	23
17	8·8	250	220	—	—	—	—	3·7	14	2	1	23
18	7·0	243	200	—	—	—	—	3·2	9	1	—	26
19	4·4	260	205	—	—	—	—	3·2	7	1	—	26
20	4·1	310	250	—	—	—	—	4·0*	8	2	—	26
21	3·9	277	240	—	—	—	—	3·0*	3	—	—	26
22	3·2	290	243	—	—	—	—	3·2*	4	—	—	27
23	2·8	325	270	—	—	—	—	3·7*	5	1	1	26

* Observations less than ten.

PROF. R. A. MILLIKAN (OBITUARY) — *Continued from page 57*

honorary memberships of various academies of America, Europe and Asia, and honorary doctorates of almost all the important universities of America and elsewhere. He was the recipient of the Hughes Medal of the Royal Society of London, the Faraday Medal, the Edison Medal and nine other medals of great value. He was awarded the Nobel Prize for Physics in 1923 for his work on the uniform electric charge and the photoelectric effect. He was elected President of the American Physical Society (1916-18), and of the American Association for the Advancement of Science (1929). During the years 1922-32 he was the American representative on the Council of International Co-operation of Science.

Dr. Millikan is also the author of numerous books in physics. With his passing away a bright star has set in the firmament of experimental physics and we, along with his numerous friends and the staff of the California Institute of Technology, deeply mourn the loss of a truly great and much-loved physicist.

R. S. Krishnan

Colloid Science & Rubber Technology

ERNST A. HAUSER
Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

IN stark contrast to the literature now available on rubber technology, comparatively little information is yet available pertaining to the morphological problems involved in the use of natural or synthetic rubbers. This refers specifically to the colloid science of the natural and synthetic products.

The first book on *Latex, Its Occurrence, Collection, Properties and Technical Applications* was published in German in 1927[1] and was translated into English by W. J. Kelly, and published in 1930[2]. In November 1927, E. A. Hauser presented the first series of Gow Lectures at the University College in London, and they were published in 1928[3]. A year later P. Stamberger offered the next series of Gow Lectures and they appeared in 1929[4]. In 1933 W. H. Stevens wrote a book on *Rubber Latex*[5], but it pays no attention to the morphological problem of latex and its industrial applications. The book does offer, however, a complete list of British patents pertaining to the concentration of rubber latex and its industrial uses. In 1936 R. J. Noble published a book on *Latex in Industry*[6], and in 1938 C. Falconer Flint's book on *The Chemistry and Technology of Rubber Latex* appeared[7]. French contributions of that time referred only to these books and for that reason they have not been cited here specifically.

It was not until 1944, however, that really serious attention was paid to the morphology of natural and synthetic rubber and to the technological problems pertaining thereto. In that year the first observations were made with the electron microscope, and they were published shortly thereafter[8]. It is more than questionable, however, whether the electron microscope actually shows a truly correct picture because the electron bombardment definitely results in the embrittlement of the formed rubber fibres and even causes them to break. It also seemed doubtful whether the globules were formed immediately or if this happened only gradually. It was, therefore, decided to study the morphological phenomena involved with a different type of instrument. The Ultropak microscope (FIG. 1) was selected for this purpose because it is the only instrument which permits the light rays (which emanate from a low-voltage lamp located in the attachment to the microscope tube) to enter the preparation from the top; this is accomplished by the use of a tube mirror which has an opening through which the light reflected from the preparation passes directly into the eyepiece. The mirror orients the light through a set of collecting lenses which are independent of the objective and, therefore, permit the adjustment of the focal point of the light where it would give the best reflection. This instrument also permits heating the preparation while it is under investigation, or even subjecting it to vulcanization[9-12].

In comparing Figs. 2, 3 and 4 one will immediately notice the change which the preparation undergoes with time. The reason for this change is that the low molecular weight fraction present in natural rubber will

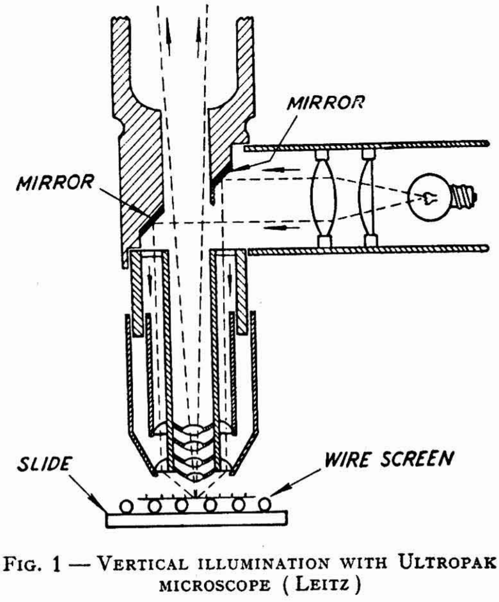

FIG. 1 — VERTICAL ILLUMINATION WITH ULTROPAK MICROSCOPE (LEITZ)

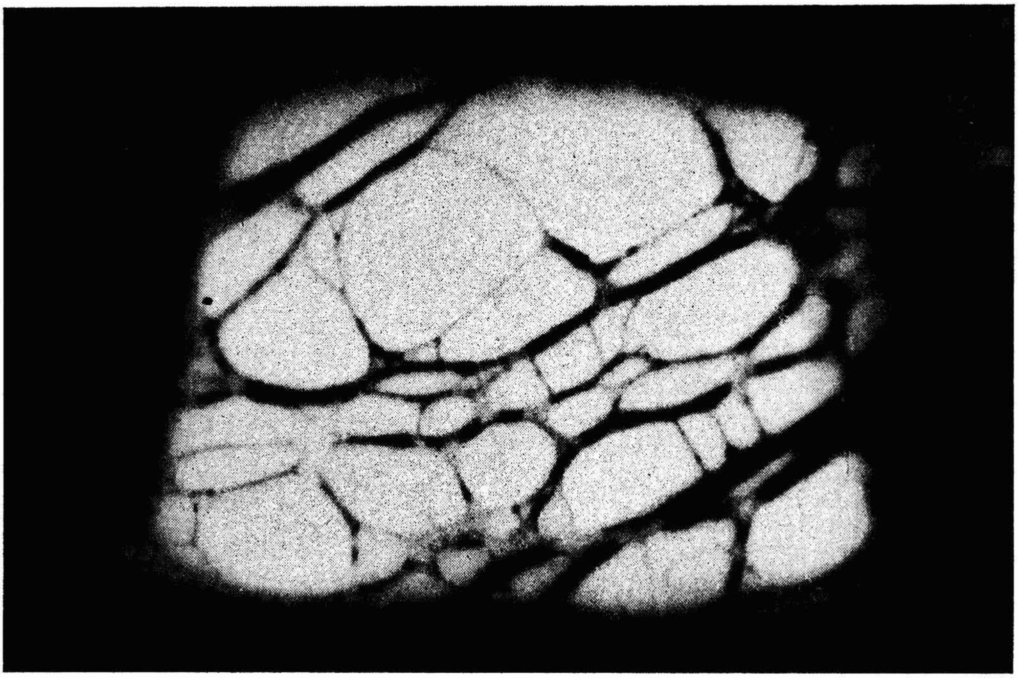

FIG 2 — *Cryptostegia grandiflora* RUBBER (FRESH PREPARATION) [Original magnification 550]

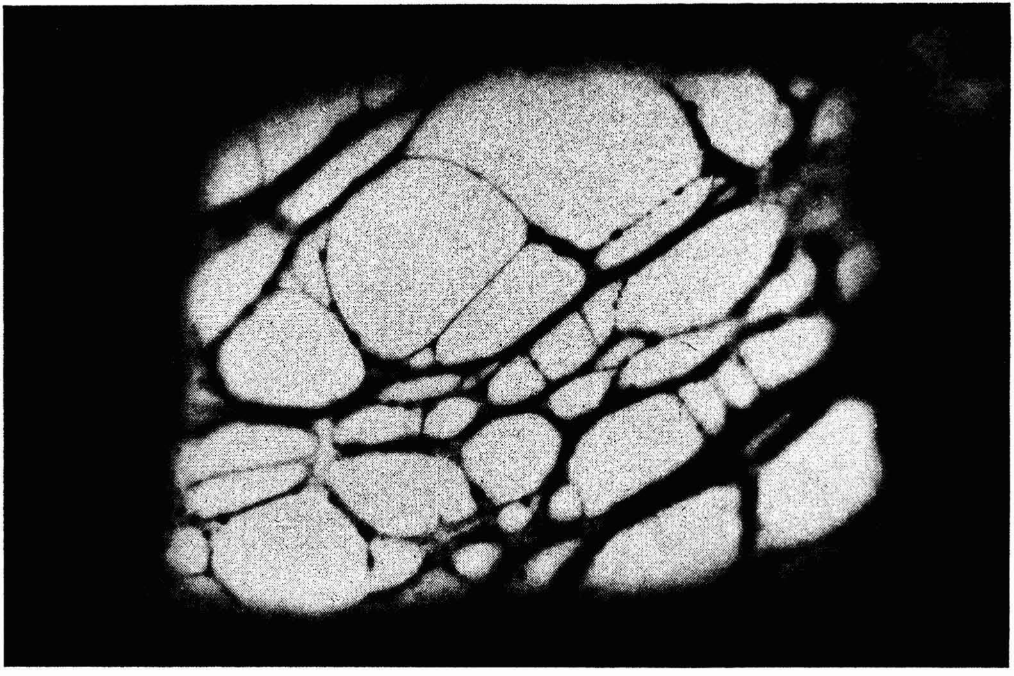

FIG. 3 — *Cryptostegia grandiflora* RUBBER (AFTER 5 HOURS' STORAGE) [Original magnification 550]

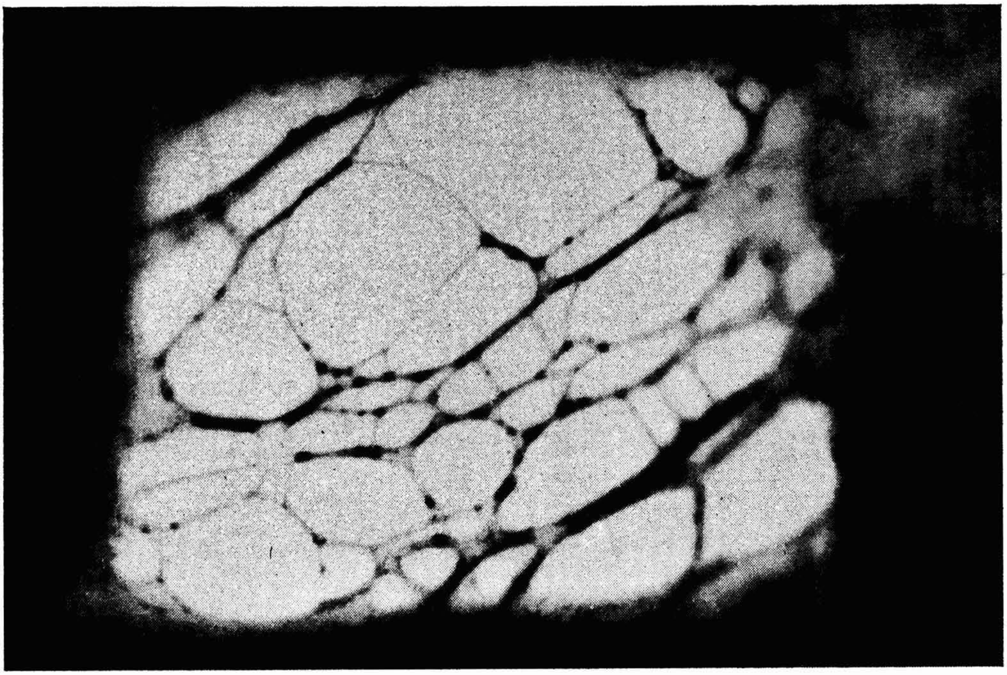

FIG. 4—*Cryptostegia grandiflora* RUBBER (AFTER 20 HOURS' STORAGE) [Original magnification 550]

be squeezed out when the fibre is under tension, thereby causing the formation of the droplets. A standard butadiene-styrene copolymer does not show this phenomenon at all. This is demonstrated in Fig. 5. Butyl rubber, a copolymer of isobutylene and isoprene, does show this phenomenon to a minor extent, as can be seen from Fig. 6. 2-Chloro-1, 3-butadiene, which is known as neoprene, shows this phenomenon just barely (FIG. 7).

This is a problem of which every rubber technologist should be aware. The temperature of rubber milling and the amount of milling which rubber has to undergo are something which should be taken into serious consideration. The more that natural rubber is milled in the presence of air, the more oxidation will occur, and this will lead to a pronounced reduction in the molecular weight of the polymer. After rubber has been milled it will no longer show the fine network, but will be composed mainly of one or two connecting strings to which one finds attached the formed low molecular weight fractions. These low molecular weight fractions are absolutely necessary for the phenomenon known as " reinforcement " because carbon black cannot be introduced into the high molecular weight fraction of natural rubber. This has already been clearly demonstrated by the techniques previously discussed. The ultraphotomicrographs also reveal the difference between the natural product and any of the synthetic ones. All the samples investigated so far reveal that almost no low molecular weight fraction is available in synthetic rubbers, even after prolonged milling. This is clearly evidenced in the pictures of the polybutadiene-styrene copolymer, butyl rubber and neoprene.

A solution of rubber which has been deposited on a fine wire screen will show the formation of networks, threads, globules, or coherent films (depending on its composition) upon evaporation of the solvent. Low molecular weight fractions are generally deposited as films which collapse completely upon evaporation of the solvent. Very high molecular weight fractions or polymers, composed of molecules with great stearic hindrance for flow, will form threads. Globule formation is the result of syneresis of the low

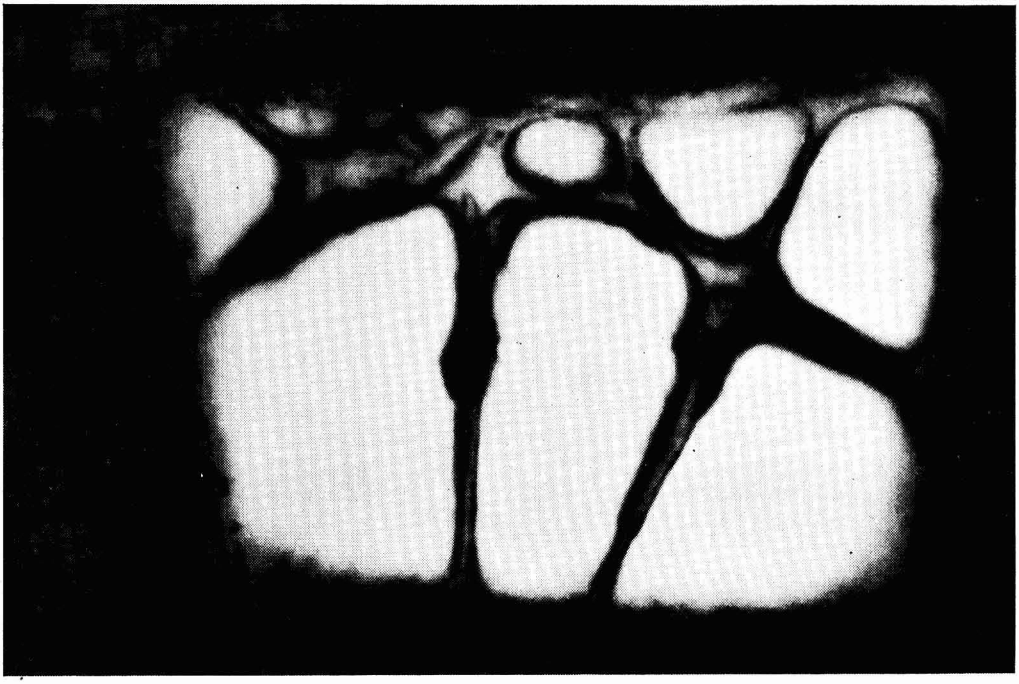

FIG. 5 — BUTADIENE-STYRENE (GR-S) [Original magnification 550]

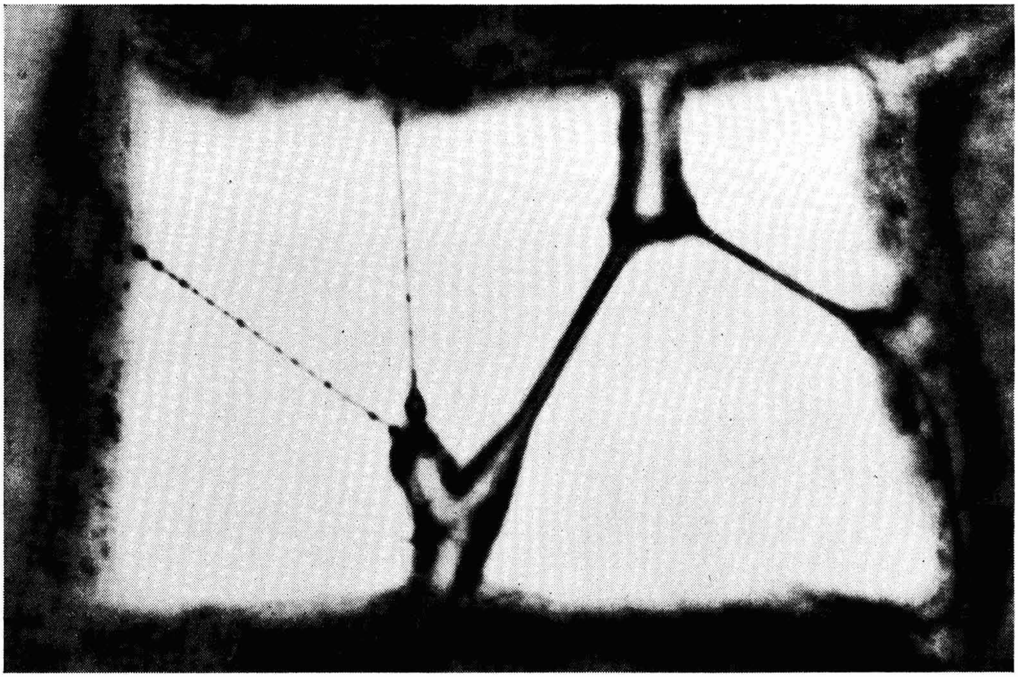

FIG. 6 — BUTYL RUBBER (ISOBUTYLENE AND ISOPRENE) [Original magnification 550]

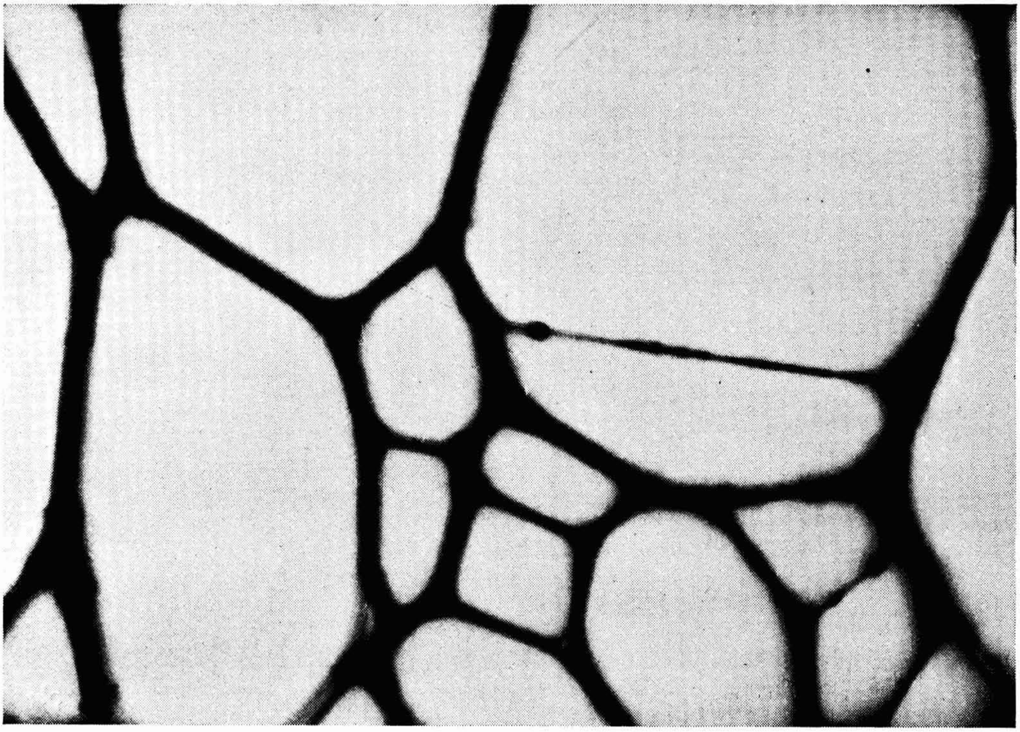

FIG. 7 — NEOPRENE (2-CHLORO-1, 3-BUTADIENE) [Original magnification 550]

molecular weight fraction when the solvent evaporates, and the high molecular weight fraction is thereby put under tension. This is only possible if the system under investigation is polydispersed. In this connection it should be pointed out that there exists a relationship between elasticity and ease of globule formation. A comparison of the morphology of preparations made from Hevea, Cryptostegia and Guayule[10] has offered visual proof of this. Hevea, which has the most uniform distribution of threads and globules of varying sizes, is pronouncedly more elastic than Cryptostegia, which exhibits only very fine globules and thin threads, and than Guayule, which shows exceptionally large globules.

To exhibit elasticity to any reasonable degree the system must be of the two-phase type, where the solute is in the continuous phase and is solvated by the solvent. The definition of the two-phase theory must not be taken too literally, however. All that the term should imply is that the elasticity of colloids depends on the presence of at least two phases, one being the solvent, the other the solute. In systems like rubber, the former in itself is composed of a wide range of molecular weights, but this fraction acts as the solvent for the insoluble fraction, which will also not be composed of only one molecular weight of the colloid[13].

Conclusions

The main conclusion which may be drawn from the foregoing discussion is that an elastomer owes its properties not only to the molecular configuration of the substance but to the composition of the colloid as a whole. These are facts which might explain to the rubber technologist the main differences found today between natural and synthetic rubbers. It is now up to the rubber technologist to learn how he can improve his processing techniques to produce polymers that are more satisfactory for the various purposes to which they are put.

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Interference of Polarized Components of the Radio Wave in the Ionosphere

R. SATYANARAYANA & DHARAMBIR RAI

Banaras Hindu University, Banaras

IT was shown by Appleton and Beynon[1] that the magneto-ionic components of the radio wave in the ionosphere caused by the earth's magnetic field produced interference and yielded periodic fading patterns during the evening hours, when there was a continuous decrease in the electron density of the ionosphere. The initial " slow " periodic fading observed by them on 9·53 Mc./s. was considered as due to the interference of the lower-trajectory ordinary and extraordinary waves. The rapid periodicity observed subsequently started only when the upper-trajectory waves (often called the " Pedersen " rays) were received at the same time. A number of periodic fading patterns observed with short-wave signals by Khastgir and Das[2] and with medium-wave signals by Tantry and Khastgir[3] and later by Rai and Rao[4] showed a " slow " type of periodicity which could be attributed to the interference of the ordinary and extraordinary waves in the ionosphere in the evening hours. The quicker periodicity observed in the records of these workers was attributed to the vertical movement of the ionospheric layer or layers in the manner already described by them. In these experiments with medium-wave radio signals the transmission distance ranged from 120 to 270 km. and the M.U.F. value for the E layer for the average transmission distance was in the neighbourhood of 3-4 Mc./s. in the evening and early night hours. The frequencies of the signals in these experiments were much lower than the M.U.F. value. It is, therefore, a reasonable conjecture that the interference between the ordinary and extraordinary components would give rise to a very slow periodic pattern, if that is at all discernible. It is, however, difficult to calculate the periodicity for such periodic fading of magneto-ionic origin. The object of the present communication is to furnish direct experimental evidence showing that the " slow " periodic patterns observed with medium-wave signals in the evening hours are really due to the interference of the two magneto-ionic components in the ionosphere.

Experimental arrangements

The medium-wave signals from the A.I.R. transmitting stations at Allahabad and Lucknow were received at Banaras during the evening and early night hours using an ordinary loop aerial capable of rotation about a vertical axis and connected to a super-het receiver with its A.V.C. made inoperative and with a suitable sensitive mirror galvanometer in the anode circuit of the second detector valve. With the plane of the frame aerial adjusted parallel to the plane of the wave reflected from the E layer, the galvanometer deflections due to the varying intensities of the received signals were recorded on a rotating drum system which was similar to the one originally used by Subba Rao and Subrahmanyam[5] in their work on recording atmospherics and by Khastgir and Das[2] in recording periodic fading. When a " slow " periodic pattern was recorded, it was arranged to suppress one of the two polarized components by using a selective aerial system and to record the intensity variation of only one component as received by the same super-het receiver when connected to the selective aerial system.

The selective aerial system, which was essentially the same as that used by Ratcliffe and White[6] in their circularly polarized receiver, consisted of a pair of similar " crossed " loop aerials, 6 ft. sq. each, capable of rotation as a whole about a common axis. One of the loop aerials was used when it was desired to receive both the ordinary and extraordinary components. The two loop aerials L_x and L_y were tuned separately by the variable condensers C_x and C_y, each condenser being symmetrically placed between a pair of coils of suitable inductances in each loop aerial circuit. The mutual inductance between the two sets of coils in the two loop aerial circuits was capable of variation by tilting the coils relative to each other. A commutator K was inserted in the circuit of the frame aerial L_y for reversing the direction of current flowing through the circuit. The condenser C_x, the two sets of coils and the commutator K were enclosed in a shielded box placed immediately under the common axis of the " crossed " aerial system. The output terminals across the tuning condenser C_y were connected to the input terminals of the super-het receiver. The circuit diagram of the aerial system with the associated connections is shown in Fig. 1.

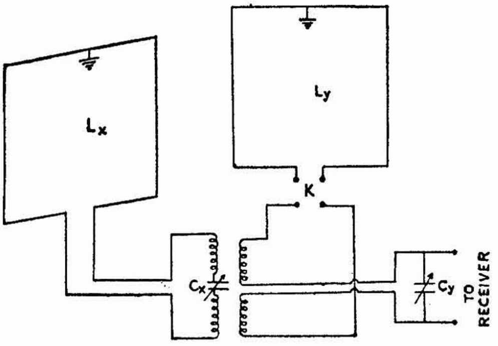

FIG. 1 — TUNED CROSSED LOOP-AERIAL SYSTEM WITH ASSOCIATED CIRCUITS

The main reason for choosing transmitting stations close to Banaras, viz. Allahabad and Lucknow, was the necessity of having the ground waves from these stations at Banaras. The ground waves were received during the daytime when the sky waves were absent and adjustments were made so that one or the other of the two magneto-ionic components could be suppressed under suitable conditions. These adjustments were (1) the tuning of the two loop aerials for each setting of the mutual inductance between the coils in the two aerial circuits; and (2) the adjustment of the mutual inductance between the coupling coils at a critical value, when the voltage developed across the tuning condenser C_y in the circuit of the loop aerial L_y was found to be independent of the orientation of the " crossed " loop aerial system as a whole.

With the above adjustments made with the ground waves during the day, the sky waves were received by the aerial system in the evening or early night hours. The voltage developed across the tuning condenser of the loop aerial L_y produced deflections in the receiver galvanometer and the deflections were recorded on the rotating drum system. It was known from the direct observations on the polarization characteristics of the downcoming waves of medium wavelengths, reported earlier by Satyanarayana and Khastgir[7], that the ordinary wave which was left-handed was very much stronger in intensity than the right-handed extraordinary wave. It was also known from the polarization patterns that the observed polarization was usually elliptic, at times circular and occasionally linear. For circular polarization, it can easily be shown that the "crossed" loop aerial system, after the mutual inductance adjustment mentioned before, should respond either to the left-handed or to the right-handed component according to the commutator position corresponding to the "direct" or the "reverse" current flow in the circuit of the loop aerial L_y. In the present experiments with medium-waves, where the ordinary component was much stronger than the extraordinary, it can be shown that the "crossed" loop aerial system, after the mutual inductance adjustment making the receiver response independent of the orientation of the aerial system, should respond to only one magneto-ionic component, *even for elliptical polarization*. If the "slow" periodic fading observed when the signal was received by an ordinary loop aerial was really due to the interference of the ordinary and extraordinary components, then the selective aerial system receiving only one component should not reveal the "slow" periodic pattern when the deflections of the receiver galvanometer were recorded. This has been substantiated in the present investigation.

Theoretical considerations

Referring to Fig. 1, which shows the aerial system and the associated circuits, let i_x, i_y and z_x, z_y denote respectively the currents and the vector impedances of the two loop aerials L_x and L_y. We then have

$$\left.\begin{aligned} i_x z_x &= E_x - M\frac{\partial i_y}{\partial t} \\ i_y z_y &= E_y - M\frac{\partial i_x}{\partial t} \end{aligned}\right\} \quad \ldots\ldots (1)$$

where M is the mutual inductance between the coupling coils of the two aerial circuits, and

$$\left.\begin{aligned} E_x &= -A_x\frac{\partial H_y}{\partial t} \\ E_y &= -A_y\frac{\partial H_x}{\partial t} \end{aligned}\right\} \quad \ldots\ldots (2)$$

where E_x and E_y are the e.m.f. induced when the magnetic fields of the wave link with the effective areas A_x and A_y of the two loop aerials. Since the instantaneous current is of the form

$$i = Ie^{jpt}$$

where I is the current amplitude and $\frac{p}{2\pi}$ the frequency of the incoming wave, the equations (1) and (2) can be written as

$$\left.\begin{aligned} I_x z_x &= -jpA_xH_x - jpMI_y \\ I_y z_y &= -jpA_yH_y - jpMI_x \end{aligned}\right\} \quad \ldots\ldots (3)$$

which give

$$I_x = \frac{-jpA_xH_x + \frac{jpM}{z_y}\cdot jpA_yH_y}{z_x + \frac{p^2M^2}{z_y}} \quad \ldots\ldots (4)$$

The impedances z_x and z_y of the tuned aerial circuits can be put equal to the resistive components R_x and R_y of the same circuits. During the daytime, when only the ground waves are received, we can, therefore, write

$$I_x = \frac{-jpA_x\cos\theta + \frac{jpM}{R_y}\cdot jpA_y\sin\theta}{R_x + \frac{p^2M^2}{R_y}} \,.\, H_o$$

where H_o is the magnetic field of the ground wave and θ the angle which the plane of the loop aerial L_x makes with the direction of the ground wave. For the scalar magnitude of I_x, we can write

$$|I_x| \propto \left[A_x^2\cos^2\theta + \frac{p^2M^2}{R_y^2}A_y^2\sin^2\theta\right]^{\frac{1}{2}} \cdot H_o \quad \ldots (5)$$

When the mutual inductance M between the coupling coils of the aerial circuits is adjusted during daytime, so that the receiver response is independent of θ, it is evident that

$$pM = \frac{A_x}{A_y}R_y \quad \ldots\ldots\ldots (6)$$

Under such condition, when the sky waves are received, we have

$$I_x = -\frac{jpA_x}{R_x + \frac{p^2M^2}{R_y}}[H_x - jH_y] \quad \ldots\ldots (7)$$

where M is taken as positive. When the commutator K is reversed, M is negative, and we can write

$$I_x = -\frac{jpA_x}{R_x + \frac{p^2M^2}{R_y}}(H_x + jH_y) \quad \ldots\ldots (8)$$

Let us now take the general case when the ordinary and extraordinary components are elliptically polarized. The ordinary component, which is left-handed, is then represented by

$$\left.\begin{aligned} x &= ae^{jpt} \\ y &= -\,jbe^{jpt} \end{aligned}\right\} \text{ (left-handed)} \quad \ldots \ (9)$$

while the *extraordinary* component, which is *right-handed*, is represented by

$$\left.\begin{aligned} x &= a'e^{jpt} \\ y &= jb'e^{jpt} \end{aligned}\right\} \text{ (right-handed)} \quad \ldots \ (10)$$

In (9) and (10) a and b and a′ and b′ denote the semi-major and semi-minor axes of the ordinary and extraordinary components respectively. The corresponding magnetic fields can then be expressed as

$$(H_x e^{jpt}, H_y e^{jpt}) \text{ and } (H'_x e^{jpt}, H'_y e^{jpt})$$

so that for the ordinary wave

$$\left.\begin{aligned} H_x &= a \\ H_y &= -jb \end{aligned}\right\} \text{ (left-handed)} \quad \ldots \ (11)$$

and for the extraordinary wave

$$\left.\begin{aligned} H'_x &= a' \\ H'_y &= jb' \end{aligned}\right\} \text{ (right-handed)} \quad \ldots \ (12)$$

Thus for $M = +\text{ve}$, when the crossed loop aerial system gives a response in the receiver which is independent of the orientation of the aerial system, it can be seen from (7) that the receiver responds to $(a-b)$ of the ordinary wave and to $(a'+b')$ of the extraordinary wave. When the commutator is reversed, M is negative and it is evident from (8) that the receiver responds to $(a+b)$ of the ordinary and to $(a'-b')$ of the extraordinary wave. When the polarization is circular, $a = b$ and $a' = b'$, so that for one position of the commutator the receiver responds only to the extraordinary wave, the response being proportional to $(2a')$. For the " reverse " position of the commutator, it can be seen that the receiver responds only to the ordinary wave, the response being proportional to $(2a)$.

In the case of medium-waves, the ordinary wave is found to be very much stronger than the extraordinary so that we can write $a' = \frac{a}{n}$ and $b' = \frac{b}{n}$, where $n >> 1$. Under such conditions, for the reversed position of the commutator $(M = -\text{ve})$, the receiver response should be proportional to $(a+b)$ of the ordinary and to $\frac{a-b}{n}$ of the extraordinary component. Here $\frac{a-b}{n} << a+b$, so that it is not possible for the ordinary and extraordinary components to produce any discernible interference effect. For the other position of the commutator $(M = +\text{ve})$, the receiver response for the ordinary is proportional to $(a-b)$ and that for the extraordinary is proportional to $\frac{a+b}{n}$. Both the ordinary and extraordinary responses may, therefore, be comparable in this case, but since each response individually is small, the interference effect between the ordinary and extraordinary components is not expected to be perceptible. Thus with the loop aerial system connected to the receiver and adjusted for the particular value of mutual inductance between the coupling coils of the two aerials, making the receiver response of the ground-wave signal independent of the orientation of the aerial system, the periodic type of fading due to the interference of the ordinary and extraordinary components is not to be expected, while on the other hand such periodic patterns may be observed when the downcoming wave is received by a single loop aerial in the usual way.

Critical mutual inductance adjustment between the two aerial circuits during daytime

For any value of the mutual inductance M between the coupling coils of the associated circuits of the two loop aerials, the detector current output of the received signal showed a marked variation between two wide limits as the aerial system as a whole was rotated. The difference $\Delta\theta$ in the maximum and the minimum values of the detector currents observed on rotating the aerial system was noted for each setting of the mutual inductance. At some critical value of M, this difference in the maximum and minimum values of the detector current output was reduced to zero. On either side of this critical value, $\Delta\theta$ was found to increase. A representative curve showing the difference in the maximum and minimum detector current values for different settings of the mutual inductances between the coupling coils is shown in Fig. 2 for signals from Allahabad ($\lambda = 394{\cdot}7$ m.).

Photographic records with polarized and unpolarized receiver

Photographic records of the intensity variations of the downcoming wave as received at night by an ordinary loop aerial were taken continuously for some minutes. Immediately after such records, the aerial system (adjusted in the daytime in the manner already described) was switched on and continuous records were taken on the same bromide paper for the "direct" and "reverse" positions of the commutator alternately for a definite interval of time. Records were taken with medium-wave signals from both Lucknow and Allahabad. A typical record is shown in Fig. 3 for the downcoming waves of medium frequency from Allahabad. The photographic records with the polarized and unpolarized receiver revealed that whenever there was indication of "slow" periodic patterns with the unpolarized receiver, the records of the same signal, taken immediately before or after, with the polarized receiver did not show the same "slow" type of periodic fading. In some photographic records, however, the comparatively "quick" and "very quick" types of periodic patterns were observed. It was found that when these quicker types of periodic fading were present in the records taken with the ordinary loop aerial, the same types of periodic patterns were also present in the records taken, immediately before or after, with the polarized receiver. All photographic records taken with the polarized receiver showed that the signal intensity for the position of the commutator corresponding to the ordinary wave reception was much stronger than the signal intensity for the other position of the commutator corresponding to the extraordinary wave reception. In Fig. 3 the fading curve marked A was obtained with an ordinary

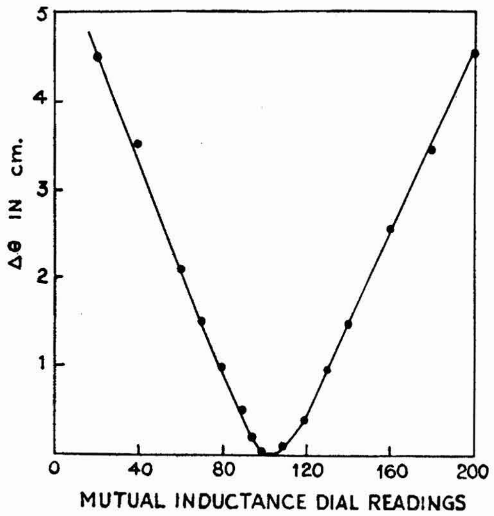

FIG. 2 — DIFFERENCE IN THE VALUES OF THE MAXIMUM AND THE MINIMUM CURRENT BY ROTATING THE AERIAL SYSTEM FOR DIFFERENT SETTINGS OF THE MUTUAL INDUCTANCE BETWEEN THE COUPLING COILS

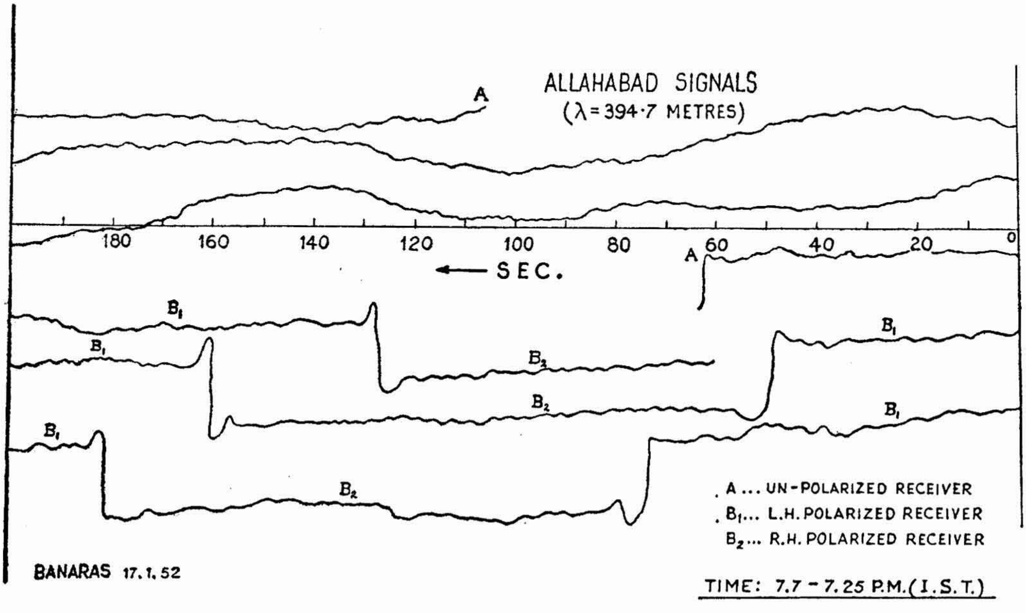

FIG. 3 — RECORDS OF ALLAHABAD SIGNALS (λ = 394·7 M.) TAKEN AT BANARAS WITH UNPOLARIZED AND POLARIZED RECEIVER

loop aerial, whereas the curves marked B_1 and B_2 were obtained with the left-handed and right-handed polarized receiver respectively.

Conclusions

From the theoretical considerations it can be concluded that the absence of the " slow " periodic fading in the records taken with both left-handed and right-handed polarized receiver, when similar records taken with an ordinary loop aerial immediately before or after showed unmistakably the " slow " type of periodic pattern, was a *direct* evidence to show that the " slow " type of periodic fading observed with ordinary loop aerial was caused by the interference of the magneto-ionic components in the ionosphere. Such evidence has been previously obtained by Mitra[8] on short-waves by employing a different experimental arrangement. The " slow " type of periodic fading observed with medium-wave radio signals can thus be definitely attributed to the interference between the magneto-ionic components, the left-handed ordinary component being much stronger than the right-handed extraordinary. The comparatively " quick " and " very quick " types of periodic patterns, which were observed, were attributed to the vertical movements (either " large scale " or " regional ") of the ionospheric layer, causing the " Döppler-beat " type of periodic fading. According to this view, the " quick " periodic patterns would be observed with both polarized and unpolarized receiver. The photographic records of periodic fading substantiated this view. The photographic records showed some random intensity variations. This was expected as the ground-waves were invariably present along with the downcoming waves from the ionosphere causing the usual phase-fading.

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Studies on Natural Fats: Part IX — Proof of Simple Chance Distribution in Natural Fats of High Fully Saturated Glyceride Contents

A. R. S. KARTHA
Maharaja's College, Ernakulam*

LITTLE experimental data has so far been recorded on the proportions of the different non-GS_3 glycerides in natural fats containing more than *c.* 40 per cent of GS_3 (the symbols G, S, U and A are used for glyceryl, saturated acid, unsaturated acid and azelaic acid radicals respectively in this paper). The more important natural fats containing above *c.* 40 per cent GS_3 are almost exclusively tropical seed fats from plants belonging to *Palmacae, Lauracae, Myristicacae, Simarubae, Salvadoracea* and a few other related natural orders. These fats generally contain above *c.* 80 per cent saturated acids, the major portion of which invariably consists of myristic and lower acids. The presence of these acids increases substantially the solubility of the glycerides in different solvents so that crystallization methods are of limited use in investigating the glyceride structure of these fats.

The crystallization studies of Bomer and colleagues[1-4] on a number of fats of this type showed that simple triglycerides could be detected only when one saturated acid formed the predominant constituent: for the most part these fats consisted of various mixed triglycerides. This indicated the possibility that the unsaturated acids also may be present mainly as mixed saturated-unsaturated glycerides.

The GS_3 contents of a number of fats of this type have been determined using the method of Hilditch and Lea[5] (TABLE 1). The values are in general somewhat higher than those required by chance distribution or the even distribution rule of Hilditch. On the basis of these GS_3 values it has been suggested that probably in fats with above *c.* 80 per cent saturated acids, simple chance distribution prevails[10].

Hilditch suggested that fats from *Myristica malabarica, Laurus nobilis* and probably *Pycnanthus combo* may be considered as exceptions to the even distribution rule[15], and that the fats from the other sources, all of which contained above *c.* 80 per cent saturated acids, showed GS_3 contents approximately as required by even distribution[16], the difference between theoretical and experimental values being attributed to possible experimental error in the determination of S and GS_3. If this view is correct then the non-GS_3 portions in these fats would consist of GS_2U alone and an examination of the non-GS_3 glycerides would show whether even distribution rule is obeyed or not. However, crystallization methods are not sensitive enough for use in the study of this class of fats and no other method was as yet available. No experimental data could, therefore, be obtained as to the proportions of GS_2U, GSU_2 and GU_3 present in these fats.

It has recently been shown that the method of Hilditch and Lea[5] for determining GS_3

TABLE 1 — PROPORTIONS OF GS_3 IN SOME FATS OF HIGH SATURATED ACID CONTENT

FAT	SAT. ACID mol. %	GS_3 FOUND mol. %	GS_3 CHANCE DIST. mol. %	GS_3 EVEN DIST. mol. %
Coconut oil[6]	94	86	83	82
do	93	84	80	79
Irvingia barterii[7]	92	81	78	76
Maniccaria saccifera[8]	92	82	78	76
Myristica fragrans[9]	90	73	73	70
Astrocryum tucuma[8]	88	73	68	64
Babassu kernel oil[16]	87	67	66	61
Acrocomia sclerocarpa[8]	86	69	64	58
Palm kernel oil[6]	85	66	61	55
Pycnanthus combo[11]	75	38	42	25
Myristica malabarica[12,13]	59	19	21	nil
do	56	16	18	nil
Laurus nobilis[14]	59	41	21	nil

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*Present address: Indian Agricultural Research Institute, New Delhi.

contents is liable to appreciable positive error[17]. The difference between experimental values for GS_3 determined by the above method and the values required according to chance distribution may possibly be due to this.

Methods have been developed recently to eliminate hydrolysis of azelaoglycerides during acetone permanganate oxidation of fats which is the principal source of error in the method of Hilditch and Lea, and also to isolate and examine the various azelaoglycerides formed by the oxidation of the non-GS_3 glycerides[18]. Since according to the even distribution rule the non-GS_3 glycerides in fats of the above type should consist of GS_2U alone, it appeared interesting to investigate the non-GS_3 portions of these fats using the above methods, if applicable. In case the former consists entirely of GS_2U, then only mono-azelaoglycerides will be formed and no GSA_2 will be present in the products of oxidation. Further the GS_2A formed could be quantitatively isolated from other oxidation products by converting to magnesium salts.

A specimen of *Myristica malabarica* fat, prepared and refined as described in the experimental section and which contained 82 per cent (mol) of saturated acids, was oxidized by the acetic acid-acetone permanganate method[18]. The GS_3 and unchanged fat were separated from acidic oxidation products as described in the experimental section. The azelaoglycerides thus obtained in dilute potassium carbonate solution were directly converted to magnesium salts by adding ammonium chloride and magnesium sulphate as usual. After settling for 15 min. the precipitated magnesium salts were filtered off and washed. The filtrate and washings were combined and total acidic matter recovered by acidification with dilute sulphuric acid and extraction with ether. This was hydrolysed with alcoholic potash and the acids recovered were submitted to the Bertram separation twice. An appreciable amount, 2-3 per cent on original fat, of higher fatty acids was recovered, which showed a mean molecular weight of 230-232, which is the same as shown by the total saturated acids in the fat. It has been shown[18] that mono-azelao-disaturated glycerides are insoluble in water at 30°C.[18]. The saturated fatty acids recovered by Bertram separation from the filtrates were hence derived from GSA_2. This indicated the presence of appreciable amounts of GSU_2 and possibly also of GU_3 in the original fat. Hence the fat does not obey the even distribution rule.

The determination of the glyceride type composition of *M. malabarica* fat was, therefore, of interest, particularly in view of the fact that the glyceride type composition of a large number of natural fats from different biologic sources, and of widely differing component acid compositions, were shown to obey a new simple rule, namely the rule of glyceride type distribution in natural fats[19]. However, the oxidative determination of GS_2U, which led to the discovery of the latter rule, can be applied as such only to fats wherein the saturated acids are such as can be quantitatively isolated by the Bertram separation. Bertram claimed that his method of separation can be used for quantitative isolation of lauric and higher saturated acids[20]. Subsequent workers had experienced difficulty in confirming Bertram's claim as regards lauric and myristic acids[21]. Hence attempts were made to ascertain the reason for this difference in observations, and if possible to develop methods for quantitative isolation of lauric and myristic acids from the oxidation products produced during acetic acid-acetone permanganate oxidation of fats.

Investigations carried out by the author have shown that (1) magnesium soaps of palmitic and higher saturated acids show very little solubility in the reactant solutions employed in Bertram separation even at higher temperatures, whereas magnesium soaps of myristic acid were slightly soluble and of lauric acid somewhat more soluble at 100°C.; (2) magnesium soaps of palmitic and higher saturated acids are insoluble in water at 30°C. (used for washing the precipitate) whereas those of myristic acid are very slightly and of lauric acid somewhat more soluble in water at 30°C.; (3) magnesium soaps of myristic and lauric acids which dissolve to a limited extent in reacting solutions at 100°C. during Bertram separation are not always completely precipitated immediately on cooling to 30°C. The precipitation requires some time for completion and an interval of 3-4 hr. is found to be necessary after cooling to 30°C.; and (4) when a mixture of water (100 cc.), 15 per cent magnesium sulphate solution (15 cc.), and

10 per cent ammonium chloride solution (10 cc.) is used for washing the precipitates, the loss of magnesium soaps by solution in wash water is minimized.

Based on these findings the following improved procedure for Bertram separation has been evolved.

The hydrolysed acidic products of oxidation from 5 g. of fat (acetic acid-acetone permanganate oxidation) are dissolved in 250 cc. of water with the help of excess of ammonium hydroxide, heated to 98°-100°C. by immersion in a boiling water bath and magnesium soaps precipitated by adding 25 cc. of 10 per cent ammonium chloride and 45 cc. of 15 per cent magnesium sulphate (a large excess, about double the usual amounts). The reaction mixture is heated on the water bath for 1·5-2 hr. with frequent shaking, to complete solution of soluble magnesium salts. If necessary, ammonia is added to keep the solution strongly alkaline. It is then cooled to 25°-30°C. and allowed to precipitate completely by keeping at this temperature for 3-4 hr. with occasional shaking. After precipitation is complete, the separated magnesium soaps are filtered off in an ordinary funnel and the filter paper and the precipitate washed with a solution containing magnesium sulphate and ammonium chloride as already mentioned. The separation may be repeated once more and the fatty acids isolated as usual.

The myristic and lauric acids lost when submitted to the improved Bertram procedure has been studied using the crystallized acids. This loss has been determined by isolating and weighing the fatty acids remaining behind in the combined filtrate and washings. Using quantities of reagent solutions and washings as required for 5 g. of original fat or fatty acids in the usual procedure, it was found that the amount of myristic acid lost in filtrate and washings was only of the order of 3-4 mg. per separation. The amount of lauric acid thus lost was somewhat higher and varied between 6 and 8 mg. In the customary two separations adopted in the usual Bertram procedure, about 6-8 mg. of myristic acid and 12-16 mg. of lauric acid may be lost. With palmitic and higher acids there is practically no loss. On the basis that 5 g. fatty acids are taken for analysis the loss of myristic acid is negligible and within the limits of experimental error, and loss of lauric acid comes only to somewhat less than 0·5 per cent. It is, therefore, to be concluded that the improved procedure can be usefully applied for the quantitative separation of myristic acid and almost quantitative separation of lauric acid.

Fats containing large amounts of C_{14} and lower acids frequently contain varying amounts of C_{10} and lower acids and these will be lost during Bertram separation. Hence before applying the improved separation procedure to fats of this type each fat has to be separately tested to see whether it contains any C_{10} and lower acids. This may be done in either of the following two ways: (1) The mixed fatty acids are converted to the esters which are then oxidized with permanganate in acetone solution. The saturated acid esters are recovered as usual from the products of oxidation, hydrolysed and the acids thus obtained are submitted to the Bertram separation, and the amount of fatty acids remaining behind in the filtrate and washings are determined as before. Unlike azelaoglycerides the fatty acid esters are quite stable towards carbonate developed during acetone permanganate oxidation and comparative experiments show that there is practically no difference in yields of saturated acid esters irrespective of whether the mixed esters are oxidized by the acetone permanganate or the acetic acid-acetone permanganate method; and (2) in cases where the amount of unsaturated acids is very small, the mixed acids may directly be submitted to the improved Bertram separation and the amount of lower acids left in solution determined.

The mixed fatty acids of the specimen of *Myristica malabarica* fat were tested for the presence of lauric and lower saturated acids by the first method. 6·76 g. of total saturated acids prepared by oxidation of mixed acid esters by the acetone permanganate method were submitted to the Bertram separation using volumes of reagents as required for 10 g. of original fatty acids. The amount of fatty acids lost in the filtrate and washings amounted to less than 20 mg., that is less than 0·3 per cent. The amount of lower fatty acids which will be lost during Bertram separation will be quite small and the improved Bertram separation may be applied to the fatty acids of *M. malabarica* fat to give sufficiently accurate results.

Making use of the above observations the glyceride type composition of *M. malabarica* fat was determined as described in the experimental section. The fat was oxidized by acetic acid-acetone permanganate technique and GS_3 separated under conditions which will produce minimum possible hydrolysis. The carbonate solutions of azelaoglycerides obtained were directly precipitated as magnesium salts and different fractions analysed. The filtrate and washings contained appreciable amounts of combined saturated acids which were recovered as in the preliminary experiment already described. The azelaoglycerides recovered from precipitated magnesium salts contained only 65·7 per cent saturated fatty acids against 67·14 per cent theoretically required for GS_2A in this fat. This must be due to the presence of GSA_2 and lends further support to the presence of appreciable amounts of GSU_2 in original fat.

The mixed fatty acids contained 79 per cent saturated acids and 21 per cent unsaturated acids by weight. By molecules, the acids contained 82 per cent saturated and 18 per cent unsaturated acids. The glyceride type composition according to simple chance or random distribution will be GS_3, 55; GS_2U, 37; GSU_2, 7 and GU_3, 1 per cent respectively by mols. The GS_3 experimentally determined was 55 per cent by weight which comes to 57 per cent in mols. The GS_3 actual is thus practically the same as GS_3 chance (the small increase in the former may tbe due to slight hydrolysis during working up and there is no method at present known to eliminate this) and hence the proportions of the other glyceride types required according to the glyceride type distribution rule are the same as those required according to chance.

The glyceride type composition arrived at by the present methods (experimental section) is GS_3, 57; GS_2U, 33; GSU_2, 8 and GU_3, 2 per cent respectively by mols. and this agrees well with those required according to chance. According to the even distribution rule of Hilditch the fat should consist of GS_3, 46 and GS_2U, 54 per cent respectively by mols, and will contain neither GSU_2 nor GU_3.

The present results thus show the following:

1. In fats which contain GS_3 in proportions as required by chance, and which also contain high proportions of GS_3, the proportions of all the other glyceride types are also approximately the same as required by chance. It has been shown by the author earlier[19] that in natural fats which contain less than about 25-30 per cent saturated acids where the proportions of GS_3 required according to chance are very small, the proportions of all the other glyceride types present are practically the same as required by chance. It may now be stated with considerable experimental basis that all natural fats which contain GS_3 in proportions as required by chance will contain all the other glyceride types also in chance proportions.

2. The rule of glyceride type distribution in natural fats is obeyed by the class of fats containing large proportions of GS_3 and those containing large proportions of myristic and lower saturated acids. This forms further experimental confirmation of the suggestion that perhaps the rule of glyceride type distribution, which was originally shown to be obeyed by fats containing mainly C_{16} and higher acids, may be applicable in general to all natural fats irrespective of biologic source or component acid composition[19].

Experimental procedure

Extraction and purification of fat — The seeds of *Myristica malabarica* used for the investigation were collected from the forests of Cochin. They were dried in the sun and then kernels separated from the husks by hand. The separated kernels were powdered in an iron mortar and further air dried for a few days by exposure in thin layers to a blast of air from a fan. Drying at higher temperatures was avoided because the seeds contain large proportions of highly unsaturated resinous matter which may undergo changes if exposed to air at higher temperatures. The air-dried powder contained only 5 per cent moisture as determined by drying in an oven at 105°C. The dried powdered kernels were exhaustively extracted with redistilled benzene in a large soxhlet. After extraction was complete, benzene was distilled off from the solution, first under atmospheric pressure, and then the last traces under vacuum (1-2 mm.) at 100°-101°C. This left a yellow viscous residue amounting to about 38-45 per cent of the dry weight of the kernels. The residue gave a deep red colour with sodium hydroxide or carbonate, and contained plenty of resinous acidic matter.

For removal of the acidic matter and recovery of neutral fat, the residue was dissolved in a large volume of sulphuric ether to give about 2-3 per cent solution and washed repeatedly with 1 per cent potassium hydroxide solution, the washings being re-extracted with ether. The alkaline extracts were deep red in the beginning, but remained colourless by the time all acidic matter was removed. From the alkali washed ethereal solution, solvent was removed, first under atmospheric pressure, and last traces under vacuum (1-2 mm.) at 105°C. till a constant weight was reached and the neutral fat was recovered. This amounted to 10-12 per cent on the dry seed kernels, the balance being mostly resinous matter.

The acidic resinous matter was recovered from the alkaline extracts by acidification with dilute sulphuric acid, separated and washed with water, and the free fatty acids remaining in this were extracted by refluxing repeatedly with petroleum ether (b.p. 50°-80°C.). The free fatty acids thus recovered amounted to 3-4 per cent on the weight of the extracted kernels. The total fatty matter extracted amounts to 15-16 per cent and this agrees well with the 16 per cent yield of fatty matter free from unsaponifiables reported by Collin[13] on extracting *M. malabarica* seeds with low boiling petroleum ether.

The purified fat had a yellow colour and a characteristic smell. It showed an iodine value of about 22. The saponification value could not be determined as usual since the fat still contained some amount of resinous material which gave a deep red colour on saponification.

Component acid composition — The fat showed Hehner value of 94·75, indicating little loss of non-glyceridic matter during saponification and recovery of acids. Unsaponifiable matter isolated in the form of a sweet-smelling oil amounted to 2 per cent.

An attempt was made to determine the amount of non-glyceridic matter remaining in the purified fat, assuming that it is converted to resin acids during saponification. The mixed fatty acids (4 g.) were esterified according to Twitchell's method for estimating rosin acids, employing 50 cc. of absolute ethyl alcohol containing 5 per cent by weight of concentrated sulphuric acid, and boiling under reflux for 8 hr. The unesterified acids were isolated as usual. This amounted to 1 per cent by weight on the acids and consisted of a transparent resin with the characteristic smell of the original fat. The mixed acids consist approximately of 80 per cent saturated acids with mean molecular weight 231 and 20 per cent of oleic acid and will, therefore, have a mean molecular weight of 236. On this basis and from the weight of ester recovered, a loss in weight of 1 per cent became evident. During esterification with larger amounts of mixed acids (triplicates), the same loss in weight of 1 per cent was observed when correction was made for the amount of fatty acids remaining unesterified. This loss is probably due to conversion of a portion of the non-fatty matter into water soluble form by the action of alcoholic sulphuric acid. Total non-glyceridic matter other than unsaponifiables thus amounts to 2 per cent, and the glyceride content of fat is only 96 per cent.

Fat (12·25 g.) on acetic acid-acetone permanganate oxidation and after removal of acidic oxidation products gave 6·54 g. of GS_3 fraction having iodine value 0·5. This, therefore, contains 6·18 g. saturated acids. The saturated acids in the acidic oxidation products were recovered by hydrolysis and improved Bertram separation, and amounted to 2·54 g. Total saturated acids thus amount to 8·72 g. from 12·25 g. of fat of Hehner value 95, unsaponifiables 2 per cent and non-glyceridic matter 2 per cent. Total saturated acids isolated by acetone permanganate oxidation of mixed acid esters showed mean molecular weight of 231. Saturated acids from the GS_3 fraction showed the same value. Saturated acids recovered from acidic oxidation products also showed practically the same value. The total saturated acids as well as saturated acids from the GS_3 fraction showed titre of 119°F., which is identical with the value of 119°F. for a mixture of 86·27 per cent pure myristic acid and 13·63 per cent of pure palmitic acid (mol) recorded by Schuette and Vogel[22]; it is, therefore, likely that the saturated acids consist of a mixture of myristic and palmitic alone.

The isolated saturated acids come to 78·2 per cent of the mixed fatty acids and allowing for the 0·3 per cent saturated acids which may be lost during Bertram separation, the total saturated acids come to 79 per cent by weight in round numbers. The unsaturated acids consist almost entirely of oleic. The proximate fatty acid composition is, therefore, myristic 69, palmitic 10 and oleic 21 per cent by weight and myristic 72, palmitic 10 and oleic 18 per cent by molecules respectively.

GS_3 content of fat — The purified fat contains larger amounts of non-glyceridic matter than usual: this tended to influence slightly the melting points of fat and mixed acids. The m.p. of fat by the method reported earlier[23] was 118°-19°F. and that of mixed acids was 114°F. The difference is 4°-5°F. The GS_3 isolated by acetic acid-acetone permanganate oxidation showed m.p. 127°F. and its mixed acids had m.p. 123°F. The difference between the two is 4°F., same as that of melting points of GS_3 and saturated acids derived from these in chance distributed fats[23]. The slight difference in the value for original fat might possibly be due to the presence of non-glyceridic matter.

The difference between the melting points of the fat and its mixed acids being nearly 4°F., the D.M.P. value will be zero and, therefore, the GS_3 constant will have value of one[24]. Actual GS_3 content will, therefore, be the same as required by chance distribution. Since saturated acid content is 82 per cent (mol), GS_3 required by chance distribution is 55 per cent (mol). This calculated value agrees well with the experimental value of 57 per cent (mol).

Glyceride type composition of fat from Myristica malabarica — Fat (12·25 g.) was oxidized by acetic acid-acetone permanganate technique employing 60 g. of permanganate. The total reaction time was 10-12 hr. on a water bath. The oxidation products were worked up as usual and obtained in ethereal solution (about 600 cc.) in a 2 l. separating funnel. This was washed 5-6 times with small quantities of distilled water to remove acetic and lower acidic products of oxidation as much as possible. All washings were re-extracted with ether.

Removal of water insoluble oxidation products is the next step and care has to be taken to see that minimum excess of carbonate solution is used and that extraction is finished as quickly as possible. A few drops of phenolphthalein solution are added to the solution in the separating funnel and then 1 per cent potassium carbonate solution is added in small lots, with shaking after each addition till the aqueous layer remains pink after shaking. The solution is allowed to settle and the aqueous layer removed. Shaking is repeated once more with 20-30 cc. of 1 per cent carbonate. Finally the solution is washed 3-4 times with distilled water in small quantities till washings are neutral. The carbonate extracts and washings are once again extracted with ether, ethereal solutions combined and solvent removed to constant weight when 6·54 g. of residue was obtained. This had an acid value less than 0·2 and iodine value 0·5; therefore, it may be taken as made up of 6·44 g. of GS_3 and 0·1 g. GS_2U.

The carbonate extract and washings are combined and a current of air is passed through the extract at room temperature to remove all traces of ether. Ten per cent ammonium chloride solution (30-40 cc.) is added, shaken well and then 15 per cent magnesium sulphate added till no further precipitate is formed. The precipitate is allowed to settle for 15 min., filtered off and washed with water to remove the mother liquor. The acidic matter is recovered from the precipitate by heating it with dilute sulphuric acid till decomposition is complete, cooling and extracting with ether as usual. The azelaoglycerides thus obtained amounted to 3·53 g. The higher saturated acids were recovered from this by hydrolysing with alcoholic potash and submitting the hydrolysed acids to the improved Bertram separation. The weight of saturated acids recovered was 2·32 g.

The filtrate and washings from the magnesium salt precipitation of azelaoglycerides were combined, acidified with dilute sulphuric acid, saturated with common salt and extracted with ether. The acidic matter recovered was hydrolysed with alcoholic potash and the higher fatty acids were recovered by the improved Bertram separation. The weight of fatty acids thus recovered was 0·22 g.

From the above data the glyceride type composition of the fat is calculated. The fat contains 96 per cent of glycerides, i.e. 12·25 g. of fat contains 11·76 g. of glycerides. Of this 6·44 g. is GS_3, i.e. about 55 per cent.

A mixture of GS_2A and GSA_2 (3·53 g.) was obtained having a saturated acid content of 65·7 per cent. The mean molecular weight of the saturated fatty acids in this fraction was the same as that of the saturated fatty acids in the whole fat and had a value of 231. The S contents of pure GS_2A and GSA_2 when S has the mean molecular weight of 231 are 67·14 and 35·81 per cent respectively. The azelaoglyceride mixture from precipitated magnesium salts, therefore, contains 95·41 per cent of GS_2A, and this amounts to 3·37 g. This will be derived from the oxidation of 3·83 g. of GS_2U. Allowing for 0·1 g. of unchanged GS_2U in the GS_3 fraction, the total GS_2U comes to 3·93 g. This works out to 34 per cent.

The weight of GSA_2 present in precipitated magnesium salts is 0·16 g. Further, 0·22 g. of saturated acids recovered from soluble magnesium salts must have been combined as GSA_2, and this will give an additional 0·61 g. of GSA_2. The total GSA_2 formed in the oxidation is thus 0·77 g. This will be derived from oxidation of 1 g. of GSU_2, which works out to 8·6 per cent or in round numbers, 9 per cent.

The glyceride type composition of the fat is hence GS_3, 55 ; GS_2U, 34; GSU_2, 9 and GU_3, 2 per cent by weight. In molecules the type composition is GS_3, 57; GS_2U, 33; GSU_2, 8 and GU_3, 2 per cent respectively.

Summary

The glyceride type composition of *Myristica malabarica* fat, which contains 82 per cent (mol) saturated acids, has been studied by new and improved methods of analysis. The proportions of different glyceride types present agree well with those required according to simple chance distribution. The fully saturated glyceride content agrees well with that estimated from the saturated acid content and the D.M.P. value of the fat. The fat obeys the Rule of Glyceride Type Distribution in Natural Fats.

The proportions of different non-fully saturated glycerides in fats containing large amounts of myristic and lower acids have been experimentally studied for the first time. By effecting certain improvements in the Bertram separation it has been found that myristic acid can be quantitatively and lauric acid almost quantitatively isolated.

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REVIEWS

NUTRITION IN INDIA, by V. N. Patwardhan (Hind Kitabs Ltd., Bombay), 1952, pp. viii + 345. Price Rs. 10

The book deals with human nutrition in India and does not concern itself with animal nutrition. The author is the Director of the Nutrition Research Institute at Coonoor and the aim is to present in a readable form a well digested survey of the knowledge already gained and of matters requiring further study. As such it will command the attention of workers in the fields of nutrition, public health and agriculture, who will read it with pleasurable anticipation.

Research on human nutrition in India has been in progress for nearly half a century. There has been as yet no connected account of the results giving a clear picture of Indian foods and their nutritive values. This lacuna has given occasion to didactic statements about nutrition problems in India by people who have had no means to distinguish between points of view and established facts. The deficiency has been supplied by Dr. Patwardhan. He has collected and collated the information lying scattered in many journals and departmental reports, indicated the progress made and has drawn attention to the gaps to be filled.

The book, which is primarily addressed to workers in the field of human nutrition and public health, covers a reasonably comprehensive field in twenty-three chapters. The discussions and apprisal seem to be based on a generally cautious and detached analysis. In matters of detail the treatment given is occasionally uneven and less informative, but references have been given for supplementary reading. Some of the discussions and conclusions are less happy. For instance, the author's findings about vanaspati or vegetable ghee or hydrogenated vegetable oils are hardly convincing both from the scientific and economic points of view. The evidence considered is imposing, but that has not impressed the reviewer that the last word has been said. The long continued use of hydrogenated oils as fatty foods for human nutrition has yet to be studied. Meanwhile it cannot be forgotten that the nation's food is more than ever the concern and responsibility of nutrition and health officials and the business of producing and processing the food supply of the population and the interest of the consumer must always come before the convenience and profits of those who supply the foods.

There are significant omissions also. The chapter on population and food supplies relies on the figures for undivided India of about a decade ago and there is no discussion on the significance of the present policy and plans for nutritional welfare. Nothing has been said either about adulteration of foods or about investigations on the nature, extent and effects of the use of chemicals as preservatives in foods. Perhaps it would be unfair to hold up the author to a standard which he did not aim at, and only wanted to review the work done on foods and diets. That has been done admirably well. In view of the title of the book, however, one would expect to find these aspects to have been dealt with.

The great interest of this book lies in that the data and discussions enable the appreciation of established facts of nutrition in India *vis-à-vis* points of view of nutrition reformers (scientific and lay) and in revealing the fallacies in the much published ideas and ideals. Although one would like to see in a book of this kind a historical review of the evolution of foods and food habits of Indians, the absence of that does not, in the least, distract the interesting and instructive nature of the narrative. The geographical location of the major food crops of India suggests demarcation into wheat India, rice India and millet India. The diet surveys indicate the dietary habits of the people. The changes in nutritive values accompanying the preparation of foods ready for eating have been described and discussed. It has been shown that the major cereals and pulses, which are in common use, are not nutritionally as inferior as basic food sources for the supply of carbohydrates and proteins as many people suppose, and that they are adequate for building up nourishing diets around them.

That brings about the realization that the problem of nutrition in India is not so much of quality as of quantity and that the realistic approach lies more in combining quantity and quality in the crops now grown than in attempting the introduction of new crops and new methods and diets.

Although the book is mainly intended for scientific workers in the fields of nutrition, public health and agriculture, the data and the discussion on the food crops and diets are of interest to the general reader also.

B. VISWA NATH

GEOLOGY OF INDIA, by D. N. Wadia (Macmillan & Co., London), 1953, Third Edition, pp. 531 + xix plates. Price 50*s*.

It is more than fifteen years since the revised second edition of this book was published and much has been achieved in the progress of geological investigations in India during the World War II and succeeding years, especially in the field of economic geology and mineralogy. This has rightly justified the bringing out of a third edition of the book. Advanced students of geology will definitely appreciate Dr. Wadia's lucid and systematic presentation of the complex subject of Indian stratigraphy. The book, from a modest beginning as a manual for students preparing for the Punjab University examinations, has grown into an excellent treatise on the subject. As a text-book on the geology of India, there will be hardly any geological library in English-speaking countries of the world where this book will not find a place.

Much of the text of the previous edition has been retained with slight modifications, but at the same time this edition embodies the latest information and recent reviews of eminent geologists, thus bringing it up to date. The important departure in this edition is that the chapter on the geology of Kashmir, which appeared as an appendix in previous editions, has been eliminated, and rightly too, and incorporated in the body of the main text. Consequently, there has been a certain amount of reshuffling of the subject-matter dealing with the geology of the extra-peninsular region like that of Simla area, Hazara, etc.

The treatment of the topics is clear and exhaustive. The book is divided into twenty-six chapters and the contributions are on many topics, some of which are based on the author's first-hand knowledge of the subject-matter. Among the new features of the present edition, mention may be made of (1) the detailed treatment of the Dharwars of Mysore, together with a note on the correlation of Mysore Dharwars; (2) a fuller account of the Archaean geology of Singhbhum and Orissa area, giving the recent views based on the work of Dunn; (3) the treatment of the Lower Vindhyans of Rajputana in greater detail; and (4) the discussion of the age and origin of the Saline Series at greater length and the incorporation of the views of geologists like Dr. V. S. Dubey regarding the occurrence of a diamondiferous plug in Rewah conglomerate in Panna State, of Dr. C. Mahadevan on some aspects of Puranas of South India, of Dr. Rajnath on his contributions to the Jurassic stratigraphy of Cutch, and many others which are not found in the previous editions. A table showing the standard stages of the Geological Record is also added in the beginning.

The chapters on the tertiary deposits have been brought up to date. The notable features are the inclusion of a table showing the correlation of tertiary formations, the expansion in the treatment of Siwaliks giving more information on the ice age in N.W. India and the discussion on the origin of petroleum. Finally, the treatment of the human epoch is expanded to include the views of F. E. Zeuner regarding the classification of the Pleistocene and recent deposits into Palaeolithic, Microlithic and Neolithic periods.

There are, of course, one or two points which deserve special mention. Going through the book, one finds that the author has preferred to retain the same treatment of the chapters on the Archaean and the Gondwana systems of India. The former are discussed separately under two chapters, one dealing with the gneisses and schists and the second, the Dharwarian rocks. To quote the author himself, " the difference of name does not denote difference of systematic position " and " the most ancient metamorphosed sedimentary rock-systems of India are as old as, and in some cases older than, the basement gneisses and schists described in the last chapter ". The exact relationships between the Archaean gneisses and schists and the metamorphosed sediments which are often so metamorphosed and that at several localities these sediments are found to be indisputably older than the gneisses and schists, do not warrant such a treatment of the subject separately under Archaean and Dharwar systems.

Many of the petrological types listed by the author (pp. 80-84), as included in the Archaean gneisses and schists, are now regarded as either Dharwars or post-Dharwars in age and their proper place would be in the succeeding chapter on Dharwar system. The general consensus of opinion amongst the geologists about the three gneissic Archaean groups of India — Bengal gneisses, Bundelkhand gneisses and the charnockites — is that none of them are the oldest rocks, but are younger than the associated Dharwars. This opinion is likely to be confirmed by other workers in the field when these rocks are studied in the light of recent views on the phenomena of granitization and injection metamorphism so commonly observed in the Archaean shields.

Again as regards the treatment of the Gondwana system, the author has followed the old three-fold classification of the most important coal-bearing formations of India as originally suggested by Fiestmantel and followed by Vredenburg. Apparently this classification has been adopted in preference to the two-fold classification adopted by the Geological Survey of India on the evidence supported by the intervention of climatic conditions of an arid continental type which is further revealed by the assemblage of vertebral remains in the middle portion of the Gondwanas. The two-fold classification has been strongly supported by C. S. Fox who has done pioneering work in the Indian coalfields and who is considered an authority on the subject. The evidences afforded by a critical study of the Gondwana flora turn the scale in favour of the two-fold classification as against the old tripartite one, however much the latter may be tempting enough and nicely fits into the three great groups corresponding to the European standard scale. It is legitimate to adopt a classification of the coal-bearing strata on the basis of the characteristic flora, which has been evidently coexistent with the formation of the rocks containing them rather than on the basis of land vertebrates whose occurrences are rarer and sporadic, and much less on the climatic conditions during those times.

The last chapter deals with the economic geology of the Indian formations wherein are described the occurrences and uses of scores of economically important minerals which have come to light in recent years. A note on the geological and geographical distribution of India's minerals, which was wanting in previous editions, is also added. The potential oil-bearing tracts in India are discussed at some length. A short account of the main soil groups of India is given at the end.

The author has rightly emphasized in the preface that geology knows no political barriers and accordingly has dealt with the geology of India as one structural unit including Burma and Pakistan.

There is no doubt that the book written with scientific precision and in lucid style will continue to serve the purpose of a good text-book on the subject as it has done in the past.

Like the other publications of Macmillan & Co., this book is neatly printed and attractively got up, and the type is bolder than in the previous editions. Probably this explains the high cost of the book, but the publishers will do well to bring out a cheaper edition to suit the pockets of Indian students. We hope the author will request the publishers to do so.

N.L.S. & T.N.

CHEMICAL CONSTITUTION — AN INTRODUCTION TO THE THEORY OF THE CHEMICAL BOND, by J. A. A. Ketelaar (Elsevier's Publishing Co. Ltd., London, Amsterdam, New York), 1953, pp. viii + 398. Price 40*s*.

The book under review is the Dutch counterpart of Pauling's well-known book on chemical bond and so the emphasis is on work carried out on the eastern side of the Pacific.

Four types of chemical bonds, namely ionic bond, atomic bond, metallic bond and van der Waal's bonding, form the main subject of discussion of the book. A highly relieving feature of the book to a conventional chemist is that it uses least mathematics and still attempts to give an accurate picture of the various types of bond without undue oversimplification and with emphasis on those aspects which are of interest to chemists. And in this attempt the author has succeeded admirably.

The formation of various types of compounds as also their physical properties have been discussed with reference to the particular type of bond existing therein. The discussions are factual and critical, pointing out the strength as also the weakness of the existing concepts.

It has been a pleasure for the reviewer to have come across so much new information in going through the book, and to find many already known facts viewed in a new light. One disturbingly new information for the reviewer is that on page 351, the boiling points of a homologous series are given by a relation $T_b^2 = n A + B$ " which has long been known ", whereas in a paper published lately by Y. P. Varshni, the latter claims to have discovered a relation which is equivalent to the above long known relation. The reviewer recommends the book to all students and workers of chemistry who desire to understand the theory of chemical bond from chemist's standpoint. The tables and extensive references to European literature are additional valuable features of the book.

SANTI R. PALIT

AYURVEDIC FLORA MEDICA: PART I, by N. S. Mooss (Vaidyasarathy Press, Kothayam, Travancore-Cochin), 1953, pp. xiv + 128 + 44 illustrations. Price Rs. 12

The publication deals with 45 Indian medicinal plants used in ayurveda arranged in alphabetical order according to their botanical names. The information included deals with the distribution and description of the plants, and description, properties and uses of the plant parts actually used for medicinal purposes. There are 40 well-executed line drawings and four coloured plates.

A feature of this publication is the inclusion of special notes, mainly citations from Sanskrit treatises, to identify the plants correctly. All the available Sanskrit and vernacular names of the plants and their synonyms have been given. The botanical nomenclature of the plants is up to date. This is a commendable achievement.

This volume is Part I of a series of publication and the plants treated cover the letters A to V. This does not give any idea as to the scope and contents of the succeeding parts.

The book is a welcome and useful addition to the ayurvedic literature.

R.C.S.

PROCEEDINGS OF SYMPOSIA IN APPLIED MATHEMATICS, VOL. IV — FLUID DYNAMICS, Edited by M. H. Martin (McGraw-Hill Book Co. Inc., New York), 1953, pp. v + 186. Price $ 7.00

This book contains 14 papers which were presented at the Fourth Symposium on Applied Mathematics of the American Mathematical Society held at the University of Maryland on 22 and 23 June 1951, the subject being Fluid Dynamics.

The first paper in the publication is by Prof. S. Chandrasekhar of the Yerkes Observatory and deals with " Some Aspects of the Statistical Theory of Turbulence ". After describing how velocity correlation tensors could be constructed for an incompressible fluid so as to satisfy the isotropic property, the author extends the method to axi-symmetric tensors and gives an application to magneto-hydrodynamics. Passing to compressible fluids it is shown that correlations in density and pressure fluctuations could be made the basis of study (instead of velocity correlations) and this is applied to study the gravitational stability of an infinite homogeneous turbulent medium. It is followed by a paper by Prof. C. C. Lin of the Massachusetts Institute entitled " A Critical Discussion of Similarity Concepts in Isotropic Turbulence ". The paper discusses the extent of " self-preservation " among the various components of the spectrum and derives various laws of decay which are compared with the experimental evidence.

Nearly half the papers in the symposium deal with transonic and supersonic flows. Prof. Adolf Busemann of the Langley Aero Laboratory shows that transonic potential flow past bodies of general shape is non-existent, this being a property of the mixed elliptic and hyperbolic differential equation and the required boundary conditions. The separation of supersonic flow from curved profiles and of a shock which occurs at the end of a profile but not attached to the vertex is discussed by Prof. T. Y. Thomas of the Indiana University and compared with experimental results. Profs. G. F. Carrier and K. T. Yen of the Brown University explain a new method of constructing flow patterns in which sonic or supersonic speeds characterize a portion of the flow field. The method consists essentially in taking the Fourier transform in the hodograph plane of the stream function of an incompressible flow and inverting it with a hypergeometric function. Profs. Martin and Thickstun of the University of Maryland deal with an example of transonic flow for the Tricomi gas. Prof. J. M. Burghers of the Technische Hoge School, Delft, has a paper on the non-uniform propagation of plane shock waves. Prof. A. Weinstein of the University of Maryland explains in his paper his " generalized axially symmetric potential theory " which is essentially the study of the generalized Stokes-Beltrami differential equations with parameter p (which is connected with axially symmetric flows in p + 2 dimensions). The basic singular solutions are used to construct incompressible flows by the method of sources and sinks, to connect flow problems with electrostatic problems in a space of two or more dimensions, and also applied to the hodograph plane to discuss the transonic flow about a wedge in a channel using Tricomi's approximation.

On wave motion there are two papers; one an abstract by Prof. R. E. Myer of Maryland on waves of finite amplitude in ducts, and a paper on gravity waves by Prof. A. E. Heins of the Carnegie Institute, Pittsburgh. There are two papers on numerical methods. One of them reviews various methods of mapping a smooth curve on to a circle and also analogous methods for " free boundary " problems by iterative processes and is by Profs. G. Birkhoff, D. M. Young and E. H. Zarentello of Harvard. The other is by Prof. J. L. Synge of Maryland and deals with the flow of viscous fluids through pipes and canals. On propeller theory, Prof. Theodorsen of the University of Maryland has a paper where he uses the result that the case of minimum induced loss corresponds to the vortex wake far behind the propeller displacing itself backward with a constant velocity, to show how thrust, torque and induced loss may be obtained by the study of conditions far behind the propeller. However, this method gives an excess pressure in the wake and so does not yield the theory of the actuator disc as a limiting case. Lastly there is the paper by Prof. S. R. De Groot of Maryland on hydrodynamics and thermodynamics, where hydrodynamical equations are developed from the viewpoint of the thermodynamics of irreversible processes. Systems with several components are taken in which, besides viscous flow, there are other irreversible processes such as heat conduction, diffusion, chemical reaction and cross phenomena. Mixtures in which there is an inhibition of the transfer of momentum between particles of different kinds leading to separate entropy laws for each of the constituents are considered. The case of liquid helium has been considered wherein it is regarded as a mixture of normal and superfluid atoms.

The book containing a collection of papers by experts in their fields with list of references is valuable for the advanced worker. The publication is admirably printed.

A. NARASINGA RAO

PUBLICATIONS RECEIVED

RADIO ENGINEERING, Vol. I, by E. K. Sanderman (Chapman & Hall Ltd., London), 2nd ed., 1953, pp. xxiv + 779, price 60*s*.

SURVEY OF INDIA TECHNICAL REPORT — 1952, PART III — GEODETIC WORK (Surveyor General of India, Dehra Dun), 1952, pp. x + 90, price Rs. 6

POISONOUS PLANTS OF INDIA, Vol. I, by R. N. Chopra, R. L. Badhwar & S. Ghosh (Manager of Publications, Govt. of India Press, Calcutta), 1949, pp. liv + 762, price Rs. 30

THE PHARMACOGNOSY OF AYURVEDIC DRUGS (TRAVANCORE-COCHIN), Series I, No. 2 (The Central Research Institute, Trivandrum), 1953, pp. vi + 104

TELEVISION RECEIVER DESIGN, by P. A. Neeteson (Philips Technical Library, N. V. Philips Gloeilampenfabrieken, Eindhoven), 1953, pp. 156, price Rs. 10

INDUSTRIAL INORGANIC ANALYSIS, by Roland S. Young (Chapman & Hall Ltd., London), 1953, pp. vii + 368, price 36*s*.

STARCH AND ITS DERIVATIVES, by J. A. Radley (Chapman & Hall Ltd., London), 1953, pp. xi + 465, price 65*s*.

STATISTICAL METHODS IN ELECTRICAL ENGINEERING, by D. A. Bell (Chapman & Hall Ltd., London), 1953, pp. viii + 175, price 25*s*.

TECHNIQUES OF TECHNICAL TRAINING, by H. R. Mills (Cleaver-Hume Press Ltd., London), 1953, pp. 195, price 10*s*. 6*d*.

RELAYS FOR ELECTRONIC AND INDUSTRIAL CONTROL, by R. C. Walker (Chapman & Hall Ltd., London), 1953, pp. xi + 303, price 42*s*.

INTRODUCTION TO A STUDY OF MECHANICAL VIBRATION, by G. W. van Santen (Philips Technical Library, N. V. Philips Gloeilampenfabrieken, Eindhoven), 1953, pp. xv + 296

DATA AND CIRCUITS OF TELEVISION RECEIVER VALVES, by J. Jager (Philips Technical Library, N. V. Philips Gloeilampenfabrieken, Eindhoven), 1953, pp. 011 + 216, price Rs. 10

STRENGTH OF MATERIAL — A Text Book for Degree Students, by G. H. Ryder (Cleaver-Hume Press Ltd., London), 1953, pp. x + 278, price 21*s*.

NOTES & NEWS

Acrizane, a new antiseptic

ACRIZANE, 9-p-HEXYLOXYPHENYL-10-methylacridinium chloride, is a new antiseptic that is more effective than any mercurial or quaternary ammonium compound now in use. Acrizane is a powerful and quick germicide against both Gram-positive and Gram-negative bacteria. It kills *Staphylococcus aureus* in 5-10 min. at dilutions of 1: 50,000; against the same organism it is bacteriostatic for 48 hr. at dilutions up to 1: 10 million. While the compound is bound by proteins and suffers a marked reduction in germicidal titre in the presence of serum, it still compares favourably with the best of other antiseptics. It also causes a certain amount of phagocytosis, but is safe at dilutions up to 1: 3,000. It has the drawback of staining clothes lemon yellow [*Chem. Engng. News*, **31** (1953), 3861].

Erythromycin B

TWO ZONES OF ANTIBIOTIC ACTIVITY were detected in the paper chromatographic analysis of fermentation broths, when *Streptomyces erythreus* was grown on a medium composed of inorganic salts, sucrose, glycine and alanine. Erythromycin appeared in the more mobile zone, while the less mobile one was associated with a new substance, erythromycin B.

Extraction of the fermentation broth at *p*H 9·5 with chloroform or amyl acetate resulted in a crude concentrate of the active substances. They were separated by column chromatography on powdered cellulose with 0·01N ammonium hydroxide saturated with methyl isobutyl ketone as the developing and eluting solvent. Separation was also achieved by countercurrent distribution with a solvent system containing acetone, methyl isobutyl ketone and water. Erythromycin B is a basic compound, sparingly soluble in water, but extremely soluble in ether, chloroform, ethyl acetate and benzene [*Chem. Engng. News*, **31** (1953), 3978].

Penicillin O

PENICILLIN O IS A NEW FORM OF penicillin developed as a result of a research programme aimed at the development of a form which would be free from the allergic reactions of the standard penicillins. The problem of penicillin sensitivity has been troublesome ever since its introduction. Some of the early reactions which were observed were thought to be due to the impurities present in the penicillin preparations. However, later studies with highly purified forms of the antibiotic demonstrated conclusively that many of these reactions were directly attributable to the drug itself.

Work on non-allergenic penicillin first centred on penicillin S, which showed some promise as being free from allergens, but had a disagreeable odour and taste. Another form of the molecule (allylmercaptomethylpenicillin), similar to penicillin S, was prepared. This was found to be free from allergic and tongue irritating properties and was still much less objectionable as far as taste and smell were concerned than the S form.

The production by fermentation processes of the new O form of penicillin became feasible when strains of the mould, which favoured the production of the O form, were eventually isolated and utilized for fermentation production. Although the mould strains were preferential in synthesizing the O form, there were still quantities of the G type being produced by the mould. Analytical methods were developed to determine the amount of the G form present in the fermentation product.

Clinical tests have demonstrated that about 90 per cent of the individuals who are sensitive to the previous G type penicillin are free from allergic reactions when the O form is used. Another interesting result of the clinical trials is that many G-sensitive persons, after treatment with penicillin O, were able to tolerate the G type without the former allergic reaction [*Chem. Engng. News*, **31** (1953), 4012].

Syntheses for cortisone intermediates

THE RECENT DEVELOPMENT OF the bio-oxidation method for the conversion of progesterone to cortisone made the development of a practical synthesis of progesterone highly desirable. A new synthesis of progesterone is reported from ergosterol, which has always been a very attractive starting material because of its almost unlimited potential supply from fermentation processes. Synthesis of another cortisone intermediate, pregnane-3, 20-dione, from either stigmasterol or ergosterol, has also recently been announced.

Ergosterol is easily oxidized by the Oppenauer method to give 4, 7, 22-ergostatrien-3-one in 77 per cent yield. This reaction was carried out with cyclohexane and aluminium isopropoxide in boiling toluene, and was essentially complete in 10 min. Progress of the reaction was checked by the analysis of the ultraviolet spectra of samples isolated consecutively from the orange-red reaction mixture. The 4, 7, 22-ergostatrien-3-one was purified by washing and recrystallization. A mixture of this compound in methanol was then refluxed until solution occurred; a small amount of hydrochloric acid was then added. The acid caused the immediate precipitation of a white crystalline material from the orange-red solution. Upon further addition of acid and heating, the precipitate redissolved Sodium bicarbonate was added, and after filtering, washing and distillation under reduced pressures, a light yellow precipitate of 4, 6, 22-ergostatrien-3-one (isoergosterone) was formed. The yields of 4, 6, 22-ergostatrien-3-one from 4, 7, 22-ergostatrien-3-one, without isolation of the enol ether intermediate, were 75-80 per cent.

The next step in the synthesis of progesterone is catalytic hydrogenation of the trienone to a dienone, 4, 22-ergostadien-3-one. Because of the difficulty of separating the desired dienone from the starting materials and the co-products, an efficient reduction is necessary. With palladium-carbon catalysts in alcoholic sodium or potassium hydroxide, conversions of 80 per cent or better were obtained. Optimum selectivity of the reduction system was found to be dependent on the reduction of the catalyst prior to the addition of the steroid, and on the concentration of alkali. Uniformly high conversions were observed in media 0·0010-0·010N in potassium hydroxide.

The side chain double bond of 4, 22-ergostadien-3-one can be easily cleaved by ozonolysis, to produce 3-ketobisnor-4-cholenaldehyde in better than 90 per cent yield. From this aldehyde 22-(N-piperidyl)-bisnor-4, 20(22)-choladien-3-one was prepared in 99 per cent yield, using 1·00 g. of p-toluenesulphonic acid monohydrate per mole of steroid as an acid catalyst to increase the rate of condensation. This product is oxidized in a sodium dichromate-benzene-acetic acid system to produce the progesterone. The overall yield from ergosterol to progesterone was 37 per cent.

Pregnane-3, 20-dione, which can also be converted to cortisone by means of microbiological oxidation, can be made from stigmasterol or ergosterol by way of the corresponding 3-keto-bisnor-cholan-22-al. Stigmasterol can be converted by the Oppenauer oxidation to 4, 22-stigmastadien-3-one. Ergosterol in the same reaction yields 4, 7, 22-ergostatrien-3-one which is isomerized with acid to 4, 6, 22-ergostatrien-3-one (isoergosterone).

Isoergosterone and stigmastadienone can be catalytically reduced to the corresponding saturated 3-ketones, but to be of value for the production of cortical hormones this reaction must be stereospecific. Hydrogenation of stigmastadienone with palladium catalyst on several supports, including charcoal, calcium carbonate and barium sulphate, in alkaline medium, has been developed to a high order of stereospecificity. This procedure can also be applied to isoergosterone to give 5 β-ergost-22-en-3-one in 88 per cent yield. Both the stigmasterol and ergosterol derivatives can be converted to pregnane-3, 20-dione through ozonization and subsequent oxidation. The ozonization product is 3-keto-bisnor-cholan-22-al. This aldehyde can be converted to 22-N-piperidylbisnor-20(22)-cholen-3-one which, upon oxidation with sodium dichromate, yielded the desired pregnanedione [*Chem. Engng. News*, **31** (1953), 3977].

Benzene hexachloride by green irradiation

IT HAS RECENTLY BEEN OBSERVED that when chlorination of benzene is carried out in a green light, the yield of the γ-isomer of benzene hexachloride is very considerably increased, being doubled or trebled. This discovery is of great significance, since it is the γ-isomer which is the most effective constituent of the insecticide gammexane. The source of green light is preferably a lamp which produces green fluorescent light, but other light sources provided with colour filters to give light of wavelengths 4,900-5,800Å may be used.

In an experiment, 3·3 lb. chlorine gas was passed into 10 lb. benzene while irradiating with green light of wavelength 4,900-5,800Å provided by a type TL 40/17 lamp made by Deutsche Philips G.m.b.H. of Hamburg. The reaction mass was cooled to prevent the temperature rising above 30°-40°C. and, on completion of the reaction, surplus benzene was distilled off. About 4 lb. of benzene hexachloride containing 30-50 per cent of the γ-isomer were obtained. By the conventional method, using ultraviolet light, the yield of γ-isomer would have been 15 per cent only. Furthermore, there would have been a considerable formation of undesirable oily byproduct which is suppressed to a large extent in the new process [*Chem. Prod.*, **16** (1953), 424].

Aralkyl ketones — a new method of preparation

A NEW METHOD FOR THE PREPARATION of aralkyl ketones by the direct condensation of glycerides with benzene in the presence of aluminium chloride is described. The glyceride was dissolved in a large excess of benzene. At least 2·1 moles of aluminium chloride were necessary for each equivalent of glyceride. About one-third of the aluminium chloride to be used was added portion-wise during the first half hour on the steam bath, and the balance of the catalyst was introduced thereafter. The mixture was shaken vigorously at frequent intervals during the reaction period. After standing overnight, it was drowned in ice water acidified with hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic portions were washed with water and dried. The ketones were isolated by distillation. Glycerine was recovered by making the aqueous solution slightly basic, filtering the precipitated aluminium hydroxide, and washing with water.

In a typical experiment, 660 g. (2·3 equiv.) hydrogenated acidless tallow, 1,800 g. (23 moles) benzene, and 7·66 g. (5·75 moles) aluminium chloride were allowed to react, and the mixture was worked up in accordance with the above method. A 530 g. fraction distilling at 90°-255°C./2·0 mm. was collected leaving a 162 g. residue. The glycerine recovered weighed 12·8 g. The yield of the ketone in the experiment was 86 per cent, glycerine recovery being 29 per cent. Alkylation with glycerol as a probable side reaction may account for the low glycerol recoveries and for the residue of unknown materials [*J. Amer. Oil chem. Soc.*, **30** (1953), 350].

Vanillin from sulphite waste liquor

A METHOD FOR OBTAINING HIGH yield of vanillin at a low cost from lignosulphonic acid in sulphite waste liquor by atmospheric oxidation has been recently patented. Waste liquors from sulphite pulping process, low in cellulose content, particularly those which have had their content of non-lignin material further reduced by alcoholic fermentation, are most suitable for the process. To the liquor 70-80 parts by weight of caustic soda per 100 parts by weight of waste sulphite liquor solids are added. The solution heated to 100°-185°C. in an autoclave and air diluted with nitrogen or steam, whereby the mixed gas has an oxygen partial pressure below about 6·6 lb./sq. in., is bubbled through. Copper and certain copper compounds are effective oxidation catalysts for promoting the partial oxidation degradation of the lignin molecule. Two to four parts by weight of copper sulphate pentahydrate per 100 parts by weight of waste sulphite liquor solids is a recommended catalyst [*Industr. Chem.*, **29** (1953), 502].

Manganese sulphate from low grade manganese ores

A NEW METHOD IS DESCRIBED FOR converting manganese dioxide into manganous sulphate by treating manganese wad with gaseous sulphur dioxide. The reaction proceeds over a wide range of temperatures and sulphur dioxide partial pressures, but above 400°C. the reaction between iron and sulphur dioxide becomes appreciable. At lower temperatures the utilization of sulphur dioxide for sulphate ion formation approaches 100 per cent, and sulphate ion corresponds stoichiometrically to manganous ion. At furnace temperatures of 300°-400°C., using a gaseous reactant containing 15 per cent of sulphur dioxide, 60-70 per cent of the manganese in the wad is converted into soluble sulphate, the limiting factor being the decreasing concentration of manganese dioxide as the reaction proceeds. For higher conversions, the reaction temperature may be increased, a richer gas may be used, or the sulphate first formed may be removed by leaching and the residue resubmitted to reaction with sulphur dioxide (*Science Newsletter*, No. 130, Item No. 1909, Scientific Liaison Office, India House, London).

Metal recovery from mineral residues

SYSTEMATIC STUDIES OF THE chemical reactivity of solid materials have been carried out with particular consideration to the conversion of metal oxides in minerals or mineral residues into water soluble salts by dry treatment with sodium carbonate. As a result of these studies a method was developed to recover tungsten in the form of sodium tungstate from the metallic dust derived in the production of ferrotungsten by dry treatment with a limited quantity of soda at 650°C. Yield and purity of the recovered tungsten are much better than in the conventional regeneration process.

A method for the recovery of soluble vanadium from metallurgical slags has also been evolved by the same process. The maximum of over 90 per cent recovery is reached with an addition of 100 per cent of soda. The quantity of silica going simultaneously into solution is small, up to 30 per cent of soda, but rises sharply above this quantity. The optimum temperature for the recovery of vanadium by dry heating lies between 700° and 800°C. depending on the silica content of the starting material. Rising temperature has the same effect on yield as increasing addition of soda.

In a successful attempt to apply the new method to the production of sodium bichromate from chromium ores, the following conditions were found to give the best results: selective sieving of the crushed chromite, mixing with 100 per cent of soda and certain quantities of lime and magnesia or dolomite, and heating the mixture for 1 hr. to 1,000°C. Silica or iron oxide may be used as inert thinners, but not alumina, which diminishes the solubility of chromium, probably due to the formation of a complex chromium-aluminate [*Industr. Chem.*, **29** (1953), 503].

Urea-formaldehyde fertilizers

UREA-FORMALDEHYDE COMPOUNDS made by the acid-catalysed reaction of urea with formaldehyde have been found to be useful fertilizers for supplying nitrogen at uniform rate. They differ from the highly insoluble urea-formaldehyde resins of the plastics field in that a urea-formaldehyde mole ratio of greater than one is employed. Depending upon the reaction conditions, a range of products is formed — including those that nitrify in soil almost as rapidly as urea to those requiring two to three years. The available water soluble nitrogen in urea-formaldehyde products is evaluated from the percentage of cold water soluble nitrogen that dissolves in a hot aqueous phosphate buffer solution. Values obtained are an index of the availability of the cold water insoluble nitrogen which approximates the amount of insoluble that nitrifies in about six months.

Greenhouse and field tests prove the ability of urea-formaldehyde fertilizer compounds to supply nitrogen at a uniform rate throughout a growing season. Most of these trials have been and are being conducted with turf because the nitrification characteristics of these compounds make them well suited for this type of long season crop. The desirable nitrogen response for turf can be obtained with a single application of a suitable compound containing about 38 per cent nitrogen, of which three quarters is in the slowly available form. Four lb. of nitrogen per 1,000 sq. ft. applied in this form will supply an average turf with sufficient nitrogen for a full year of satisfactory growth. The efficiency of a single application equals or exceeds that of multiple applications of the soluble nitrogen fertilizers. High quality urea-formaldehyde fertilizer compounds are equal or superior to the other forms of slowly available nitrogen such as the natural organic materials, sewage sludges and tankages [*Chem. Engng. News*, **32** (1953), 3858].

Fertilizer insecticide mixes

THE NEW PRACTICE OF USING insecticides mixed with fertilizers is evoking considerable interest in both the insecticide and fertilizer industries as a consequence of the discovery that some of the newer insecticides are economically effective for the control of insects which spend a susceptible phase of their life cycle in the soil. Saving of time and labour are big factors in their favour.

A number of the chlorinated organic insecticides, such as DDT, lindane (purified gamma isomer of benzene hexachloride), chlordan, aldrin and dieldrin, which have been so spectacular in general insect control, are also effective for control of insects in the soil. Of this group, chlordan and aldrin have been most widely used. Aldrin has been gaining wide acceptance because of its general effectiveness, lack of toxicity to growing plants, freedom from off-flavour effects and low cost of treatment. A more recent chemical, heptachlor, has also been demonstrated to be effective. The most satisfactory stage for the addition of insecticides is during the blending and grinding operation after the fertilizer has cured, and just prior to bagging. Addition of pesticides to the mixer during this operation has proved very satisfactory if adequate blending and proper formulations have been used [*Chem. Engng. News*, **31** (1953), 3859].

New cyclic process for peroxides

A NEW CYCLIC PROCESS WHICH affords a convenient and economical synthesis of oxides, peroxides and peroxyhydrates of the alkali and alkaline earth metals in an anhydrous medium is reported. The process involves the use of easily oxidizable organic compounds, such as hydrazobenzene, as intermediates; the resulting azobenzene is reduced with an amalgam of the alkali metal desired in the final product. Alkaline earth metals can be introduced in another step, by the removal of alkali metal alcoholate formed in the reaction and substitution of the alkaline earth alcoholate.

Careful control of the temperature, alcoholate to peroxide ratio, alcoholate to solvent ratio, and other factors determines the exact product. Besides the oxides, peroxides and peroxyhydrates that may be formed in the process, high purity alkali metal and alkaline earth alcoholates, high strength hydrogen peroxide, and superoxides can also be obtained. An attractive feature of the synthesis is that it involves the use of an electrolytic cell that makes possible the production of chlorine without byproduct caustic. This cell is used in the preparation of the alkali metal amalgam.

The reduction takes place in a mixture of benzene and methyl alcohol. Oxygen bubbled through the reaction mixture forms hydrogen peroxide with the hydrazobenzene, which then interacts with the alkali metal alcoholate to form the diperoxyhydrate. The product, formed in 90 per cent yield continuously, can be used as an inexpensive bleaching agent, as a source of high strength hydrogen peroxide or to make superoxides for military uses [*Chem. Engng. News*, **31** (1953), 4012].

Versatile photometric goniometer

A GONIOMETER OF UNUSUAL VERSATILITY and precision has been devised by the National Bureau of Standards, U.S.A. Designed for use on a 100 ft. photometric range, the NBS goniometer was specially designed to combine accuracy with flexibility. The new goniometer has three possible axes of rotation, and can be used as any one of the three conventional types of goniometers. Of the three axes of rotation, only one, which measures horizontal angles, is permanently fixed. Of the other two axes, both of which may be rotated, one measures " horizontal " angles while the other measures "vertical" angles.

Backlash and variable torque errors have been greatly reduced by the adjustable balancing arrangement and the constant torque device. The accuracy of the new goniometer was evaluated, and no error greater than 0·03° in the measurement of angular intervals up to 90° was found with either of the rotary tables. Errors in the measurement of vertical angles with the inner U-frame drive system were found to vary with angular intervals from a maximum of 0·02° in a 1° traverse to a maximum of 0·01° in a 90° traverse [*J. Franklin Inst.*, **256** (1953), 266].

" Cellular " electronic circuits

PRINTED ELECTRONIC CIRCUITS, IN which conducting patterns etched on plastics take the place of conventional wiring, have not yet gained widespread acceptance on account of the difficulty of connecting components and tubes to them. In a novel approach to the problem currently being investigated, small 3-contact moulded blocks or cells, each containing one or two circuit elements — resistors, capacitors, inductors — are pressed against the etched circuit pattern by means of springs that are extensions of the tube socket contacts. No soldering is needed.

The individual moulded cells are *c.* $\frac{7}{8}$ in. high by $\frac{1}{2}$ in. wide by $\frac{1}{4}$ in. thick. Each has three contacts, one on the top and two on the bottom. The cells are grouped together in " building blocks ", each comprising two tubes and twelve cells held in a compact bundle by means of a suitable frame. The top surface of the block consists of a spring assembly containing the tube sockets and the necessary spring contacts. When the block is fastened to the printed base plate by means of screws, springs in the spring assembly apply substantial pressure to the top terminal of each cell and hold the two bottom terminals firmly in contact with the printed circuit pattern. Positive and noise-free electrical connection is further assured by the application of a thin film of grease to the cell contacts.

The two-tube block is considered an optimum-sized subassembly in the new system. Any number of the blocks can be mounted on a suitably printed base plate of sufficient area. Potentially inexpensive, they are compact (*c.* $2\frac{1}{4} \times 1 \times 1\frac{3}{16}$ in., exclusive of tubes) and are easy to store and to handle. They are extremely rugged, and as long as a block is secured to the base plate none of the cells can vibrate or shake loose.

A noteworthy feature of the technique is the achievement of quick replaceability — of both blocks and cells — without the use of plugs or connectors. In case of trouble, an entire block can be easily removed for repair or replacement simply by loosening the screws that hold it to the base plate [*J. Franklin Inst.*, **256** (1953), 268].

Air lubricated bearings

A LEONARD GENERATOR SET which uses air lubricated bearings has been recently exhibited. The set operates at 3,000 r.p.m., develops 16 kW. and carries a shaft weighing 95 kg. The air for the bearing is fed at atmospheric pressure. Experiments with a simple testing equipment have shown that higher friction is obtained with liquid lubricated bearings than is obtained with air lubricated bearings. The saving in lubricating costs and increased efficiency due to reduction in friction losses are some of the advantages (*Science Newsletter*, No. 132, Item No. 1936, Scientific Liaison Office, India House, London).

Type transparencies

TYPE TRANSPARENCIES WHICH DO away with the need for a type pull and photographic negative have received considerable attention in the trade in recent years. There are two processes in general use — (1) United States Government Printing Office method (U.S.G.P.O.) and (2) the Erwa method (a German process) — the relative merits of which have been evaluated recently.

In the U.S.G.P.O. method, the film used is ethyl cellulose (0·003 in. thick), and employs a special ink based upon octylene glycol which dries in a few seconds. Using a proof press, both sides of the film are printed in register by first pulling impressions upon a rubber blanket which takes the place of the normal cylinder packing. When the film is printed, the impression on the blanket offsets on to the reverse of the film. The ink film is kept spare to avoid squash and three impressions are taken on the blanket with two on the face of the film. The transparency is then ready for use.

The Erwa process employs a special light-sensitive paper which has been made transparent and sufficiently slow to light to permit handling in diffuse daylight. A pull, taken again on a proof press, is made on this with a thin film of special ink, using hard packing to avoid squash. After impression, the paper is exposed to light, partially developed, and the ink removed to reveal a negative image of the original type. Following fixation, the negative is ready for use, the whole process taking between 10 and 15 min. By suitable modifications to the processing a positive may be obtained by reversal.

A comparison of the results obtainable by the two processes shows that, where surface plates are in use, the Erwa method has the advantage of providing a negative directly, whereas a contact negative would have to be prepared from the U.S.G.P.O. positive in such a case. It is found that although both processes require a precision proof press, the Erwa method does not need a roller film tensioning device. It is important for both the processes to have the type face thoroughly clean and free from grease. A solvent made up of equal parts of trichloroethylene and ethyl acetate is effective with final brushing of the type with an electrotyper's rubber [*PATRA News*, No. 34 (1953)].

Spheroidal graphite cast iron

THE MOND NICKEL CO., WHO ARE manufacturing spheroidal graphite cast irons, have brought out a publication entitled *Spheroidal Graphite Cast Iron (S.G. Iron) Engineering Properties and Applications* to provide the engineer with a concise review of the properties and applications of these materials.

The spheroidal graphite irons are classified according to the structure of the matrix. Ordinary compositions, when cast into sections ranging from $\frac{1}{2}$ to 2 in. (12-50 mm.), will normally give a pearlitic matrix, similar to that found in the ordinary high duty cast iron. This S.G. iron will have a tensile strength of 35-45 t.s.i. (55-71 kg./sq. mm.) with a measurable elongation. Sections below $\frac{1}{2}$ in., and other sections which are quickly cooled, tend to chill as in the case of ordinary cast iron. The greater part of the carbon is combined and a hard white cast iron is produced.

The magnesium-treated irons, both grey and white as cast, can be softened by heating to 900°C. for a few hours followed by slow cooling. This treatment breaks down the combined carbon, giving a matrix of ferrite, with all the carbon as spheroidal graphite. The tensile strength of the iron will be 27-35 t.s.i. (47-55 kg./sq. mm.) with an elongation of 10-25 per cent.

In practice, S.G. iron is generally used either as cast with a predominantly pearlitic matrix, or annealed to the ferritic type. Heavier sections — 2 in. (50 mm.) and more in thickness — which cool more slowly, generally show a structure consisting of a mixture of pearlite and ferrite.

The tensile strength of the S.G. iron as cast is about double that of flake graphite cast iron. On annealing for high ductility and toughness, however, the strength is reduced but is still strikingly higher than that of any other cast iron, including malleable. The yield point is high and markedly superior to malleable cast iron, so that S.G. iron can sustain higher loads without permanent deformation. The elastic modulus is 17,600 kg./sq. mm. and is independent of the matrix condition. The combination of high yield strength, high modulus and good elongation together signify that although S.G. iron has sufficient ductility to permit deformation by twisting and bending, it is nevertheless stiff and rigid, and requires considerable force to cause permanent deformation. The Brinell hardness of S.G. iron is usually some 20-40 points higher than flake graphite iron of similar matrix structure. The tensile/hardness relationship is 0·16 for as cast S.G. iron and 0·19 for annealed material which, therefore, closely approaches that of steel at 0·21 and is vastly different from the flake graphite irons at 0·07-0·09.

S.G. iron is about a dozen times tougher than ordinary cast iron. It is markedly superior to other materials including cast plain carbon steel in endurance limit — a feature of considerable importance for moving parts. The damping capacity of the S.G. iron lies between those of flake-graphite cast iron and steel.

The creep strength of S.G. iron at moderate temperatures is good. Its shock resistance at 900°-950°C. is reported to be two to three times that at normal temperature. S.G. irons are similar to flake graphite irons as regards coefficient of thermal expansion.

The magnetic permeability and electrical conductivity of S.G. are both superior to those of flake graphite iron. The S.G. irons have been employed to produce many types of castings ranging in thickness from $\frac{1}{16}$ to 40 in. and in weight from an ounce to 50 or 60 tons; light section castings are always annealed but for larger castings it is unnecessary. All normal foundry production methods including sand, chill and centrifugal casting can be applied.

The fall in strength and other mechanical properties with increasing section is less in the case of S.G. irons than with flake graphite. There is no special difficulty in producing pressure-tight castings with these irons and intricate castings can be made. S.G. iron, as cast or annealed, has excellent machining qualities and takes a high finish. It may be machined wet or dry and high speeds can be employed for the annealed S.G. iron, which can give long, continuous turnings like those of wrought steel. The iron can be worked to a limited extent in both the hot and cold conditions. The castings may be cold bent, a feature of importance in reclaiming distorted or warped parts.

S.G. iron can be readily welded using normal techniques. The dense close structure of the iron facilitates the surface coating of castings by all known methods. It can be tinned and galvanized. S.G. iron castings may be surface hardened by flame and induction methods.

Service tests show that the heat resistance of S.G. iron is much superior to that of flake graphite iron. It is more resistant to growth and oxidation and has greater stability at elevated temperatures than the conventional types. The corrosion resistance of S.G. iron is approximately the same as for flake graphite irons.

The S.G. iron promises application in many engineering fields.

It is used to secure improved mechanical properties by replacing normal grey cast iron in the field of engineering practice where severe stress and shock may cause failure of the castings, as in agricultural machinery, traction equipment, forging plant and in marine castings. It can be used to reduce section thickness and consequently weight as well as to secure toughness and ductility in castings which are too thick for malleablizing. S.G. iron, because of its castability, can be used for intricate castings which would be very difficult to produce in steel. Another field where it can replace steel is in steel forgings, such as crankshafts.

Most applications for which S.G. iron has been or may be adopted depend on the combination of several properties. A few examples are enumerated here. S.G. iron castings, which combine the corrosion resistance of cast iron with strength approaching that of steel and a measure of ductility, are finding increasing use in heating-pipe systems for tankers with valves and fittings. S.G. iron is also used in water circuits for power stations and paper mills and other industrial plants. Due to its superior mechanical properties, good castability and pressure tightness, S.G. iron can be adopted for many castings subjected to high pressures, such as diesel engine and compressor heads, which cannot be produced economically as steel castings.

The combination of toughness, compressive strength and rigidity plus hardenability may be utilized to produce cutting edges. Good results have already been achieved with domestic cutting or pinking shears. Of special interest is the use of S.G. iron for blanking dies in which the die can be cast accurately to form, and after finishing the cutting edges are hardened by local treatment, such as flame or induction hardening. Some applications of S.G. iron depend on the high degree of finish to which it can be brought. With the modifications of matrix structure made possible by alloying and heat treatment, most types of wear encountered in service may be met. S.G. iron has replaced even bronze for bearings on run-out tables in rolling mills, and in its various types it is worthy of consideration for diesel engine parts and many other machine tool and machinery parts where rubbing friction is involved.

Ready castability and good strength combined with interesting electrical and magnetic properties have led to the use of S.G. iron for switchgear parts and other components of electrical machinery such as motor frames and brush holders. Some of the austenitic S.G. irons are non-magnetic and may with advantage replace the weaker flake graphite non-magnetic irons and even non-ferrous alloys or non-magnetic steels for armature clamps and end rings or other parts where excessive eddy currents would develop in a magnetic material.

Caustic soda with Kreb's mercury cells

THE TRAVANCORE-COCHIN CHEMICALS have recently installed Kreb's mercury type cells for the production of high grade caustic soda to meet the demand of viscose rayon plants that are being installed in the country. The daily production capacity of the plant is 20 tons of caustic soda in the form of 50 per cent lye (750 g./l. of NaOH) which may also be fused into solid and flakes in an auxiliary plant. Under carefully controlled conditions, a lye strength of 850 g./l. of sodium hydroxide can be made. The purity of the product is very high and it has only *c.* 0·2 per cent sodium carbonate and 0·02 per cent sodium chloride in it based on 100 per cent caustic by weight.

The plant consists of 64 cell units connected in series and designed for a load of 10,000-12,000 amp., though they can be operated at higher loads under certain conditions. Each cell unit is independent of the other and any desired cell can be cut off from the series with suitable short circuiting device, thus providing a wide flexibility in the operation of the plant.

Each cell consists of two parts, the electrolyser (primary cell) and the denuder (secondary cell). In the primary cell, brine is electrolysed between graphite anodes dipping in it and mercury over iron cathode. In the secondary cell the amalgam formed undergoes anodic dissolution with graphite grills as cathode.

The primary cell is a long trough with rubber-lined side panels and a grooved iron bottom which facilitates uniform flow of mercury. It is assembled in four sections joined together by bolting, the overall dimensions being length, *c.* 40 ft., width, 18½ in. and depth, 6½ in. The slope of the primary cell along its length is so adjusted that it takes about 50-55 sec. for a small metallic disc placed over the bed of mercury to travel from one end to the other. Attached to the high end of the primary cell is an open mercury inlet box into which mercury is being continuously pumped from the secondary cell. This inlet box has a mercury seal that allows only pure mercury to enter the electrolyser section proper. At this end there is an inlet pipe for the flow of brine into the electrolysing section. At the lower end of the primary cell there is an outlet piece through which the amalgam formed in it flows out. Just before this outlet piece is an overflow pipe through which the depleted brine is being continuously withdrawn and sent back to the brine plant for re-processing. The amalgam outlet piece has a double mercury seal, of which one is fixed and the other adjustable with a sluice valve and normally allows only the amalgam to come out of the primary cell and enter the secondary cell. The top of the electrolyser section proper is covered with a number of stoneware slabs which support 72 graphite anode plates, each plate being suspended by two tight-fitting graphite rods which lead in the current from busbars through copper clamps.

The secondary cell consists of an amalgam inlet box, the denuder and a mercury outlet piece. The denuder is made up of four sections joined together by bolting and measures *c.* 40 ft. × 11 in. × 18 in. The amalgam inlet box has got two mercury seals to prevent impurities and brine from entering denuder section and help their removal by occasional washing. The denuder section is packed with graphite grills which aid decomposition of the amalgam. The secondary cell has covers dipping in water seals which help to maintain the purity of hydrogen formed inside.

The total amount of mercury charged per cell is between 700 and 750 kg. The sodium content of the amalgam as it enters the secondary cell is of the order of 16-20 g./l. of mercury at

10,000 amp. Decomposition of the amalgam is effected practically to completion leaving only a sodium content of *c.* 0·1 g./l.

The working temperature of the cell at full load is *c.* 50°-60°C. The electrolyte is a chemically treated solution of commercial sodium chloride (300-350 g./l.). The depleted brine from the cell containing *c.* 260-270 g./l. sodium chloride is treated with a little hydrochloric acid to decompose the hypochlorite in it, and adjusted to the requisite concentration by passing through a bed of salt.

The current efficiency of the cell is *c.* 95-96 per cent; the energy efficiency is *c.* 55 per cent. The voltage of full load is 3·9-4·3 V. depending on the distance between the electrodes. Power consumption is 3,600 kWh./ton of caustic soda.

The byproducts produced are 670 lb. of chlorine and 18·9 lb. of hydrogen per working day. The two gases are burnt together to produce hydrochloric acid.

Textile Printing Technology — Symposium

IN A SYMPOSIUM ON TEXTILE Printing held by the Society of Dyers & Colourists in Lancashire, Dr. P. Krug described a new reducing agent for use in textile printing. The new material is thiourea dioxide (formamidine-sulphinic acid) marketed under the trade name Manofast. Thiourea dioxide is produced by the oxidation of thiourea with hydrogen peroxide. As such, thiourea dioxide has neither oxidizing nor reducing properties, but with alkalies in the cold or on heating in aqueous solution, molecular rearrangement takes place leading to a compound the structure of which is probably sulphinic and which has reducing properties. This rearrangement is reversible. While alkaline conditions convert thiourea dioxide into an unstable reducing agent, acidic solutions show great stability and develop reducing powers only at elevated temperatures (*c.* 100°C.) in presence of moist saturated steam. Manofast is of principal interest as an acidic reducing agent under conditions in which fibres can be printed with a minimum of degradation and with a greater safety of production. The new technique has so far been developed for the use of vat dyes in the printing of acetate rayon, wool and silk.

In another paper to the symposium, Dr. F. Gunn discussed recent developments in the application of the phthalocyanines in textile printing. One such material in wide use in important printworks in Europe is Phthalogen Brilliant Blue IF3G, which is not a finished phthalocyanine but a phthalocyanine precursor which is converted to the actual phthalocyanine pigment on the fibre by application in the form of a printing paste containing the metal (copper or nickel) and 10-20 per cent of special solvent mixtures. Very bright blues or greenish blues of high fastness to light, weather and boiling are obtained.

The equipment and methods used in the Vigoureux or mélange process for printing wool, rayon staple or polyamide slubbing were described by F. Buxtorf and A. Wiazmitinow. The process consists broadly in printing a wide web of slubbing with diagonal or lateral stripes of colour, a proportion of the slubbing being left unprinted, so that during subsequent gilling and combing a uniform yarn and finally a uniform coloured-and-white fabric is produced.

Recent developments in the application of the azoic dyes in printing were discussed by B. Jomain. "Neutrogenes" (N-substituted anthranilic acids) which have been recently introduced are claimed to give, with suitable stabilizing agents, completely reliable developments in neutral steam. The range to date consists of eleven dyes, many of which can be mixed to give compound shades. They are expected to constitute very effective replacements for the vat reds and scarlets of the indigoid type in textile printing.

Work on the mechanism of the reduction of vat dyes in printing pastes was discussed in a paper by W. J. Marshall and R. H. Peters. The times required for complete reduction of these dyes cover a wide range, but for most dyes they are a substantial proportion of the time allowed for steaming and must be taken into consideration when the printing efficiency of a dye is assessed. Provided the dye is completely reduced the maximum fixation is determined almost wholly by its affinity for the fibre. In another paper, A. G. H. Michie and R. Thornton described a method for the assessment of vat dye prints involving the determination of the amount of dye applied to a cotton fabric by a roller printing technique and the amount fixed at various stages during the after-printing process. Seventeen vat dyes applied by the potassium carbonate-Formosul process were studied, and marked differences in the sensitivity to Formosul concentration in the print paste were found. Provided the required amount of Formosul was added to the print paste and remained on the print up to the time of steaming, all vat dyes could be satisfactorily printed [*Chem. Tr. J.*, **133** (1953), 821].

Stanvac Magazine

THE INAUGURAL ISSUE OF THE *Stanvac Magazine* [**1** (1953), No. **1**] published by Standard Vacuum Oil Co. is a welcome addition to the existing technical periodicals. The journal is devoted to the dissemination of information about the mineral oil industry.

With the establishment of oil refineries in India, petroleum products are bound to play an important role in the development of the country. It is but natural, therefore, that dissemination of information about various phases of the oil industry and the industries dependent on petroleum products should receive adequate attention. The *Stanvac Magazine* is a step in this direction.

The first issue contains interesting technical and popular articles pertaining to the industry. One of the features — News Briefs — brings together recent developments in techniques and processes and other relevant information.

Mineral production during 1952

THE YEAR 1952 RECORDED THE highest production in coal, manganese ore, iron ore and gypsum in India, according to the Geological Survey of India's review of mineral production during 1952. Compared with the production in 1947, the first year of independence, the increase in the output of coal was about 20 per cent; in the case of manganese ore the increase was more than 200 per cent; in the case of gypsum it was more than 700 per cent, while in the case of gold and iron ore the increase was about 47 and 57 per cent respectively.

The total value of coal produced in 1952 was about Rs. 53·6 crores, gold and salt about Rs. 6 crores each, iron ore about Rs. 2·7 crores and copper ore Rs. 1·6 crores. The value of manganese ore exported from India during the year amounted to about Rs. 22 crores and that of mica exported was more than Rs. 9·5 crores. The total pit mouth value of minerals produced in India during 1952 is estimated at Rs. 111 crores against Rs. 107 crores in 1951.

Indian Standards

THE FOLLOWING STANDARDS HAVE been recently issued by the Indian Standards Institution: (1) Standard specification for mild steel and high tensile bars and hard-drawn steel wire for concrete reinforcement; (2) Standard for silica refractories for general purposes; and (3) Revised standard for moderate and high heat duty fireclay refractories.

Standard for salt for human consumption

THE GOVERNMENT OF INDIA FIXED the minimum standard for salt for human consumption in 1953 at 94 per cent sodium chloride content. In practice, however, the percentage enforced was 93·5, as fractions of 0·5 and above over 93·5 were treated as equivalent to 1 and the total as 94. It was intended that the percentage to be enforced for 1954 should be 95 per cent. After a careful consideration of the representations that have been made by the salt manufacturers and their associations regarding the hardships caused to the manufacturers, the Government of India have decided to maintain the minimum standard for salt for human consumption in 1954 at 94 per cent sodium chloride content *without* any allowance for fractions between 93·5 and 94. Government's aim is to attain the standard of 96 per cent sodium chloride content for salt for human consumption as early as possible.

Unesco Advisory Committee on Scientific Research

THE EXECUTIVE BOARD OF Unesco has approved the establishment of an International Advisory Committee on Scientific Research. The task of the committee will be to assist Unesco in carrying out and developing its scientific programme, and in promoting international co-operation between national councils and centres of research. The committee will be composed of 15 members, of whom 12, of different nationalities, will represent national research organizations. The other three members will be representatives of the International Council of Scientific Unions, the Council for International Organizations of Medical Scienes, and the Union of International Engineering Organizations. The first annual meeting of the committee will take place as early as possible in 1954.

Announcements

National Institute of Sciences Research Fellowships — The National Institute has announced the award of four Senior and seven Junior Research Fellowships during 1954-55. The Fellowships are tenable at any university or institute in India. The value of the Senior and Junior Fellowships would be Rs. 500 and Rs. 350 p.m. respectively. In addition a sum of Rs. 1,000 per annum would be made available in each case for approved expenses. Candidates for Senior Fellowships should not be above 45 years in age and should produce evidence of their ability to carry on research work independently, and should, therefore, be prepared to outline a proposed scheme of research, and to state the lines on which they would desire to work. The minimum qualifications for a Junior Fellowship are a Master's degree and some research experience. The age is not to exceed 35 years.

Seven copies of application on prescribed form obtainable from the Secretary, National Institute of Sciences of India, Mathura Road, New Delhi 1, should reach him not later than 3 March 1954. All requests for forms of applications should be accompanied by a large addressed and stamped (as. -/6/-) envelope.

Imperial Chemical Industries (India) Research Fellowships — The Imperial Chemical Industries will award four Research Fellowships tenable ordinarily for two years in Physics (including Mathematics), Chemistry or Biology (Botany and Zoology) at any university or institution in India. The Fellowship is of the value of Rs. 400 p.m. In addition Rs. 600 a year is available for approved expenses. The minimum qualifications required are a Master's degree and some research experience. The age is not to exceed 35 years. Seven copies of application on prescribed form obtainable from the Secretary, National Institute of Sciences of India, Mathura Road, New Delhi 1, should reach him not later than 3 March 1954. All requests for forms of applications should be accompanied by a large addressed and stamped (as. -/6/-) envelope.

The Third British Plastics Exhibition will be held at Olympia, London, from 1 to 11 June 1955. A convention will be held concurrently with the exhibition which will represent all sections of the industry, including raw material suppliers; manufacturers of moulding powders, synthetic resins, plastics sheeting; the moulders and fabricators; manufacturers using laminated plastics and reinforced plastics; the manufacturers of moulding plant and other essential equipment.

Dr. E. D. Adrian, F.R.S., has been elected president of the British Association for 1954. Dr. Adrian was awarded the Nobel Prize for Medicine in 1932. He has been the President of the Royal Society since 1950.

A temporary Foundrymen's Training Centre to run short industrial courses in modern foundry practice is being opened in March next at the Indian Institute of Technology, Kharagpur. The Ministry of Commerce and Industry, Government of India, the U.S. Technical Co-operation Administration in India, the Institute of Indian Foundrymen, Calcutta, and the Indian Institute of Technology, Kharagpur, are co-operating in organizing the course. The Indian Institute of Technology, Kharagpur, is giving all the necessary facilities to the Centre while the U.S. Technical Co-operation Administration are providing some of the equipment.

Twenty trainees could be accommodated in the Centre every three months and five courses covering a period of 15 months have been planned. Admission to the Centre is open primarily to foundrymen sponsored by foundries in India. It may also be possible to consider for admission trainees from Government technical institutions and other Asian countries, and also Engineering or Metallurgical Graduates and apprentices wishing to undergo training in foundry practice.

Those interested may contact the Registrar, the Indian Institute of Technology, Kharagpur, for particulars and application forms.

National Institute of Sciences — The following office-bearers have been elected to the Council of the National Institute of Sciences for the year 1954: *President*, Dr. K. S. Krishnan; *Vice-Presidents*, Prof. S. K. Banerji and Dr. B. Mukerji; *Treasurer*, Prof. D. S. Kothari; *Foreign Secretary*, Prof. P. C. Mahalanobis; *Secretaries*, Prof. R. C. Majumdar and Dr. B. P. Pal.

INSTRUMENTS AND APPLIANCES

TESTING STANDARD SIEVES

The micrometer projector developed by Andhra Scientific Co. Ltd., Masulipatam, can be used to project the different portions of a sieve on a screen for general inspection as well as for measuring the aperture widths and wire diameters.

The essential components of the apparatus are: (1) an illuminating unit, (2) a sieve holder, (3) a projection lens system and a microscope with micrometer eyepiece (which are interchangeable) and (4) a linear scale accurate to 0·01 mm.

When clamped in position, the projection lens or the microscope receives a collimated beam of light reflected vertically upwards by a mirror fitted below the base.

In the modified form (FIG. 1) now being fabricated, a micrometer unit is fitted to a swan-neck bracket whose height above the sieve holder is adjustable. The micrometer eyepiece of the microscope is replaced by a Ramsden eyepiece. The micrometer unit with the microscope fitted in position gives readings accurate to 1 μ directly. The microscope can be rotated through 90° over a precision cone bearing for measuring aperture widths across warp and weft at one setting. Another reported advantage is that the microscope can be replaced by the projection unit for visual inspection of the sieve mesh on the screen.

FIG. 1 — MICROMETER PROJECTOR FOR TESTING STANDARD SIEVES

GRATING SPECTROGRAPH

The new Bausch and Lomb grating spectrograph (FIG. 2) employs certified precision grating which makes for fine line quality. The instrument can be employed for examination of non-ferrous metals, alloys, carbon steels and unalloyed grey irons, inorganic chemicals, lubricants, dyestuffs, pharmaceutical products and biological materials. The spectrograph has concave 40 × 80 mm. grating, fixed type slits, 10 and 50 μ widths, Hartmann slide with seven 2 mm. step apertures, quartz stigmatizing

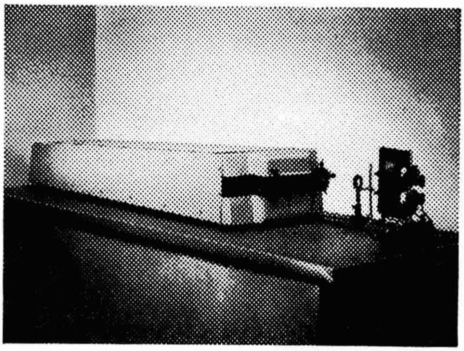

FIG. 2 — GRATING SPECTROGRAPH

TABLE 1

	MODEL No. 10	MODEL No. 11
Grating grooves per mm.	415	450
Spectrum range	2250-6250A (first order)	3700-7400A (first order) 1850-3700A (second order)
Dispersion	16A/mm. (first order)	15A/mm. (first order) 7·5A/mm. (second order)
Resolving power	32000	35000

lens, and takes 10 in. length of 35 mm. film. Short exposures give high sensitivity for trace elements.

Two gratings — models 10 and 11 (specifications given in TABLE 1) — are available for research institutions and industrial laboratories.

Specimen spectrogram and further information on the apparatus are available from Martin & Harris Ltd. (Scientific Department), Savoy Chambers, Wallace Street, Bombay 1.

E.V.T. VISCOMETER

The E.V.T. viscometer (FIG. 3) for measuring directly the equiviscous temperature of road tars, pitches, bitumens, etc., has been developed by A. Gallenkamp & Co. Ltd., London, in co-operation with the South-Eastern Gas Board. The E.V.T. is defined as the temperature at which a material has a viscosity of 50 sec. Viscosities can be determined to an accuracy of ±0·2°C. with a sample of approximately 7·5 cc.

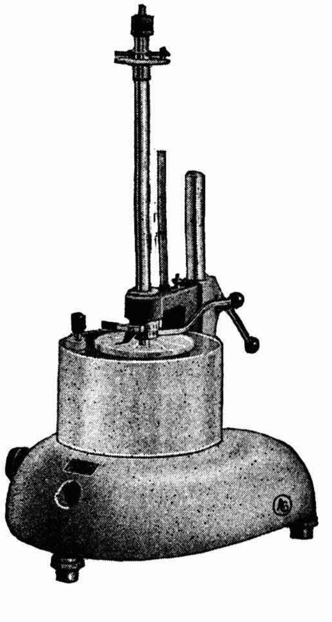

FIG. 3 — E.V.T. VISCOMETER

The determination is independent of the temperature susceptibility of the tar and one apparatus covers the whole range of materials likely to be tested.

The actual viscosity measurement, depending on the damping of the oscillation of suspended rotating cylinder, is almost instantaneous.

ANALYSIS AIDS

Chemical analysis of plating solutions can be performed with accuracy and speed by the use of an electropolarizer and a portable galvanometer, according to Patwin Instruments Co. and the General Electric Co., U.S.A., respective developers of the equipment. The Patwin model polarizer employs the polarographic method of analysis which saves half the time formerly consumed by the chemical method. Most plating solutions including copper cyanide, zinc cyanide, cadmium, brass and nickel can be analysed with the equipment.

The electropolarizer eliminates the need for maintaining and standardizing several solutions.

GE's galvanometer used with the polarizer measures the low values of current or voltage. The high sensitivity of the galvanometer is made possible by alnico magnets, which provide a field of more than twice the strength obtainable with chrome steel magnets.

ORGANIC CHEMICALS

Ten new chemicals have just been added to the list of organic research chemicals produced by Distillation Products Industries Division of Eastman Kodak Co. The list includes acrylamide; 4-amino-2, 6-dimethylpyrimidine; 2, 5-dimethylfuran; 5, 5-dimethyl hydantoin; 2, 5-diphenyloxazole; formamide; malonic acid; phthaloyl chloride; γ-valerolactone; and m-xylene.

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Progress Reports

BOSE RESEARCH INSTITUTE

THE THIRTY-SIXTH ANNIVERSARY MEETING OF THE Bose Institute was held on 30 November 1953, when Dr. N. K. Bose, Director, River Research Institute, delivered the 16th Acharya Jagadish Chandra Bose Memorial Lecture on " The Role of Silt and Sand in Multipurpose River Valley Projects ". In the course of his address Dr. Bose said that sand and silt, which form fertile lands providing means of subsistence for the humanity, are derived from erosion of soil in the upper region. Man has long endeavoured to strike, with limited success, a balance between the opposing activities of soil erosion and land formations, and it has only recently been realized that great benefit expected out of some of the multipurpose river valley projects is going to be short-lived owing to the silt problem. After discussing the various evil effects of sand and silt, and the efforts made by man to overcome them, the lecturer described the various investigations carried out so far to discover the fundamental principles of " soil and sand movement " and concluded with the remarks that though by research and experimentation we might be able to reduce the evil effects of sedimentation to a considerable extent, the only sure way they can be completely brought under control is by developing sound soil conservation practices among the people of the upper valley.

Dr. D. M. Bose, Director, in presenting his report on the working of the Bose Institute for the past year, said that completion of many projects commenced during the past few years was being delayed for want of funds. The Institute has, on invitation from the National Institute of Sciences of India, submitted a five-year scheme of fundamental investigations on the mutagenic action of different kinds of radiation on plants. Preliminary investigations started during last year have disclosed that the beta radiation from radioactive phosphorus, which is selectively adsorbed in plant nuclei, is a very convenient tool for inducing mutation in plants. By this method new types of effects have been obtained in certain varieties of jute plants in addition to those obtained after irradiation trials with X-rays.

At the experimental plant pathological laboratory, Mayapuri, Darjeeling, work has begun on the breeding of new hybrids of potatoes resistant to several virus and fungal infestations using locally available potatoes as one of the parent and imported resistant strains as the other. The Institute has reported the presence of potato wart disease, hitherto not known to occur in India, in one of the farm's plots sown with an imported variety of potatoes known as Furore.

Mayapuri is also being developed as a centre for cosmic ray research. On a request from the Council of Scientific & Industrial Research, a scheme with detailed plans and estimates for erection of laboratory and workshop for cosmic ray research has been submitted. The Institute has received a new grant from the Board of Research on Atomic Energy for investigations on the use of radioactive isotopes of carbon and phosphorus for investigations on photosynthesis and on mutagenic action of beta rays of phosphorus.

The microbiology department has received a grant from the C.S.I.R. on the production of antibiotics isolated from *Streptomyces* spp. which have some remarkable bactericidal properties.

THE BRITISH NON-FERROUS METALS RESEARCH ASSOCIATION — THIRTY-THIRD ANNUAL REPORT, 1952

SATISFACTORY SPECIMENS OF BICRYSTALS HAVE BEEN made for studying the mechanical properties of the grain boundaries between them, and a technique has been developed for their examination.

The study of the mechanical properties of titanium alloys at elevated temperatures was continued, and certain promising binary alloys have been selected as the basis for the preparation of ternary alloys; some of the ternary alloys developed exhibited high resistance to creep.

Employing automatic gauge control and strip rolling methods, it has been possible to eliminate variations in gauge of rolled strip resulting from the speed variations when the mill is started up or shut down.

A simple inexpensive instrument has been designed for the inspection of tungsten carbide wire-drawing dies. Equipment has been developed for studying the deformation of steel at temperatures and strain rates attained in hot forging.

There has been further development of the process for hot-dip aluminium coating of steel using a pilot plant capable of taking strip or wire. Data have been obtained on the viscosity of molten metals. Electrodeposition and resistance to corrosion of zinc-iron alloys of a wide range of compositions are being investigated.

Studies on grain refinement of cast copper alloys have revealed that in some of these materials grain refinement does not offer the benefits which it confers on aluminium casting alloys.

Hot rolling behaviour of tin-bronzes has confirmed that small additions of certain other elements considerably improved the working behaviour of the alloys. Investigation of hot stamping brasses, in which cracking occasionally occurs associated with a coarse grain, has continued, and the reasons for the formation of the large crystals have been elucidated. In the light of the information gained, it is now possible to produce extruded forging stock which does not develop large crystals on reheating.

Studies on the extraction of copper and elementary sulphur from copper ores have shown that copper and sulphur can be separated from the sulphide by electrolysis in fused salt baths. Copper and sulphur can be recovered with high efficiency from sulphidic copper concentrates by an acid leaching process.

Studies on extrusion of satisfactory lead pipes over bridge cores have confirmed that clean billets are essential if satisfactory pressure welds are to be made in such pipes.

The results of the earlier studies on the adhesion of electrodeposits of aluminium using the sodium-zincate replacement method have been successfully applied to a commercial process in which the initial zinc deposit is formed by electrodeposition. This process involves heat treatment of the plated material to ensure good adhesion, but has been modified to improve the initial adhesion of the zinc deposit and the inconvenient heat treatment can be avoided. It also appears that it will be possible to use bright instead of dull nickel deposits, so that a further substantial advantage will accrue from the elimination of a polishing operation.

THE ALUMINIUM DEVELOPMENT ASSOCIATION — ANNUAL REPORT, 1952

THE RESEARCH COMMITTEE DEVOTED CONSIDERABLE attention to problems encountered in the jointing of aluminium electrical conductors, particularly stranded cables. A review was also made of the information on hot dipped aluminium coatings for the protection of steel. The general question of soldering of aluminium was also reviewed, together with data on the properties of soldered joints.

Large riveted joints — The possibility of driving large rivets in the high strength copper-bearing alloys has received consideration, and a programme of work in conjunction with an aircraft builder has already given promising test results. Experimental work was also begun on the driving of freshly quenched heat treatable alloy rivets as an alternative to hot driving.

A study is being made of variations in the design of counter-sunk rivet points with a view to evolving a shape giving optimum ease of drive and adequate strength. Attention has also been devoted to the development of improved driving equipment for larger rivets.

Corrosion — The work of the Corrosion Subcommittee has continued both on fundamental metallurgical questions involving corrosion and on *ad hoc* matters arising from other aspects of the Association's work. Further reports have been received on exposure tests involving such diverse substances as peat, road wash and mine waters. Progress was also made with the tests on the behaviour of aluminium in contact with timber in collaboration with the Forest Products Research Laboratory. The corrosion tests on riveted joints including those made with steel rivets were continued and observations were also made on riveted structures already in existence. Experience with the corrosion resistance of fusion welded joints was the subject of a review which revealed the need for further investigations, particularly on welds made by the newer processes.

Finishes — Following publication of details relating to the Vogt process of electroplating on aluminium which marks the best industrial technique so far for plating aluminium, the Finishes Subcommittee recommended that a programme of exposure tests of chromium-plated aluminium should be undertaken to obtain data on the service life of various alloys electroplated by the available processes. The progress of further experiments with hard anodic coatings was closely followed and the subcommittee received a report on test results obtained.

Marine research — In the marine field there has been the experimental work in connection with superstructures on large ships, continuation of the work undertaken jointly with the British Shipbuilding Research Association on channels and bulb angles and investigations on the design of bulkheads; a programme of fire tests culminating with the " burn out " of a test cabin was outlined in a paper before the Institution of Naval Architects; a full-scale welding trial organized in conjunction with the British Welding Research Association yielded valuable information in the construction of an aluminium alloy deckhouse for a launch.

The Association's development work is described under the headings of Structural Engineering, Marine, Building, Road and Rail Transport, Mining Equipment, Electrical Engineering, Castings and Standards. Considerable work has been undertaken on investigating strut instability with particular reference to BS 1161 and there have also been some interesting enquiries in connection with roof structures and cranes.

INDIAN PATENTS — *Continued from page* 100

50131. Method of producing high gloss surfaces on aluminium and aluminium-base alloys: *The objects after previous degreasing are treated with solutions which contain ions of hydrogen, ammonium, nitrate and fluorine* — VEREINIGTE ALUMINIUM-WERKE AKTIENGESELLSCHAFT

47424. Herbicidal compositions: *Containing in admixture with another herbicidally active compound, a herbicidal aryl alkyl urea compound* — E. I. DU PONT DE NEMOURS & CO.

47794. Process and apparatus for the de-dusting and classification of granular materials: *A distributed stream of granular material is contacted with a stream of gas, counter current to the granular material* — RUHRCHEMIE AKTIENGESELLSCHAFT

INDIAN PATENTS

[A few of the Patent Applications notified as accepted in the *Gazette of India*, Part III, Section 2, for December 1953, are listed below.]

Chemicals, plastics, rubber, paints and allied products

47288. Anthelmintic compounds: *Reacting hexylresorcinol with a compound of formula RCOX where R is aliphatic, cyclic or phosphoric acid radical and X is halide or other anionic acid group* — Strong Cobb & Co. Inc.

48275. Waterproofing of boards used for soundproofing purposes: *Treating sound-proof boards with wetting agent, dipping the boards in latex compounded with stabilizer, zinc oxide, sulphur, accelerator and antioxidant, and vulcanizing the dipped boards* — Council of Scientific & Industrial Research

49011. A method for the production of p-aminosalicylic acid phenylester: *Reacting 4-acetamino-2-acetoxybenzoic acid with an inorganic acid chloride, esterifying with phenol and splitting off the acetyl group by hydrolysis or alcoholysis* — Abildgaard-Elling

49043. Improved process and apparatus for the manufacture of porous and homogeneous plastics having a basis of polyurethane: *Wherein an activator, namely one or more cross-linking agents and/or reaction accelerators, is injected into the reaction mixture undergoing polyaddition* — Farbenfabriken Bayer

49698. Production of N-aryl-N′-aminoalkyl-ureas: *By reacting a reactive functional derivative of 2:6-dimethyl- or 2:4:6-trimethyl-carbanilic acid with a diaminoalkane* — J. R. Geigy A.-G.

50137. Manufacture and use of polymerizable compounds: *Wherein (a) a condensation product of formaldehyde with a compound of the amino-triazine or urea group, (b) a nitrile or amide of an unsaturated polymerizable acid and (c) a compound containing at least one active hydrogen atom are reacted with one another such that the final product contains one double bond* — Ciba Ltd.

50183. Copolymerizable compositions: *A mixture of a polyglycidal ester of a polycarboxylic acid, an alpha, beta unsaturated acid and a styrene* — American Cyanamid Co.

48538. A new cyclopentanopolyhydrophenanthrene derivative and methods for its production: *A cyclopentanopolyhydrophenanthrene having a free hydroxyl group is reacted with a derivative of β-phenyl propionic acid* — Organon Laboratories Ltd.

48770. Manufacture of 3 : 5-dioxo-pyrazolidine derivative: *Di-substituted malonyl chloride, (Br) (Butyl)* $C(COCl)_2$, *is reacted with hydrazobenzene* — Sudhir Lal Mukherjee & Albert David Ltd.

48771. Manufacture of 3″: 5-dioxo-pyrazolidine derivatives: *Di-substituted malonyl halide, viz. (Hal)* (R_1) $C(COR'')_2$ *where Hal means halogen, R″ means chlorine or bromine and* R_1 *means lower alkyl, is reacted with hydrazobenzene* — Sudhir Lal Mukherjee & Albert David Ltd.

49580 and 49581. A process for the manufacture of 3″: 5-dioxo-pyrazolidine derivatives: *3, 5-Dioxo-1, 2-diphenyl-4-alkyl-4-halogeno pyrazolidines are reacted with hydrazobenzene, phenyl hydrazine or hydrazine hydrate.*

3, 5-Dioxo-1, 2-diphenyl-4, -n-butyl-4-bromo-pyrazolidine is reacted with hydrazobenzene, phenyl hydrazine or hydrazine hydrate — Sudhir Lal Mukherjee & Albert David Ltd.

49019. Process for the manufacture of a new ether: *Reacting N-methyl-trimethyl-colchinic acid with methyl ether forming agent, separating individual isomers and isolating N-methyl-desacetyl-iso colchicine* — Ciba Ltd.

49754. Manufacture of optically active 3-hydroxy-N-methyl-morphinanes: *Splitting racemic 1-(p-methoxybenzyl)-2-methyl-1, 2, 3, 4, 5, 6, 7, 8-octahydroisoquinoline and cyclizing the optically active compound* — F. Hoffmann-La Roche & Co.

47398 and 47399. Preparation of acylamino diol compounds: *Oxidizing a 2-aliphatic acylamino-1-(4-hydrocarboxylmercaptophenyl)-1, 3-propane diol by treating with a per-compound.*

Reducing alpha-aliphatic-carboxylic acylamino-beta-hydroxy-4-hydrocarboxylmercaptopropiophenone with an oxidizable aluminium alkoxide — Sterling Drug Inc.

47820. Stabilized sodium aluminate: *Comprising a mixture of sodium aluminate containing 1·2-1·4 moles of* Na_2O *per mole of* Al_2O_3 *and 0·01-0·1 per cent of iron oxide as impurity, and mannitol or sorbitol* — I.C.I. Ltd.

48424. Preparation of lower titanium chlorides: *In electrolytic cell having titanium anode, cathode and molten electrolyte of halide salts of alkali, alkaline earth metal or magnesium* — Titan Co. Inc.

48791. Process for the production of oxygen-containing hydrocarbon compounds: *Reacting carbon monoxide and hydrogen at temperatures above 400°C. in the presence of catalysts free from compounds of metals of the iron group and containing compounds of metals of the 2nd to 7th group, thereafter causing the participant to react in the presence of metals of the iron group* — Metallgesellschaft Aktiengesellschaft

47442. Sugarcane wax: *Heating crude wax with hydroxylic solvent and absorbent materials, filtering and crystallizing wax, again filtering and melting filter cake to separate solvent from refined wax* — Wiggins & Davison

47538. Production of meso-substituted aza-acridines: *Comprises heating an aza-acridine with primary amine* — Ward Blenkinsop & Co. Ltd.

49637. Process for the production of aldehydes and aldehyde derivatives from dicyclopentadiene: *Dicyclopentadiene is partially hydrogenated below 100°C. and the product subjected to the oxo-synthesis reaction for the addition of CO and hydrogen* — Ruhrchemie Aktiengesellschaft

50064. Malonic acid derivatives and process for the manufacture thereof: *Coumarin derivatives are produced by condensing an alkali derivative of dialkyl (1′-p-chlorophenyl-alkyl) malonate with acetyl salicylic acid halide, and heating the product with a cyclizing and hydrolysing agent* — F. Hoffmann-La Roche & Co. Aktiengesellschaft

50249. Process for the manufacture of substituted tropic acid N-(γ-picolyl)-amides: *Reacting tropic acid chloride, which may be acetylated with methyl-, ethyl- or allyl (γ-picolyl)-amine* — F. Hoffmann-La Roche & Co.

47575. Process for the manufacture of new pyridazones: *Taking 2-aryl-pyridazone (3) compounds which in the 6-position carry a substituent convertible into an amino group and converting said substituent into amino group* — Ciba Ltd.

47875. Improvements in or relating to the manufacture of interpolymers of styrene with polyhydric alcohol esters of unsaturated fatty acids: *Heating styrene or nuclear alkyl or halogen substituted styrene with polyhydric alcohol esters of one or more fatty acids* — Lewis Berger & Sons Ltd.

49888. Process for preparing d-N-N-diethyl-N′ (2-tetrahydro-1, 2, 3, 4-naphthyl) glycin amide and products obtained: *d, 1,-N, N-diethyl-N′ (2-tetrahydro, 1, 2, 3, 4-naphthyl) glycin amide is resolved into its optical isomers by means of salification with optically active acid and fractional crystallization from solvent* — Farmaceutici Italia S.A.

Chemical processes, engineering and equipment

48333. A centrifugal pump: *Nozzle or diffuser surrounding entire or part of periphery of impeller acting as injector pump extracting air* — Volland

49768. A process and apparatus for concentrating hydrogen peroxide: *Obtaining equilibrium between vapour and liquid in tubes* — Laporte Chemicals Ltd.

47589. Improvements in distillation columns: *Superposed perforated plate structures are provided and each structure has a seal trough* — The A. P. V. Co. Ltd.

49433. Method of recovering oils from oleaginous meats of nuts, beans, seeds and the like: *Pressing the meat to expel the juice, centrifuging the juice before fermentation to yield an oil-containing cream, subjecting the cream to enzymic action without acid formation and centrifuging it to separate the oil* — Coconut Processes Inc.

50297. Process of obtaining water-white oil from fresh coconut meat: *Pressing the coconut meat, cooling the cream obtained, agitating and heating the cream and then separating the oil from the cream and finally filtering and pasteurizing the oil under vacuum* — Floro

48876. A new or improved electrolytic cell of the diaphragm type: *Comprising in combination with electrolytic bath an anode, at least two cathodes and porous electrically non-conductive diaphragms in the bath to segregate the solubilization cathode from other cathodes and the anode from each of the cathodes* — Titan Co. Inc.

49632. Apparatus for the treatment of finely divided fluidizable solid material: *Comprising a retort having heat conducting side-walls, a horizontal porous diaphragm dividing the retort into a gas chamber and a fluidizing chamber* — Aluminium Laboratories Ltd.

50258. Apparatus for extraction of sulphur from sulphur ores: *Heating the ore with a concentrated solution of calcium chloride or magnesium chloride between 118° and 150°C. and filtering the molten sulphur at 128°-138°C. by suction or by application of pressure* — Elliott

50300. Improvements relating to lead acid accumulators: *Comprising calcium from 0·03 to 0·01 per cent, tin from 1 to 2 per cent, aluminium from 0·01 to 0·1 per cent and balance lead* — The Chloride Electrical Storage Co. Ltd.

50301. Improvements relating to the grids of lead acid electric accumulators: *Containing 6-12 per cent antimony, 0·3-3·0 per cent tin and balance lead* — The Chloride Electrical Storage Co. Ltd.

Physics — general

49831. Magnetic cores: *Core is made up of at least two layers of ferromagnetic ferrite material, at least one of the layers consists of a material having a temperature coefficient of permeability which is different from that of the material of at least one of the other layers* — N. V. Philips' Gloeilampenfabrieken

49936. Low pressure mercury vapour discharge lamps: *Coated on the lamp wall with a luminescent material made from red luminescent magnesium arsenate in which the ratio between magnesia and arsenic pentoxide lies between 4: 1 and 10: 1 and activated with manganese between* 1×10^{-3} *and* 10×10^{-3} *atom per magnesium atom and with another luminescent layer on said luminescent material* — N. V. Philips' Gloeilampenfabrieken

49643. Improvements in or relating to movable equipment for electromagnetically controlled devices having a shuttle forming a magnetic core adapted for reciprocating movement: *Having a shuttle forming a magnetic core comprising an elongated element the centre portion of which forms a portion of larger diameter which in turn supports a tubular element having bundles of laminations* — Reutter

Food and kindred products

47505. Improvements in baking of food products in an oven: *Projecting the gaseous heating medium in spaced jets towards the food product and circulating said medium in a closed circuit at a volume rate of flow per minute which is a substantial multiple of the total volume of the medium in the circuit* — Spooner Food Machinery Engineering Co. Ltd.

Drugs and pharmaceuticals

47366. Method of preparing solutions of endocrine glands and other animal cellular tissues: *Dissolving the tissues and forming a colloidal suspension by treatment with an aqueous alkali* *containing aliphatic sulphate or sulphonate as emulsifying agent* — FITZGERALD

48585. Condensation products of hydrocarpic acids: *The acid chlorides of hydrocarpus oil are reacted with 4, 4: -diamino-diphenyl sulphone* — SMITH, STANISTREET & CO. LTD.

49477. Manufacture of a vitamin active powder: *Forming an emulsion containing vitamin active material, water, gelatin, and/or gum acacia, and sugar, converting the emulsion to droplets and collecting the droplets in a mass of starchy powder* — HOFFMANN-LA ROCHE & CO. AKTIENGESELLSCHAFT

49048. Manufacture of isonicotinic acid derivatives: *Iso-nicotinyl halide or hydro-halide thereof is reacted with a hydrocarbon-substituted hydrazine of the formula* R_1-NH-NR_2R_3 *or alternatively a substituted iso-nicotinyl hydrazine of the formula iso-nicotinyl*-NH-R_2R_3 *is treated with an alkali metal dissolved in lower alkanol and subsequently with an alkyl, aralkyl or alkenyl halide* — F. HOFFMANN-LA ROCHE & CO. AKTIENGESELLSCHAFT

49129. Improvements in the production of penicillin: *Penicillin producing mould is fermented under deep culture conditions in a cornsteep liquor medium containing a thiosulphate and a penicillin precursor* — GLAXO LABORATORIES LTD.

48400 and 50093. Apparatus for the administration of analgesics and anaesthetics: *Comprising container for analgesic an open-ended, tube, a duct for delivering analgesic from container to tube and means located within the tube for accelerating the rate of flow therein.*

Comprising a gas capacity which forms part of or communicates with the section of conduit that is downstream of analgesic-conveying duct outlet — NATIONAL RESEARCH DEVELOPMENT CORPORATION

48408. Manufacture of new aminobenzenesulphonamides: *A compound of the formula* p-R-C_6H_4-SO_2-X, *X and R standing for halogen and amino group respectively, is reacted with a substituted halogenated pyridazine and, if desired, the resulting product is converted into its salts* — CIBA LTD.

Metals and metal products

50304. Desulphurization and desiliconizing of cast iron: *Treating cast iron with a slag having substances for desulphurizing and a quantity of oxides to effect oxidation of silicon* — SOCIETE D'ELECTRO-CHIMIE, D'ELECTRIC-METALLURGIE ET DES ACIERIES ELECTRIQUES D'UGINE

49444. Centrifugal casting of metals: *Molten metal from a tundish delivered into a tubular element while the element is rotating and then discharged into a mould* — ALLIED IRONFOUNDERS LTD.

49559. Process for producing pulverulent metallic titanium: *Reacting Al-Ti alloy with a reagent reacting differently with the alloy metal* — SOCIETE D'ELECTRO-CHIMIE, D'ELECTRO-METALLURGIE ET DES ACIERIES ELECTRIQUES D'UGINE

49571. Melting and casting of high melting point metals or alloys: *Arc melting and casting metals and alloys under an inert atmosphere in a cooled crucible communicating through a centrally disposed orifice in its base with a separable mould* — I.C.I. LTD.

50233. Process for reducing low grade ores: *Effecting contact between melted ore and molten metallic reducing bath, the mass of reducing bath being much greater than theoretically necessary* — SOCIETE D'ELECTRO-CHIMIE, D'ELECTRO-METALLURGIE ET DES ACIERIES ELECTRIQUES D'UGINE

49823. Apparatus for extruding metal: *Comprising a hydraulic apparatus including a ram and a cylinder, a die with an operative face clear of obstruction, means for maintaining the billet in operative position, a pressure fluid accumulator for storing fluid under a pre-determined pressure* — CRITTALL-LUXFER LTD. & FIELDING & PLATT LTD.

49828. Blowing installation for the production of steel: *Oxygen is blown into molten metal by means of a lance which is bent so as to be moved into and out of the converter on a curved path* — DEMAG AKTIENGESELLSCHAFT

Glass and ceramics

49660. Continuous production of glass filaments or fibres: *A stirrer is located between the container and the feeding chamber to stir the molten glass* — OWENS-CORNING FIBERGLAS CORPORATION

Leather and leather products

48568. Apparatus suitable for use in compacting hides: *Having a movable head member which causes the compacting means to work and the anvils to occupy an operative relation to each other* — THE BRITISH UNITED SHOE MACHINERY CO. LTD.

Miscellaneous

48753. Method for the concentration of sea water for the extraction of salts: *Several concentrating steps submitting sea water to pulverization in the air obtained by mechanical or pneumatic means to provide evaporation in spatial volume* — VOUVARD

49891. A device for making sugar floss or wool: *Comprising a cage having slots formed in its walls, mounted on a revolving platform and means for heating the cage* — SUNDARAM

49400. Machinery for defibring husks and particularly coconut husks: *Arranging a set of rotary scrappers and endless gripping conveyors holding coconut husks in a manner that the scrappers cut with gripping conveyors to defibre husk* — FLORO

47229. Compositions for use in killing weeds: *Comprising weed-killing substances, and adhesive and wetting and/or dispersing and/or suspending agent* — HALLCHURCH

46875. Manufacture of refractory and heat-insulating compositions: *Comprising a fired mass containing paddy husk ash bound with lime* — BURN & CO. LTD. & SUBRAMANIAN IYER

47359. Liquid soap-making pot: *Having four parts, an outer compartment for liquid soap, an inner compartment for liquefying soap cakes, a water supply arrangement and a delivery unit* — BARVE

47466. Method and apparatus for stabilizing the flames of pre-mixing burners: *Jet divided into partial jets whose discharge axes are at an angle with respect to each other* — N. V. DE BATAASFSCHE PETROLEUM MAATSCHAPPIJ

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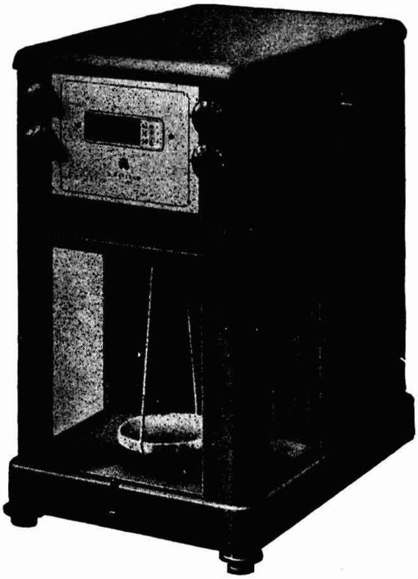

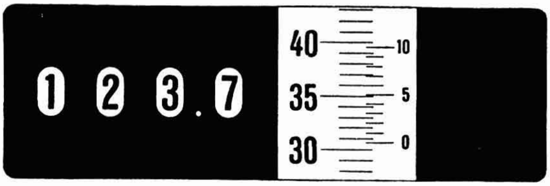

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Diffraction of Light by Several Ultrasonic Beams: Intensity of the Combination Lines

S. PARTHASARATHY, M. PANCHOLY & HARKRISHAN SINGH
National Physical Laboratory of India, New Delhi

The relation established in our previous studies between the intensities of combination lines in a superposed diffraction pattern produced by the passage of light through two ultrasonic beams has been found to hold good when three ultrasonic beams were used in the same medium to produce a complex diffraction pattern. The intensities of the satellite lines show that the effects reported for two ultrasonic beams generally hold good for several sound beams.

IT is now well known that the Debye and Sears diffraction pattern produced by oscillations of the transducer simultaneously at two frequencies consists of lines corresponding to the two frequencies as also combination lines corresponding to the sum and difference frequencies[1-3]. Aggarwal and Parthasarathy[4] have shown that the ratio of intensities of a pair of side bands is given by R^2 where

$$R = \frac{\sin\left[\frac{\pi l\lambda}{2}\left(\frac{1}{\lambda_1^*}+\frac{1}{\lambda_2^*}\right)^2\right]}{\sin\left[\frac{\pi l\lambda}{2}\left(\frac{1}{\lambda_1^*}-\frac{1}{\lambda_2^*}\right)^2\right]}\cdot\frac{\left(\frac{1}{\lambda_1^*}-\frac{1}{\lambda_2^*}\right)^2}{\left(\frac{1}{\lambda_1^*}+\frac{1}{\lambda_2^*}\right)^2}$$

λ being the wavelength of the light used, λ_1^* and λ_2^* the wavelengths of the two sound waves and l the width of the sound beams.

In an earlier paper[5], it has been shown that there is a good qualitative agreement between the theoretical and experimental values of the relative intensities of the combination lines and that for every pair of these side bands the inner line is stronger than the corresponding outer line. The present investigation was undertaken with a view to finding out if these results hold good generally for any number of sound beams and, therefore, diffraction produced jointly by three sound beams was studied.

Experimental procedure

The experimental set up used was the usual diffraction arrangement developed by Debye and Sears and Lucas and Biquard and is shown in Fig. 1. Three piezoelectric quartz crystals were placed in a special holder inside the large parallel plate cemented glass cell containing xylol. Each of these generators, consisting of independent variable oscillator, power amplifier and matching network, were used to excite each crystal at its resonance frequency. The diffraction pattern was first taken on a ground glass viewing screen and after adjustment was recorded photographically. A high pressure mercury vapour lamp served as a source of light and a monochromatic filter was used to give only the green mercury line 5461A (FIG. 1).

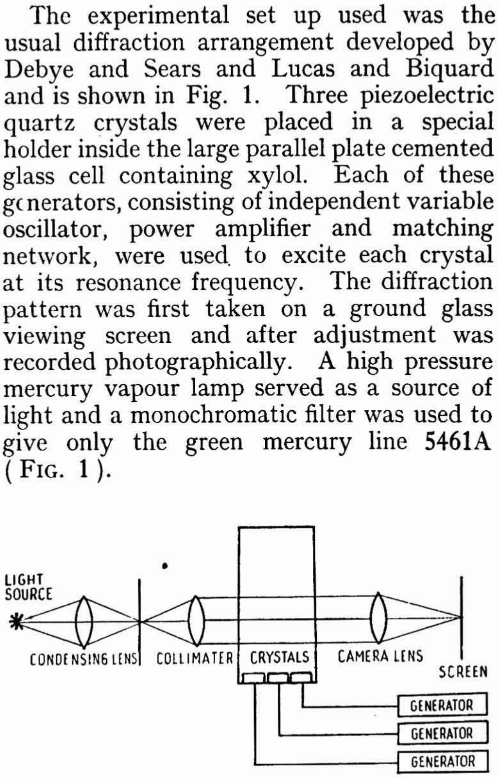

FIG. 1 — EXPERIMENTAL SET UP OF THE DIFFRACTION APPARATUS

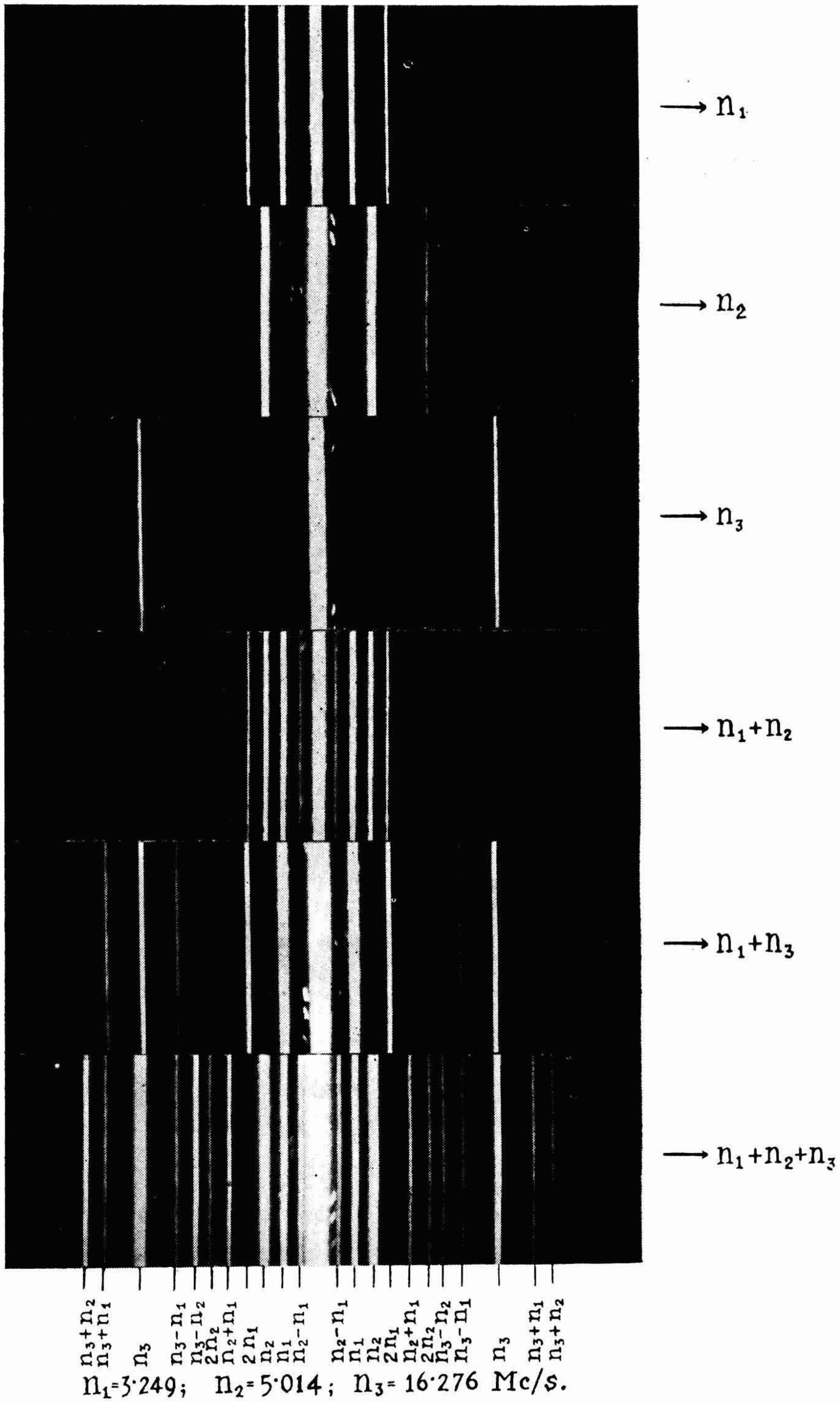

FIG. 2 — DIFFRACTION PATTERNS WITH MORE THAN TWO FREQUENCIES

Power to the crystals was switched on one at a time and the output was adjusted so as to get on the ground glass screen a bright first order and a weak second order with no third order. For identification, these single frequency diffraction patterns were first photographed individually and their respective frequencies were measured by a heterodyne wavemeter. Then all the crystals were simultaneously excited and the complex diffraction pattern was photographed giving an exposure of a fraction of a second.

The intensities of the various lines were estimated by measuring the densities of the recorded lines on a recording type of microphotometer.

Results and discussion

Five sets of frequencies were taken, each consisting of three frequencies and each set was repeated twice. Fig. 2 shows the results of one set of observations. The top three patterns in Fig. 2 corresponding to the three individual frequencies are designated here as n_1, n_2 and n_3; the fourth and fifth patterns show diffraction patterns obtained by using two frequencies at a time, namely n_1, n_2 and n_1, n_3 respectively; the bottom pattern is obtained by using all the three frequencies simultaneously. The lines corresponding to the component frequencies are denoted by n_1, $2n_1$, etc., where the prefix denotes the order of the diffraction lines. The combination lines or the side bands are marked $n_1 + n_2$, $n_2 - n_1$, etc.

It is observed that in dealing with any one pair of side bands in these diffraction patterns, only two frequencies are involved and the positions of the diffraction lines concerned are given by the formula

$$\sin \theta = \pm r \frac{\lambda}{\lambda_1^*} \pm s \frac{\lambda}{\lambda_2^*}$$

where θ is the corresponding angle of diffraction and r and s are integers.

TABLE 1 — INTENSITY MEASUREMENTS

FREQUENCY Mc./s.	FREQUENCY OF COMBINATION LINES		INTENSITY RATIO OF INNER TO OUTER LINE	
	Difference	Sum		
3·2494	1·7645	8·2633	1·2	1·4
5·0139	13·0261	19·5249	1·1	0·7
16·2755	11·2616	21·2894	1·3	1·2
5·0139	3·8485	13·8763	1·8	2·0
8·8624	11·2561	21·2839	1·1	1·3
16·2700	7·4076	25·1324	2·1	1·4
5·0139	2·1401	12·1679	2·4	1·5
7·1540	11·2561	21·2839	1·4	1·4
16·2700	9·1160	23·4240	3·6	2·0
5·7230	1·4310	12·8770	4·4	5·6
7·1540	4·0260	15·4720	2·0	1·5
9·7492	2·5950	16·9030	2·1	3·3
4·5897	2·5589	11·7383	2·4	1·2
7·1486	8·3707	17·5401	1·9	1·7
12·9504	5·8018	20·0990	2·3	1·6

The results of intensity measurements are shown in Table 1. Column 1 gives the frequencies of the three ultrasonic beams; the frequencies corresponding to the difference and sum side bands are shown in columns 2 and 3, and the ratio of intensity of the inner line to the outer line for each pair is shown in columns 4 and 5.

It is seen from the results in Table 1 that the difference line is always higher in intensity than the corresponding outer line. This extends the validity of results earlier obtained for the intensity of side bands in a diffraction pattern produced by two ultrasonic beams to a general case of diffraction pattern produced by several ultrasonic beams.

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Theoretical Basis of Badger's Rule for the Force Constant of Molecules

YATENDRA PAL VARSHNI
Department of Physics, Allahabad University, Allahabad

Assuming that the valence electrons of a diatomic molecule form a Fermi gas and that the variations in the force constant are mostly due to changes in the repulsive force, Badger's relation, viz. $K_e(r_e-d_{ij})^3=$ constant, has been shown to have a semi-theoretical justification for the different electronic states of a diatomic molecule.

IT was shown by Badger[1,2] empirically that the following relation holds good for the different electronic states of a diatomic molecule

$$K_e(r_e-d_{ij})^3=C \quad \ldots\ldots\ldots \quad (1)$$

where K_e is the force constant, r_e the internuclear distance, and d_{ij} is a constant which is different for each type of molecule. C may be taken to be approximately the same for all molecules. However, a somewhat better agreement is obtained if C is given slightly different values for different types of molecules[3]. The Badger relation is also found to be true for poly-atomic molecules[4].

The purpose of the present paper is to show that the relation has a theoretical basis at least for the different electronic states of the same molecule.

Simultaneous attractive and repulsive forces go to form a molecule. However, the repulsive force contributes more to the magnitude of the force constant since it varies more rapidly with the distance than the force of attraction[5]. At the equilibrium distance the repulsive force and the attractive force are equal. K_e is given by the difference of the derivatives of these forces. Thus, it is obvious that a given law for the repulsive force should give an approximation for the variations of the force constant.

We will consider a diatomic molecule formed of the same element. As a first approximation we can consider the molecule to be a prolate spheroid. A section through the major axis is shown in Fig. 1. The shaded portions represent the closed electronic shells of the two atoms.

It is well known that it is only the valence electrons that go to form the molecules. We consider these electrons as forming a Fermi gas. The number of electrons involved is rather small and the application of Fermi theory is not absolutely correct. However, several workers[6,7] have applied it to atoms with low atomic numbers and have obtained satisfactory results, so far as the order of magnitude is considered.

Let Z be the number of valence electrons forming the molecules and V the volume in which they can move. Then V is obviously the volume due to the revolution of the unshaded portion. The most important contribution to the repulsive force will be due to the pressure of this electronic gas.

Now V = volume of spheroid — volume of closed shells

$$=\frac{4}{3}\pi\left(\frac{r+2\sigma}{2}\right)b^2-\frac{4}{3}\pi r_1^3$$

$$=\frac{2}{3}\pi b^2\left[r+2\sigma-\frac{4r_1^3}{b^2}\right]$$

and $b\sim\sigma$ and r_1 will be slightly less than σ, say $(9/10)\sigma$. Therefore, $2\sigma-\frac{4r_1^3}{b^2}$ will be

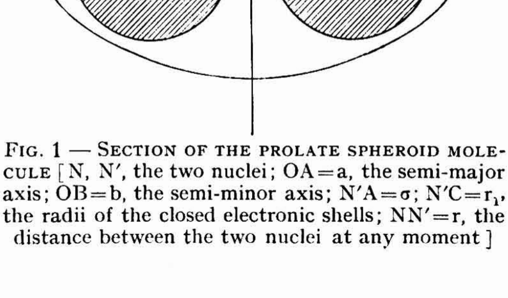

FIG. 1 — SECTION OF THE PROLATE SPHEROID MOLECULE [N, N', the two nuclei; OA = a, the semi-major axis; OB = b, the semi-minor axis; N'A = σ; N'C = r_1, the radii of the closed electronic shells; NN' = r, the distance between the two nuclei at any moment]

negative. Let this be represented by $(-d)$. It can be verified that $d < r_e$. Finally for V we have

$$V = \frac{2}{3}\pi b^2 (r-d) \quad \ldots\ldots \quad (2)$$

The energy of the Fermi gas is

$$E = \frac{3}{40}\frac{h^2}{m}\left(\frac{3}{\pi}\right)^{2/3}\frac{Z^{5/3}}{V^{2/3}} \quad \ldots\ldots \quad (3)$$

$$= \frac{3}{40}\frac{h^2}{m}\left(\frac{3}{\pi}\right)^{2/3}\left(\frac{3}{2\pi b^2}\right)^{2/3}(r-d)^{-2/3} \text{ by } (2)$$

$$K_e = \left[\frac{d^2E}{dr^2}\right]_{r=r_e}$$

$$= \frac{10}{9}\times\frac{3}{40}\frac{h^2}{m}\left(\frac{9}{2\pi^2}\right)^{2/3}\frac{Z^{5/3}}{b^{4/3}}(r_e-d)^{-8/3}$$

$$\text{or } K_e(r_e-d)^{8/3} = \frac{1}{12}\frac{h^2}{m}\left(\frac{9}{2\pi^2}\right)^{2/3}\frac{Z^{5/3}}{b^{4/3}}$$

For any particular molecule Z and b are constant. Thus for the different electronic states of the same molecule

$$K_e(r_e-d)^{8/3} = D \quad \ldots\ldots\ldots \quad (4)$$

where D is a constant.

The exponent $8/3 \approx 3$, and hence

$$K_e(r_e-d)^3 = \text{constant} \quad \ldots\ldots \quad (1a)$$

which is Badger's relation.

It is apparent that with such an approximate theory no numerical test of the equation 3 would be justified. However, it is interesting to note that while the empirical value of the constant is $1{\cdot}12 \times 10^{-16}$, the calculated value is also $\sim 10^{-16}$.

In the discussion below formula 1 is referred to as formula B and formula 4 as formula BV.

Discussion

It is interesting to compare formulae B and BV. In Table 1 are collected the constants for all states of C_2, N_2 and O_2 for which reliable data are available[8]. These molecules belong to KK period and Badger has recommended the value 0·68 for d_{ij} for such molecules. It may be that the d of BV formula is not exactly equal to d_{ij} of Badger, due to the different exponents of $(r_e - d_{ij})$

TABLE 1 — VALUES FOR THE FORCE CONSTANTS OF MOLECULES FOR ALL STATES OF C_2, N_2, O_2 CALCULATED ACCORDING TO FORMULAE B AND BV

MOLECULE	STATE		ω_e	r_e IN A° U.	K_e IN 10^5 DYNES/CM.	$K_e(r_e-0{\cdot}68)^3$	% DEVIATION	$K_e(r_e-0{\cdot}68)^{8/3}$	% DEVIATION
C_2	d	$^1\Sigma_u^+$	1829·6	1·238	11·82	2·28	11·4	2·74	12·0
	c	$^1\Pi_g$	1809·1	1·273	11·56	2·41	16·2	2·86	15·7
	b	$^1\Pi_u$	1608·3	1·318	9·14	2·37	14·7	2·76	12·7
	a	$^1\Sigma_g^+$	1855·6	1·242	12·16	2·16	6·5	2·61	7·6
	B	$^3\Pi_g$	1106·6	1·535	4·32	2·70	25·1	2·85	15·4
	A	$^3\Pi_g$	1788·2	1·266	11·30	2·28	11·4	2·71	11·0
	X	$^3\Pi_u$	1641·3	1·312	9·52	2·40	15·8	2·80	13·9
N_2	C	$^3\Pi_u$	2035·1	1·148	17·08	1·75	15·4	2·25	7·1
	B	$^3\Pi_g$	1734·1	1·212	12·40	1·87	8·0	2·30	4·7
	A	$^3\Sigma_u^+$	1460·4	1·293	8·79	2·02	0·0	2·38	1·3
	x	$(^1\Sigma_g^-)$	1910·0	1·180	15·04	1·88	7·4	2·37	1·7
	a′	$(^1\Sigma_u^-)$	1527·0	1·280	9·61	2·08	2·9	2·46	2·0
	q	$^1\Sigma_u^+$	715·0	1·470	2·18	—	—	—	—
	b	$^1\Sigma_u^+$	751·7	1·450	2·33	—	—	—	—
	a	$^1\Pi_g$	1692·0	1·213	11·81	1·79	12·9	2·21	9·1
	X	$^1\Sigma_g^+$	2359·6	1·098	22·96	1·63	21·8	2·19	10·0
O_2	B	$^3\Sigma_u^-$	700·4	1·604	2·31	1·82	11·0	1·87	28·9
	b	$^1\Sigma_g^+$	1432·7	1·227	9·66	1·58	27·8	1·93	24·8
	a	$^1\Delta_g$	1509·0	1·215	10·73	1·65	22·5	2·03	18·7
	X	$^3\Sigma_g^-$	1580·4	1·207	11·76	1·68	19·7	2·13	13·1
	Mean		—	—	—	2·02	13·9	2·41	11·6

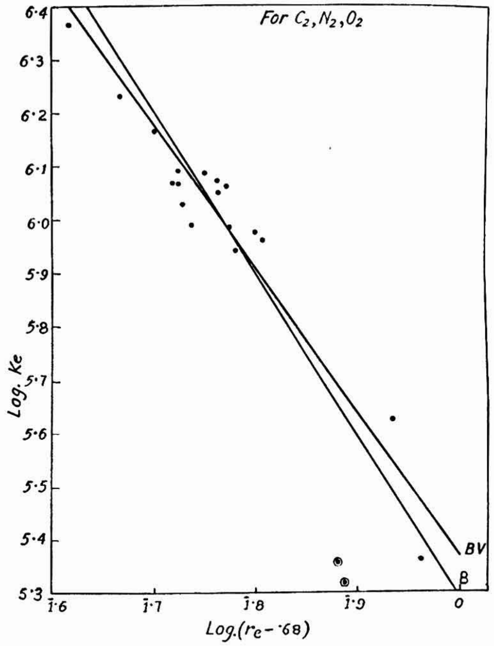

FIG. 2 — GRAPHICAL COMPARISON OF FORMULAE B AND BV

and ($r_e - d$). However, it is convenient to consider d and d_{ij} to be equal. K_e is in 10^5 dynes/cm. and r_e and d in Å.

The mean values of $K_e(r_e - d_{ij})^3$ and $K_e(r_e - d)^{8/3}$ are 2·02 and 2·41 respectively (TABLE 1). In terms of fundamental units, viz. K_e in dynes/cm. and r_e and d in cm., the values of C and D are $2{\cdot}02 \times 10^{-19}$ and $1{\cdot}12 \times 10^{-16}$ respectively. It is clear that the value of the constant is very sensitive to the exponent of ($r_e - d$). The two values of N_2, shown by dots enclosed in circles in Fig. 2, have been neglected.

The percentage errors in the calculation of different constants are tabulated in Table 2.

The comparison is illustrated graphically in Fig. 2.

It is clear from the graph as well as from the numerical calculation that there is hardly any significant difference between the two formulae.

However, it is not clear from the above theory why the constant should be the same for different molecules. If we assume that it is so, equation 3 shows that $Z^{5/3} \propto b^{4/3}$. But in the above theory b is a very ill-defined quantity, because a molecule resembles more the shape of two pressed elastic spheres than a spheroid and hence no definite conclusions can be drawn about variation of b with Z.

TABLE 2 — ERRORS IN THE CALCULATION OF FORCE CONSTANTS

	ERROR IN THE CALCULATION OF DIFFERENT CONSTANTS ACCORDING TO FORMULA	
	B %	BV %
C or D	13·92	11·65
$r_e - d$	4·64	4·37
r_e	~2·30	~2·20

TABLE 3 — MEAN VALUES FOR THE FORCE CONSTANTS OF DIFFERENT MOLECULES

Z	MOLECULE	C	$C\sqrt{Z}$	D	$D\sqrt{Z}$
8	C_2	2·37	6·70	2·76	7·80
10	N_2	1·86	5·88	2·31	7·30
12	O_2	1·68	5·82	1·99	6·89

Actually the constant is not same for all the molecules. The mean values for the different molecules are shown in Table 3. The constant decreases with the increasing number of valence electrons. Sutherland[9] and Clark and Webb[10] have suggested that the Badger relation should be corrected for electronic structure by multiplying by $\sqrt{N}$ where N is the " group number " (equal to Z in this paper). It is found that there is no appreciable improvement by this modification. Table 3 illustrates the point.

From similar considerations it can be shown that the relation will also hold for molecules formed from different elements.

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Distribution of Radioactivity in the Rocks of South India: I—Charnockites & Associated Rocks

U. ASWATHANARAYANA
Department of Geology, Andhra University, Waltair

Representative specimens of charnockites and associated rocks drawn from Ananthagiri, Kondapalli, Pallavaram and Trichinopoly areas in Madras State have been examined for their radioactivity and the data so obtained are studied in conjunction with environmental factors and geological history. The radioactivity is shown to be closely related to the order of decreasing basicity. It is suggested that the marked contrast in the radioactivity of the four groups of charnockites reflects the nature of the petrogenetic processes responsible for their formation.

Attention is drawn to the scope and limitations of the β-activity method in radioactivity studies.

CHARNOCKITES as a petrological entity have been attracting considerable attention ever since they were designated as such by Sir Thomas Holland[1]. These hypersthene-bearing granulites have been studied by petrologists from various localities in India and abroad and conflicting views have been expressed to account for their genesis. The present work is an extension of the investigations in progress in the Geology Department of the Andhra University since 1945 on the petrography, petrochemistry and petrogenesis of charnockites of the Eastern Ghats of the Circars districts, occurring in association with khondalites. In view of the marked divergence of opinion regarding the genesis of charnockites of South India, expressed by research workers of different areas, it was felt that the study of their radioactivity would throw new light on their genetic history. Accordingly, an attempt is made in this paper to examine the charnockite problem from a new angle — the radioactivity distribution.

Investigations on the radioactivity of charnockites, besides contributing to the solution of the charnockite problem in a general way, are also of importance in the elucidation of problems connected with the generation of radioactive heat in the lithosphere and production of chemical changes in the underground fluids[2]. Though there are six nuclides — U_{238}, Th_{232}, K_{40}, Rb_{87}, Sm_{152} and Lu_{176} — capable of these functions, the first three alone are of any importance, the others being so scarce in the crustal layers as to make their contribution insignificant[3].

The published work on the petrographical, petrochemical and petrogenetic studies of charnockites is fairly extensive. Amongst recent publications, *Charnockites of Mysore* by Ramarao[4] and *Charnockite Series of Verberg District, on the South-western Coast of Sweden* by Quensel[5] give a fairly exhaustive summary of the previous work. Though Evans and Goodman[6] and Senftle and Keevil[7] worked on the radioactivity of various types of rocks, there are no similar published data with regard to the charnockites.

Experimental procedure

Geiger-Mueller counter system — The β-activity of charnockites and associated rocks has been studied with a G.M. counter system, rigged up by the author while at the Tata Institute of Fundamental Research, Bombay. This system consists of the following three units:

(1) *The power unit* is a 300 V. L.T. and 2,000 V. H.T. electronically stabilized, multipurpose power unit. A modified form of circuit described by Elmore and Sands[8] has been followed.

(2) *The scaling unit* is a model 200 pulse counter with six Higginbotham's scale-of-two units, making it a scale-of-sixty-four. Pulses can be recorded either with a telephone call counter or with a cyclotron specialities mechanical register. The former type is more useful for radioactivity work on rocks, as it is inexpensive and rugged and

records low pulse rates reliably. The cyclotron specialities mechanical register is, however, indispensable for recording the high speed pulses met with in the examination of radioactive ores, as the telephone call counter is incapable of responding to fast pulses, because of its higher mechanical inertia. The timing switch is operated manually, though alternate arrangements have been made for its operation with a Londex timer.

(3) *The G.M. tube* is of type EA-3B, a product of Electronic Associates, Toronto, Canada. It is what is generally described as an envelope type of tube. It has a wall thickness of 3 mg./sq. cm. and an effective projected area of approximately 13 sq. cm. The tube has a plateau of about 250 V. and is operated at 1,000 V. The tube is surrounded by a 2 in. thick inactive lead shield and this is found to cut down the background emission by about one-third.

Two ebonite rings of 1·5 mm. thickness are snugly attached at the two ends of the sensitive area of the β-tube. A glass envelope with a 2 mm. slit is slid over the rings and the rock powder (40-60 mesh) is introduced through the slit, so as to fill in the annular space between the tube and the envelope. The volume of the annular space being constant, the weight of the rock powder introduced becomes a function of the density of rock, being highest in ultra-basic rocks and least in the case of granites.

Calibration was effected with a samarskite sample, kindly supplied by Dr. J. Shankar of the Atomic Energy Commission (India). The sample contains 11·15 per cent uranium and 0·545 per cent thorium. The thorium content is converted into equivalent uranium content on the basis of the β-emission ratio, U : Th = 6 : 1. Hundred mg. of this mineral sample were mixed intimately with 100 g. of non-radioactive plaster of Paris and made into a paste. After drying, the mixture was powdered and sieved to get the requisite quantity of 40-60 mesh powder. Such a procedure reduces the pulse rate to a level comparable to that met with in rocks and has been adopted to satisfy the requirements of statistical computation. The pulses were continuously recorded for a period of 3 hr. to reduce the statistical error to a minimum and thereby insure reproducibility. The uncertainty factor was always less than 10 per cent and in most cases less than 5 per cent.

Limitations of the β-activity method for determining the absolute radioactivity of a rock

The determination of the radioactivity of the rock from its β-activity introduces certain factors which must be taken cognizance of when computing its accuracy.

(1) β-rays are not uni-energy particles, but constitute an energy spectrum. The extent to which the softer fraction of the radiation is cut off depends upon the constitution of the rock particle through which it has to pass before being recorded. Further, most of the rocks contain members of both uranium and thorium series, which have different β-energy spectra.

(2) The absorption is an exponential function of the effective density of the rock sample surrounding the counter. " This density involves not only the intrinsic density of the rock itself but also the size distribution of the ground sample and the degree of packing among the constituent particles.... Ideally the sample should be of the original intrinsic particle size of the rock body. Practically, however, this condition is difficult to realise[2] ". Normally the sample is reduced to some convenient mesh range, but the extent to which the final sample represents the original rock depends upon the granularity of the rock and the hardness of the individual mineral constituents. The less the variation in the sizes of the minerals constituting the rock the better representative the sample will be.

(3) In the case of investigations on the radioactivity of rocks, it is necessary that the G.M. tube should be calibrated with a rock powder of comparable radioactivity and effective density, of the type supplied by the National Bureau of Standards, U.S.A. Thus, when calibration is effected with activated plaster of Paris, which has got a low "effective density " and hence low absorption ratio, it introduces another factor affecting the accuracy of the method.

Although the radioactive content of the samples cannot be claimed as absolute in view of the complications involved, the relative values are reliable in almost all the cases.

Results and discussion

Twenty-two representative samples of charnockites and associated rocks drawn from Ananthagiri, Kondapalli, Pallavaram

TABLE 1 — RADIOACTIVITY MEASUREMENTS OF ROCK SAMPLES

SL. No.	NO. OF THE SPECIMEN	LOCALITY	NATURE OF THE ROCK	EQUIVALENT U CONTENT g. of U/g. of rock
1	B/2	Ananthagiri	Acid charnockite, highly felspathized	$37\cdot27\times10^{-6}$
2	B/4	do	Acid charnockite	$22\cdot45\times10^{-6}$
3	B/1	do	Basic charnockite	$5\cdot909\times10^{-6}$
4	B/5	do	Garnetiferous basic charnockite	$4\cdot626\times10^{-6}$
5	B/3	do	Khondalite	$1\cdot056\times10^{-6}$
6	P/2/49	Pallavaram	Acid charnockite	$36\cdot78\times10^{-6}$
7	P/6/49	do	Leptynite	$24\cdot62\times10^{-6}$
8	P/4/49	do	do	$20\cdot92\times10^{-6}$
9	P/1/49	do	Intermediate charnockite	$7\cdot791\times10^{-6}$
10	P/3/49	do	do	$6\cdot386\times10^{-6}$
11	P/7/49	do	Basic charnockite	$5\cdot826\times10^{-6}$
12	P/5/49	do	do	$4\cdot783\times10^{-6}$
13	T/3	Trichinopoly	Garnetiferous acid charnockite	$25\cdot68\times10^{-6}$
14	T/24	do	Garnetiferous leptynite	$12\cdot84\times10^{-6}$
15	T/2	do	Basic charnockite	$2\cdot899\times10^{-6}$
16	T/11	do	do	$2\cdot869\times10^{-6}$
17	T/13	do	do	$2\cdot645\times10^{-6}$
18	K/39	Kondapalli	Acid charnockite	$10\cdot75\times10^{-6}$
19	K/13	do	Garnetiferous leptynite	$7\cdot602\times10^{-6}$
20	K/28	do	Intermediate charnockite	$6\cdot052\times10^{-6}$
21	K/43	do	Basic charnockite	$4\cdot051\times10^{-6}$
22	K/27	do	do	$3\cdot153\times10^{-6}$

and Trichinopoly areas in Madras State, which are roughly spaced at intervals of about 200 miles, were examined for their radioactivity and the data thus obtained (TABLE 1) were studied in conjunction with relevant environmental factors. The distribution of the radioactivity in the charnockites and associated rocks is studied from two aspects — firstly the variations in the radioactivity with the variations in mineralogical constitution and secondly the regional variation in their radioactive content and its possible significance in petrogenetic studies.

Mineralogical constitution and radioactivity

It can be seen from Table 1 that in charnockites from all the four areas, the radioactivity progressively decreases from acid to basic varieties or, in other words, with increasing basicity. This accords well with the work of Evans and Goodman[6] and Senftle and Keevil[7], who find that in igneous rocks radioactivity generally decreases with increasing basicity. The averages calculated also corroborate this surmise, as is evident from the data presented in Table 2.

TABLE 2 — CALCULATED VALUES OF RADIOACTIVITY OF ROCKS

NATURE OF THE ROCK	NO. OF SPECIMENS EXAMINED	RADIOACTIVITY g. of U/g. of rock
Acid charnockite	5	$26\cdot590\times10^{-6}$
Intermediate charnockite	3	$6\cdot743\times10^{-6}$
Basic charnockite	9	$4\cdot085\times10^{-6}$

The average acid charnockite is thus about six times more radioactive than its basic variety — an observation which is fully consistent with the work of Keevil and Senftle[7]. The intermediate charnockites, as can be expected, have a radioactivity intermediate between acid and basic varieties, but nearer to the latter. This is perhaps due to the relative rarity of typical intermediate charnockites. Most of the charnockites associated with the Eastern Ghats come under either acid or basic varieties, but relatively few of them strictly correspond to intermediate charnockites.

The radioactivity of average leptynite ($16\cdot496\times10^{-6}$ g. of U/g. of rock) stands in marked contrast to that of khondalite ($1\cdot056\times10^{-6}$). Dr. M. S. Krishnan[9] opines that khondalites and leptynites " are essentially of the same character ". According to him " the differences that may be found in their mineralogical composition are incidental to regional variation in the nature and composition of sediments (though of essentially similar nature) as we are dealing here with comparatively large areas." The few observations that have been made on their radioactivity appear to warrant the view that leptynites are not mere variants of the khondalites, as the introduction of extraneous material has to be recognized to account for the higher radioactivity of the leptynites. Turner's[10] description of migmatites suggests that the leptynites are typical migmatites — a view which is supported by the radioactivity data. Whatever might be the process of migmatization — whether it is magmatic injection (Goldschmidt), magmatic soaking (Quirke and Collins) or differential fusion (Holmquist) — it has certainly been responsible for the introduction of radioactive elements into the leptynites, thus giving them a markedly higher radioactivity, when compared with the parent rock khondalite.

As garnet is a common constituent in all the rocks belonging to the charnockitic group and also in view of its importance in petrogenetic studies of charnockites and associated rocks, an attempt has been made to study the nature of the relationship between the garnet content and the radioactivity. While the available data do not permit an unambiguous solution, there are good reasons to believe that high garnet content is correlatable to low radioactivity. The garnets in the charnockites and leptynites are believed to have been largely derived from the pre-existing khondalites and thus the garnet content becomes an index of the extent of the retention of the khondalitic material in the charnockites and leptynites. It is not, therefore, surprising that in the case of rocks in which garnets occur in some abundance, the radioactivity is relatively low.

Regional variation in the radioactivity and petrogenesis

The consolidated data bearing on the regional variation of the radioactivity of charnockites and associated rocks are given in Table 3 in the order of decreasing radioactivity (in terms of equivalent uranium content in g. of U/g. of rock).

Variations in the radioactivity can be caused by any combination of the following possibilities: (a) inadequate sampling of the specimen or rock body; (b) irregular localization of radioactive elements in crystals of accessory minerals and (c) the effects of differentiation in the distribution of radioactive minerals within the intruded mass[11]. It is no doubt possible that these processes are responsible for the variations between two rocks of the same type obtained from different points in the same zone. In the present case, however, the variations are too systematic and the relationship with petrogenetic processes too obvious to attribute them to reasons mentioned above. They cannot possibly be described as fortuitous, as they appear to have a profound significance in petrogenetic studies as is shown below.

In the Ananthagiri area, the manifestations of the processes of granitization are clearly discernible[12]. Felspathization, which may be taken as a particular case of granitization, appears to have markedly influenced the mineralogical constitution of the rocks of the area, as can be evidenced by the large-scale development of potash felspars as porphyroblasts. The alternating bands of sialic and mafic minerals are suggestive of the mechanism of granitization, which appears to have been effected dominantly along the weak planes of the rock. That the granitization processes have been all-pervasive is borne out by the relatively higher content of micas and amphiboles even in the basic rocks, which suggests that their normal constitution has been modified to some extent by the later hyperfusible constituents. The granitic ichor, rich in radioactive constituents, slowly rises into the superposed rocks and diffuses the radioactive material into the surrounding zones[13]. According to Bugge[14], the radioactive elements are often mobilized in remelting and migrate in the ichor, which is capable of moving to distances ranging from a few millimetres to several kilometres. The high radioactivity associated with Ananthagiri charnockites, both individually and collectively, is thus a direct result of the processes of granitization.

At Kondapalli the basic and ultra-basic varieties of charnockites form a sizable proportion of the total charnockitic rocks[15-17]. The association of chromite as well as the

TABLE 3 — REGIONAL VARIATION IN THE RADIOACTIVITY OF CHARNOCKITES AND ASSOCIATED ROCKS

SOURCE	AVERAGE RADIOACTIVITY OF CHARNOCKITES	HIGHEST RADIOACTIVITY ASSOCIATED WITH ACID CHARNOCKITES	HIGHEST RADIOACTIVITY ASSOCIATED WITH LEPTYNITES
Ananthagiri area, Visakhapatnam district	$17\cdot654\times10^{-6}$	$37\cdot27\times10^{-6}$	Not determined
Pallavaram area, Madras	$12\cdot813\times10^{-6}$	$36\cdot78\times10^{-6}$	$22\cdot77\times10^{-6}$
Trichinopoly area	$8\cdot523\times10^{-6}$	$25\cdot68\times10^{-6}$	$12\cdot84\times10^{-6}$
Kondapalli area, Krishna district	$6\cdot002\times10^{-6}$	$10\cdot75\times10^{-6}$	$7\cdot60\times10^{-6}$

mineralogical and chemical composition of the basic and ultra-basic varieties are clearly suggestive of their predominantly igneous origin, as differentiation products of a basic magma. The magma, which had given rise to these rocks, appears to have been poor in hyperfusible constituents to start with, as is suggested by the low radioactivity of even the acid charnockites of this area. It is, therefore, not surprising that a group of rocks with such a petrogenetic history as Kondapalli charnockites should be characterized by low radioactivity.

The chief interest of Pallavaram and Trichinopoly groups of charnockites lies in the fact that their radioactivity is intermediate between the Ananthagiri and Kondapalli groups of charnockites.

The Pallavaram charnockites, like those of Ananthagiri, exhibit the development of potash felspars as porphyroblasts. There is also evidence to show that metasomatic processes and magmatic differentiation have been dominant in this area[18-20]. It is significant that the chromite is not associated even with ultra-basic types. As can be expected, the radioacitivity range of Pallavaram charnockites is considerably higher than that of Kondapalli charnockites, and comes quite near to that of Ananthagiri. The leptynites of this area too exhibit a corresponding difference.

The Trichinopoly group has a radioactivity intermediate between Pallavaram and Kondapalli groups of charnockites, but is nearer to the former than the latter. The degree of intensity of the processes capable of introducing radioactive elements appears to be less here than at Pallavaram. It is an interaction zone of Dharwars and Peninsular complex and it is possible that interaction of granites with the precursors of charnockites might have influenced the radioactivity distribution in this area.

Conclusions

1. The radioactivity of charnockites decreases with increasing basicity.

2. The leptynites are surmised to be not mere variants of khondalites. The markedly high radioactivity of the leptynites, when compared with khondalites, suggests that leptynites might have been derived by migmatization of khondalites.

3. High garnet content appears to be correlatable to low radioactivity.

4. The granitization processes normally increase the radioactive content of a rock to an appreciable extent, their degree of intensity determining the extent of enrichment in radioactive constituents. Among the four groups of charnockites examined, the Ananthagiri group of charnockites, which shows evidence of granitization, has the highest radioactivity and the Kondapalli charnockites, which appear to have been derived essentially by differentiation of a basic magma (poor in hyperfusible constituents ?), exhibit the least. The Pallavaram and Trichinopoly groups of charnockites are intermediate in their radioactivity between those of Ananthagiri and Kondapalli, which is in keeping with their genetic history.

It is suggested that the study of the radioactivity of charnockites gives a valuable clue to their genetic history.

Though the limited number of observations that have been made on the radioactivity of charnockites and associated rocks have yielded encouraging and interesting results, and thereby demonstrated the essential soundness of the new approach, it must be mentioned that this work is of an exploratory nature. Intensive and systematic examination of the radioactivity of charnockites and associated rocks from different areas is bound to lead to interesting results.

The results of these radioactivity investigations open up several problems, some of which are briefly enumerated below:

(a) The relationship between the extent and the mineral constitution of the leptynites and their genetic history in an area.

(b) Garnet content as an index of the degree of migmatization in the case of leptynites, and hybridism in the case of garnetiferous charnockites.

(c) Study of mechanism and extent of diffusion of radioactive elements by systematic sampling of a granitized body of rock.

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Electron Microscope Study of Diatom Wall Structure: II—Genus *Chaetoceros* Ehrenb.

T. V. DESIKACHARY & KANWAR BAHADUR

University of Saugar, Saugar & National Physical Laboratory of India, New Delhi

Three species of *Chaetoceros*, *C. lorenzianus*, *C. didymus* and *C. paradoxum*, were studied under the electron microscope and their structure described. Their walls show fine perforations and do not show any clear aereolae formation.

The spines in *Chaetoceros* spp. similarly show minute to large perforations on their wall, the pores being arranged differently in different species.

THE first paper of this series[1] was concerned with the study of eight species of diatoms belonging to the genera *Synedra*, *Desmogonium*, *Cymbella*, *Navicula*, *Epithemia* and *Nitzschia*. The present communication deals with the genus *Chaetoceros* Ehrenb. Not much is known regarding the wall structure of this genus except that in a few cases fine punctae, which show a somewhat radial arrangement, have been observed[2]. The authors studied a number of species of this genus collected from the coast near Madras. The different species are *Chaetoceros lorenzianus* Grun. [FIG. 1 (1, 2)], *Chaetoceros didymus* Ehrenb. [FIG. 1 (4, 10, 11)], and *Chaetoceros paradoxum* Cleve. [FIG. 1 (8)]. In addition to these a number of species have been studied for their spine structure [FIG. 1 (3, 5-7, 9, 12)].

In all these species the diatom wall did not show any aereolae formation such as is seen in many other *Centrales* investigated. The wall seems to be merely perforated [FIG. 1 (1, 8, 10)]. The pores are very small varying from 0·07 to 0·2 μ in diameter. These are often very closely packed in somewhat vertical rows when seen from the girdle view.

This type of wall structure recalls the wall structure described by Fott and Rozsival[3] in *Attheya zachariasii* Braun, wherein the wall is merely perforated. But it differs from *Attheya* in that the spines also show pores in the present genus.

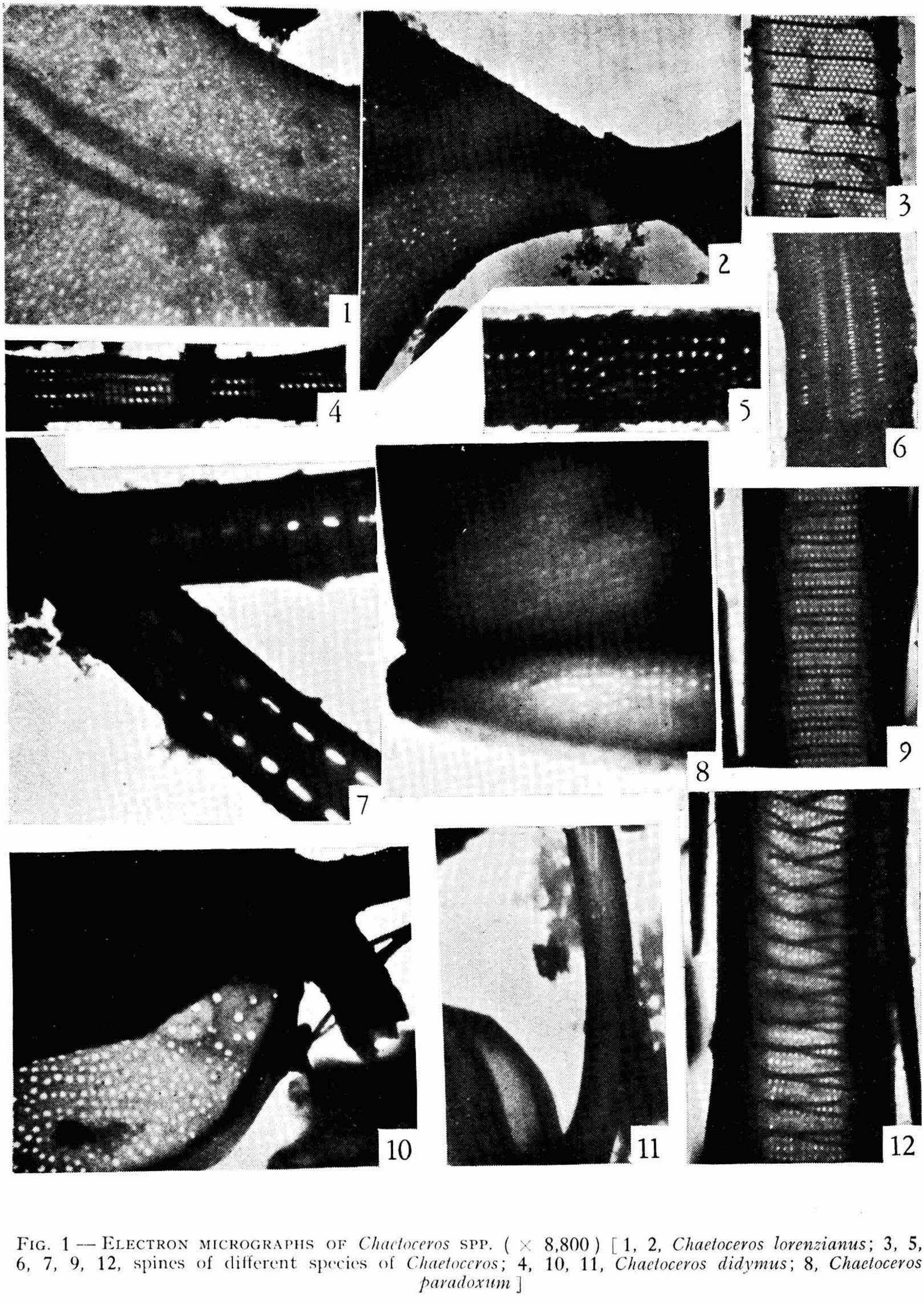

Fig. 1 — Electron micrographs of *Chaetoceros* spp. (× 8,800) [1, 2, *Chaetoceros lorenzianus*; 3, 5, 6, 7, 9, 12, spines of different species of *Chaetoceros*; 4, 10, 11, *Chaetoceros didymus*; 8, *Chaetoceros paradoxum*]

Many species of *Chaetoceros* have been described to possess spines showing aereolae or striations. This seems to be very common in all the species studied. The pores on these spines vary very much in their size and arrangement. They vary from fine pores to very prominent ones [FIG. 1 (4, 7)]. The arrangement of the pores varies with the species and often imitates the fashion of punctation of the Pennales [FIG. 1 (3, 6, 9, 12)]. Even a species such as *C. didymus*, which does not show pores under the optical microscope, reveals fine pores arranged in longitudinal rows [FIG. 1 (4, 11)].

The authors' observations, as also of Fott and Rozsival[3] and of Desikachary[1], confirm Kolbe's observation[4] that there is no homogeneous membrane in the diatoms. The walls are all perforated. The forms with a slightly silicified wall seem to have simple perforations without any aereolae formation.

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Formation of Molybdo-oxalate Complex

D. V. RAMANA RAO & S. PANI

Department of Chemistry, Ravenshaw College, Cuttack

The complex formation between molybdate and oxalate has been studied by the electrical conductivity method and evidence has been obtained for the existence of the compound $Na_2[MoO_2(C_2O_4)_2]$. This has been substantiated by *p*H measurements. Distinction has been made between complex formation and aggregation process using sodium oxalate and oxalic acid respectively as titrants.

MOLYBDATES can be reduced to different stages using different reducing agents. The extent to which reduction proceeds is controlled, *inter alia*, by the hydrogen ion concentration[1] of the reaction medium. It has been observed that oxalate ion is quite stable in sulphuric acid medium, even on warming, against potassium permanganate, if considerable quantities of molybdic acid are present[2]. A partial or complete prevention of the precipitation of ammonium phosphomolybdate can also be brought about by masking the phosphate ion in the presence of excess of oxalate ion[3,4]. It is of interest, therefore, to investigate the possibility of complex formation between molybdate and oxalate ions in solution. Various methods like the measurements of surface tension, refractive index, etc., are employed for ascertaining the formation of complexes. The conductimetric titration method has been employed by us in the present work.

Experimental procedure

Sodium molybdate ($Na_2MoO_4.2H_2O$) and sodium oxalate (Merck A.R. quality) were employed. Standard solutions of molybdate and oxalate were prepared containing 14·699 g. and 29·69 g. respectively per litre. Four cc. of a standard sodium molybdate solution (14·699 g./l.) were taken in a 500 cc. pyrex conical flask and diluted to 200 cc. to avoid the error due to volume effect during titration. The standard sodium oxalate solution (29·69 g./l.) was added from a microburette and conductivity of the resulting solution measured using a dip-type conductivity cell. Readings were taken with different amounts of added oxalate solution. The titration was repeated starting with different volumes of sodium molybdate solution. The results obtained are graphically represented by curve A, Fig. 1. A blank titration was carried out employing 200 cc. of water and adding different volumes of sodium oxalate solution and the results are given by curve B, Fig. 1. In another set of observations, 4 cc. of sodium molybdate solution were titrated against a standard solution of oxalic acid (19·95 g./l.). The results are represented graphically in Fig. 2. The *p*H values of mixtures of solutions of sodium molybdate-sodium oxalate and sodium molybdate-oxalic acid were measured in a Marconi *p*H meter. The results are recorded in Table 1.

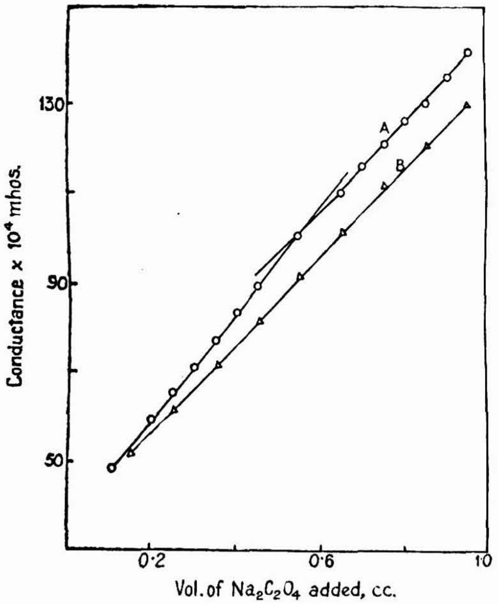

FIG. 1 — CONDUCTIMETRIC TITRATION CURVE OF SODIUM MOLYBDATE AGAINST SODIUM OXALATE

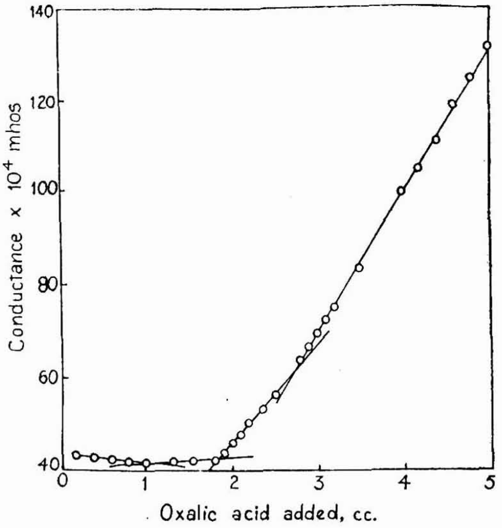

FIG. 2 — CONDUCTIMETRIC TITRATION CURVE OF SODIUM MOLYBDATE SOLUTION AGAINST OXALIC ACID

TABLE 1 — *p*H OF MOLYBDATE-OXALATE AND MOLYBDATE-OXALIC ACID MIXTURES

(*Volume of sodium molybdate solution taken, 4 cc.*)

VOL. OF SODIUM OXALATE ADDED cc.	*p*H	VOL. OF OXALIC ACID ADDED cc.	*p*H
0·0	7·64	nil	7·8
0·5	8·42	1·00	6·5
1·0	8·47	1·80	4·5
1·5	8·64	2·75	3·1
2·0	8·64	5·00	2·7
2·5	8·52	—	—
3·0	8·34	—	—
3·5	8·50	—	—
4·0	8·50	—	—

Results and discussion

The breaks in the conductimetric curve indicate the formation of complexes. A break occurs corresponding to the titre value of 0·55 cc. of sodium oxalate solution (curve A, FIG. 1). This corresponds to 2 mols of sodium oxalate for 1 mol of sodium molybdate. The reaction can be represented by the following equation:

$$Na_2MoO_4 + 2Na_2C_2O_4 + 2H_2O \rightarrow Na_2[MoO_2(C_2O_4)_2] + 4NaOH \quad . . . \quad (1)$$

This involves the liberation of sodium hydroxide. The slow-moving complex ion $MoO_2(C_2O_4)_2^{=}$ decreases the resultant conductivity while the liberated NaOH increases it. The net result is an overall increase in conductivity and this is clearly brought about by the divergence of the curves A and B (FIG. 1) up to the break. After the complex formation is complete the curves run almost parallel to each other.

This assumption has also been substantiated from the *p*H measurements. According to equation 1, the liberation of sodium hydroxide would mean increase in *p*H and the results in Table 1 are in agreement with this. Measurements of *p*H round about the value 7 will be erroneous due to the absorption of atmospheric carbon dioxide[5]. The values shown in the table, however, indicate an increase in *p*H up to the break.

Sodium oxalate supplies oxalate ions for the purpose of complex formation and the resulting variation in *p*H is between 7·64 and 8·64. Jander[6], working on the aggregation process in molybdate solutions, obtained evidence for the existence of various species of aggregates at different *p*H ranges. In the range 14-6·5, $(MoO_4)^{2-}$ is stable and between 6·3-4·5 and 4·5-1·5, the trimolybdate ion $(Mo_3O_{11})^{4-}$ and hexamolybdate ion $(Mo_6O_{21})^{6-}$ are formed. Hence, during the addition of sodium oxalate (*p*H 7·64-8·64) only $(MoO_4)^{2-}$ is stable and changes in conductivity are due to the complex formation alone. On the other hand, when oxalic acid was added the *p*H changed from 7·8 to 2·7 and the graph closely resembles that of Jander indicating the formation of different isopolyacids as envisaged above[7]. It is, therefore, necessary that investigations on molybdate-oxalate complex formation should be carried out under conditions not favouring aggregation process.

Acknowledgement

Our thanks are due to Prof. S. S. Guha Sirkar for his keen interest and kind encouragement in the work.

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Separation of Starch by Elutriation

K. S. GILL & F. A. KINCL

National Chemical Laboratory of India, Poona

An experimental unit, working on the elutriation principle, has been developed for separating starch particles from coarser particles and pulp during the manufacture of starch from tapioca. The influence of slurry concentration and velocity of flow on the total starch recovered as overflow has been studied, and the unit has been found to run efficiently at slurry concentrations between 2 and 3 per cent and at flow velocities between 1·8 and 2·0 mm./sec.

IN the tapioca starch manufacture one of the important steps is the separation of the released starch from the coarse pulp. This is usually carried out with the help of sieves. The types of sieves in general use are the stationary sieve, the brush washer sieve, the vibrating sieve and the rotating cylindrical sieve. With the possible exception of the last one, all other sieves suffer from the serious disadvantage that the gummy materials present in the starch liquor tend to agglutinate with the fibres and plug the sieve openings[1]. To overcome this difficulty, a method for the separation of starch from the coarser particles has been developed on the principle of elutriation.

A survey of the existing literature on the subject showed that elutriation is used mainly as an analytical tool for sizing subsieve particles[2-4] or occasionally as an aid in the ore dressing industry[5].

The present paper describes the work carried out to study the separation of -160 mesh starch particles from coarser ones using the elutriation principle.

Experimental procedure

The experimental unit (Fig. 1) was developed after considerable experimentation in

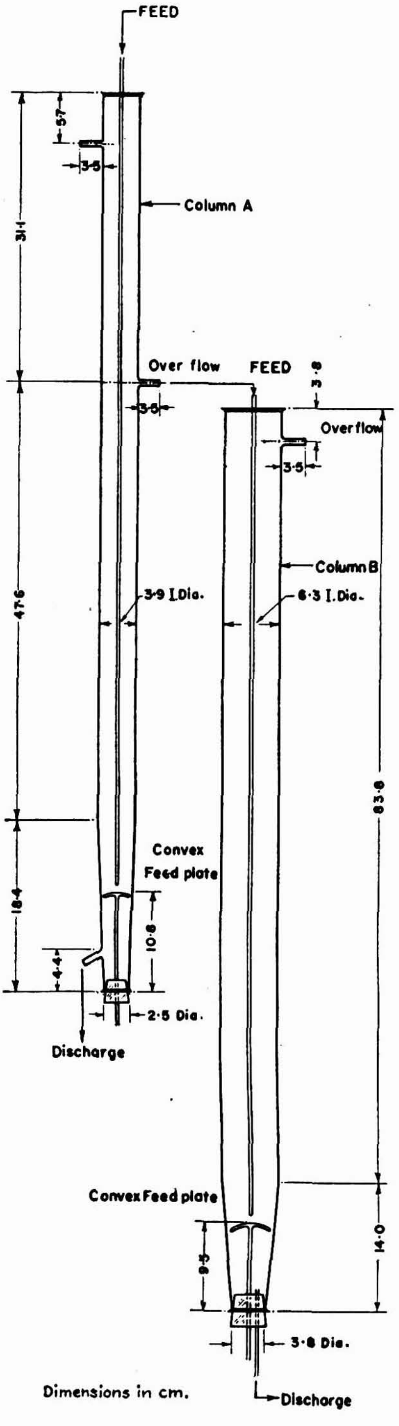

FIG. 1 — EXPERIMENTAL UNIT FOR SEPARATING STARCH PARTICLES

feeding, discharging and stirring arrangements. The unit consisted of two pyrex glass columns A and B. Column A was of 3·9 cm. inside diameter and 97·1 cm. high while column B was of 6·3 cm. inside diameter and 97·8 cm. high. The distances between the top of the convex feed plate and the overflow for the two columns were 55·2 cm. and 84·5 cm. respectively. In each column the feed was introduced through a feed tube (0·7 cm. outer diameter) on top of the convex plate, located in the centre of the conical portion of the column. The function of the feed plate was to reverse the direction of flow, making the particles momentarily stationary so that the larger ones settled out rapidly around the plate. Proper adjustment of the feed tube and the plate is important as an off centre position results in a disturbed flow decreasing appreciably the settling rate.

The starch powder was made by grinding dried tapioca root in a hammer mill and collecting the −20 mesh fraction, which consisted of 35 per cent of +160 mesh and 65 per cent of −160 mesh portions. The slurry of the desired concentration was placed in a 10 l. aspirator bottle fitted with a stirrer. About 6 l. of the liquid were allowed to pass through the unit before collecting to ensure that equilibrium had been attained in both columns. The coarse particles, collected in the form of 10-15 per cent slurry, were withdrawn periodically as bottoms and the starch was collected continuously as overflow from the second column. The total quantity collected varied between 2 and 3 l. The various fractions were graded by sieving through a 160 mesh silk sieve, the solids dried in an oven to a constant weight and weighed.

Slurry concentrations were varied between 1 and 4 per cent solids and the terminal velocities in the larger column were varied between 0·632 and 3·6 mm./sec. corresponding to a flow of 7-40 l./hr.

Results and discussion

When a spherical non-porous incompressible particle is allowed to settle freely in an incompressible fluid, the maximum (or terminal) velocity attained is given by

$$\mathrm{Vm} = \frac{4(\rho_s - \rho_l)gD}{3\rho_l(fD)}$$

where Vm is maximum velocity; ρ_s, density of particles; ρ_c, density of fluid; g, acceleration due to gravity; D, diameter of the particle; and fD, friction factor.

When the flow is laminar, Stokes' law applies and the terminal velocity is given by

$$Vm = \frac{(\rho_s - \rho_l)}{18\mu} gD^2$$

where μ is viscosity of the fluid.

The terminal velocity of a single spherical particle, 0·1 mm. diameter (about −160 mesh) and density 1·53 (starch), in water at 25°C. would be

$$Vm = \frac{981}{18}\left(\frac{1{\cdot}53-1}{0{\cdot}00894}\right)(0{\cdot}01)^2 = 0{\cdot}324 \text{ cm./sec.}$$

When a large number of particles are present in the fluid, the rate of settling would be less than the calculated value due to mutual interference in the motion of the particles.

For 0·1 mm. quartz particles ($\rho_s = 2{\cdot}65$) in water, the settling velocity observed was 6·0 mm./sec.[6]. On this basis, the settling velocity of starch particles of the same diameter would be

$$Vm_1 = Vm_2\frac{(\rho_{s_1}-\rho_{l_1})}{(\rho_{s_2}-\rho_{l_2})} = 6\frac{(1{\cdot}53-1)}{(2{\cdot}65-1)}$$
$$= 1{\cdot}93 \text{ mm./sec.}$$

The flow at the velocities tested (3·6 mm./sec. max.) is viscous, as indicated by the calculated Reynolds number which is 0·4 (for laminar flow Reynolds number should be ≤ 3)[7].

Data collected are presented in Table 1. The recovery is plotted against the velocity (in larger column) in Fig. 2. From the curves (FIG. 2) it is evident that the recovery of starch is a linear function of the feed velocity for a particular concentration. Below the critical range this relationship can be expressed by the equation

$$y = 1{\cdot}90 \ cx$$

where y is recovery in g./hr./sq. cm.; x, velocity in mm./sec.; and c, concentration

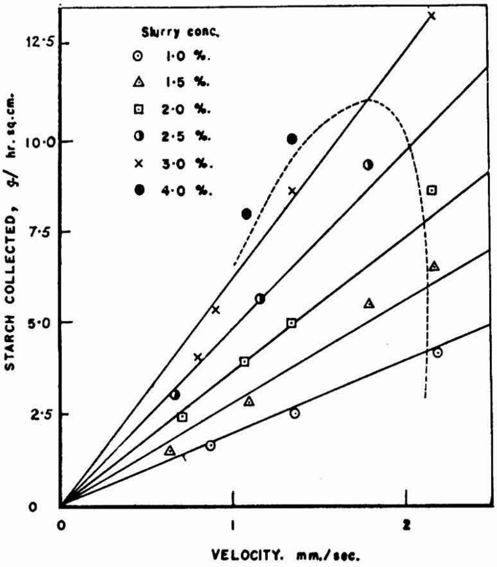

FIG. 2 — EFFECT OF LINEAR VELOCITY OF STARCH SLURRY ON THE TOTAL RECOVERY OF STARCH

TABLE 1 — OPERATIONAL AND CALCULATED DATA FOR THE EXPERIMENTAL ELUTRIATION UNIT

CONC. OF SLURRY %	RATE l./hr.	COLUMN A, BOTTOMS		COLUMN B				VELOCITY (LARGER COLUMN) mm./sec.	STARCH IN OVERFLOW g./hr. sq. cm.	EFFICIENCY (STARCH IN OVERFLOW) / TOTAL STARCH %
				Bottoms		Overflow				
		+160 %	−160 %	+160 %	−160 %	+160 %	−160 %			
1·0	9·8	25·0	—	9·0	12·0	—	54·0	0·88	1·72	82·0
1·0	15·0	17·5	—	18·0	14·0	—	51·0	1·35	2·48	79·0
1·0	24·0	13·0	—	22·0	7·0	Traces	58·0	2·17	4·51	89·0
1·0	40·0	5·5	—	26·0	4·5	2·0	62·0	3·60	8·05	—
1·5	7·0	22·0	—	11·0	10·5	—	46·0	0·63	1·57	70·0
1·5	12·0	17·0	—	20·0	12·0	—	50·0	1·08	2·92	81·0
1·5	20·0	13·0	—	21·0	9·5	—	57·0	1·80	5·55	86·0
1·5	24·0	11·0	—	23·0	8·0	1·0	57·0	2·17	6·65	—
2·0	7·7	20·0	4·0	15·0	13·0	—	47·0	0·70	2·37	73·0
2·0	12·0	18·0	—	20·0	11·0	—	51·0	1·08	3·96	82·0
2·0	15·0	14·0	—	21·0	13·0	—	52·0	1·35	5·05	80·0
2·0	24·0	10·0	—	24·0	8·0	2·5	55·5	2·17	8·66	—
2·5	7·6	20·0	5·0	14·0	14·0	—	47·0	0·68	2·90	71·0
2·5	13·0	19·0	—	14·0	11·0	—	55·0	1·17	5·80	83·0
2·5	20·0	11·0	—	24·0	7·5	—	58·0	1·80	9·40	89·0
3·0	8·8	19·0	5·0	14·0	16·0	—	46·0	0·79	3·92	68·5
3·0	10·0	17·0	—	16·0	9·0	—	58·0	0·90	5·65	86·5
3·0	15·0	16·0	—	18·0	7·0	—	59·0	1·35	8·70	89·5
3·0	24·0	8·0	—	23·0	6·0	5·0	58·0	2·17	13·50	—
4·0	12·0	18·0	—	15·0	16·0	Traces	51·0	1·08	7·95	76·0
4·0	15·0	13·0	—	22·0	11·0	2·0	52·0	1·35	10·10	—

as percentage solids in the slurry. The maximum deviation between the observed and the calculated values from the above equation is +13·4 per cent and −13·0 per cent and the average deviation is +0·13 per cent. Thus it can be seen that the equation is fairly representative.

The dotted line envelop (FIG. 2) shows the critical velocity region beyond which coarser particles (+160 mesh) are lifted in the overflow. The critical velocity varies between 1·08 mm./sec. and 2·17 mm./sec. for concentrations of 4 to 1 per cent respectively. The unit, therefore, can be run most efficiently between 2 and 3 per cent concentrations and around velocities of 1·8-2·0 mm./sec.

The efficiency (starch in overflow/total starch in feed) is plotted against the terminal velocity in Fig. 3. The efficiency rises sharply for velocities between 0·6 and 1 mm./sec. and levels off up to 2·1 mm./sec. Beyond this range the efficiency should be considered zero as the final product is contaminated with coarser particles.

Conclusion

On the basis of the data presented it can be safely predicted that the unit developed would be suitable for use in the starch industry to replace the usual sieving operation. A unit fitted with two columns of 1 ft. and 2·5 ft. diameters would be capable of processing 1 ton starch per day.

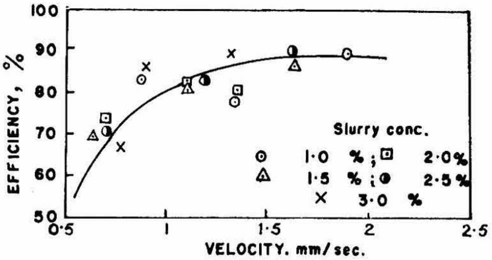

FIG. 3 — EFFECT OF LINEAR VELOCITY OF STARCH SLURRY ON THE EFFICIENCY OF RECOVERY

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Studies on the Concentration & Cyanidation of Auriferous Pyrite from Harewood Mine, Wynaad, Nilgiris

G. V. SUBRAMANYA & P. I. A. NARAYANAN
National Metallurgical Laboratory, Jamshedpur

A study has been made on the recovery of sulphides and gold from an auriferous pyrite sample from Harewood mine by tabling, magnetic separation, flotation and cyanidation. The sample, highly weathered and complex from the point of view of mineral dressing, was found to contain 2·4 per cent sulphur and 3·7 dwt. of gold per ton. Sulphur is present in the form of pyrite, pyrrhotite, marcasite and sulphates. Flotation recovers 50 to 64 per cent sulphur, the concentrate grades being 30 to 18 per cent sulphur.

The possibility of recovering gold and some of the sulphur as byproducts from the ore and the factors which affect the dissolution of gold in cyanide solutions have been investigated. Optimum particle size for cyanidation has been found to be 65 mesh. Use of lead acetate accelerates the dissolution of gold. Direct cyanidation of the ore after removal of magnetic minerals at −35 mesh results in lower consumption of cyanide. Flotation of pyrite and gold, followed by roasting of the flotation concentrate at 750°C. and cyanidation of the calcine recovers 92·0 per cent of the total gold, with a cyanide consumption of 0·21 lb./ton of ore.

THE investigation reported in this paper forms part of beneficiation work carried out, at the instance of the Geological Survey of India, on three samples of auriferous pyrite from the old abandoned mines of Harewood and Alpha in the Wynaad area of Nilgiris, Madras. In spite of the low sulphur contents of the samples, investigations were undertaken on account of the strategic importance of sulphur.

Sample — Ten cwt. of lode material consisting of lumps of 3 in. and below were received for investigation. This material seems to be more highly mineralized than the samples from Alpha mine and has higher sulphur and gold contents, but it is of a weathered (oxidized) type and consequently is more complex from an ore-dressing standpoint.

Concentration studies

Chemical analysis and mineralogical composition — Chemical analysis (TABLE 1) shows that it contains 2·42 per cent total sulphur and 3·7 dwt. gold per ton of ore.

The chief gangue minerals are quartz and magnetite with minor amounts of siderite, calcite, haematite, feldspar and chloritic minerals.

The sulphide minerals present are pyrite, marcasite, pyrrhotite and traces of chalcopyrite. Pyrite occurs as aggregates of coarse crystals while other sulphides occur closely associated with magnetite and the gangue minerals.

Gold is in a very fine state of division and is mostly associated with pyrite, the other sulphide minerals being almost barren. Polished sections of the pyrite indicate the presence of small particles of gold in the pyrite.

The ore is highly oxidized as evidenced by the presence of oxides and sulphates of iron.

Sieve analysis, heavy liquid separation and microscopic examination — Table 2 gives the size distribution of the −10 mesh roll-crushed product.

Microscopic examination of the sized fractions reveals that all the pyrite particles are liberated at −65 mesh and there is fair liberation at 35 mesh.

Heavy liquid separation tests done with the various fractions using acetylene tetrabromide showed that the sink product con-

TABLE 1 — CHEMICAL ANALYSIS

	%
Total S	2·42
SiO_2	65·50
Total Fe	15·50
S present as pyrrhotite	0·56
Gold	3·70 dwt./ton (fire assay)

stitutes about 30 per cent. Both the sink and float products were examined under the microscope. The pyrite particles are free at −65 mesh but are always associated with transparent minerals in the coarser fractions.

Tabling — Although a high grade of pyrite concentrate could not be expected by gravity methods, on account of the presence of other heavy minerals, two tabling experiments were carried out with material ground to −65 mesh and −35 mesh. Recoveries of sulphur in the two tests were 63·9 and 63·7 per cent in the concentrates of grade 6·05 and 6·78 per cent sulphur respectively. Recoveries of gold were 80·5 and 88·0 per cent respectively.

Flotation — A large number of flotation tests were carried out to recover gold as well as pyrite. Except where otherwise stated, the flotation feed was prepared by grinding the −10 mesh ore in a rod mill for 15 min. with 66 per cent solids to the size given in Table 3.

Conditioning period was 5 min. in all the experiments for modifying agents, 3 min. for collectors, and each of the 3 floats was taken for 2 min. The floats were taken at 5 min. intervals, the first with 0·125 lb./ton of amyl xanthate and the subsequent floats with 0·05 lb./ton each. Pine oil was employed as frother in all the tests.

TABLE 2 — SIEVE ANALYSIS OF −10 MESH PRODUCT

SIZE (mesh)	WT. %
− 10 + 14	26·6
− 14 + 20	19·2
− 20 + 28	12·8
− 28 + 35	9·1
− 35 + 48	7·2
− 48 + 65	5·6
− 65 + 100	5·0
−100 + 150	3·8
−150 + 200	2·1
−200 + 270	2·1
−270	6·5

TABLE 3 — SIEVE ANALYSIS OF FEED USED IN FLOTATION

SIZE (mesh)	WT. %
+ 48	0·4
− 48 + 65	6·0
− 65 + 100	21·1
−100 + 150	18·3
−150 + 200	12·0
−200 + 270	8·6
−270	33·6

TABLE 5 — FLOTATION WITH AMYL XANTHATE AND REAGENT 208

PRODUCTS	WT. %	ASSAY % S	RECOVERY % S	GOLD dwt./ton	RECOVERY % Au
Flotation conc.	4·6	28·00	56·0	74·2	92·3
Tailing	95·4	1·06	44·0	0·3	7·7
	100·0	2·30	100·0	3·7	100·0

Due to the oxidized nature of the ore, the *p*H of the pulp was 6·1 using distilled water for grinding. The *p*H could not be brought to the alkaline side with even 3 lb./ton of sodium carbonate. This may be due to the buffering action of salts produced by the oxidation of sulphides. Flotation without the use of any modifying agent proved non-selective. Addition of copper sulphate in the presence of sulphuric acid gave higher grade and recovery of sulphur. It is thought that the sulphuric acid might function as a cleansing agent for slime coatings and iron oxide, thus aiding the adsorption of copper ions by the pyrite surface. On the other hand, use of copper sulphate with sodium carbonate lowered the grade of concentrate as well as recovery. The results obtained when sulphuric acid (1 lb./ton) and copper sulphate (0·5 lb./ton) were employed are given in Table 4.

In another set of experiments the collectors were varied keeping sulphuric acid and copper sulphate constant. Amyl xanthate and Reagent 208 (American Cyanamid Co.) (0·3 lb./ton) have given a fairly good recovery of sulphur (TABLE 5) and the best gold recovery.

Amyl xanthate and Aerofloat 31 when used as collectors did not improve the results.

A mixture of pentasol amyl xanthate and potassium ethyl xanthate in the ratio 2: 1 gave a better recovery and grade of sulphur

TABLE 4 — FLOTATION WITH AMYL XANTHATE

(*Grinding, 15 min.*)

REAGENTS lb./ton	*p*H	PRODUCTS	WT. %	ASSAY % S	RECOVERY % S	GOLD dwt./ton
Sulphuric acid, 1·0	—	Conc. 1	4·15	30·21	55·0	—
Copper sulphate, 0·5	—	Conc. 2	1·17	11·39	5·9	—
—	5·8	Conc. 3	0·65	8·49	2·4	—
—	—	Tailing	94·03	0·89	36·7	0·9

but the gold loss in the tailing was high (TABLE 6).

Repetition of test of Table 4 with a material ground finer (grinding time 20 min. instead of 15 min.) slightly increased the recovery and grade, with only two floats (TABLE 7) taken for 10 min. (5 + 5) as against 15 min.

It is observed that in the flotation tests the recovery of sulphur varies from 50 to 65 per cent, the grade varying from 30 to 18 per cent sulphur. The low recovery of sulphur is due to the highly oxidized nature of the ore, as well as to the presence of pyrrhotite and marcasite which are intimately associated with the gangue. No pyrite is visible in the tailing. Recovery of gold is well over 90 per cent in the flotation concentrates while it is 80-88 per cent in the table concentrates.

Magnetic separation — Results of magnetic separation of the ore roll crushed to −10 mesh, −28 mesh and −35 mesh are given in Table 8.

These experiments are important as they throw some light on the association of sulphides and gold in the ore. Pyrite is found interlocked with a transparent mineral but not with magnetite, whereas pyrrhotite and marcasite are closely associated with magnetite. This accounts for the presence of more than 50 per cent of the sulphide in the magnetic portion. It is clear from these experiments that most of the gold is either associated with pyrite or other non-magnetic gangue. Recovery of gold is 98·64 per cent in the non-magnetic product when the magnetic separation is carried with ore crushed to −35 mesh.

TABLE 6 — FLOTATION WITH A MIXTURE OF PENTASOL AMYL XANTHATE AND POTASSIUM ETHYL XANTHATE

PRODUCTS	WT. %	ASSAY % S		RECOVERY % S		Au dwt./ton
Float 1	3·6	34·83	30·0	53·6	60·1	—
Float 2	1·1	13·93		6·5		
Tailing	95·3	0·98		39·9		0·75
	100·0	2·341		100·0		—

TABLE 7 — FLOTATION WITH MATERIAL GROUND FOR 20 MIN.

PRODUCTS	WT. %	ASSAY % S		RECOVERY % S
Concentrate 1	4·2	30·7	25·25	56·4
Concentrate 2	1·7	11·6		8·6
Tailing	94·1	0·85		35·0
	100·0	2·30		100·0

Cyanidation

Numerous studies on the dissolution of gold in cyanide solutions are reported in literature. The chemical reaction involved in cyanidation using potassium cyanide is represented by a number of equations of which the most important are those of Elsner, Bodlaender and Janin. The work of Barsky *et al.*[1] on the calculation and comparison of free energies and equilibrium constants for these equations limits the acceptable equations to that of Bodlaender and Elsner. The thermodynamic calculations of Reynolds[2] also indicate that both these equations are possible and that oxygen is necessary to the dissolution of gold. The recent investigations of Mitsuo Kameda[3] favour Bodlaender's equation. So the chemical reactions involved in cyanidation can be represented by:

(i) Elsner's equation:

$$4Au + 8KCN + O_2 + H_2O = 4KAu(CN)_2 + 4KOH$$

(ii) Bodlaendar's equation:

$$2Au + 4KCN + O_2 + 2H_2O = 2KAu(CN)_2 + 2KOH + H_2O_2$$

$$2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH$$

TABLE 8 — MAGNETIC SEPARATION

SIZE (mesh)	PRODUCTS	WT. %	ASSAY % S	RECOVERY % S	Au dwt./ton	RECOVERY % gold
−10	Magnetic	39·0	4·67	71·5	—	—
	Non-magnetic	61·0	1·19	28·5	—	—
		100·0	2·55	100·0	—	—
−28	Magnetic	38·6	4·06	68·5	—	—
	Non-magnetic	61·4	1·17	31·5	4·4	—
		100·0	2·29	100·0	—	—
−35	Magnetic	18·9	6·66	51·8	—	1·36
	Non-magnetic	81·1	1·45	48·2	4·5	98·64
		100·0	2·44	100·0	—	100·00

It has been shown by Barsky *et al.* that excess of alkali has a depressing effect on the rate of dissolution of gold and this is more pronounced with lime than with sodium or potassium hydroxide. This is attributed by Mitsuo Kameda[4] to the prevention of the second stage of Bodlaender's reaction, either by the elimination of H_2O_2 as calcium peroxide or by the stabilizing effect of alkalies on the decomposition of hydrogen peroxide. This effect calls for the correct control of alkalinity during cyanidation.

Although there is no agreement as to the concentration of KCN which induces the maximum velocity of gold dissolution (0·25 per cent KCN according to Maclaurin and 0·027 per cent according to White), plant practice is to use about 0·06 per cent KCN or even less in cyaniding gold ores.

Results of a detailed study of the various factors which affect the dissolution of gold from the sample from Harewood mine are presented below.

Results and discussion

DIRECT CYANIDATION

Particle size distribution of the material (wet ground in the ball mill) used in the various cyanidation experiments are given in Table 9 and represented by A, B and C.

TABLE 9 — PARTICLE SIZE DISTRIBUTION OF THE ORE USED IN CYANIDATION TESTS

MESH (T.S.S.)	WT. % A	WT. % B	WT. % C
+ 48	2·1	—	—
− 48+ 65	13·6	4·6	—
− 65+100	26·1	9·0	3·2
−100+150	16·9	17·9	9·7
−150+200	9·8	14·9	13·7
−200	31·5	53·6	73·4

Cyanidation experiments were carried out at a solid liquid ratio of 1: 2·5 keeping the concentration of potassium cyanide at 0·06 per cent and of lime at 0·025 per cent. These reagents were added at intervals after determining the strength of these in the agitated pulp.

Effect of particle size and time of agitation — The effects of particle size and time of agitation on the dissolution of gold are demonstrated by the results given in Table 10.

It is general experience that the rate of dissolution of gold increases with decrease in particle size. But in the present case the rate of dissolution is maximum with the size B which corresponds to the size at which pyrite is completely released from the gangue. With coarser or finer feeds the dissolution is slower. The rapid dissolution of gold may be attributed to the fact that most of gold is in good contact with a cathodic sulphide mineral, pyrite. With finer sizes than −65 mesh, some gold may get released from the pyrite and escape dissolution, as postulated by Thompson[5] on the basis of electrochemical nature of dissolution of gold.

Maximum recovery of gold is 92 per cent with 48 hr. agitation and using grind B the consumption of cyanide being 6·75 lb./ton.

Subsequent tests were carried out with size B.

Effect of pre-aeration — Pre-aeration with excess lime for a period of 0·5 and 24·0 hr. has not improved the results of direct cyanidation (TABLE 11). On the other hand, it has resulted in reduced extraction of gold.

TABLE 10 — EFFECT OF PARTICLE SIZE AND TIME OF AGITATION ON THE DISSOLUTION OF GOLD

TEST NO.	GRIND	DURATION OF AGITATION hr.	CONSUMPTION lb./ton KCN	CONSUMPTION lb./ton CaO	Au, ASSAY OF RESIDUE dwt./ton	EXTRACTION OF GOLD %
1	A	24·0	2·90	6·09	2·20	40·6
2	B	24·0	5·15	6·60	0·84	77·2
3	C	24·0	5·30	7·80	1·70	54·0
4	A	45·5	4·45	6·96	1·16	68·6
5	B	48·0	6·75	7·65	0·30	92·0
6	C	48·0	7·15	8·30	0·40	89·2

TABLE 11 — EFFECT OF PRE-AERATION

TEST NO.	DURATION OF PRE-AERATION hr.	DURATION OF AGITATION hr.	CONSUMPTION lb./ton KCN	CONSUMPTION lb./ton CaO	Au, ASSAY OF RESIDUE dwt./ton	EXTRACTION OF GOLD %
7	0·5	24·0	5·2	7·50	1·2	67·6
8	0·5	47·0	6·6	7·05	0·8	78·4
9	24·0	44·0	6·1	12·00	1·0	73·0

Effect of removal of solubles — Removal of soluble salts produced during grinding in order to effect reduction in the consumption of cyanide has not yielded the expected results (TABLE 12).

Effect of cyanidation at low *p*H — Cyanidation at a low *p*H of about 8·0 has reduced the gold recovery to 67·6 per cent (TABLE 13) as the concentration of cyanide will be decreased at low *p*H. It may be stated that all the previous tests were done at a *p*H over 10.

The large consumption of cyanide in all the tests is due to the presence of cyanicides in the ore. Of the three iron sulphides, pyrite is more stable while marcasite and pyrrhotite decompose[6] in cyanide solutions, giving various products of which thiocyanate and ferrocyanide are the most important from the point of view of cyanide consumption.

Analyses of the pregnant solutions from experiments 5 and 12 are given in Table 14. It is evident that low alkalinity favours the formation of ferrocyanide whereas high alkalinity helps the production of thiocyanate.

Cyanidation of non-magnetic material — Removal at −35 mesh of the magnetic material which contains very little gold and the subsequent cyanidation of the non-magnetic portion have resulted in the reduced consumption of cyanide and lime (TABLE 15).

Recovery of gold is 93·4 per cent after agitation for 48 hr., the consumption of lime and potassium cyanide being 6·9 and 4·1 lb./ton of non-magnetic material (equivalent to 5·65 and 3·36 lb./ton of ore).

TABLE 12 — EFFECT OF REMOVAL OF SOLUBLE SALTS

TEST No.	DURATION OF AGITATION, hr.	CONSUMPTION lb./ton		Au, ASSAY OF RESIDUE dwt./ton	EXTRACTION OF GOLD %
		KCN	CaO		
10	24	5·35	5·55	3·1	18·92
11	47	6·60	7·05	0·6	83·80

TABLE 13 — CYANIDATION AT *p*H 8·0

TEST No.	DURATION OF AGITATION hr.	CONSUMPTION lb./ton		Au, ASSAY OF RESIDUE dwt./ton	EXTRACTION OF GOLD %
		KCN	CaO		
12	48	7·75	3·6	1·2	67·6

TABLE 14 — ANALYSIS OF PREGNANT SOLUTION OF TESTS 5 AND 12

TEST No.	*p*H	KCNS g./l.	$K_4Fe(CN)_6$ g./l.
5	Above 10	1·368	0·338
12	8	0·720	0·510

TABLE 15 — CYANIDATION OF NON-MAGNETIC MATERIAL

DURATION OF AGITATION hr.	CONSUMPTION lb./ton		ASSAY OF RESIDUE dwt./ton Au	EXTRACTION OF GOLD %
	KCN	CaO		
18·0	3·0	6·0	2·3	48·8
24·0	3·0	6·0	1·7	62·2
48·0	4·1	6·9	0·3	93·4

TABLE 16 — PARTICLE SIZE DISTRIBUTION OF ORE EMPLOYED IN STUDYING THE EFFECT OF LEAD ACETATE

SIZE (mesh)	WT. %			
	D	E	F	G
− 65 + 100	20·2	—	—	—
−100 + 150	21·0	14·8	—	—
−150 + 200	13·6	21·0	24·6	2·5
−200 + 270	11·1	14·6	19·0	14·2
−270	34·1	49·6	56·4	83·3
	100·0	100·0	100·0	100·0

Effect of addition of lead salts on cyanidation — It has been observed by a number of workers[7-9] that lead salts accelerate the dissolution of gold. According to Clennel[10] lead is electro-negative to gold in cyanide solutions. Russel[11] suggests that the cathodic reduction of lead by gold in cyanide solution is responsible for the enhanced rate of reaction. Fink and Putnam[8] attribute the phenomenon to the deposition of lead on the gold providing cathodic areas. A lower limiting concentration of cyanide as well as metal ion is necessary to give the accelerating effect and the control of alkalinity is important.

In order to study the accelerating effect of lead acetate on the rate of dissolution of gold, the ore was dry ground to give the grind samples listed in Table 16.

Agitation with cyanide and lead acetate was carried out with each of the grinds for different periods keeping the solid liquid ratio at 1 : 3. Lime and cyanide were added in excess before the commencement of agitation.

The effect of concentration of lead acetate on the dissolution of gold is indicated in Table 17 and graphically represented in Fig. 1. The extraction of gold is maximum (94·6 per cent) at a concentration of 0·01 per cent lead acetate.

The changes in the extraction of gold caused by varying the grind of ore and the time of agitation are shown in Fig. 2 and Table 18, when 0·01 per cent lead acetate was employed as an accelerator.

When lead acetate is used, grinds D and E give almost the same extraction of gold, but

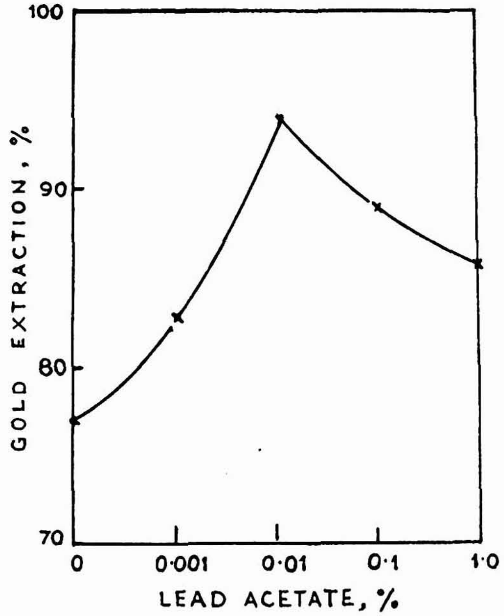

FIG. 1 — EFFECT OF LEAD ACETATE ON THE EXTRACTION OF GOLD

TABLE 17 — EFFECT OF CONCENTRATION OF LEAD ACETATE ON GOLD EXTRACTION — SIZE E

% LEAD ACETATE	DURATION OF AGITATION hr.	GOLD, ASSAY OF RESIDUE dwt./ton	EXTRACTION OF GOLD %
0·000	48	0·80	78·4
0·000	20	0·85	77·0
0·001	20	0·60	83·8
0·010	20	0·20	94·6
0·100	20	0·40	89·2
1·000	20	0·50	86·5

TABLE 18 — EFFECT OF PARTICLE SIZE AND DURATION OF AGITATION ON THE DISSOLUTION OF GOLD USING LEAD ACETATE AS ACCELERATOR

GRIND	CONSUMPTION lb./ton KCN	CONSUMPTION lb./ton CaO	RESIDUE ASSAY dwt./ton Au	EXTRACTION OF GOLD %
Duration of agitation 6 hr.				
D	3·92	7·00	0·6	83·8
E	5·18	7·20	0·6	83·8
F	5·72	7·70	1·2	67·6
G	6·80	8·20	1·5	59·5
Duration of agitation 18 hr.				
D	6·08	7·66	0·4	89·2
E	7·40	8·24	0·2	94·6
F	7·70	8·33	0·8	78·4
G	7·82	8·68	1·0	73·0
Duration of agitation 24 hr.				
D	6·74	7·89	0·2	94·6
E	7·58	8·28	0·2	94·6
F	8·30	8·58	0·8	78·4
G	8·66	8·79	0·4	89·2
Duration of agitation 48 hr.				
D	7·94	8·40	0·1	97·3
E	8·54	8·64	0·1	97·3
F	9·17	8·91	0·3	91·9
G	9·20	8·94	0·2	94·6

the consumptions of cyanide and lime are more with grind E; so D is the optimum size for best cyanidation. With finer sizes not only is the gold extraction low but the consumption of potassium cyanide is high. With only 6 hr. agitation, the percentage extraction of gold is 83·8 in these experiments, whereas without lead acetate agitation for even 48 hours dissolves only 78·4 per cent of gold. Consumption of cyanide in the present experiment is only 3·92 lb./ton, while in the absence of lead acetate it is 8·35 lb./ton. The maximum dissolution obtained is 97·3 per cent gold when agitated for 48 hr., the consumption of lime and cyanide being 8·45 and 7·94 lb./ton respectively, when 0·01 per cent lead acetate is used.

FLOTATION, ROASTING AND CYANIDATION OF CALCINES

Flotation — Flotation experiments were carried out in the unit flotation cell keeping the pulp density at about 18 per cent solids. The reagents employed were:

	lb./ton
Sulphuric acid	1·00
Amyl xanthate	0·10
Reagent 208	0·10
Pine oil	0·08

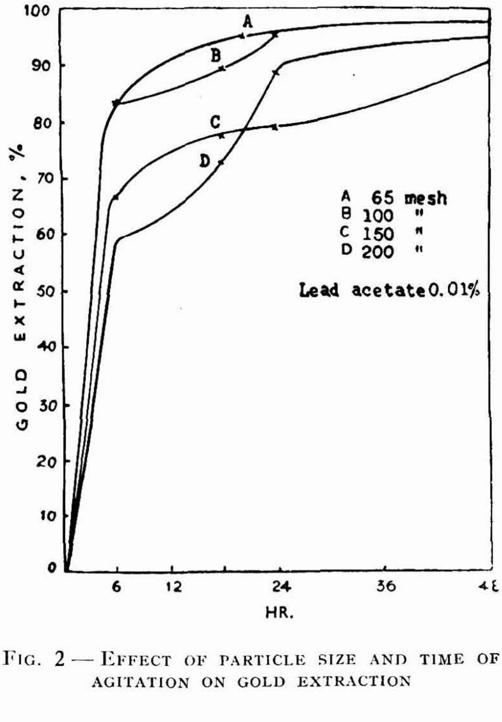

FIG. 2 — EFFECT OF PARTICLE SIZE AND TIME OF AGITATION ON GOLD EXTRACTION

The results are given in Table 19. Recovery of gold in the flotation concentrate is 92·3 per cent.

Roasting of flotation concentrate — The roasting or air oxidation of pyrite is a highly complicated process, producing a large number of products but the final products of oxidation are haematite and sulphur dioxide, under the conditions of roasting usually carried out with the auriferous flotation concentrates. Wienert[12] has given a critical review of the present knowledge on the roasting of auriferous pyrites.

Particle size distribution of the flotation concentrates and the calcines obtained after roasting the flotation concentrate at different temperatures are given in Table 20. The particle size of the calcine gradually increases as the temperature increases from 450° to 650°C. but at 750°C. there is a decrease in size.

Analysis of washed calcines is given in Table 21. There is a gradual decrease in the total sulphur content as the temperature of roasting increases. The temperature of roasting and the sulphur content of the final calcine are important from the point of view of cyanidation of the product.

TABLE 19 — FLOTATION TEST WITH AMYL XANTHATE AND REAGENT 208

PRODUCTS	WT. %	ASSAY % S	GOLD dwt./ton	RECOVERY % Au
Flotation concentrate	4·78	30·0	71·43	92·3
Flotation tailing	95·22	—	0·30	7·7
	100·00	2·4	3·70	100·0

TABLE 20 — SIZE DISTRIBUTION OF FLOTATION CONCENTRATE AND OF ROASTED CALCINES

MESH (T.S.S.)	FLOTATION CONC. wt. %	CALCINES ROASTED AT 450°C. wt. %	550°C. wt. %	650°C. wt. %	750°C. wt. %
+ 65	8·1	12·4	14·8	16·0	14·0
− 65 + 100	14·7	14·4	17·0	18·4	15·2
−100 + 150	12·1	11·2	13·6	18·6	10·8
−150 + 200	5·7	8·0	15·2	18·8	8·0
−200 + 270	11·1	9·6	10·6	8·0	9·2
−270	48·3	44·4	28·8	20·2	42·8
	100·0	100·0	100·0	100·0	100·0

TABLE 21 — ANALYSIS OF WASHED CALCINES

TEMP. OF ROASTING °C.	% S	% Fe_2O_3	GOLD dwt./ton
450	0·09	80·0	91·26
550	0·07	79·9	92·72
650	0·03	84·5	98·30
750	0·01	80·1	91·26

TABLE 22 — CYANIDATION OF CALCINES

(48 *hr. agitation*)

TEMP. OF CALCINATION °C.	CONSUMPTION lb./ton KCN	CaO	HEAD	ASSAY OF RESIDUE dwt./ton	% EXTRACTION Au
450	6·42	1·62	91·26	5·6	93·90
550	6·60	1·71	92·72	21·8	76·47
650	6·24	1·57	98·31	3·4	96·52
750	5·64	1·42	91·26	0·4	99·56

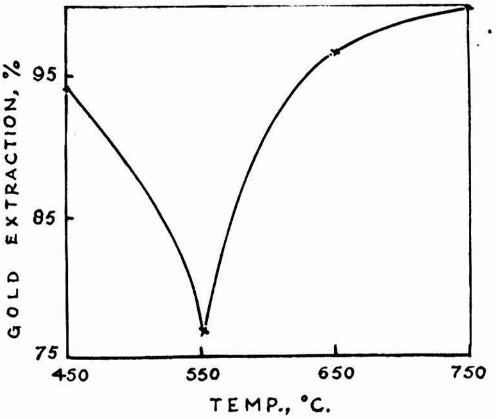

FIG. 3 — EFFECT OF ROASTING TEMPERATURE ON GOLD EXTRACTION

Cyanidation of calcines — Results of cyanidation of the calcines at 1: 3 solid/liquid ratio at a concentration of 0·12 per cent potassium cyanide and 0·03 per cent CaO are presented in Table 22 and graphically represented in Fig. 3.

Extraction of gold from the calcine obtained at 450°C. is higher than that from 550°C., whereas the calcines obtained at 650° and 750°C. yield increasing amounts of gold. The recovery is maximum at 750°C. (99·6 per cent). The consumption of cyanide and lime are 0·21 lb. and 0·053 lb./ton respectively on the basis of the original weight of ore. Extraction of gold when the calcines are ground is invariably lower.

Summary

The chief gangue minerals present in the auriferous pyrite ore from Harewood mine, Wynaad, Nilgiris, are quartz and magnetite with minor amounts of siderite, calcite, haematite, feldspar and chlorite minerals. The mineral is weathered and contains sulphates. The sulphide minerals present are pyrite, marcasite, pyrrhotite and traces of chalcopyrite. Gold is finely divided and is mostly associated with the pyrite.

The presence of heavy minerals limits the grade of concentrate that can be obtained by gravity methods.

Flotation recovers 50 to 64 per cent sulphur, the concentrate grades ranging from 30 to 18 per cent sulphur. The low recovery of sulphur is attributed to the presence of a large amount of sulphur in the form of sulphates. The best result from the point of view of recovery of both gold and sulphur is obtained by using a mixture of amyl xanthate and Reagent 208 as collectors. Recovery of gold is 92 per cent.

Magnetic separation at −35 mesh gives a non-magnetic product which contains 98 per cent of the total gold, eliminating pyrrhotite and part of marcasite, which are cyanicides.

Particle size is very important for cyanidation, the optimum size for the best recovery being −65 mesh. Maintenance of the alkalinity during cyanidation at 0·025 per cent CaO and cyanide strength at 0·06 per cent KCN by additions at intervals gives the best results, rather than one addition of the requisite quantity of lime and cyanide in the initial stage.

Pre-aeration and removal of solubles prior to cyanidation have not the desired effect by way of improved gold extraction or lower consumption of reagents.

Consumption of potassium cyanide and lime for straight cyanidation are very high due to the presence of pyrrhotite and marcasite. Removal of pyrrhotite and part of the marcasite by magnetic separation at −35 mesh results in low consumption of lime and cyanide, the overall extraction of gold being 92·12 per cent.

Lead acetate accelerates the dissolution of gold during cyanidation and reduces the consumption of cyanide. With only 6 hr. agitation in the presence of lead acetate, extraction of gold is 83·8 per cent, consumption of cyanide being 3·92 lb./ton while even with 48 hr. agitation the recovery of gold is only 78·4 per cent and the consumption of cyanide is 8·35 lb./ton if lead acetate is not employed as an accelerator. Use of lead acetate during cyanidation of the non-magnetic product may further reduce the consumption of cyanide.

A study of the effect of roasting of the flotation concentrate on cyanidation indicates that the extraction of gold is maximum when roasting is carried out at 750°C. The total extraction of gold is then 92·0 per cent, consumption of lime and cyanide being 0·05 and 0·21 lb./ton of original material respectively.

The results indicate the possibility of recovering gold and some of the sulphur as a byproduct from the ore from Harewood mine.

Acknowledgement

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Enzyme Systems of the Silk-worm, *Bombyx mori* Linn.: Part I — A Preliminary Study

B. BHEEMESWAR* & M. SREENIVASAYA†

A study has been made of the enzyme systems — proteases, carboxy and amino peptidases, carbohydrases, nucleolytic enzymes and oxidation-reduction enzymes—associated with the principal tissues and tissue fluids (intestine, haemolymph and silk gland) of the silkworm (*Bombyx mori* Linn.).

The tissues have been found to be associated with a practically complete and a rich proteolytic system including the carboxy and amino peptidases.

The significance of the dehydrogenase systems associated with the gland with special reference to glutamic acid dehydrogenase is indicated.

IN connection with our experiments on the nutrition of the silk-worm, a study of the enzyme systems associated with the more important organs and tissue fluids of the organism has been undertaken. The present communication deals with a preliminary study of four groups of enzymes: (a) carbohydrases; (b) proteoclastases; (c) nucleolytic enzymes associated particularly with the nucleic acid rich silk gland; and (d) oxidation-reduction enzymes connected with the respiratory system.

Earlier work on the enzymes of insects is meagre; considering the economic importance of the silk-worm, enzyme studies on this organism are neither comprehensive nor satisfactory. Lichtenstein[1,2] and his coworkers have reported that glycerol extracts of diapause eggs of silk-worm hydrolyse the peptones of casein and gelatin, L-leucyl glycine, L-leucyl glycyl glycine and chloracetyl tyrosine but do not split either casein or gelatin, either with or without glutathione or cyanide. They obtained, however, a definite cleavage of casein with extracts of actively developing eggs, prepared a few days before hatching. Other papers[3,4] dealing with proteoclastic enzymes describe the work carried out with intestinal extracts as the source of the enzyme. The haemolymph of the silk-worm[5] has been reported to contain tyrosinase, catalase, phenolase, invertase, maltase, lipase and two proteases in varying concentrations depending upon the age and stage of development.

Recent work of Yamafugi and his collaborators[6,7] has elucidated the mode of incorporation of inorganic forms of nitrogen into amino compounds. They have shown, in this connection, the occurrence of an enzyme in the tissues of the silk-worm, oximase, which brings about the reduction of oximes. This enzyme has been shown to be activated by hydroxylamine and nitrite.

Experimental procedure

Enzyme extracts for these investigations were prepared by grinding the carefully and freshly isolated tissues either with 60 per cent glycerol (5 vol.) or with M/15 phosphate buffer, *p*H 7·4. For a determination of the amylolytic and ribonuclease activities, glycerol homogenates were employed as the source of the enzyme, while for a study of the oxidation-reduction enzymes and proteoclastic enzymes, the homogenates were prepared with the buffer. Well-developed crossbred worms (Mysore × *C. nichi*), 3 to 4 days after the fourth moult, were employed for the preparation of the homogenates.

The haemolymph or the body fluid of the worm was squeezed out by making an incision at the fourth segment of the worms before the carcass was dissected for isolating the other tissues of the worm — glandular and intestinal. Homogenates prepared from these tissues were preserved under toluene at 0°C.

Proteoclastic activity was determined by the papyrographic method employing casein and gelatin and a few peptides at *p*H 8 [BHEEMESWAR, B. and SREENIVASAYA, M. (in press)]. Methods for the determination of

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*Indian Institute of Science, Bangalore 3.
†17th Cross Road, Malleswaram, Bangalore 3.

the amylase and ribonuclease activities have been described previously$^{8-10}$. Necessary live and boiled enzyme controls were simultaneously conducted and corrections applied in calculating the activity. The activity of the oxidation-reduction enzymes was determined by the anaerobic Thunberg methylene blue reduction technique^{11}. The results are presented in Tables 1-3.

TABLE 1 — HYDROLYTIC ENZYMES (PROTEASES AND PEPTIDASES)

Substrates	Enzyme source, M/15 phosphate buffer homogenate of		
	Intestine	Gland	Haemolymph
Proteases			
(*p*H *of the reaction*, 8·0; *temp. of the reaction*, 37°C.)			
Casein	+ + + + +	+ + +	+ +
Gelatin	+ + + + +	+ +	+
Peptidases			
(*p*H *of the reaction*, 7·4; *temp. of the reaction*, 37°C.)			
Carboxy chloracetyl L-leucine	+ + + +	+ + +	+ + + +
Carboxy chloracetyl L-tryptophane	+ +	+ + +	+ + + +
Carboxy chloracetyl L-tyrosine	+ +	+ +	+ +*
Amino L-alanyl glycine	+ + + +	+ + +	+ + + +
Amino L-diglycyl glycine	+ +	+ +	+ +
Amino L-glycyl glycine	+ + +	+ +	+ +
Amino L-glycyl L-leucine	+ + + +	+ + +	+ + +
Amino L-glycyl L-tyrosine	+ + +	+ + +	+ +*
Amino L-glycyl L-tryptophane	+ + +	+ +	+ + +
Amino L-leucyl glycyl glycine	+ + +	+ + + +	+ + +
Amino L-leucyl glycine	+ + + +	+ + + +	+ + +

*Reaction mixtures darken due to melanin formation by the action of tyrosinase present in the haemolymph.

TABLE 2 — HYDROLYTIC ENZYMES (CARBOHYDRASES AND NUCLEASES)

(*p*H *of the reaction*, 5·2; *temp. of the reaction*, 37°C.; *source of enzyme, glycerol homogenate of gland*)

	Substrate	Method of determination	Units
Carbohydrases	Starch	Estimation of maltose	23
Nucleases	Yeast ribonucleic acid	Estimation of organic phosphorus	80

TABLE 3 — OXIDATION-REDUCTION ENZYMES

(*p*H *of the reaction*, 7·4; *temp. of the reaction*, 37°C.; *source of enzyme*, *M*/15 *phosphate buffer homogenate of gland*)

Substrates	Time taken for 50% Me blue reduction min.
Alcohol	50
Glucose	60
Lactic	60
Citric	50
Malic	50
Succinic	144
Oxalic	—
Formic	—
Fumaric	—
Maleic	—
Glutamic	60

Discussion

From the results given in Tables 1 and 2 it will be seen that the intestinal homogenate is associated with a practically complete and a particularly rich system of proteolytic enzymes. In addition to proteases (tryptic enzymes) capable of hydrolysing casein, the homogenate contains both the carboxy and the amino peptidases which in combination are capable of splitting a variety of peptides as shown in Table 3. We may, therefore, expect a complete digestion of the leaf proteins, thereby securing an efficient utilization of the products of digestion by the worm.

The haemolymph and the gland homogenate appear to be equally rich and complete in the enzymes of the proteolytic system. These enzyme systems may be considered to be responsible for mediating transpeptidations and rearrangement of amino acid residues, an aspect of study which is being actively pursued by us. It is significant that the homogenate of the gland, which is the seat of active synthesis of silk proteins, is also associated with a powerful proteolytic system including peptidases.

During the course of our work it has been observed that when tyrosine containing proteins and peptides are employed as substrates for the proteolytic enzymes of the haemolymph, the reaction mixture darkens progressively as hydrolysis proceeds. This, however, is due to the tyrosinase present in the haemolymph.

Amylase (glycogenase) and ribonuclease activities are exhibited by the gland homogenate (TABLE 2). The gland apparently is able to utilize the glycogen present in the tissue for the energy requirements of the synthetic reactions. The high ribonuclease activity shown by the gland homogenate is to be expected in view of the exceptionally rich concentration of the nucleic acid present in the gland.

A study of the oxidation-reduction enzyme associated with the gland homogenate, by the Thunberg methylene blue technique, reveals that the alcohol, glucose, lactic, citric and malic dehydrogenase systems are present in comparatively high concentration (TABLE 3). It is interesting to find that the glutamic dehydrogenase is present in an equally high concentration. The significance of its presence is realized if attention is called to the high trans-aminase activity, which we have earlier shown to be present in the gland[12]. It is surprising that the ubiquitous succinic dehydrogenase is not present in high concentration in the gland.

Summary

A preliminary study of five groups of enzyme systems — proteases, carboxy and amino peptidases, carbohydrases, nucleolytic enzymes and oxidation-reduction enzymes (dehydrogenases) — associated with the principal tissues and tissue fluids, the intestines, the haemolymph and the gland, of the silk-worm, *Bombyx mori* Linn., has been carried out.

The tissues have been found to be associated with a practically complete and a rich proteolytic system including the amino and carboxy peptidases. This must secure for the organism not only an efficient system of digestion and assimilation of proteins but also promote protein metabolism in general and protein synthesis in particular.

The significance of the dehydrogenase systems associated with the gland, with special reference to glutamic acid dehydrogenase, is indicated.

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The Effect of Biotin on the Utilization of Glutamic Acid by Yeasts

P. R. KRISHNASWAMY & K. V. GIRI
Department of Biochemistry, Indian Institute of Science, Bangalore

The effect of exogenous biotin on the utilization of glutamic acid by two yeasts BY2 and *Rhodotorula glutinis* has been studied. BY2, for which biotin was a critical growth factor, assimilates glutamic acid only in the presence of biotin, whereas in the case of *Rhodotorula* biotin enhanced the rate of assimilation. The greater stimulatory effect of biotin on the metabolic functions of BY2 is indicated.

CONSIDERABLE evidence has accumulated concerning the role of growth factors in the metabolism of amino acids by micro-organisms[1] and in particular the function of biotin in the enzyme systems associated with the amino acid metabolism of micro-organisms[2] and metabolic functions of yeasts[3] have been the subject-matter of pioneering research by various workers. The " biotin effect " or the stimulated metabolic functions like the increased rates of fermentation or respiration and growth due to added biotin, which " perhaps brings about the greater assimilation of ammonia nitrogen resulting in the synthesis of certain materials or enzymes involved in these metabolic activities ", was studied in detail by Winzler *et al.*[3]. Growth stimulation due to utilization of certain amino acids, both individually and in combinations, has been observed, and a study has been made with regard to their role as sources of nitrogen[4]. The present investigation concerns the study of the effect of biotin on the actual utilization of glutamic acid by two strains of yeasts, for one of which (BY2) biotin was a critical growth factor[5] and a growth promoting factor for the other yeast, *Rhodotorula glutinis*. The capacity of yeasts to assimilate with ease l-amino acids of the structure $-CHNH_2$ has been noted[6].

Materials and methods

The two yeasts, *Rhodotorula glutinis* (Fres.) Harrison var. *rubescens* (saito) Lodder (R.g.) and a mutant top yeast (obtained from a bottom brewery yeast, *Saccharomyces cerevisiae*), BY2[7], were maintained on wort-agar slants.

The basal medium used in the experiments consisted of ammonium sulphate, 0·2 per cent; glucose, 2 per cent; salts solution (KH_2PO_4, 4·4 g.; KCl, 3·4 g.; $MgSO_4.7H_2O$, 1·0 g.; $CaCl_2.2H_2O$, 1·0 g.; $MnSO_4$, $FeCl_3$, H_3BO_3, 20·0 mg. each; $ZnSO_4$, 8 mg.; $CuSO_4$ and KI, 0·8 mg. each per litre of solution), 12·5 cc., per 100 cc. of medium. The *p*H was adjusted to 4·8. For ammonia-free basal medium, the other ingredients except ammonium sulphate were mixed, the water used being ammonia-free double distilled water. The different types of media employed to study the effect of biotin on the utilization of glutamic acid were compounded as indicated in Table 1. Biotin was added to give a concentration of 0·01 γ/cc. of the total volume and 0·5 cc. of l-glutamic acid solution was added from a 1 per cent solution. The total volume was made up to 5 cc. with distilled water. The flasks were sterilized for 15 min. at 10 lb. pressure and inoculated the next day.

The inoculum for experiments was obtained by transferring the yeasts from 24 hr. slants to 50 cc. conical flasks containing 5 cc. quantities of the basal medium and growing for 36 hr. at 28°C. (for obtaining sufficient inoculum in case of BY2, 0·01 γ/cc. of biotin was added to the basal medium). The cells were then centrifuged, washed five times with 0·9 per cent saline under sterile conditions and after weighing suspended in a known volume of saline to give the required weight per cc., and 0·5 cc. of such suspensions (corresponding to 0·5 mg. wet weight) were inoculated into the different flasks, which had been previously sterilized. The flasks were incubated at room temperature. Growth was measured at various intervals of time by diluting 1 cc. of the contents of the flasks to 5 cc. and reading the turbidities in a Klett-Summerson photoelectric colorimeter using a 420 mμ filter.

TABLE 1 — BASAL MEDIUM

	I	II	III	IV	V	VI
Basal medium (complete)	+	+	+	+	−	−
Basal medium (-ammonium sulphate)	−	−	−	−	+	+
Glutamic acid	−	+	−	+	+	+
Biotin	−	−	+	+	−	+

The utilization of glutamic acid at different periods of incubation was calculated by estimating the glutamic acid concentration in the culture media at different intervals. Five μcc. aliquots from the centrifuged culture media were spotted on circular discs of filter paper (Whatman No. 1, 18·5 cm. diam.) and chromatographically developed as described by Giri and Rao[8,9]. The quantitative estimation was carried out by the technique developed by Giri *et al.*[10]. For each set of conditions, flasks were kept in triplicates.

Discussion

It is clear from Table 2 that BY2 requires exogenous biotin for growth, though in the presence of glutamic acid (TABLE 2, media II and V), even without added biotin, after 24 hr. of incubation, a very slight growth is perceptible. From the results presented in Table 3 it is observed that BY2 needs external biotin for the assimilation of glutamic acid. During the first few hours of incubation, however, there is a certain assimilation (TABLE 3, media II and V), probably due to the traces of biotin initially present in the cell environment. The slight increase in growth observed, even in the absence of biotin, with added glutamic acid, may perhaps be due to this limited assimilation.

Rhodotorula can grow and assimilate glutamic acid in the absence of biotin. Its presence enhances the growth of the organism considerably and increases the rate of assimilation of glutamic acid resulting in a greater total assimilation (TABLE 3). With added biotin, BY2 is capable of utilizing more glutamic acid (TABLE 3, media IV) even in the presence of ammonia nitrogen

TABLE 2 — GROWTH OF R.G. AND BY2 IN DIFFERENT MEDIA WITH AND WITHOUT ADDED BIOTIN*

Media		Yeast strain	Period of incubation hr.					
			0	6	12	24	48	72
I	Basal medium	R.g.	6·5	8·0	12	20	40	100
		BY2	8·0	10·0	10	12	14	14
II	Basal medium+glutamic acid	R.g.	7·0	12·5	14	21	48	127
		BY2	7·0	12·0	11	25	40	40
III	Basal medium+biotin	R.g.	6·5	9·0	17	32	110	185
		BY2	8·0	19·0	80	105	180	200
IV	Basal medium+glutamic acid+biotin	R.g.	7·0	13·5	20	35	128	204
		BY2	8·0	21·0	95	145	220	235
V	Basal medium (-ammonium sulphate)+glutamic acid	R.g.	7·0	10·5	14	20	50	73
		BY2	7·0	9·0	10	29	31	30
VI	Basal medium (-ammonium sulphate)+glutamic acid+biotin	R.g.	7·0	11·0	17	30	98	120
		BY2	8·5	15·0	68	100	125	159

* Average value of triplicate turbidity readings.

TABLE 3 — ASSIMILATION OF GLUTAMIC ACID (IN MG.) WITH AND WITHOUT ADDED BIOTIN

Media		Yeast strain	Period of incubation hr.						Total assimilation
			0	6	12	24	48	72	
II	Basal medium+glutamic acid	R.g.	—	0·48	0·07	0·22	0·81	0·15	1·73
		BY2	—	0·26	0·36	—	—	—	0·62
IV	Basal medium+glutamic acid +biotin	R.g.	—	1·00	0·36	0·36	1·46	0·44	3·62
		BY2	—	0·85	0·51	0·36	2·18	0·66	4·56
V	Basal medium (-ammonium sulphate)+glutamic acid	R.g.	—	0·26	0·59	0·66	0·37	0·95	2·83
		BY2	—	0·51	0·34	—	—	—	0·85
VI	Basal medium (-ammonium sulphate)+glutamic acid+biotin	R.g.	—	0·90	0·51	0·66	2·49	—	4·56
		BY2	—	1·07	0·84	2·65	—	—	4·56

than what *Rhodotorula* does under the same conditions; this may be indicative of the greater stimulatory effect of biotin on the metabolic functions of BY2. It is interesting to note that BY2 assimilates completely all the glutamic acid present in the medium between the twelfth and twenty-fourth hour of incubation (TABLE 3, media VI) with added biotin, whereas the *Rhodotorula* takes almost double that period for a similar performance.

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Storage Effects on the Proteins of Groundnuts

M. N. MOORJANI & D. S. BHATIA

Central Food Technological Research Institute, Mysore

The effects of storing groundnuts for 18 months upon the properties of the proteins in the nuts have been determined. Decreases in total nitrogen, solubility in sodium chloride solution, protein nitrogen, amount of protein precipitable by trichloroacetic acid and digestibility are observed during storage. These changes indicate that the proteins are denatured and have undergone partial break down.

DURING the pilot-plant trials on the production of groundnut milk according to the process developed by Subrahmanyan, Moorjani and Bhatia[1], it was observed that some stored lots of groundnuts gave loosely set curds (fermented product). Since in the curdling of groundnut milk the most important factor is the coagulation of protein, it was considered necessary to determine the extent of denaturation or the changes brought about in groundnut protein during storage. Pickett[2] reported that the solubility of protein in hydraulic peanut meal showed no significant change when stored at 33°F. for 3 years; however, after 1 year in the dark and light at 75°F., the solubility of the proteins in the cake dropped from 79·7 to 76·4 and 76·6 per cent, and after 3 years to 72·9 and 70·5 per cent respectively. A more detailed study of the effect of storing groundnuts on the properties of the proteins in the nuts has been carried out, and the results are described in the present paper.

Material — Freshly harvested groundnuts of Coromandel Talquale (*Mozambique* or *Mauritius*) variety used in these studies were purchased from the local market. This variety was chosen firstly because it is extensively cultivated, and secondly because it was found suitable for the production of vegetable milk.

Storage of the material — Groundnuts in shell were stored in gunny bags in the laboratory (20°-30°C.; R.H. 30-84 per cent) and the analyses were made at the end of 18 months of storage.

Analytical procedure — Moisture and free fatty acids were determined in the shelled groundnuts according to the A.O.A.C. methods (1945). Nitrogen determinations in triplicate were made on defatted flour which was prepared by extracting the kernels with ethyl ether, drying at 50°C. and powdering it to pass through 60 mesh (the figures for nitrogen are on moisture-free basis).

In order to examine the nature and extent of changes in the properties of the proteins occurring during storage, determinations of total nitrogen, protein nitrogen, solubility and digestibility were made.

Total nitrogen was determined by micro-Kjeldahl method.

Protein nitrogen was determined according to the copper hydroxide method of Stutzer[3]. In this method, the native protein is separated from the breakdown products by converting the former into an insoluble copper derivative.

Changes in the solubility of the proteins were determined by extracting the defatted powder with sodium chloride solution. A 5 g. sample of defatted flour was shaken with 100 cc. of 10 per cent sodium chloride in a glass stoppered bottle in a mechanical shaker for 1 hr. After allowing the mixture to stand overnight in a refrigerator (4°C.), it was centrifuged and total nitrogen determined in aliquots of the extract.

The nitrogen precipitable by trichloroacetic acid was also determined in aliquots of the original sodium chloride extract. The trichloroacetic acid precipitate was separated by centrifugation and nitrogen was determined in the filtered supernatant liquid. The nitrogen in the precipitate was calculated by difference.

Digestibility of the proteins was measured by the amount of protein nitrogen rendered soluble by peptic and tryptic digestion. Defatted cake (0·5 g., moisture-free basis)

TABLE 1 — EFFECT OF STORAGE ON THE PROTEINS OF GROUNDNUTS

(*Results expressed as mg. N per* 100 *g. of defatted flour*)

DETERMINATIONS	FRESH MATERIAL		MATERIAL STORED FOR 18 MONTHS		RESULTS EXPRESSED AS % DECREASE AS A RESULT OF STORAGE
	Determined values	Expressed as % total nitrogen	Determined values	Expressed as % total nitrogen	
Total nitrogen	11400	100·0	10540	100·0	7·5
True protein nitrogen	10395	91·1	9220	87·5	11·3
Nitrogen soluble in 10% NaCl	10660	93·5	9566	90·8	10·3
Nitrogen in NaCl extract precipitate by trichloroacetic acid	9706	85·1	8284	78·6	14·6
Digestibility	10540	92·5	9709	92·1	7·9

and 0·2 g. of pepsin were mixed with 0·1N hydrochloric acid and the volume made up to 60 cc. The mixture was incubated in a 100 cc. conical flask for 48 hr. at 37°C. At the end of this period, the digestion mixture was brought to *p*H 8-9 by the addition of sodium hydroxide solution. Trypsin (0·2 g.) was added and the digestion was continued for 48 hr. During both peptic and tryptic digestions, the digests were covered with a layer of toluene and the flasks were plugged with cotton. At the end of tryptic digestion, the mixture was filtered and aliquots taken for the determination of total nitrogen. Corrections were made for the nitrogen in the enzyme used.

Results and discussion

The moisture content of groundnuts had slightly decreased from 3·5 to 3·1 per cent at the end of storage period; there was slight increase in the free fatty acid content from 0·55 to 0·63 per cent. The results of other analyses recorded in Table 1 show that the protein in the stored nuts has undergone modification during storage. The solubility of the protein in salt solution is decreased and a decrease is observed in the protein nitrogen content, protein precipitable by trichloroacetic acid and digestibility. Decrease in the solubility of the protein in salt solution indicates that the groundnut protein is denatured during storage. The decrease in true protein nitrogen and in the amount of protein precipitable by trichloroacetic acid indicates proteolysis or degradation of the protein.

The changes observed by us in the proteins of groundnut as a result of storage are similar to those observed by Jones and Gersdorff[4] and Jones *et al.*[5] in the case of wheat and corn products, the only distinctive feature being that whereas no significant change in the nitrogen content was found in wheat and corn, a significant decrease in the total nitrogen was observed in the case of groundnuts.

Irving and Fontaine[6] have reported the occurrence in peanut meal of a proteolytic enzyme and have emphasized the role of the enzyme from the standpoint of processing of peanut meal for its protein. It is highly probable that the changes observed in the protein are due to the action of the proteolytic enzyme.

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The Effect of Thiouracil & Thyroxine Feeding on the Catalase Level in the Liver of the Rat

L. K. RAMACHANDRAN & P. S. SARMA
University Biochemical Laboratory, Madras

Thiouracil administration elevates liver catalase level in both male and female rats, whereas thyroxine exerts a depressing action. In both cases males respond more markedly than female rats. Normal levels for liver catalase in female rats is lower than that for male rats.

INTEREST in the examination of factors affecting liver catalase levels in experimental animals has mainly been the result of the findings of Greenstein and his associates[1,2] concerning the marked depression of liver catalase activity in the presence of a growing tumour in rats and mice. Regarding the mechanism of the effect, evidence available[3-7] indicated that the phenomenon was due to some factor or factors — not isolated or identified — elaborated by the tumour, ultimately resulting in the interference of the synthesis of catalase in the liver. However, the way in which such factors could operate, besides being controversial at present, are very obscure. Attempting a new approach to the problem, based on the observed sex-linked difference in liver catalase activity in mice[5,6], Adams[8,9] and Begg and Reynolds[10] investigated hormonal factors influencing liver catalase activity in mice. These investigators observed the enhancing effect of cortisone and testosterone administration in such cases, and also the depressing effect of castration and adrenalectomy. Low levels in normal female mice could be heightened by testosterone administration. Thus these observations indicated that hormonal factors could operate to control the catalase activity in the liver.

Drabkin[11,12] has studied the cytochrome content of several tissues, extending the observations of Tissieres[13], demonstrating that a generalized increase of cytochrome c levels results from hyperthyroidism and a decrease from hypothyroidism. He also postulated thyroid control of metabolism through cytochrome c and pointed the liver as the source of the respiratory pigment. Extensive inquiry has been made regarding the role of enzymes in the mechanism of action of the thyroid hormone. Following the work of Drabkin, it was thought probable that altered thyroid status in experimental animals may after all have a generalized effect on chromoprotein metabolism, though the pattern of changes in the various cases need not necessarily be that observed for cytochrome c. On this assumption, catalase was selected as one amongst this important group of haem-protein enzymes and changes in the levels of this constituent in the liver of rats fed thiouracil to induce hypothyroidism and injected thyroxine to induce hyperthyroidism were examined. The latter experimental procedure was designed to bring out, if possible, by the opposite means of thyroxine deficiency and excess, any manifestations of relationship between the thyroid hormone and catalase of liver. The results of different concordant experiments led to the unequivocal conclusion that a correlation exists between thyroid function and catalase level in the liver of the rat.

Experimental procedure

Animals — Adult albino rats, 165-170 g. in weight, from a stock strain were used. The diet of the animals consisted of the stock diet mixed with water.

Procedure — In the thiouracil experiments 50 mg. methylthiouracil (Geigy) incorporated in the dietary mixture was given per day per animal. The administration was continued for a month and a half resulting in an expected marked enlargement of the thyroid tissue. In a normal control rat of 165 g. the gland weighs approximately 0·02-0·03 g. In thiouracil thyrotoxicosis the hypertrophied glands were deep purple in colour and weighed 0·13-0·16 g. despite a 11-15 per cent reduction in the body mass of these rats.

For the production of experimental hyperthyroidism, 0·5 mg. crystalline l-thyroxine sodium pentahydrate in water was injected intraperitoneally every other day, leading to 15-20 per cent reduction in the body weight of animals so treated.

Care was taken to provide sufficient time to establish the desired experimental state, it having been observed by us earlier that thiouracil administration of seven days duration or two thyroxine injections as above and examination of the liver on the third day after the last injection revealed an inappreciable change in the content of the constituent being examined.

Analytical procedure — Food was withheld on the day the animals were sacrificed and their livers dissected. Samples of whole liver homogenates, in proper dilution, were allowed to react with a large excess of 0·05M hydrogen peroxide at *p*H 7 at 29°C., the reaction being stopped after 5 min. by addition of dilute H_2SO_4 and the hydrogen peroxide left unreacted being titrated against standard permanganate.

The catalase activity is expressed in arbitrary units/mg. wet liver only since the relationships were not to be found altered in the initial few experiments when rated per mg. dry weight or per mg. N. Adams[9] has also observed that so far as liver catalase levels are concerned, substitution of tissue wet weight for dry weight or N would have had no effect on the pattern of results obtained in experimental mice.

Results

The variations in the catalase levels in the livers of the experimental rats are represented in Table 1 and the nature of distribution of individual values in each group in Fig. 1.

Thus induction of deficiency or excess of the thyroid hormone in the living animal affects the catalase activity in liver. In the male rat thiouracil treatment is followed by a 30 per cent increase in activity whereas the female responds less markedly, by 13 per cent. Thyroxine treatment, on the other hand, lowers the activity to the extent of 25 per cent in the male and to a lower extent of 13 per cent in the female. In either case (thiouracil or thyroxine treatment) the changes in the female are much less pronounced. Even the value for normal female rats is much lower (by 23·7 per cent) than the value for normal male rats. This latter observation parallels the 30-40 per cent difference in catalase level in female mice compared to normal male mice noted by Adams[9]. The "t" test applied to the above data revealed that the differences observed are all highly significant.

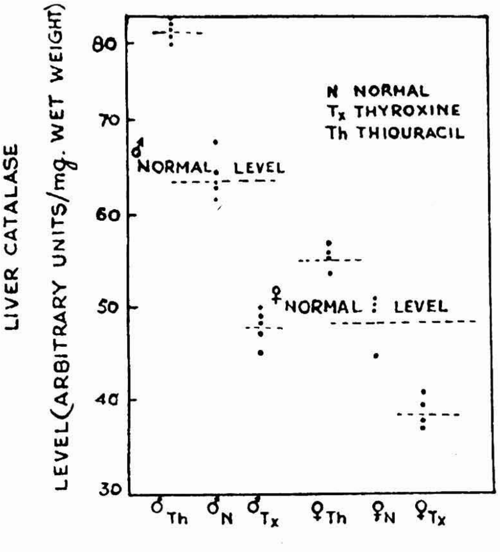

FIG. 1 — NATURE OF DISTRIBUTION OF INDIVIDUAL CATALASE LEVELS

TABLE 1 — LIVER CATALASE ACTIVITY IN NORMAL, METHYLTHIOURACIL-TREATED AND THYROXINE-TREATED RATS

No. of animals used	Sex	Treatment (1½ months)	Range units/mg. wt. of liver	Mean ± average deviation of mean	% difference from normal
5	Male	nil	61·4-66·4	63·3 ± 1·2	—
5	do	Thiouracil	80·9-84·1	82·4 ± 1·1	+30·2
5	do	Thyroxine	44·9-49·7	47·4 ± 1·3	−25·1
4	Female	nil	43·4-50·1	48·3 ± 2·4	—
4	do	Thiouracil	52·9-56·3	54·7 ± 0·9	+13·3
4	do	Thyroxine	36·4-40·3	38·2 ± 1·6	−13·2

Discussion

Marked changes in the level of liver catalase have been shown to follow thiouracil thyrotoxicosis and prolonged thyroxine administration to rats of either sex. Whether such induced changes are reversible by administration of the compound capable of effecting the opposite type of effect would remain to be found, as well as the mechanism of such changes. Whether these changes are due to influence on synthesis of enzyme protein thus affecting the effective concentration of the enzyme or the result of changes in concentration of activators or inhibitors present will have to be determined. Any direct activating or inhibiting effect of thyroxine or thiouracil would appear to be ruled out in view of lack of significant changes in catalase level during short-term therapy. Dietary factors and composition of the diet may, however, have some influence and this factor also will need investigation. Nevertheless, the ineffectiveness of short-term therapy would seem to indicate that the observed phenomenon may be a secondary one consequent on other important changes in body state.

The interpretation of the observed results in relation to the well-known effects of thiouracil and thyroxine on basal metabolism would appear to present difficulties. The role of catalase in the animal organism is itself in dispute, one school considering its biological purpose as protection of the cell from the deleterious effects of hydrogen peroxide[14] while another school doubts the validity of this theory of the biological role of catalase as a safety valve against accumulation of hydrogen peroxide and postulates a peroxidative function for catalase[15]. In the present case what is observed is an inverse relationship between catalase activity and respiratory intensity. It has not been possible to demonstrate in many organisms any relationship between catalase activity and respiratory intensity[16] in spite of the persistent belief that it may be so. And if we were to accept that the catalatic destruction of hydrogen peroxide in the living cell is a waste of energy, and if such energy is utilized by more active or increased concentration of peroxidative enzymes for oxidative metabolism, then correlation of the observed changes in catalase activity with the decreased and increased basal metabolic rates in thiouracil thyrotoxicosis and hyperthyroidism is easy. However, the evidence for such relationships will have to be sought through studies on relative concentrations of catalatic and peroxidative enzyme systems in such physiological states.

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Studies in Synthetic Neuromuscular Blocking Agents: Part II—Potency of Some Polymethylene bis-'onium Compounds

S. N. PRADHAN, K. S. VARADAN, C. RAY & N. N. DE
Central Drug Research Institute, Lucknow

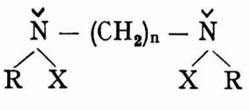
Curariform potency of some polymethylene bis-'onium compounds and their side effects on blood pressure and respiration in dogs have been studied.

N, N'-bis-benzyl decamethylene bis-piperidinium dichloride has been found to be most active. Its activity is found to be one-fifth that of *d*-tubocurarine chloride. This compound has a marked depressant effect on blood pressure and respiration.

The relation between chemical constitution and the curariform activity of the compounds has been discussed.

RECENTLY attention has been focussed on the chemical structure and curariform activity of several types of synthetic compounds. The presence of quaternary nitrogen atom, particularly two, has been stressed to be an important factor in the molecular structure of the curariform or neuromuscular blocking agents[1,2]. The activity of a compound increases with the length of the chain separating the two nitrogen atoms, till the optimum length of ten atoms (9-14Å) is reached, when the maximum potency is obtained[3-7]. Change of position of N atoms from the simple ammonium radicals to hetero-rings like piperidine and tetrahydroquinoline greatly influences the nature of curariform activity[1,4,8]. It is also claimed that adequate neuromuscular blocking activity depends not only on the length of the linking chains but also on the nature of the potentiating side chains[4,9].

On the basis of these considerations a number of polymethylene bis-'onium compounds were synthesized in the Medicinal Chemistry Division of the Central Drug Research Institute. The general molecular structure of these compounds is



$$\underset{R\quad X}{\overset{\vee}{N}} - (CH_2)_n - \underset{X\quad R}{\overset{\vee}{N}}$$

where n = 2, 3 or 10; R = methyl, ethyl, propyl, butyl, amyl or benzyl radical; X = I, Br or Cl; and N is placed either in ammonium radical or piperidinium ring[10]. Some compounds already known have also been included in this series for comparison. The present communication gives the curariform potency of 30 such compounds with their side effects on blood pressure and respiration in dogs.

Experimental procedure

Curariform activity of synthetic polymethylene bis-'onium compounds was tested on sciatic-gastrocnemius preparations as described by Burn[11] in dogs anaesthetized with sodium phenobarbitone. This method was selected, as it was described to be the most specific for assay of curariform agents and also because it provided an opportunity to observe their side effects on other organs and systems. In the nerve muscle preparations, the sciatic nerve was stimulated 15 times per minute by an electronic stimulator producing pulses of 0·001 sec. duration and the resulting muscle contraction was recorded in the usual way. Carotid blood pressure and tracheal air pressure of dogs were also recorded simultaneously along with the muscle contraction.

Aqueous solutions (1 per cent) of the compounds were used in the experiment unless otherwise mentioned. A particular dose of a compound was injected in the femoral vein of the animal and its effects on muscle contraction, blood pressure and respiration were observed. When blood pressure, respiration and, above all, muscle contraction returned to normal, a varying dose of the same compound or a dose of another compound was administered, followed afterwards by a suitable dose of *d*-tubocurarine chloride (Burroughs Wellcome & Co.; 1 per cent solution) so as to cause approximately the same degree of muscle paralysis as the previous drug or drugs. The effect of a particular dose of a compound was measured in terms of percentage depression of muscle twitch, and compared to that of an equipotent dose of *d*-tubocurarine chloride. The potency of a compound was expressed in terms of that of *d*-tubocurarine chloride, the latter being taken as unit.

The effect of a compound on blood pressure was determined by calculating the percentage of its fall below the original level produced by 1 mg./kg. dose and represented arbitrarily by number of plus depending on the degree, as described in Table 1. The respiratory stimulation or depression caused by 1 mg./kg. of a compound was represented arbitrarily by a number of plus or minus respectively. To note the effect of a new compound on blood pressure and respiration, a dose of 1 mg./kg. was employed. Previous experience indicated that this dose was more than sufficient, even for the moderately active curariform agents, to produce the desired paralysing effect.

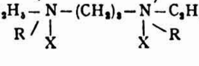
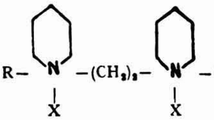
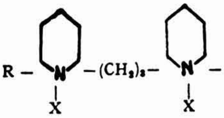
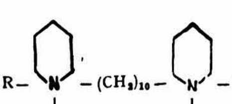
Rabbit's head-drop test by cross-over method[11] was also used to assay the potency of those compounds found to be active in dogs. Solutions containing 0·025 mg./cc. of *d*-tubocurarine chloride and 0·1 mg./cc. of the compounds were injected at the rate of 1 cc. per minute for comparison.

Molecular structures of 30 compounds with their pharmacological activities are given in Table 1.

It appears from the table that compound No. 30 (N, N′-bis-benzyl decamethylene bis-piperidinium dichloride) is the most active of the whole series, its potency being one-fifth to one-sixth that of *d*-tubocurarine chloride. It is also found to exert a marked depressive effect on blood pressure and respiration in dogs (FIG. 1).

TABLE 1 — CURARIFORM POTENCY OF POLYMETHYLENE BIS-'ONIUM COMPOUNDS AND THEIR SIDE EFFECTS ON BLOOD PRESSURE AND RESPIRATION

(*Blood pressure:* +, 1-20% *fall from the original level;* ++, 21-50%; +++, *fall of* 51% *and upwards; respiration:* +, *stimulation;* −, −−, −−−, *different degrees of depression;* −+, *depression followed by stimulation*)

GROUP	GROUP STRUCTURE	SL. No.	R	X	CURARIFORM POTENCY (TC = 1)	EFFECT ON B.P.	EFFECT ON Resp.
A.	 $R_3-\underset{X}{\underset{\vert}{N}}-(CH_2)_3-\underset{X}{\underset{\vert}{N}}-R_3$	1	C_3H_7	I	(10)*	+	+
		2	n-C_4H_9	I	(10)*	+	+
		3	n-C_4H_9	Br	(10)*	+	+
		4	Iso-C_4H_9	Br	(10)*	+	+
		5	$CH_2C_6H_5$	Cl	(2·25)*	+	+
B.	 $(C_2H_5)_2(R)\underset{X}{\underset{\vert}{N}}-(CH_2)_3-\underset{X}{\underset{\vert}{N}}(C_2H_5)_2(R)$	6	CH_3	I	(10)*	++	+
		7	C_3H_7	I	1/440	+	+
		8	n-C_4H_9	I	1/110	++	+
		9	Iso-C_4H_9	Br	1/146	++	+
		10	Iso-C_5H_{11}	I	1/150	+	+
C.		11	CH_3	I	(10)*	+	−
		12	CH_2I	I	(10)*	+	−
		13	C_2H_5	I	1/300	+	−
		14	C_3H_7	I	1/440	+	−
		15	n-C_4H_9	I	1/150	+	−
		16	Iso-C_4H_9	Br	(10)*	+	−
		17	Iso-C_5H_{11}	I	1/153	+	−
		18	$CH_2C_6H_5$	Cl	1/200	+	−
D.		19	CH_3	I	1/37	++	−+
		20	CH_2I	I	1/64	nil	−+
		21	C_2H_5	I	1/52	+	−+
		22	C_3H_7	I	1/100	+	−+
		23	C_4H_9	I	1/22	+	−+
		24	$CH_2.C_6H_5$	Cl	1/20	++	−+
E.		25†	CH_3	I	1/16	nil	nil
		26	C_2H_5	I	1/23	nil	nil
		27	n-C_3H_7	I	1/13	+	−
		28	Iso-C_3H_7	I	1/14	+	−
		29	C_4H_9	I	1/8	++	−−
		30	$CH_2C_6H_5$	Cl	1/5-1/6	+/++	−−

*Mg./kg. of the compound that failed to show any depression of muscle contraction.
†Compound tested by others.

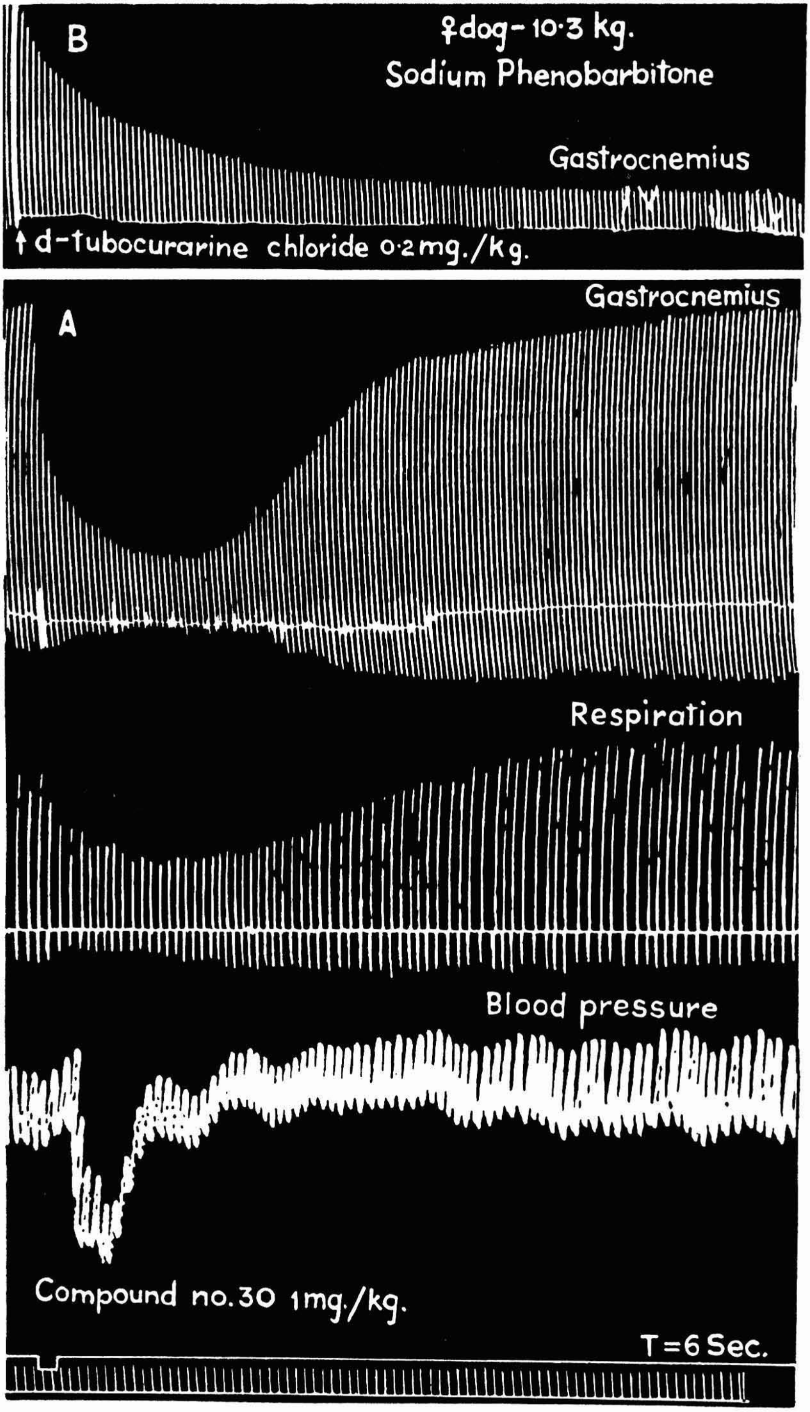


Fig. 1 — Effect of (A) compound No. 30 (1 mg./kg.) on gastrocnemius contraction, blood pressure and respiration, and (B) *d*-tubocurarine chloride (0·2 mg./kg.) on gastrocnemius contraction in a dog

In the head-drop experiments, it proved to be toxic to rabbits. The animals died almost in all the cases before regular head-drop could be produced. While dogs could tolerate 1 mg./kg. dose quite well, rabbits died even at a low dose of 0·15 mg./kg.

Discussion

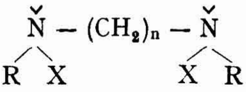
Comparing the curariform potency of compounds with different side chains from group to group, a definite influence of side chains on potency is observed. In all the groups, the compounds with butyl radical are found to be more active than those with methyl. Effects of ethyl and propyl radicals seem to be variable. Compounds with iso-alkyl radicals are found to be less potent than their normal analogues. Compounds with benzyl radicals in almost all the groups are definitely more active than those with alkyl radicals. In fact the most active compound in this series, i.e. compound No. 30, contains benzyl radical. Whether the toxic nature of this compound is associated with this benzyl radical or not, needs further investigation.

Influence of the length of the connecting chain between the two quaternary N atoms also appears to play its role as usual. Compounds of the trimethylene groups B and D are more active than the corresponding representatives of the dimethylene groups A and B, and compounds of decamethylene group E are more active than those of all other groups.

By changing the position of N atom from ammonium radical to the piperidinium ring, as seen in the groups A and C, and also in groups B and D, curariform activity seems to increase. But the activity of the compounds belonging to group E containing methyl radical (No. 25) does not prove to be greater than decamethonium (C_{10}) which is twice as active as *d*-tubocurarine chloride in dogs.

Summary

1. Thirty polymethylene bis-'onium compounds were tested for curariform activity on sciatic-gastrocnemius preparations of dogs and also by rabbit's head-drop method. Their general structure is



$$\underset{R\quad X}{\overset{\vee}{N}} - (CH_2)_n - \underset{X\quad R}{\overset{\vee}{N}}$$

where n = 2, 3 or 10; R = alkyl or benzyl radical; X = I, Br or Cl; and N is either in ammonium radical or piperidinium ring.

2. N, N'-bisbenzyl decamethylene bis-piperidinium dichloride (No. 30) was found to be most active. Its activity in dogs was found to be one-fifth that of *d*-tubocurarine chloride. It showed a marked depressant effect on blood pressure and respiration of dogs in 1 mg./kg. doses. In rabbits it proved to be too toxic. The animals died before showing head-drop.

3. Curariform activity of the compounds has been discussed in relation to their chemical constitution.

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Studies in Synthetic Neuromuscular Blocking Agents: Part III—Curariform Potency of Polymethylene bis-'onium Ether Compounds

S. N. PRADHAN, C. RAY, K. S. VARADAN & N. N. DE
Central Drug Research Institute, Lucknow

Curariform activity and side effects on blood pressure and respiration of various substituted bis-'onium compounds carrying polymethylene ether connecting chains have been studied. Twenty-five compounds were tested of which four were found to be active; their activity is one-fourth to one-seventh that of *d*-tubocurarine chloride. These compounds are toxic to dogs and rabbits. The relationship between chemical constitution and curariform activity of the compounds has been discussed.

IN earlier communications in this series[1,2] it was suggested that besides the shape of the cationic heads, the nature and the length of the connecting bridge between the two nitrogen atoms of bis-'onium compounds would be expected to play an important role in their neuromuscular blocking ability. In the present communication observations are reported upon the curariform activity and side effects on blood pressure and respiration of variously substituted bis-'onium compounds carrying polymethylene ether (with one or two oxygen atoms) connecting chains.

Experimental procedure

Curariform activity was tested on sciatic-gastrocnemius preparation[3] in dogs anaesthetized with sodium phenobarbitone. In these experiments sciatic nerve was stimulated 15 times per minute by an electronic stimulator producing pulses of 0·001 sec. duration. The potency of these compounds was compared and expressed in terms of that of *d*-tubocurarine chloride (Burroughs Wellcome & Co.). The effects on carotid blood pressure and tracheal air pressure with 1 mg./kg. dose were also studied and the results expressed in terms of plus or minus signs. Details of experiments and the mode of expression of their effects on nerve-muscle preparations, blood pressure and respiration have been described in the previous communication[2]. One per cent solution of the compounds was used in these experiments.

Rabbit head-drop test was carried out by " cross-over method "[3] to assay the potency of the compounds found to be active in dogs. Solutions containing 0·025 mg./cc. of *d*-tubocurarine chloride and 0·1 mg./cc. of the compounds were used for comparison.

Structural formulae of 25 compounds with their curariform potency and side effects on blood pressure and respiration are given in Table 1.

It appears from the table that compound Nos. 7, 20, 24 and 25 are the most active, their activity ranging from one-fourth to one-seventh that of *d*-tubocurarine chloride (FIG. 1). Side effects of all the compounds, particularly of those carrying benzyl radicals, on blood pressure and respiration in dogs are considerably depressive and, therefore, undesirable.

In rabbit head-drop experiment, compound Nos. 24 and 25 proved to be too toxic. The animals died with convulsions and showed no sign of head-drop at average doses of 0·35 mg./kg. and 1·1 mg./kg. respectively. Compound No. 20 produced various untoward manifestations like respiratory paralysis, prostration and in some cases death before head-drop was manifest. In case of compound No. 7 the approximate head-drop dose was found to be 1 mg./kg.

Discussion

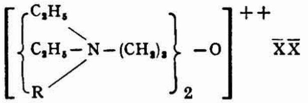
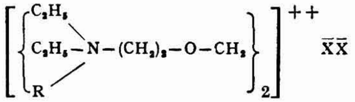
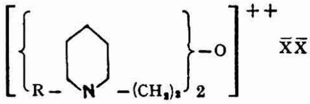
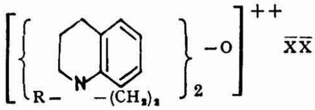
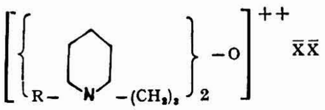
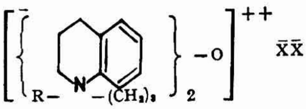
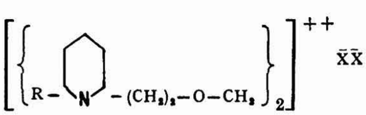
In our previous communication[2] the curariform potency of some polymethylene bis-'onium compounds has been discussed. Compounds carrying benzyl radicals seem to be the most active and also the most toxic, those with butyl radicals are more active than those with methyl group, whereas the effects of compounds carrying ethyl and propyl appear to be variable. Compounds carrying branched radicals are less active than those carrying straight alkyl chains. In these compounds, potency increases with the length of the connecting chain and also with changing the N atom from a simple ammonium radical to a piperidine ring.

In the present series of polymethylene bis-'onium ether compounds, the influence of side chains attached to the quaternary N atoms is still more impressive. Undoubtedly, the compounds with benzyl radical are the most active in the whole series, but at the same time a definite gradation in the increase of activity is observed from methyl to butyl and then to the benzyl radicals. Variation of effect with ethyl or propyl radicals is less marked. This observation is in keeping with the statement of Craig[4]. Compounds with iso-radicals are found to be less active than those with normal ones also in the series. Toxic effects of benzylated compounds both in dogs and in rabbits are again very marked in this series. This provides further evidence in favour of a possible association of toxicity with the benzyl radical.

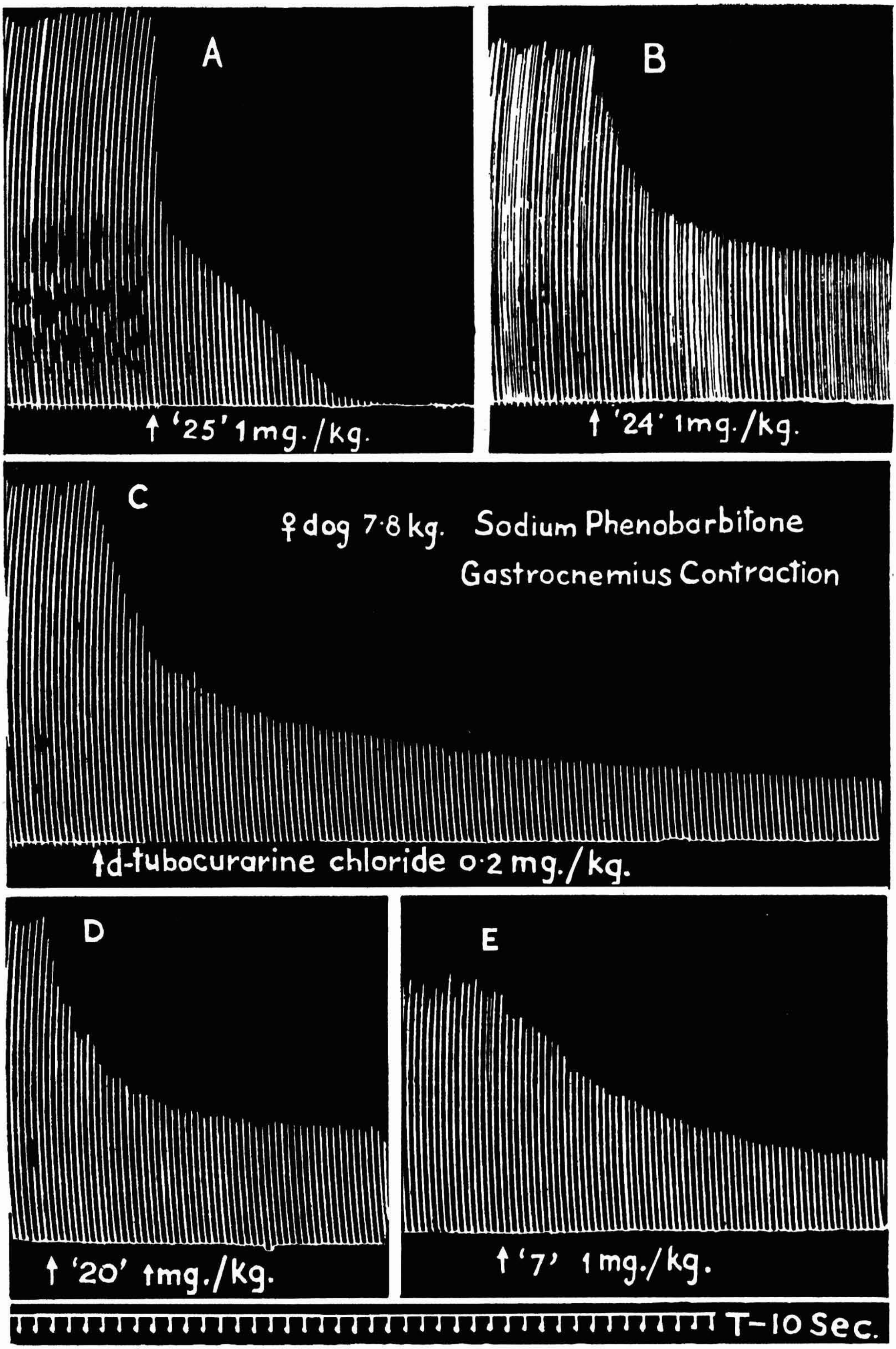
Enhancement of curariform activity in dogs due to the influence of oxygen atoms introduced into the polymethylene chain

TABLE 1 — CURARIFORM POTENCY OF POLYMETHYLENE BIS-'ONIUM ETHER COMPOUNDS AND THEIR SIDE EFFECTS ON BLOOD PRESSURE AND RESPIRATION

(*Blood pressure:* +, 1-20% *fall from the original level;* ++, 21-50%; +++, *fall of* 51% *and upwards; respiration:* +, *stimulation;* –, – –, – – –, *different degrees of depression;* – +, *depression followed by stimulation or vice versa*)

GROUP	GROUP STRUCTURE	SL. No.	R	X	CURARIFORM POTENCY	SIDE EFFECTS ON B.P.	SIDE EFFECTS ON Resp.
A.		1	CH_3	I	(10)*	+	nil
		2	C_2H_5	I	(10)*	+	nil
		3	n-C_3H_7	I	1/40	+	–
B.		4	CH_3	I	(10)*	+	+
		5	C_2H_5	I	1/8	+	–
		6	n-C_3H_7	I	1/6	+	–
		7	$CH_2C_6H_5$	Cl	1/6	+	– –
C.		8	CH_3	I	1/58	++	+
		9	C_2H_5	I	1/25	++	+
		10	n-C_3H_7	I	1/29	++	+
		11	n-C_4H_9	I	1/11	+/++	+ –
		12	Iso-C_4H_9	I	1/24	+/++	+ –
		13	$CH_2C_6H_5$	Cl	1/10	++	– –
D.		14	CH_3	I	1/11	+	nil
E.		15	CH_3	I	1/32	+	nil
		16	C_2H_5	I	1/25	+	nil
		17	n-C_3H_7	I	1/23	+	+
		18	n-C_4H_9	I	1/21	+	+
		19	n-C_5H_{11}	I	1/8	+	–
		20	$CH_2C_6H_5$	Cl	1/5-1/6	++	– –
F.		21	CH_3	I	(8)*	+	–
G.		22	CH_3	I	1/50	+	+
		23	n-C_3H_7	I	1/18	+	–
		24	n-C_4H_9	I	1/6-1/7	+	– –
		25	$CH_2C_6H_5$	Cl	1/4	++	– –

*Mg./kg. of the compound that failed to show any depression of muscle contraction.


A
↑ '25' 1 mg./kg.
B
↑ '24' 1mg./kg.
C
♀ dog 7·8 kg. Sodium Phenobarbitone
Gastrocnemius Contraction
↑d-tubocurarine chloride 0·2 mg./kg.
D
↑ '20' 1mg./kg.
E
↑ '7' 1 mg./kg.
T–10 Sec.

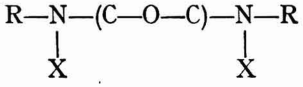
between the quaternary N atoms, as manifested in some of the compounds of this series, appears to be interesting. This is in contradiction to the observation of other workers[5]. Increase of potency in the corresponding compounds of the groups A and B, and also in E and G can only be ascribed to the insertion of one more O atom in between the rearranged CH_2 radicals whose number remains constant. Moreover, the compounds with butyl and benzyl radicals in group G (Nos. 24 and 25) are found to be more potent than the corresponding decamethylene bis-piperidinium salts. The potency of the latter has been shown to be one-eighth, and one-fifth to one-sixth of that of *d*-tubocurarine chloride respectively in the previous communication[2]. Compounds with short side chains, however, behave otherwise.

It may be noted that compounds of a series with benzyl and butyl radicals containing six carbon atoms and two oxygen atoms are more potent in dogs than the corresponding compounds of an otherwise similar series containing ten carbon atoms in the connecting chain.

Change of nitrogen atom from open chain to cyclic compounds in various bis-'onium salts, however, gives a conflicting result. Though a gradation in the increase of activity was observed from ammonium to piperidinium to tetrahydroquinolinium compounds in one series of otherwise almost similar compounds (Nos. 1, 8 and 14), no such change was visible in another series (Nos. 1, 15 and 21). It seems that it is the combined influence of the length and nature of the connecting chain between the nitrogen atoms and the nature of the potentiating side chain which is responsible for the activity of the compound and not the individual group. It is likely that the whole combination provides the " best fit " in the receptor at the neuromuscular junction before adequate potency of the drug is manifest[6].

Summary

1. Twenty-five polymethylene bis-'onium compounds were tested for curariform activity in dogs and rabbits. Their general structure is



$$R-\underset{\substack{|\\ X}}{N}-(C-O-C)-\underset{\substack{|\\ X}}{N}-R$$

where R represents alkyl or benzyl radical; X represents halogen; (C—O—C) represents polymethylene chain with ether linkage and N is placed in ammonium radical or piperidinium or tetrahydroquinolinium rings.

2. Compound Nos. 7, 20, 24 and 25 were found to be active. Their activity in dogs ranged from one-fourth to one-seventh that of *d*-tubocurarine chloride. They proved to be toxic to dogs and rabbits.

3. Influence of chemical constitution on curariform activity with respect to the series of compounds synthesized has been discussed.

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FIG. 1 — CURARIFORM ACTIVITY OF COMPOUND NOS. (A) 25, (B) 24, (D) 20, (E) 7 (1 MG./KG. EACH) AND (C) *d*-TUBOCURARINE CHLORIDE (0·2 MG./KG.) [Tests were carried out on sciatic-gastrocnemius preparation stimulated at the rate of 15 times per min. in a female dog (7·8 kg.) under sodium phenobarbitone anaesthesia]

Studies on Anaemia: Part II— Effect of Liver Extract & Vitamin B_{12} on Lead Anaemia in Rats

D. C. DHAR & S. N. PRADHAN

Central Drug Research Institute, Lucknow

The R.B.C. and haemoglobin response resulting from administration of liver extract or vitamin B_{12} have been studied in the lead anaemia of the rat. Liver extract and vitamin B_{12} produce a beneficial effect in counteracting lead anaemia. On comparing the response of liver extract (2 U.S.P.) and vitamin B_{12} (2 μg.), liver extract appeared to be much more potent than vitamin B_{12}.

IN a previous communication[1] it was reported that a macronormoblastic type of anaemia could be produced in rats by the parenteral administration of lead acetate. The anaemia thus produced reached its peak on the seventh or eighth day after the injection of lead acetate, when there was a maximum fall in erythrocyte count and in the haemoglobin content. In the present investigation an attempt has been made to find out whether the beneficial effect of liver extract or vitamin B_{12} in lead anaemia of rabbits, reported earlier by Gerlich[2] and van Klaveren *et al.*[3,4], was also manifest in the lead anaemia in rats and whether this method could be utilized for the assay of these drugs.

Experimental procedure

Rats, mainly male, from the Central Drug Research Institute Stock Colony were used in this experiment. They were maintained on a basal diet supplemented with vitamins, as described earlier[1]. Anaemia was produced either by a single intravenous injection of 6 mg. of lead acetate in 10 per cent aqueous solution or two such injections on successive days. Blood was collected from the tail vein and total R.B.C. count and haemoglobin content were determined. Liver extract or vitamin B_{12} were then given and their effects on anaemic rats studied up to the fourteenth day.

Effects of liver extract and vitamin B_{12} were also studied on the normal rat population of the colony to serve as a control. Five groups, each consisting of 5 rats, were maintained on the usual basal diet. The first group received on the first day an intraperitoneal injection of 1·8 μg. of vitamin B_{12} per 100 g. body weight and the second group received 3 U.S.P. units of liver extract in the same way. To the third group vitamin B_{12} in doses of 2 μg./100 g. body weight was given daily for five successive days by the intraperitoneal route starting on the sixth day of the maintenance of basal diet; the fourth group received 2 U.S.P. units liver extract in the same manner. The fifth group of rats received no treatment and served as control. Day-to-day blood picture of the treated rats compared with the

TABLE 1 — BLOOD PICTURE OF RATS AFTER DAILY INTRAPERITONEAL INJECTIONS OF LIVER EXTRACT FOR FIVE DAYS

(*Dosage of liver extract,* 2 *U.S.P. units*/100 *g.; red cell in million/cu. mm.; haemoglobin in g.*/100 *cc. blood*)

RATS	6TH DAY		8TH DAY		10TH DAY		12TH DAY		14TH DAY	
	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin
Normal	9·30 ±1·01	17·72 ±0·85	9·37 ±1·01	15·63 ±1·15	8·86 ±0·83	16·08 ±0·98	8·79 ±1·01	16·08 ±0·98	9·21 ±0·61	15·84 ±0·69
Anaemic (single)	6·64 ±0·83	11·44 ±1·55	7·75 ±0·63	11·10 ±1·13	8·16 ±0·76	11·09 ±0·51	7·60 ±0·54	11·00 ±0·41	8·66 ±0·90	10·74 ±1·03
Anaemic (double)	4·75 ±0·52	8·84 ±0·60	6·64 ±0·52	10·76 ±1·42	6·91 ±0·24	9·86 ±1·56	6·62 ±0·22	9·04 ±1·09	7·46 ±0·64	9·51 ±0·76

untreated group, showed no significant variation in response to the drugs.

Effect of liver extract

Effect of liver extract was studied on rats made anaemic by lead acetate (both single and repeated doses). Two U.S.P. units per 100 g. body weight of liver extract were injected intraperitoneally daily for five days beginning from the sixth day after injection of lead acetate. Table 1 gives the average figures for R.B.C. and haemoglobin with standard deviation on alternate days from sixth to fourteenth day. The degree of regeneration of each was calculated in terms of percentages, taking the sixth day figures as 100 per cent (FIGS. 1-4). The amount of regeneration in excess over the control was next determined also in terms of percentage. In either case the rate of regeneration of R.B.C. was more marked on the eighth and tenth day. In the group of rats injected with single dose of lead acetate, regeneration of R.B.C. caused by liver extract on the eighth and tenth day was 11·4 and 27·1 per cent respectively. In the group treated with repeated doses, when degree of anaemia is nearly 60 per cent, the rate of regeneration of R.B.C. was 45 and 51 per cent on the eighth and tenth day respectively. After the tenth day the regeneration of R.B.C. over control gradually slowed down, and on the fourteenth day the rate practically appeared to be the same as that of control rat, treated with repeated doses of lead. Effect on haemoglobin formation, however, is not so marked. The rate of formation of haemoglobin by injections of liver extract on the eighth and tenth day was 14 and 6 per cent respectively for single injection of lead and 23 and 9 per cent in case of repeated injections. On the subsequent days the haemoglobin formation due to effect of liver extract is very little.

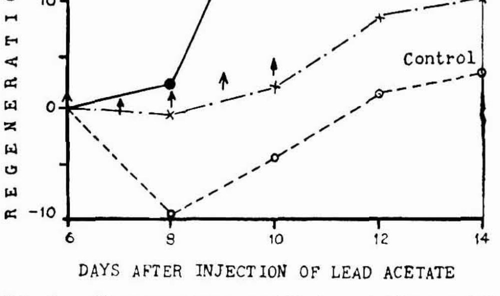

FIG. 1 — ERYTHROCYTE RESPONSE TO FIVE DAILY INTRAPERITONEAL INJECTIONS OF LIVER EXTRACT (2 U.S.P. UNITS) AND VITAMIN B_{12} (2 µG.) IN RATS AFTER SINGLE INTRAVENOUS DOSE OF LEAD ACETATE [↑ indicates time of injection]

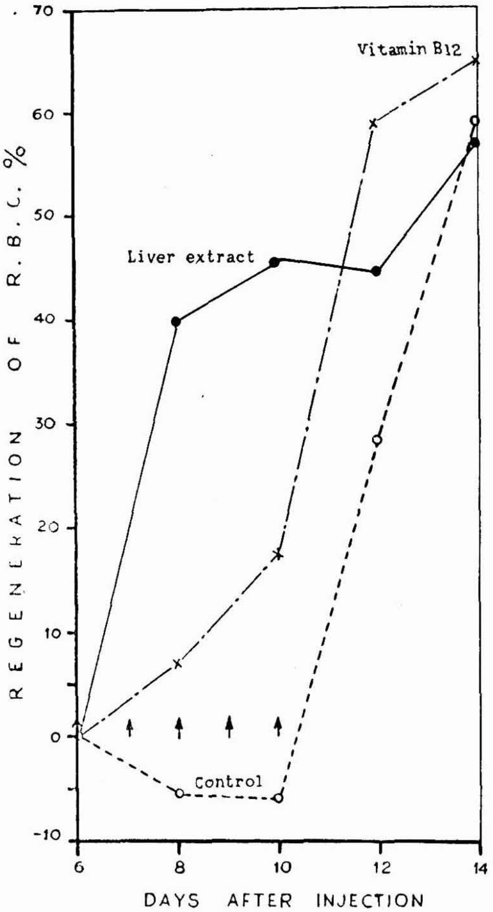

FIG. 2 — ERYTHROCYTE RESPONSE TO FIVE DAILY INTRAPERITONEAL INJECTIONS OF LIVER EXTRACT (2 U.S.P. UNITS) AND VITAMIN B_{12} (2 µG.) IN RATS AFTER REPEATED INTRAVENOUS DOSE OF LEAD ACETATE [↑ indicates time of injection]

Four groups, each consisting of 5 rats, were injected with lead acetate in the usual way. One, two and three U.S.P. units of liver extract were administered intraperitoneally in three of the respective groups on

TABLE 2 — BLOOD PICTURE OF RATS AFTER SIMULTANEOUS INJECTION OF LIVER EXTRACT OR VITAMIN B_{12} ALONG WITH LEAD ACETATE

(*Dosage: liver extract, 3 U.S.P./100 g.; vitamin B_{12}, 1·8/µg. R.B.C. in million/cu. mm.; haemoglobin in g./100 cc. blood*)

Rats treated with	Same day		2nd day		4th day		6th day		8th day		10th day		12th day		14th day	
	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin
Liver extract	8·90 ±0·29	15·20 ±0·81	9·68 ±0·89	15·40 ±0·26	8·75 ±0·54	14·80 ±0·12	9·15 ±0·37	13·80 ±0·95	9·60 ±0·96	13·80 ±1·30	8·21 ±0·81	13·30 ±0·86	7·80 ±0·09	13·80 ±0·50	8·16 ±0·52	13·30 ±0·70
Vitamin B_{12}	8·91 ±0·09	15·10 ±0·85	8·35 ±0·27	15·40 ±0·05	—	15·00 ±0·62	8·50 ±0·42	13·80 ±0·43	9·11 ±0·10	13·20 ±0·52	7·40 ±0·20	12·58 ±0·67	7·40 ±0·20	12·70 ±1·01	7·30 ±0·48	12·50 ±0·96

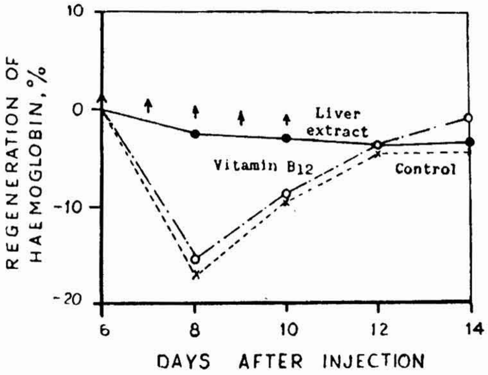

FIG. 3 — HAEMOGLOBIN RESPONSE TO FIVE DAILY INTRAPERITONEAL INJECTIONS OF LIVER EXTRACT (2 U.S.P. UNITS) AND VITAMIN B_{12} (2 µG.) IN RATS AFTER SINGLE INTRAVENOUS DOSE OF LEAD ACETATE [↑ indicates time of injection]

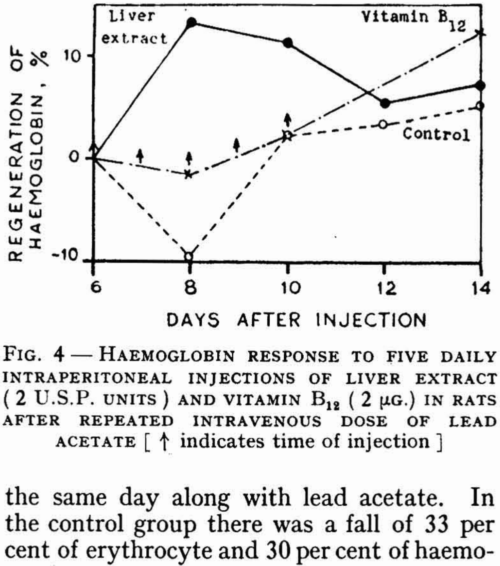

FIG. 4 — HAEMOGLOBIN RESPONSE TO FIVE DAILY INTRAPERITONEAL INJECTIONS OF LIVER EXTRACT (2 U.S.P. UNITS) AND VITAMIN B_{12} (2 µG.) IN RATS AFTER REPEATED INTRAVENOUS DOSE OF LEAD ACETATE [↑ indicates time of injection]

the same day along with lead acetate. In the control group there was a fall of 33 per cent of erythrocyte and 30 per cent of haemoglobin whereas in the other three groups the fall of R.B.C. and haemoglobin was 29·5, 14, 9·5 and 20·3, 13, 9·2 per cent respectively on the eighth day. The average blood picture of the group treated with 3 U.S.P. units of liver extract up to the fourteenth day is given in Table 2.

Effect of vitamin B_{12}

Two groups of 5 rats each were injected with lead acetate by usual single and repeated doses respectively. Starting from the sixth day, 2 µg. of vitamin B_{12} was administered intraperitoneally daily for five consecutive days. The results indicating the effect of vitamin B_{12} are represented in Table 3 and percentage of regeneration have been plotted in Figs. 1-4. The method of calculation was similar to that given in case of liver extract. The total regeneration of R.B.C. in excess over control on the eighth and the tenth day was 9·2 and 6·1 per cent respectively in groups treated with single injection of lead, and 12·2 and 23·5 per cent respectively in the group treated with repeated injection. After that slight stimulation of R.B.C. is maintained throughout up to the fourteenth day in both cases. The degree of haemoglobin formation in both cases was very little affected by vitamin B_{12} and never exceeded 3 per cent up to the twelfth day. On the fourteenth day the regeneration increased slightly.

In 5 groups of rats, single dose of 0·2, 0·4, 0·8, 1·6, 1·8 μg./100 g. of vitamin B_{12} respectively were administered intraperitoneally along with single intravenous dose of lead acetate (6 mg./100 g. body weight). The experiment was followed for the usual period of 14 days and a set of typical results on the seventh day is given in Table 4. No regular increase of haemoglobin was seen with increased doses. The average R.B.C., on the contrary, showed definite increase with the increase of vitamin B_{12} injected. Since the curative effect of 2 U.S.P. units of liver extract was found to be more than that of 2 μg. of vitamin B_{12} (FIGS. 1 and 2), a further comparison of their efficiency regarding the preventive effect was attempted and the results are given in Table 2. It would be seen from the table that the response with 3 U.S.P. units of liver extract is higher than that in the case of 1·8 μg. of B_{12}, although the former contains only 0·99 μg. of B_{12}.

With a view to find out the dose-response relationship, the average R.B.C. counts of the respective groups along with those of the control were plotted against the duration of treatment up to the eighth day. The points corresponding to each group were best fitted to a straight line, represented by the equation $Y = a + bX$, where X and Y represent line to the horizontal plane which signifies the level of R.B.C. up to the eighth day and can be measured by the tangent of the angle which it makes with abscissae. All such straight lines along with the control have been interposed in Fig. 5 keeping their respective angles constant for comparison. It appears that with the increase in dose of vitamin B_{12}, the angles of the slopes gradually decrease. Percentage of regeneration of R.B.C. corresponding to each dose is calculated according to the formula

$$100 - \frac{\text{Slope pertaining to dose}}{\text{Slope pertaining to control}} \times 100$$

and plotted against dosage. The curve

TABLE 3 — BLOOD PICTURE OF RATS AFTER DAILY INTRAPERITONEAL INJECTIONS OF VITAMIN FOR FIVE DAYS

(*Dosage of vitamin B_{12}*, 2 *μg./100 g. R.B.C., million cu. mm.; haemoglobin, g./100 cc. blood*)

RATS	6TH DAY		8TH DAY		10TH DAY		12TH DAY		14TH DAY	
	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin	R.B.C.	Haemoglobin
Normal	9·62 ±1·64	16·32 ±1·13	9·58 ±0·77	15·60 ±1·02	9·36 ±1·11	15·23 ±1·46	9·95 ±0·24	16·30 ±0·89	9·52 ±0·74	15·90 ±0·83
Anaemic (single)	6·54 ±0·55	10·91 ±0·93	6·50 ±0·76	9·17 ±1·12	6·68 ±0·87	9·80 ±0·21	7·08 ±1·11	10·50 ±0·67	7·12 ±0·74	10·90 ±0·98
Anaemic (double)	3·60 ±0·84	7·80 ±0·30	3·85 ±1·25	7·30 ±0·41	4·23 ±1·11	8·00 ±1·42	5·71 ±1·06	—	5·93 ±0·40	8·80 ±1·04

TABLE 4 — EFFECT OF SIMULTANEOUS ADMINISTRATION OF DIFFERENT DOSES OF VITAMIN B_{12} ALONG WITH LEAD ACETATE (6 MG./100 G.) ON ERYTHROCYTE COUNT AND HAEMOGLOBIN LEVEL IN ANAEMIC RATS

DOSE (μg./100 g.)	NO. OF RATS	R.B.C. COUNT (million/cu. mm.)			HAEMOGLOBIN (g./100 cc.)		
		Same day	7th day	% decrease	Same day	7th day	% decrease
Control	12	8·92	6·10	31·6	14·9	12·06	20·0
0·2	5	9·09	6·60	27·3	14·0	13·00	7·1
0·4	5	10·14	7·78	23·2	17·9	12·30	31·0
0·8	5	9·76	7·77	20·3	16·5	14·10	14·5
1·6	5	8·31	8·01	3·1	15·3	14·30	6·5
1·8	5	8·91	8·80	1·1	15·1	13·30	11·9

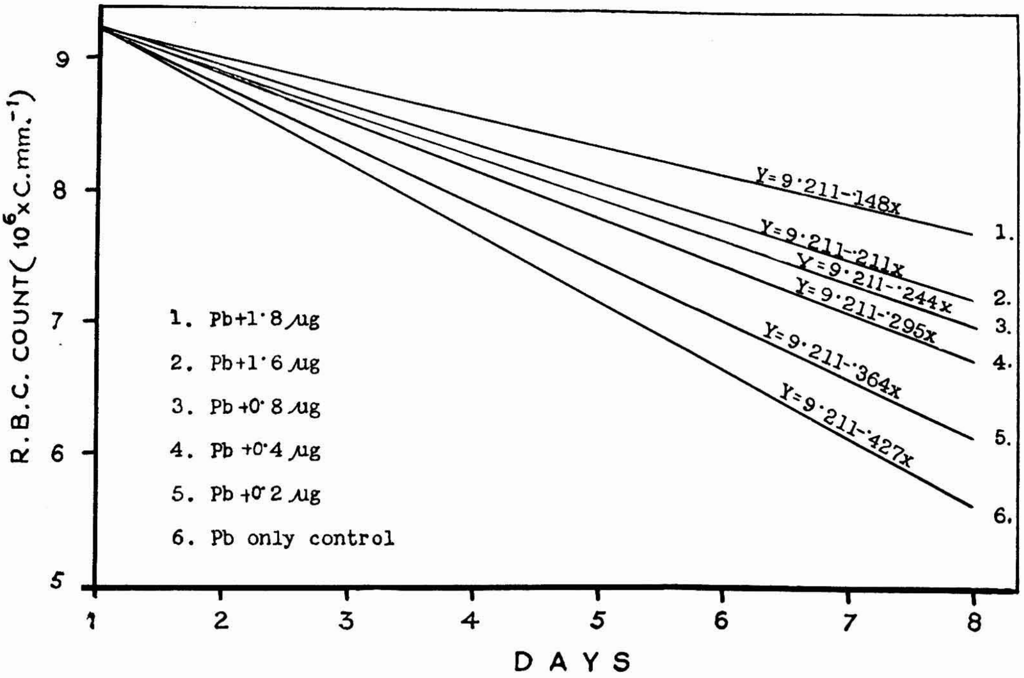

FIG. 5 — THE SLOPE OF THE STRAIGHT LINE TO THE HORIZONTAL PLANE WHICH SIGNIFIES LEVEL OF R.B.C. UP TO THE EIGHTH DAY

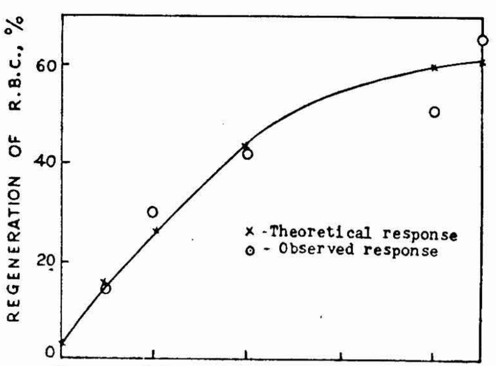

FIG. 6 — REGENERATION OF R.B.C. WITH VITAMIN B_{12}

(FIG. 6) thus drawn is exponential. In the beginning, up to 0·8 µg., the curve is almost linear, showing that the response is proportional to the dose within this limit; afterwards the response gradually diminishes below the calculated proportional dose.

Further work is in progress to determine whether this observation can be utilized for the assay of vitamin B_{12} and liver extract.

Summary

Liver extract and vitamin B_{12} administered either simultaneously with or 6 days after the injection of lead acetate produced beneficial effects in lead anaemia.

Regeneration of R.B.C. caused by liver extract or vitamin B_{12} was much more than haemoglobin formation.

Liver extract gave a much better response than B_{12} although the former contained much less of the vitamin.

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Digestibility & Absorption of Hydrogenated Blended Fats*

M. R. SAHASRABUDHE
Central Food Technological Research Institute, Mysore

Studies with fat blends containing vanaspati and hydrogenated groundnut oil melting at 41°, 45° and 50°C. have been carried out with a view to determining the influence of the hard fat portion in the blend on the digestibility and particulate absorption. Chylomicrographic observations indicate that in spite of insignificant differences in the digestibility, the trend of absorption of the fat is considerably effected in blends where a high proportion (15-25 per cent) of harder fat is incorporated.

RECENT studies[1] carried out in our laboratories on " shortenings " for biscuits indicate the beneficial effects of higher melting fats (m.p. 41°-42°C.). The beneficial effect enhancing the keeping quality of the product mainly lies in the reduced " free oil content ". Incorporation of the harder fat in a certain percentage of the total fat has also been suggested for some processed sweets (DATE, W. B. and BHATIA, D. S., unpublished data). Biscuits and sweets are generally consumed as adjuncts in our diet in moderate quantities and considering the amount of the total fat consumed in the diet, the quantity of the harder fat incorporated in these products is small. It has also been demonstrated that a harder fat (m.p. 60°C.), when fed in the form of a blend with refined oil at a level of 15-16 per cent of the total fat, has no deleterious effect as indicated in the digestibility studies, body and liver fat analysis and mineral metabolism[2-4]. Digestibility of the fat in relation to its melting point has exhaustively been studied by several workers[5-8] who conclude that fats melting below 45°C. are completely digested. However, our previous chylomicrographic studies[9] indicated that hydrogenated groundnut oil melting at 45°C. has an altered particulate absorption when compared to vanaspati melting at 37°-38°C. The blended product containing refined oil and a hardened fat (m.p. 60°C.) with a resultant melting point of 45°C. was also absorbed at a faster rate than the straight hydrogenated product melting at the same temperature, in spite of there being no significant difference in the digestibility coefficients of fat blends (viz. 92·3 and 90·2 respectively)[2].

In the investigation reported here, chylomicrographic observations (particulate absorption) and digestibility studies have been carried out using blends of hydrogenated groundnut oil melting at 41°, 45° and 51°C. respectively with vanaspati† (m.p. 37°C.) with a view to determining the influence of the harder fat portion of the blend on the trend of absorption.

The chylomicrographic technique[10-12] employed was essentially the same as developed by Nhavi and Patwardhan[13]. The experimental subjects were six normal healthy girls between the ages of 12 and 16 years. These children were selected from a group of 18 after a preliminary examination of their chylomicrographic curves for groundnut oil. This preliminary observation was necessary in order to avoid the individual variations as is indicated in our previous communication[8]. The selected subjects gave comparable chylomicrographic curves.

The fats studied were: (1) vanaspati, m.p. 37°C.; (2) vanaspati blended with the hydrogenated fat, m.p. 41°C., at 10, 15 and 25 per cent levels; (3) vanaspati blended with the hydrogenated fat, m.p. 45°C., at 10, 15 and 25 per cent levels; and (4) vanaspati blended with the hydrogenated fat, m.p. 51°C., at 10 and 15 per cent levels.

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†Vanaspati is essentially a hydrogenated groundnut oil melting within a range of 37°-39°C.

*These investigations were carried out under the C.S.I.R. scheme on " The Nutritive Value of Blended Vanaspati " in 1951, under the supervision of Dr. V. Subrahmanyan, Director, Central Food Technological Research Institute, Mysore.

The standard meal consisted of $\frac{3}{4}$ oz. of the test fat with $1\frac{1}{2}$ oz. of bread. The children were given the test meal at 8 a.m.; the last meal they had was at 5 p.m. the previous day. The first post-ingestional observation was made after 1 hr. while subsequent observations were at $\frac{1}{2}$ hr. intervals till the tenth hour. The average particle count of the fat particles at different stages of ingestion is graphically represented in Fig. 1.

Digestibility — Fat metabolism studies were carried out on the same subjects to determine the digestibility of the blends.

The experimental diet consisted of rice as the main cereal and was comparable to the standard South Indian rice diet described earlier[14]. The dietary routine observed was as follows:

8.30 a.m. — rice and ragi (5 per cent) without any added fat (50 g. of dried food)
1.00 p.m. — cooked rice (*dal*, 5 per cent, vegetable, 5 per cent) with 15 g. of added fat (150 g. dried food)
7.30 p.m. — cooked rice with 5 g. of added fat (100 g. dried food)

Major portion of the fat (15 g.) was included in the midday meal because it was easy to incorporate the fat with *dal* and vegetables. Weighed amounts of the food were individually served and the food was analysed from time to time. The weighed amounts of fat were individually added to the feeding plates and all the children consumed the entire amount of food.

Each of the test fat blends was fed for a period of 9 days, the fecal excretion being collected only for the last 4 days. The feces excreted during the 24-hr. period were individually collected, wetted with absolute alcohol and dried and the powdered collection for the entire 4-day period was stored in individual glass stoppered bottles. Determinations were made for fecal fat and the digestibility calculated from the neutral fat and fatty acid contents in the usual way. The correction for metabolic fat was determined in experiments where the diet was free of any added fat. The results (expressed as the coefficient of digestibility) are presented in Table 1.

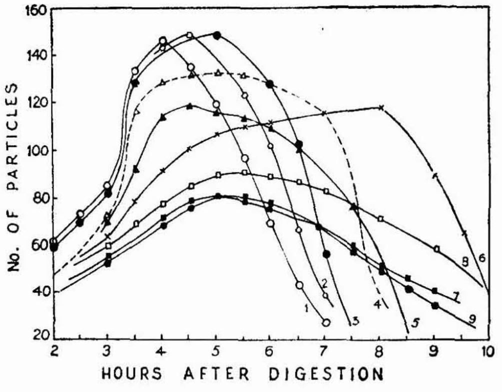

FIG. 1 — CHYLOMICROGRAPHS OF VARIOUS FAT BLENDS

TABLE 1 — MELTING POINTS AND DIGESTIBILITY COEFFICIENTS OF FAT BLENDS

BLEND No.	M.P. OF THE HARD FAT USED °C.	HARD FAT USED IN THE BLEND %	M.P. OF THE BLEND (CAPILLARY SLIP METHOD) °C.	DIGESTIBILITY COEFFICIENT
1	—	—	38·0	95·60 ± 1·60*
2	41	10	38·6	96·00 ± 1·20
3	41	15	38·8	95·70 ± 0·75
4	41	25	39·2	90·60 ± 1·30
5	45	10	39·5	95·80 ± 1·30
6	45	15	40·1	92·40 ± 1·40
7	45	25	42·6	84·20 ± 2·40
8	51	10	42·5	88·30 ± 1·20
9	51	15	44·5	87·50 ± 2·20

* Standard error of the mean.

TABLE 2 — FATTY ACID PARTITION OF FECAL AND DIETARY FAT

BLEND No.	SATURATED FATTY ACIDS OF THE DIETARY BLEND % of total fat	SATURATED FATT ACIDS IN THE FECAL FAT % of total fat
1	38·5*	32·60 ± 2·51†
2	39·2	40·30 ± 1·82
3	40·2	44·50 ± 3·03
4	42·1	44·80 ± 1·64
5	40·3	42·90 ± 2·03
6	42·7	46·20 ± 1·12
7	44·5	51·50 ± 1·74
8	48·5	51·60 ± 1·06
9	51·2	52·50 ± 0·98

* Mean of two determinations.
† Mean of six observations with standard error of the mean.

Determinations on the solid and liquid fat portions in the fecal fat as extracted with petroleum ether were also determined with the Twitchell's lead salt method. The results giving the percentage of saturated acids in the fecal fat are presented with the figures for the dietary fat in Table 2.

Discussion

There is a good deal of data in literature to indicate that a comparative serial picture of blood fat changes, as is obtained in a chylomicrograph, is more valuable than the occasional qualitative determinations of blood fat. Digestibility determinations give an overall picture of the removal of the fat from the intestine over 24 hr., whereas a chylomicrograph gives the trend of absorption of fat in the blood and its further transport to the depot tissues. Our previous studies indicated that though a blend of refined oil with a hard product (m.p. 60°C.) with a resultant melting point of 45°C. was absorbed in the blood at the same rate as oil, the subsequent removal of the fat from the blood was slow[9]. Similar flattened curves are obtained with the blends of vanaspati under present study. Though the digestibility coefficients are not very significantly different (except for samples 7, 8 and 9, FIG. 1), the chylomicrographs suggest a remarkable difference in the manner the fats undergo changes in the blood. The peak is also shifted (from 4 to 5 hr.) in blends containing the higher melting fractions, showing the retention of fat in the blood over long periods. With vanaspati, the cycle of absorption is complete within 7 hr. after ingestion of the fat, whereas in the blends, without exception, the period is extended from 8 to 10 hr. What effect this amount of fat in the blood will have on the general metabolism is not known.

The analysis of the fecal fat did not indicate any selective absorption of the solid or liquid fatty acids (TABLE 2). The effect in the blood, therefore, appears mainly due to the presence of the more saturated fatty acids.

Acknowledgement

The author is indebted to Dr. V. Subrahmanyan, Director of this Institute, for his personal interest and encouragement in this work and to the authorities of the Good Shepherd Convent Orphanage for providing facilities for this work.

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Utilization of Polyfructosan from *Agave vera cruz* by the Honey Bee (*Apis indica* F.)

I. S. BHATIA & S. V. PINGALE
Central Food Technological Research Institute, Mysore

Evidence has been presented to show that polyfructosans from *Agave vera cruz* are capable of being utilized by the bee, *Apis indica*, for the production of honey.

THE plants of the Agave family (N.O. Amaryllidae) grow widely and abundantly in almost every part of India and in many parts of the world. That the stems of these plants in general are rich sources of water-soluble polyfructosans is apparent from the works published so far on *Agave vera cruz*[1-3] and *Furcrea gigantea*[4]. It was of interest to find out, therefore, the extent to which these carbohydrates, present as such in the stem juice, or in the form of isolated polyfructosans, would be utilized by the honey bee, *Apis indica* F.

In any apiary, only facilities are provided to the bee for depositing honey in an easily accessible place and the production of honey by the bee is by the normal method practised in its native habitat, namely of collecting nectar by foraging on neighbouring flora. In the present study, however, care was taken to train the bees to forage, as far as possible, on the artificial feed composed mainly of polyfructosans, although the possibility of their having strayed outside could not be completely excluded, for want of proper facilities. Any honey-like product (hereafter referred to as honey) deposited under these conditions by the bee can be deemed to be mostly derived from the polyfructosans. Thus, evidence for the breakdown of the polyfructosans by enzymes present in the digestive tract of the honey bee would be provided. It is not claimed to produce real honey under these restricted and unnatural conditions. Perchance, the polyfructosans hydrolysed by the bee may, during the process of ripening and as a result of it, get modified and prove better than the product obtained by acid hydrolysis as a base for concoction of honey. From the economic point of view, however, prima facie the production of fructose from polyfructosans is by acid hydrolysis.

Materials and methods

Bees — Two colonies, each consisting of about 1,800 bees of *Apis indica* obtained locally, were acclimatized to the new surroundings for 15 days by being fed on a 50 per cent sugar (sucrose) solution at the rate of 150 cc. per day. The feed was filled in 3 combs kept in a small box within 10 ft. of the colony. Both the colony and the feed box were put in an enclosed shed with wire net at the top and accessible to plenty of sunlight. During the acclimatization and test periods, the feed was freshly supplied every morning, the remnants of the previous day, where left over, being removed and weighed. Invariably during the acclimatization period the feed was almost entirely consumed. Counts were taken at three different times during the day of the number of bees visiting the feed box in 5 min. and those straying outside.

After the acclimatization period, the feed was switched over to a mixture of polyfructosan and glucose (TABLE 1). At the end of the fourth week, the bees were fed on an 80 : 20 mixture. Polyfructosan was given in the form of agave juice (colony A) or in the form of aqueous solution of the pure polyfructosan isolated from the agave (colony B) at comparable levels.

TABLE 1 — COMPOSITION OF FEED

	Week			
	First	Second	Third	Fourth
Polyfructosan	50	60	60	60
Glucose	50	40	40	40

During the experimental period, the average quantity of the feed ingested was determined from the feed left over at the end of each day. After 4 weeks, the honey collected in the upper shelves of the hives (super) was expressed, qualitative composition determined chromatographically (FIG. 1) and the sugar estimated. Other normal constituents of natural honey were not looked for. The results are recorded in Tables 2-4.

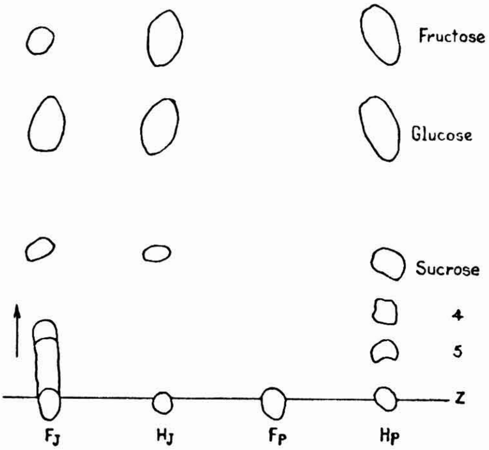

FIG. 1 — CHROMATOGRAM OF FEEDS AND OF HONEY FORMED [Agave juice feed (F_J) — corresponding honey formed (H_J); polyfructosan feed (F_P) — corresponding honey formed (H_P); solvent — butanol : acetic acid : water (4 : 1 : 5). Developed by ascending technique for 60 hr. Sprayed with benzidine trichloracetic acid]

TABLE 2 — NUMBER OF BEES FEEDING OUTSIDE AND ON THE SYNTHETIC DIET

COLONY		WEEK			
		First	Second	Third	Fourth
A	Number* feeding outside, %	4·3	3·7	3·6	4·2
	Number on synthetic diet, %	66·3	65·0	77·0	89·6
B	Number feeding outside, %	4·5	4·0	2·5	7·6
	Number on synthetic diet, %	54·6	81·5	94·5	34·6

*Expressed as percentage of the total number.

TABLE 3 — AVERAGE DAILY FOOD INTAKE AND YIELD OF HONEY

	POLY-FRUCTOSAN g.	GLUCOSE g.	HONEY COLLECTED AT THE END OF 4 WEEKS g.
Colony A (bees fed with polyfructosan in the form of agave juice)	26·80	19·55	62·0
Colony B (bees fed with polyfructosan pure)	25·60	18·10	72·0

TABLE 4 — ANALYSIS OF HONEY

COLONY	SPECIFIC GRAVITY	$[\alpha]_D^{23°}$	GLUCOSE %	FRUCTOSE (TOTAL REDUCING SUGAR-GLUCOSE/1·06) %	$\frac{\text{FRUCTOSE}}{\text{GLUCOSE}}$
A	1·3829	−11·9°	46·9	55·8	1·19
B	1·3887	−7·9°	44·6	57·9	1·30

Discussion

The amount of honey deposited in the super combs was small in comparison with the total feed. On the reckoned average production of 5 lb. of honey per hive in South India[5], the yield of honey based on the observations made for a period of 4 weeks with 2 colonies fed on the experimental diet is of the order of 33-40 per cent.

It could be reasonably concluded that the honey, small as it is, deposited in the comb is from the polyfructosan feed. This is based on the facts that (i) the number of bees foraging outside is small compared with the bees feeding on the synthetic medium and (ii) the qualitative composition of the honey (FIG. 1) has a relation to the feed. It is well to remember in this connection the known fact that when a pilot bee has located a source of nectar, the followers all go for this source only[6].

The honey formed has normal composition[7] as reflected by the fructose : glucose ratio, 1·19 from colony A and 1·30 from colony B. The other normal, though a small constituent of honey, namely sucrose, is also present as shown by the chromatogram. It is noteworthy that sucrose appears in the honey from bees fed on pure polyfructosan.

Further experiments excluding all extraneous foraging are necessary to correlate honey production in a particular period with the quantity of polyfructosan fed. The present data indicate that the polyfructosans admit of being utilized by the bee for the production of honey. It is significant that the glucose content of the feed and that of the honey are about the same (TABLES 3 and 4). The fructose in the honey must have all been derived from the polyfructosan, for it is far in excess of that which could be accounted for by isomerization of glucose, even assuming with Taufel and Reiss[7] that such a process takes place in the honey bee.

When the composition of the feed at the end of the fourth week was changed over from 60 : 40 polyfructosan : glucose to 80 : 20, the bees in the colony A (i.e. polyfructosan given in the form of whole agave juice) continued to stay and feed on, while colony B (fed on pure polyfructosan) deserted. This indicates that the bee does not tolerate this composition (80 : 20). If colony A persisted, it is probably because the composition (based on solids) of the whole agave juice was still within tolerance limits (the juice contains besides polyfructosans sucrose, glucose and fructose in small quantities[1]).

These feeding trials show that so far as the honey bee is concerned there is nothing nutritionally deleterious in the agave juice, and that enzymes in *Apis indica* are capable of hydrolysing polyfructosans from *Agave vera cruz*.

Acknowledgement

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Production of Electrolytic Manganese

N. DHANANJAYAN, H. K. CHAKRABARTI & T. BANERJEE
National Metallurgical Laboratory, Jamshedpur

The results of experiments on the production of manganese by the electrolysis of a solution containing sulphates of manganese and ammonia, and sulphur dioxide, in a canvas diaphragm cell employing stainless steel cathode and lead anodes are presented. The optimum conditions for electrolysis are: c.d., 26·4 amp./sq. ft.; temperature, 32°-35°C.; manganous sulphate in the feed electrolyte, 80 g./l.; ammonium sulphate, 150 g./l.; sulphur dioxide, not less than 0·15 g./l.; catholyte *p*H, 7·2.

At a given concentration of manganous sulphate in the electrolyte, the current efficiency of the process increases with increase in the catholyte *p*H up to a limiting value; with further increase in *p*H current efficiency rapidly falls. Increasing the concentration of manganous sulphate results in a fall in the catholyte *p*H necessary for maximum current efficiency. The relationship between the catholyte *p*H and manganous sulphate concentration has been explained on the basis of the ratio of [Mn++] and [H+] in the catholyte.

THE largest demand for manganese is from the iron and steel industry. It is commonly used in the form of ferromanganese and spiegeleisen. Manganese helps the removal of sulphur, oxygen and phosphorus from iron and also forms alloy with it imparting a high degree of toughness to the resulting product. A number of useful non-ferrous alloys, e.g. manganese bronze, high and low expansion alloys, high damping alloys, manganin, etc., contain manganese along with other constituents.

Ferro-manganese and spiegeleisen contain varying quantities of iron, carbon, silicon and smaller amounts of some other impurities. When these two materials are added in metallurgical processes for the purpose of incorporating manganese, these impurities also enter into the final product. In ferrous metallurgy, the presence of iron in the added manganese is generally not objectionable, but impurities like carbon, sulphur, silicon and phosphorus are undesirable. This is specially so when the composition of the steel is sought to be rigorously controlled, e.g. in the case of stainless steel. In non-ferrous metallurgy, ferro-manganese and spiegeleisen are unsuitable because of the presence of iron. Until recently only manganese metal prepared by carbon reduction or by thermit process was used in non-ferrous alloys. While manganese from the thermit process is too costly, and carbon-reduced manganese is not pure and contains fairly high percentage of carbon; electrolytic manganese is free from impurities and is about 99·98 per cent pure. It is also less costly than manganese produced by the thermit process[1].

The alloys prepared from electrolytic manganese are much better than those produced from other forms of manganese. According to U.S. Bureau of Mines' investigators[2], some of the high manganese alloys when prepared with carbon-reduced manganese appear to be unworkable, while the same alloys, prepared with electrolytic manganese, are free from this defect and possess many desirable qualities. This anomalous behaviour of the alloys may be due to the impurities associated with carbon-reduced manganese. If this observation is substantiated, electrolytic manganese will have a very important role to play in the future development of high manganese alloys, and, but for its present high cost of production, it could be used almost in every metallurgical practice in preference to other forms of manganese. In the manufacture of stainless steel and non-ferrous alloys, the advantages of using electrolytic manganese outweigh the disadvantage of its high cost, and it can compete with other forms of manganese[3].

In the electromotive series, manganese is perhaps the last metal that can be plated out of an aqueous solution. Because of its high negative electrode potential and low current efficiency in deposition, the consumption of electrical energy per pound of metal produced is quite high which contributes towards its high cost. Also, metals such as copper, iron, nickel, cobalt, etc., are plated out on the cathode at lower potentials. This makes it imperative that these more electro-positive metals should be completely removed from the solution. Thus purification of the electrolyte is important which adds to the cost of final product. Again, manganese metal is highly reactive. Even a slight change in the *p*H during electrolysis may bring about the dissolution of deposited manganese. A rigorous control of the conditions of electrolysis is thus necessary. The preparation of the electrolyte from ores is not a single-stage operation. The ores, which are mostly insoluble in sulphuric acid, have to be reduced and then dissolved in acids. All these factors combined, make the electrodeposition of manganese a difficult and costly process.

During World War I, import of manganese minerals into the U.S.A. became restricted and a programme of research was undertaken for the utilization of low grade domestic ores and production of manganese metal by an electrolytic process. Since then much work has been carried out in the U.S.A. and elsewhere on the production of electrolytic manganese and methods have been successfully developed for its manufacture. A survey[4] of the previous work on this subject reveals that one of the promising ways of exploiting the vast deposits of manganese ores in India is through the production of manganese metal electrolytically. Though the problem of production of electrolytic manganese has been successfully investigated to the pilot-plant stages in foreign countries, there are many uncertain features of the process which make successful reproduction of the results obtained by them rather difficult. These uncertainties are mostly with respect to optimum current density, concentration of manganous sulphate, catholyte *p*H and temperature. It is often difficult to correlate the sets of data obtained by different workers.

The method for production of electrolytic manganese involves the dissolution of the ore to form the electrolyte of proper composition and electrodeposition of manganese metal from the electrolyte. The present investigation is limited only to electrodeposition of manganese from manganous sulphate solutions.* Both manganous sulphate and chloride solutions can be used for electrodeposition. Chloride baths, however, suffer from certain disadvantages[5].

A comparative study of sulphate and chloride baths has shown that sulphate baths are convenient to use[4].

Materials and methods

Apparatus — The apparatus (FIG. 1) consisted of three main parts, namely feed electrolyte reservoir F_R, electrolytic cell E, and spent electrolyte reservoir S_R.

A glass aspirator (capacity 20 l.) was used as feed reservoir to store and maintain supply of electrolyte to the electrolytic cell. The outlet from the aspirator was connected

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*Application has been filed to cover the invention of this process by patent rights in India.

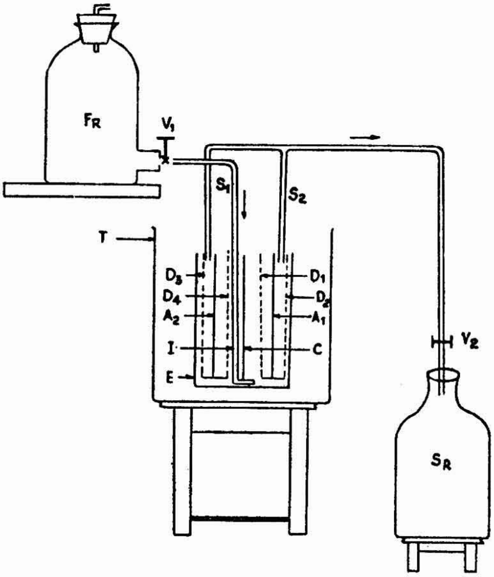

FIG. 1 — ELECTROLYTIC CELL

to the inlet tube I through the valve V_1. The feed reservoir was placed at a higher level than the electrolytic cell. The electrolytic cell was placed in a thermostat T whose temperature was controlled within ±1°C. of the desired temperature. A lead-lined wooden vat was used as the thermostat. A rectangular glass trough, measuring $5 \cdot 7 \times 3 \cdot 7 \times 8 \cdot 3$ in. in depth, was used as the cell. It was furnished with two anodic chambers, D_1, D_2, and D_3, D_4, made of cotton canvas (16 oz. quality), mounted on two wooden frames. The lead anodes, A_1 and A_2, each measuring $6 \times 2 \cdot 5 \times \frac{1}{12}$ in. in thickness, were suspended inside the two anode chambers from respective anode bus-bars. The effective area of each anode was reduced by 22 per cent by boring as many $\frac{3}{8}$ in. holes as possible[6]. The cathode C made of stainless steel and measuring $6 \times 2 \cdot 5 \times \frac{1}{24}$ in. was suspended from cathode bus-bar by stainless steel hooks between the two anode chambers and 2 in. apart from each anode. The spent electrolyte reservoir was a glass carboy (capacity 20 l.) placed at a level lower than that of the electrolytic cell.

A 12 V. lead accumulator was used as the source of electric current. It was connected to the two bus-bars through a sliding rheostat and a precision ammeter in series. A voltmeter was connected between the anode and the cathode to determine the voltage in closed circuit.

Electrolyte — The electrolyte was prepared from chemically pure manganous sulphate and ammonium sulphate. The *p*H of the electrolyte was adjusted with chemically pure sulphuric acid and ammonia. Sulphur dioxide gas was passed to obtain the desired concentration of the gas in the electrolyte. The feed electrolyte from the feed reservoir was let in through a valve V_1 and it entered the cathode chamber through the spray inlet tube. The electrolyte from cathode chamber passed through the canvas diaphragm into the anode chamber and passed out through the siphon tubes S_1 and S_2 and valve V_2 to the spent electrolyte reservoir. The movement of the electrolyte through the system could be controlled by the two valves. The spent electrolyte was regenerated and used again.

Electrolysis — The electrolytic cell was filled with the feed electrolyte and its *p*H adjusted to the required value. The *p*H of feed electrolyte was generally much lower than that of the catholyte. The valves V_1 and V_2 were so adjusted that the flow of the electrolyte was sufficient to keep the *p*H of the catholyte constant during the experiment. The lead anodes were coated with a thin layer of adherent manganese dioxide. The stainless steel cathode was mechanically polished and finally electrolytically polished in a bath containing sulphuric and phosphoric acids. It was then washed thoroughly with water, dried and weighed. The electrodes were then suspended from the respective bus-bars. After adjusting the temperature, the current was switched on and each experiment was allowed to run for 5 hr. During the period of experiment the rate of electric current passing through the cell, temperature, catholyte *p*H and bath voltage were recorded at intervals and controlled as desired. At the end of an experiment the cathode was removed from the bath and washed immediately with large volume of water. It was rinsed with alcohol, dried by hot air (60°C.), cooled in a desiccator and weighed to determine the weight of metal deposited. The deposited manganese was detached in the form of shiny flakes by bending the cathode.

Spent electrolyte — The spent electrolyte was regenerated by replenishing the deficient ingredients. Any manganese dioxide carried down from the anode chamber was converted into manganous sulphate during regeneration by passing sufficient amount of sulphur dioxide. The solution was filtered before being used again.

Analyses — Manganese metal in the deposit was estimated by dissolving it in acid and estimating the manganese content by Volhard's method[7]. For the presence of impurities, the samples were tested spectrographically.

Volhard's method was used for determining the manganese content of the electrolyte also. Ammonium sulphate in the electrolyte was determined by evolution method[8].

The *p*H of the electrolyte was measured with glass electrode, Marconi, model TF 511D, *p*H meter and Beckmann, model G, *p*H meter.

The current efficiency of the process and the amount of electrical energy consumed per pound or kilogram of manganese produced were calculated in the usual way.

Results

The results are from experiments each conducted for 5 hr. It was difficult to maintain the system under exactly the same conditions during this long period and there were slight fluctuations. But for all purposes the readings were reproducible. The data on influences of current density, temperature, concentration of manganous sulphate and *p*H of catholyte on cathodic current

TABLE 1 — INFLUENCE OF CURRENT DENSITY ON CURRENT EFFICIENCY

(*Composition of feed electrolyte: manganous sulphate*, 42 *g./l.; ammonium sulphate*, 150 *g./l.*; SO_2, 0·3 *g./l.; catholyte: p*H, 8-8·5; *temp.*, 32°C.)

CURRENT DENSITY amp./sq. ft.	BATH VOLTAGE V.	CATHODE CURRENT EFFICIENCY %	ENERGY CONSUMED		NATURE OF DEPOSIT
			kWh./lb. Mn	kWh./kg. Mn	
19·2	4·23	47·77	3·91	8·64	Silver white
24·0	4·26	55·76	3·37	7·45	Slightly grey, with striations
26·4	4·28	61·15	3·09	6·82	Silver white with small black blister
28·8	4·29	60·50	3·13	6·92	Silver white
36·0	4·33	58·24	3·29	7·27	do
43·2	4·48	56·13	3·53	7·79	Two small blisters; fine deposit
48·0	4·53	55·54	3·61	7·96	Silver white; treeing at the edges
57·6	5·13	54·12	4·19	9·26	do

TABLE 2 — INFLUENCE OF TEMPERATURE ON CURRENT EFFICIENCY

(*Composition of feed electrolyte: manganous sulphate*, 42 *g./l.; ammonium sulphate*, 150 *g./l.*; SO_2, 0·5 *g./l.; catholyte: p*H, 8-8·5; *cathodic current density*, 24 *amp./sq. ft.*)

CATHOLYTE TEMP. °C.	BATH VOLTAGE V.	CATHODE CURRENT EFFICIENCY %	ENERGY CONSUMED		NATURE OF DEPOSIT
			kWh./lb. Mn	kWh./kg. Mn	
16·5	4·42	55·04	3·55	7·83	Slightly grey; peeling off from the cathode; treeing
23·0	4·38	56·72	3·42	7·54	Quite satisfactory
32·0	4·26	55·76	3·37	7·45	Slightly grey; striations
40·5	4·18	—	—	—	Black slimy coat on the cathode

TABLE 3 — INFLUENCE OF CONCENTRATION OF MANGANOUS SULPHATE ON CURRENT EFFICIENCY

(*Composition of feed electrolyte: conc. of manganous sulphate as in the table; ammonium sulphate*, 150 *g./l.*; SO_2, 0·4 *g./l.; catholyte temp.*, 32°C.; *cathodic c.d.*, 33·6 *amp./sq. ft.*)

CONC. OF $MnSO_4$ g./l.	BATH VOLTAGE V.	CATHOLYTE *p*H	CATHODE CURRENT EFFICIENCY %	ENERGY CONSUMED		NATURE OF DEPOSIT
				kWh./lb. Mn	kWh./kg. Mn	
42·0	4·31	8·0 - 8·5	58·52	3·26	7·19	Silver white
63·6	4·54	8·0 - 8·5	61·98	3·24	7·15	do
80·0	4·64	8·2 - 8·3	62·94	3·26	7·19	do
99·0	4·59	7·8 - 8·1	61·93	3·28	7·24	do
120·0	4·62	7·8 - 7·9	61·95	3·30	7·28	do
138·8	4·81	7·3 - 7·8	61·53	3·46	7·64	Treeing at the edges
161·7	4·85	6·9 - 7·5	61·16	3·51	7·74	do
181·0	4·72	7·2 - 7·8	62·03	3·37	7·43	Increased treeing at the edges
196·0	4·66	7·4 - 7·5	63·04	3·27	7·21	do

TABLE 4 — INFLUENCE OF CATHOLYTE *p*H ON CURRENT EFFICIENCY

(*Composition of feed electrolyte: conc. of manganous sulphate as in table; ammonium sulphate*, 150 *g./l.*; SO_2, 0·4 *g./l.*; *cathodic c.d.*, 33·6 *amp./sq. ft.*; *catholyte temp.*, 32°C.)

*p*H	BATH VOLTAGE V.	CATHODE CURRENT EFFICIENCY %	ENERGY CONSUMED		NATURE OF DEPOSIT
			kWh./lb. Mn	kWh./kg. Mn	
A. Conc. of manganous sulphate, 80 g./l.					
4·60	5·00	46·67	4·74	10·46	Bright
5·05	4·80	53·47	3·97	8·76	do
5·20	4·85	54·12	3·96	8·75	do
6·85	4·72	63·51	3·29	7·25	Silver white
7·75	4·67	65·58	3·15	6·95	do
8·25	4·64	62·94	3·26	7·19	do
B. Conc. of manganous sulphate, 120 g./l.					
4·45	4·96	52·83	4·15	9·16	Bright
5·05	4·90	58·29	3·72	8·20	do
6·30	4·76	63·16	3·33	7·36	do
7·45	4·69	64·30	3·22	7·12	Silver white
7·73	4·78	63·08	3·35	7·38	do
7·85	4·62	61·95	3·30	7·28	do
C. Conc. of manganous sulphate, 196 g./l.					
4·30	4·96	52·83	4·15	9·15	Bright; treeing at the edges
4·75	4·82	57·63	3·70	8·16	do
6·75	4·74	64·49	3·25	7·17	Silver white
7·25	4·47	64·54	3·06	6·75	do
7·45	4·66	63·04	3·27	7·21	do

TABLE 5 — INFLUENCE OF CONCENTRATION OF MANGANOUS SULPHATE ON CATHODIC CURRENT EFFICIENCIES AT VARIOUS *p*H VALUES OF THE CATHOLYTE*

(*Composition of feed solution: conc. of manganous sulphate as in the table; ammonium sulphate*, 150 *g./l.*; SO_2, 0·4 *g./l.*; *cathodic c.d.*, 33·6 *amp./sq. ft.*)

CATHOLYTE *p*H	% CATHODIC CURRENT EFFICIENCY AT CONC. OF MANGANOUS SULPHATE		
	80 g./l.	120 g./l.	196 g./l.
5·05	53·47	58·29	59·50
6·00	59·50	62·30	63·30
6·80	63·30	64·30	64·70
7·20	64·70	64·80	64·60
7·40	65·30	64·60	63·50
7·60	65·50	64·00	61·70

*Values of the current efficiencies of this table have been taken from Fig. 2.

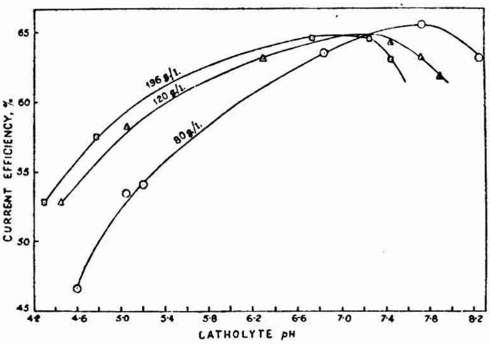

FIG. 2 — INFLUENCE OF *p*H OF THE CATHOLYTE ON CATHODIC CURRENT EFFICIENCY AT DIFFERENT CONCENTRATIONS OF MANGANOUS SULPHATE

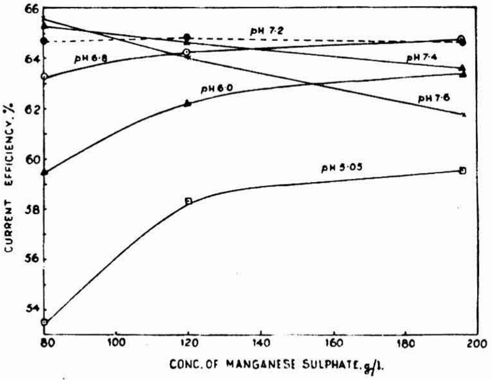

FIG. 3 — INFLUENCE OF CONCENTRATION OF MANGANOUS SULPHATE IN THE CATHOLYTE ON CATHODIC CURRENT EFFICIENCY AT DIFFERENT *p*H VALUES OF THE CATHOLYTE

efficiency and consumption of electrical energy per kilogram and per pound of product have been presented in Tables 1-3, 4 A, B, C and 5 respectively. Tables 4 and 5 are represented graphically in Figs. 2 and 3 respectively.

Discussion

Before discussing the results recorded in Tables 1-5 and Figs. 2-3 it may be of interest to examine the results of unsuccessful experiments. In these experiments, the deposition of manganese was often observed to stop completely. This may have been due to the following causes: (1) when the electrolyte contains more electropositive ions such as Cu^{++}, Ni^{++} or Co^{++}, hydrogen evolution is accelerated and the catholyte *p*H goes up. As a result, oxides of manganese are formed which settle on some parts of the cathode causing rapid dissolution of the deposit; (2) if the current through the cell fails even for a short while, the deposited metal, being very reactive, begins to dissolve raising the *p*H of the catholyte. Once this phenomenon starts re-establishment of the power circuit alone fails to arrest the dissolution which continues unabated till the cathode is completely denuded of all the deposit. If the flow of the electrolyte is not uniform or is slow for some time, a rise in the *p*H of the catholyte facilitates the settling of manganese oxides on the cathode with the usual result. In the above cases, a local couple[9] seems to develop on the cathode plate where the deposited manganese metal acts as anode and dissolves away in no time. Nothing short of beginning afresh after completely overhauling the cell can initiate deposition of manganese again.

Current density — From the results of experiments recorded in Table 1, it is evident that the current efficiency goes on increasing rapidly with increase in the current density and reaches a maximum value when c.d. is 26·4 amp./sq. ft. Beyond this optimum c.d. the current efficiency decreases rather slowly with further increase in c.d. As manganese is sufficiently electronegative, the cathode has to be polarized to a greater extent for a steady deposition of the metal. At low current densities, the voltage requirement is not fully satisfied and, therefore, low efficiencies are obtained. At the optimum cathode potential and corresponding current density, maximum current efficiency is realized. With further increase in c.d. the applied cathode potential increases causing loss of current through hydrogen evolution. Also, at high current densities, specially when the concentration of manganous sulphate is not very high, concentration polarization develops causing growth of nodules and trees on the cathode plate. These abnormal growths fall down from the cathode plate and being very reactive quickly dissolve in the electrolyte. This phenomenon is also partly responsible for low efficiencies at high current density. It is possible that at higher concentrations of manganous sulphate, high current densities will give higher current efficiency. The amount of energy consumed per pound of metal deposited is minimum at a c.d. of about 26·4 amp./sq. ft. The c.d. recommended by earlier workers[10-16] varies from 18 to 60 amp./sq. ft. The wide variation in the working ranges of current densities employed is perhaps due to the fact that the desirable current density for electrolytic production of the metal involves consideration of many factors other than current efficiency alone. Increasing the current density increases the output of the cell and decreases capital cost, floor space, etc.[17]. Though it is not possible to arrive at the optimum c.d. without pilot-plant studies, it is safe to assume that it should not be lower than 25 amp./sq. ft.

Temperature — The results recorded in Table 2 show that increasing the temperature of the electrolyte beyond certain limits has a deleterious effect on the deposition of manganese. At low temperatures, current efficiency does not change appreciably and voltage requirement rises with corresponding increase in energy consumption. Poor adhesion and treeing are also noticeable in deposits obtained at low temperatures. At temperatures higher than 35°C. smaller amounts of deposit, and at times no deposits, are obtained. Manganese being highly reactive, its chances of dissolution increase when the electrolyte is hot. Therefore, at high temperatures poor efficiencies are likely to result.

Earlier workers have recommended a temperature around 35°C. as the optimum, though Agladze[15] recommends 20°-25°C. as most suitable. From our experience it is felt that initiation of deposit is easier at a low temperature, say, at 20°-25°C., while actual deposition is convenient and profitable at a higher temperature, say, about 32°-35°C. This procedure may ensure uniform deposition at reasonable energy consumption. In large-scale production of the metal, a cooling system should be incorporated in the cell.

Concentration of manganous sulphate in the feed

The results presented in Table 3 show that current efficiency rises with concentration and reaches a maximum of 62·9 per cent at a concentration of 80 g./l.; it remains almost unchanged at higher concentrations. The optimum concentration of manganous sulphate in the feed recommended by other workers[11,13,14,18] varies between 66 and 88 g. of manganous sulphate per litre. Agladze[15], however, suggests a wide range between 20 and 70 g./l.

The energy consumption per pound of manganese produced is minimum in the range 63·6-80 g./l. and does not appreciably change beyond this limit. To ensure better strip from the electrolyte, a higher concentration, as far as practicable, is to be favoured. But a concentrated solution of manganous sulphate containing in addition ammonium sulphate (150 g./l.) will be susceptible to crystallization at various stages of its handling and thus create difficulties. It, therefore, appears desirable that for maximum efficiency the concentration of manganous sulphate should be maintained near about 80 g./l.

A reference to Table 4A will show that the current efficiency of 62·9 per cent at 80 g./l. is likely to go up to 65·6 per cent if the *p*H of the catholyte is maintained at 7·75 instead of 8·25.

The *p*H values of the electrolyte at which these experiments were carried out for obtaining a good deposit show a tendency to go down with increase in the concentration of manganous sulphate. In other words, deposition from a dilute solution is possible at high *p*H but is difficult at the same *p*H from a concentrated solution. Thus it appears that efficiency of deposition from solutions of varying concentrations is related to the *p*H of the solutions.

*p*H *and concentration* — Table 4 and Fig. 2 show how the *p*H values affect the current efficiency at three selected concentrations. The curve (FIG. 2) recording the current efficiencies at different *p*H values of the electrolyte of concentration 80 g./l. shows that when the *p*H of the electrolyte rises from 4·6 to 7·7, the current efficiency steadily rises and reaches a maximum at 7·7. When the *p*H rises beyond 7·7, the current efficiency shows a sharp fall. The curves for concentrations of 120 g. and 196 g. are similar in nature, but the *p*H values for maximum efficiency are 7·25 and 7 respectively. Thus it is evident that optimum *p*H for maximum current efficiency decreases with increasing concentration of manganous sulphate. It is interesting to note that energy consumption is minimum at the optimum *p*H at all the three concentrations.

The effect of concentration of manganous sulphate on current efficiency at *p*H values 5·05, 6·0 and 6·8 (TABLE 5, FIG. 3) shows that the current efficiency registers a rise with increasing concentration while at *p*H values 7·4 and 7·6 a fall is observed. The curve for *p*H value 7·2 is almost parallel to the concentration axis showing the independence of current efficiency from variations in concentration.

From the above observations it appears that the *p*H of the catholyte should be maintained at about 7·2 so that variations in electrolyte concentration with respect to manganous sulphate will leave the current efficiency unaffected. A similar observation has been made by Jacobs[19] with manganous chloride and ammonium chloride bath.

The interrelation between *p*H and concentration of manganous sulphate with respect to current efficiency may possibly be due to the following reactions.

Reactions at the cathode:

(a) $Mn^{++}+2e = Mn$; (b) $H^{+}+e = \frac{1}{2}H_2$

The chemical reaction occurring in the catholyte, specially on the surface of the cathode, where the evolved hydrogen is leaving the zone alkaline may be represented as follows: (c) $Mn^{++}+2OH^{-} = Mn(OH)_2$ (sparingly soluble). If K is the solubility product under the conditions of experiment

$$K = [Mn^{++}]\times[OH^{-}]^2 \quad \ldots\ldots \quad (1)$$

The deposition potential of manganese or hydrogen will depend upon their respective activities. Therefore, under a constant current density, the ratio of deposited manganese to evolved hydrogen, i.e. efficiency of manganese deposition, under otherwise identical conditions, will virtually depend upon the ratio

$$\frac{\text{Conc. of } Mn^{++} \text{ in the catholyte}}{\text{Conc. of } H^{+} \text{ in the catholyte}}$$

Thus, if the concentration of Mn^{++} is kept constant and the *p*H raised, thereby decreasing the H^{+} ion concentration, efficiency of Mn^{++} deposition is expected to rise. A corroboration of this expectation is found in the lower *p*H range in all the three curves in Fig. 2. Alternatively, if the *p*H is kept constant in the lower range and concentration of Mn^{++} increased, the current efficiency of deposition will rise. This is borne out by the curves for lower *p*H range (FIG. 3).

At higher *p*H range, OH^{-} ions preponderate and we shall have to take into account the reaction (c) occurring on the cathode layer. Manganese hydroxide will precipitate out as soon as local concentrations of the two relevant ions exceed the limiting value of K in eqn. 1. The moment some hydroxide gets deposited on the cathode, the deposition of manganese is greatly hindered[9]. This effect is quite sharp and is connected to the critical *p*H beyond which the current efficiency falls rapidly with increasing *p*H. Both Mn^{++} and OH^- ions take part in attaining this value of K. Thus in a dilute solution where $(Mn)^{++}$ is low, this value of K will be reached at a higher *p*H, i.e. the critical *p*H will be higher in dilute solutions. Similarly, it can be shown that for a more concentrated manganous sulphate solution the critical *p*H will be lower. The curves in Fig. 2 bear out the above conclusions on the basis of which it is possible to explain the apparently varying optimum *p*H ranges suggested by different workers for different concentrations of manganous sulphate.

The following data will make the point clearer:

Suggested conc. of manganous sulphate, g./l.	*Suggested optimum pH range*
71-66[14]	7·2-7·5
70-20[15]	6·5-8·0
137-110[20]	6·0-7·2

Ammonium sulphate — Bright and silver white deposits are obtained by using 150 g./l. of ammonium sulphate in the electrolyte.

Sulphur dioxide — The cell functions normally when the concentration of sulphur dioxide is not below 0·1 g./l. of the feed electrolyte. In our experiments a higher concentration of sulphur dioxide has been employed to prevent manganese dioxide formation at the anode.

Voltage — The recorded voltages in the foregoing tables are influenced to some extent by the resistance offered by the diaphragm besides other factors. The resistance of the diaphragm depends on its condition and in spite of cleaning it to certain definite standard before each experiment, its resistance is not constant. However, the error thus introduced in the calculation of energy consumption is quite small.

Purity of the product — The samples of manganese metal obtained in our experiments have been spectrographically examined. They are free from all heavy metals and the manganese content of the samples has been found to be of the order of 99·95 per cent by chemical analysis (the co-deposited hydrogen has not been taken into consideration in arriving at this figure).

Conclusion

Current efficiencies of the order of 65 per cent, corresponding to the consumption of about 3·2 kWh. of energy per pound of manganese, can be obtained employing a feed electrolyte containing 80 g. of manganous sulphate, 150 g. of ammonium sulphate and not less than 0·15 g. sulphur dioxide per litre. The catholyte should be maintained at a *p*H about 7·2 and a temperature of about 32°-35°C. Electrolysis should be carried out in a canvas diaphragm cell with arrangement for the flow of electrolyte. Stainless steel sheets (18: 8 quality) can be profitably used as cathodes and perforated lead sheets coated with an adherent layer of manganese dioxide as anodes.

A suitable current density cannot be recommended for the process based on the results of this investigation and it is necessary to carry out large-scale trials to arrive at an optimum current density for a given set of conditions. Work on a semi-pilot-plant scale is in progress.

Acknowledgement

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Letters to the Editor

THE ELECTRODE SURFACE AS THE SEAT OF "AGEING" IN THE PRODUCTION OF THE JOSHI EFFECT

The interpretation of "ageing"[1,2], namely the development with time of the Joshi effect $\pm\Delta i$ under discharge at constant applied potential V, in *freshly prepared* discharge tubes, as due to growth on the electrode walls of an adsorption-like layer of particles from the discharge space and a consequent lowering of the surface work function, has mainly been based on Joshi's postulate[3-6] that the formation of such a layer is primary to the production of the *effect*. Experimental evidence now adduced, however, demonstrates conclusively that the electrode surface is fundamental to "ageing".

The electrodes of an all-glass (Indian soft soda) Siemens' tube, previously washed repeatedly with chromic acid mixture and finally with conductivity water, were partially coated, over half their length, with a 2·5M aqueous solution of "Analar" potassium chloride. The tube was vacuum dried, and filled with pure oxygen[8] at 100 mm. Hg (29°C.) pressure. Equal lengths of the two portions, blank and potassium chloride coated, were excited separately, excluding the extremities, at 3·74 kV. r.m.s. (50~; temp., 34°C.) and $-\Delta i$ observations made at regular time intervals till a constant maximum $-\Delta i_{\max}$ was recorded in each case.

The mean values of the specific rate k of the process, given by the equation[2]

$$k = \frac{2\cdot303}{t}\log\frac{(-\Delta i_{\max})-(-\Delta i_{o})}{(-\Delta i_{\max})-(-\Delta i_{t})}$$

where $-\Delta i_o$ and $-\Delta i_t$ are the values of $-\Delta i$ at the commencement of the discharge ($t = 0$) and after an interval of time t respectively, are blank, 0·0212, and potassium chloride coated, 0·0795 min^{-1}. That a change in the nature of the electrode surface should bring about a (large) variation in the kinetics of "ageing" shows that the seat of "ageing" is located in the electrode surface.

Grateful thanks are due to Prof. S. S. Joshi for his keen interest in the work.

S. R. Mohanty
T. D. Prasada Rao
R. Ramaiah

Department of Chemistry
Banaras Hindu University
Banaras
29 *May* 1953

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DEPENDENCE OF THE "THRESHOLD POTENTIAL" IN SILENT ELECTRIC DISCHARGE ON THE NATURE OF THE ELECTRODE SURFACE

THE IMPORTANCE OF THE "THRESHOLD potential" V_m (defined as the minimum potential V at which a gas breaks down as a dielectric) in chemical or quasi-chemical changes under discharge, as a determinant of their rate and nature, and in the Joshi effect, has been emphasized by Joshi[1,2]. In the case of elementary gases, V_m is identifiable with, or is a simple function of, the corresponding Paschen potential, and is marked by a sudden increase in the current i passing through, and the wattage dissipated in, the system.

The author has observed that V_m for oxygen diminishes with "ageing" under discharge (unpublished data). The findings of Ramaiah[3] in water vapour are similar. V_m varies sensibly linearly with the gas pressure p[2,4,5]. That, however, the diminution in V_m due to "ageing" is much larger than can be accounted for by a similar change in p, brought about by removal of the gas from the discharge space through sorption on, or/and chemical reaction with, the electrodes, can be shown from the known magnitude of dV_m/dp. The chemisorbed layer[6], formed during "ageing" on the electrode walls (and responsible for $\pm\Delta i$[7-9]), changes the nature of the latter. It would appear, therefore, that V_m is dependent, not only on the nature and number of gas particles in the discharge space, but partly also on the nature of the electrode surface, an aspect not considered hitherto in studies of the Joshi effect. The results of the present investigations, only a typical set of which is considered below, confirm the validity of the above conclusion.

The (sensibly exactly concentric) electrodes of an all-glass Siemens' tube were coated, over half their length, with a 2·5M aqueous solution of "Analar" potassium chloride, and vacuum dried. The tube was then filled with purified oxygen at 100 mm. Hg pressure (29°C.) and sealed off. The two portions, i.e. blank and potassium chloride coated, were excited separately, excluding the extremities, at a given applied V, till no further time variation of i was noticed in either case; the length of the discharge column was the same in both. The V-i characteristics were then determined on a vacuo-junction-galvanometer system with increasing V (2-6 kV., r.m.s.), also separately, and are shown graphically in Fig. 1. Values for V_m obtained by extrapolation are, blank 2·64 kV. and potassium chloride coated 2·43 kV. Similarly, with chlorine in a Siemens' tube at 150 mm. Hg pressure, V_m for blank was 2·67 kV. and for sodium chloride coated 2·56 kV. This variation in V_m, with the nature of the electrode surface, similar to that observed in the case of the Paschen potential[10], can be ascribed to the surface dependence of γ.

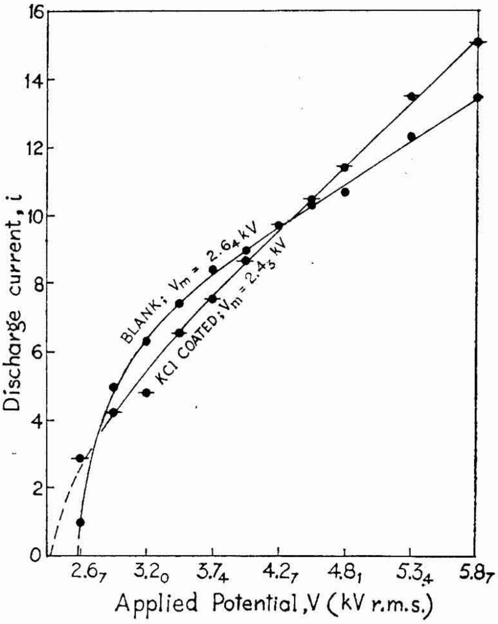

FIG. 1 — V-i CHARACTERISTICS FOR (GLASS) ELECTRODES, BLANK AND KCl COATED [pO_2, 100 mm. Hg (29°C.); temperature, 34°C.; 50 cycles; vacuo-junction detection]

Grateful thanks are due to Prof. S. S. Joshi for his keen interest in the work.

S. R. MOHANTY

Department of Chemistry
Banaras Hindu University
Banaras
15 *April* 1953

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FOSSIL WOODS BELONGING TO *GUTTIFERAE, CELASTRACEAE, LEGUMINOSAE, SONNERATIACEAE* & *EUPHORBIACEAE* FROM TERTIARY ROCKS OF SOUTH ARCOT DISTRICT, MADRAS

IN A PREVIOUS NOTE[1] THE AUTHOR DESCRIBED some fossil woods resembling the genera *Shorea*, *Mangifera* and *Albizzia* from Tertiary rocks (? Cuddalore Series) near Mortandra, 5 miles north-west of Pondicherry. Further study of the petrified woods from this locality has brought to light several other interesting types.

Guttiferae — The fossils resemble the wood of *Garcinia* in the following features: Vessels usually solitary, fairly large, often tylosed; pits on vessels alternate and hexagonal. Vessel ray pits transversely elongated, 3-5 per cell.. Fibres unseptate. Parenchyma apotracheal, in tangential bands 1-3 cells wide. Rays numerous, 3-6 seriate, 13-55 cells high, mostly homogeneous, often weakly heterogeneous.

Celastraceae — The woods show the following characters: Vessels moderately small, usually solitary; perforations simple, rarely scalariform; pits on vessels alternate, hexagonal. Vessel ray pits bordered and many per cell. Ground tissue composed only of fibre-tracheids; pits to fibre-tracheids numerous, bordered and circular. Parenchyma apotracheal, in very short bands usually 1-2 cells wide. Pits between parenchyma and vessels large, elongate and bordered. Rays 1-5 seriate, 10-70 cells high, heterogeneous to almost homogeneous. It has not yet been possible to make generic comparisons.

Leguminosae — The specimens show resemblances to the genera *Cassia* and *Dalbergia*. The fossils resembling *Cassia* are characterized by faint growth rings. Vessels mostly solitary; pits to vessels small and alternate. Vessel ray pits simple and many per cell. Fibres of same size as in the living genus *Cassia*, with few simple pits. The fibrês of *Cassia* are septate, but in the present fossils the septate condition is not clearly seen. Parenchyma abundant, confluent, rarely aliform; faintly developed terminal bands also present; parenchyma cells not storied. Rays 1-4 seriate, 5-15 cells high and weakly storied; rays usually homogeneous, occasionally heterogeneous. Gum-ducts absent.

The fossil woods resembling *Dalbergia* possess the following characters: Vessels medium to large, mostly solitary, often in oblique patterns in the transverse section; vessel pits numerous, small and alternate. Vessel ray pits small and many per cell. Parenchyma abundant, paratracheal (aliform to confluent, often forming irregular bands) as well as apotracheal (in fairly broad bands); parenchyma cells storied. Fibres unseptate with simple pits. Rays 1-4 seriate, 8-25 cells high, homogeneous to heterogeneous. The tangential surface of the fossil wood shows distinct ripple marks, owing to storied arrangement of the rays.

Sonneratiaceae — Two genera, *Sonneratia* and *Duabanga*, seem to be represented. The fossil woods resembling *Sonneratia* possess vessels which may be solitary or in many radial groups of 2 or 3 members. Inter-vessel pits alternate and vestured. Fibres septate with simple pits. Parenchyma absent. Rays numerous, mostly uniseriate, 3-12 cells high, homogeneous with small procumbent cells.

The woods resembling *Duabanga* show the following characters: Vessels mostly solitary, medium to large; pits to vessels alternate and vestured. Vessel ray pits also vestured. Fibres aseptate with simple pits. Parenchyma present in the form of narrow to wide vasicentric sheaths. Rays 1-3 seriate, 2-20 cells high, always heterogeneous; pits on the tangential walls of rays many and simple.

Euphorbiaceae — The specimens afford striking similarities with *Glochidion* and *Bridelia*. Those resembling *Glochidion* possess the following features: Growth rings faint, vessels solitary or in radial groups of 2-4. Inter-vessel pits alternate and bordered with lenticular pore. Vessel ray pits many, apparently simple and circular. Fibres thick walled and septate. Parenchyma absent. Rays 1-4 seriate; usually 20-60 or more cells high, markedly heterogeneous.

The specimens resembling *Bridelia* are characterized by the following features:

Growth rings distinct. Vessels in numerous radial groups of 2-6, usually plugged with dark solid deposits. Inter-vessel pits alternate and vestured. Vessel ray pits apparently simple, oval to circular and 2-4 per cell. Fibres septate. Parenchyma in limited quantities, usually vasicentric. Rays numerous, 1-4 seriate, 12-35 cells high and weakly heterogeneous; ray cells commonly filled with dark solid deposits.

The author is very much indebted to Dr. R. V. Sitholey for his help.

C. G. K. RAMANUJAM

Birbal Sahni Institute of Palaeobotany
Lucknow
18 *Dec.* 1953

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CHEMICAL EXAMINATION OF THE ROOTS OF *CAESALPINIA DIGYNA* ROTTLER

Caesalpinia digyna ROTTLER (N.O.: *Leguminosae*; Hindi: *Vakeri*) is a large, profusely branched scrambling shrub copiously armed with recurved prickles and is chiefly found in Assam, Bengal, Bombay, Bihar and Ceylon. The dark brown roots are astringent and are reported to be efficacious in the treatment of phthisis, scrofulous affections and diabetes[1].

The pods of *C. digyna* are rich in tannins[2], consisting of monodigalloyl glucose[3]. Brazilin has been isolated from the woody parts of other species of *Caesalpinia* like *C. brazilian*, *C. crista*, *C. echinata* and *C. sappan*. *C. bonducella* has been reported to contain a bitter glucoside, bonducin[4]. Dividivi, the dried seed pods of *C. coriaria*, contains ellagitannin[5], while algarobilla, the pods of *C. brebifolia*, contains methyl gallate[6]. Apart from the isolation of tannins from the pods no other reference is available in literature in regard to the other chemical constituents of *C. digyna*, and in view of the importance of the roots in the indigenous system of medicine, a systematic examination of the roots was undertaken.

As a result of the present investigations, a crystalline phenolic substance, provisionally named as Vakerin, $C_{15}H_{18}O_{10}$, has been isolated in a yield of nearly 3 per cent on the weight of the air-dried powdered roots. The powdered drug was exhaustively extracted with alcohol and the alcoholic extracts were concentrated under reduced pressure at 40°C. The dark red viscous concentrate, which was soluble in hydroxylic solvents, but almost insoluble in non-hydroxy solvents, was diluted with water and kept in the cold for a week, when a deposit of a dark brown crystalline mass separated out. On repeated crystallization of the crude crystallizate from methanol and finally from boiling water (norit), vakerin was obtained in the form of colourless plates giving a meniscus at 155°C., resolidifying on further heating and remelting at 235°C. The melting point on recrystallization from methanol rose to 238°C. without any previous melting at 155°C. It showed $[\alpha]^{27}_{D} = -39°$ in 1 per cent methanol solution; found: C, 49·90; H, 5·20; OCH_3 (after Zeisel), 8·25; $C_{15}H_{18}O_{10}$ requires: C, 50·27; H, 5·02; OCH_3 (for one), 8·68 per cent.

Vakerin is soluble in alcohol, methanol and water in the hot but sparingly so in the cold. It is insoluble in acetone, benzene, chloroform and other solvents. It is feebly acidic to litmus but does not give any effervescence with sodium bicarbonate. It dissolves in dilute caustic soda and caustic potash and is precipitated out on acidification. It develops a light yellow colour on standing in aqueous alkali and a light red with dilute acids. With alcoholic ferric chloride, vakerin gives a violet colouration. It dissolves in concentrated sulphuric acid with a reddish colouration and on dilution with water the colour lightens and the original compound is recovered. It reduces Fehling's solution and ammoniacal silver nitrate solution. It does not react with semicarbazide hydrochloride or with 2:4-dinitrophenyl hydrazine hydrochloride. It does not give Molisch's test and is recovered unchanged on heating with dilute acids or dilute alkalies.

On acetylation with acetic anhydride in pyridine or in the presence of fused sodium acetate, vakerin gives a penta-acetyl derivative, m.p. 205°C.; found: C, 52·62; H, 5·09; CH_3CO, 39·0; OCH_3, 6·20; $C_{15}H_{13}O_{10}(CH_3CO)_5$ requires: C, 52·80; H, 4·90; CH_3CO (for five), 37·8; OCH_3 (for one), 5·45 per cent. The acetyl derivative does not give any colouration with ferric chloride and does not reduce Fehling's solution or Tollen's reagent.

With diazomethane vakerin yields a dimethyl ether, m.p. 199°C.; found: C, 52·64; H, 5·94; OCH_3, 23·93; $C_{15}H_{16}O_8(OCH_3)_2$ requires: C, 52·85; H, 5·70; OCH_3 (for three), 24·10 per cent. The dimethyl ether also does not reduce Fehling's and Tollen's reagents and gives no colouration with ferric chloride.

The dimethyl ether on acetylation with acetic anhydride in presence of a drop of perchloric acid gives triacetyl vakerin dimethyl ether, m.p. 130°C.; found: C, 53·82; H, 5·64; OCH_3, 18·40; CH_3CO, 26·0; $C_{17}H_{19}O_{10}(CH_3CO)_3$ requires: C, 53·90; H, 5·46; OCH_3 (for three), 18·16; CH_3CO (for three), 25·20 per cent.

On alkali fusion with potassium hydroxide, vakerin gave a volatile acid along with shining needles of another acid, m.p. 103°C. The solid acid does not give any colouration with ferric chloride. The quantities of the two acids were, however, too small to permit a detailed study.

Further work is in progress.

G. R. CHAUDHRY
V. N. SHARMA
M. L. DHAR

Central Drug Research Institute
Lucknow
·18 *Nov.* 1953

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A COMPARATIVE STUDY OF THE COMPOSITION & BITTERNESS OF LOOSE JACKET ORANGES GROWN IN INDIA

A NUMBER OF VARIETIES OF LOOSE JACKET oranges are grown extensively in the hilly regions of different parts of India and often go to waste either for want of proper transport facilities or lack of demand. The present communication reports the results of a comparative study on the composition of loose jacket oranges grown in Coorg, Wynaad, Nagpur and Assam.

Ripe fruits of medium to large size (weighing 140-160 g. each) were taken for analysis. The juice was pressed from the segment by means of a basket press or by squeezing by hand the crushed segments in cloth. In the case of the lye-treated segments, the segments were dipped in 1 per cent boiling sodium hydroxide solution and then rinsed with water to remove traces of alkali. In the case of the tight-skinned Sathgudi orange, the juice was reamed by means of a revolving spindle. The total soluble solids in the juice were noted by means of a refractometer (at 20°C.). Acidity was determined by titration against standard sodium hydroxide solution and expressed as anhydrous citric acid. The reducing and total sugars were determined by Lane and Eynon's method, total ascorbic acid by titration with standard 2:6-dichlorophenol indophenol dye solution and true ascorbic acid by means of the formaldehyde modification of the xylene extraction procedure of Robinson and Stotz[1]; *p*H was determined with a Beckmann *p*H meter. The juice was bottled by the overflow pasteurization method.

The results of analysis (TABLE 1) show that loose jacket oranges of average size and quality from Coorg, Nagpur, Assam and Wynaad areas are almost similar in composition as regards total soluble solids, acidity, *p*H, sugars and ascorbic acid content. The juice of Assam oranges is free from bitterness, while that of Coorg, Wynaad and Nagpur oranges has a marked tendency to turn bitter on processing, which is a serious handicap in the commercial processing of these oranges into juice or concentrate. Although the bitterness in oranges has been the subject of several investigations, which have recently been reviewed by Siddappa, Pruthi and Takerkhede[2], a completely satisfactory method for removing bitterness from the juice has not so far been worked out. This study has shown that bitterness in the juice is almost completely removed by treating the segments in boiling dilute lye solution to remove their outer covering, prior to expression of the juice. This process has the additional advantage of removing some of the pectic substances which often lead to gelation and clarification of juice concentrates. The lye treatment of the segments has, however, one disadvantage, namely that the yield of juice is slightly lowered.

TABLE 1 — ANALYSIS OF ORANGE JUICES

	GAUHATI ORANGE JUICE		KHASI ORANGE JUICE		COORG ORANGE JUICE		NAGPUR ORANGE JUICE		WYNAAD ORANGE JUICE		SATHGUDI ORANGE JUICE FROM REAMING MACHINE
	Hand pressed	From lye-treated segments	Hand pressed	From lye-treated segments	Hand pressed	From lye-treated segments	Extracted in basket press	From lye-treated segments	Hand pressed	From lye-treated segments	
Yield of juice, %	38·40	40·10	49·00	49·90	52·60	46·30	54·70	47·30	—	44·00	44·00
Total soluble solids, 20°C.	11·30	9·30	14·56	12·76	10·66	9·43	11·43	10·13	8·86	7·35	13·61
Acidity (anhydrous citric acid), %	0·54	0·47	0·40	0·37	0·46	0·40	0·53	0·47	1·44	0·76	0·43
Total ascorbic acid, mg./100 g.	20·24	19·71	19·82	20·67	28·78	27·36	25·61	20·36	31·65	27·67	52·89
True ascorbic acid, mg./100 g.	—	—	15·74	16·68	—	—	—	—	—	—	—
*p*H	3·78	3·78	4·25	4·35	3·90	3·90	3·90	3·90	3·15	3·20	3·90
Reducing sugars (as invert sugar), %	3·92	3·37	5·33	4·67	3·06	—	3·92	—	2·12	—	3·22
Total sugars (as invert sugar), %	8·68	7·45	11·65	10·36	6·36	—	8·26	—	6·14	—	11·47
Quality of fresh juice	Not bitter	Not bitter	Not bitter, but flat in taste	Not bitter, flat taste, but slightly less so than in untreated juice	Slightly bitter taste; normal flavour	Not bitter; less acidic taste, weak flavour	Slightly bitter (½ hr. after extraction)	Not bitter	Slightly bitter; normal flavour	Not bitter; weak flavour	Not bitter; good taste and flavour
Quality of bottled juice	do	do	Not bitter, but flat in taste (slightly fermented)	do	Bitter taste, normal flavour	Not bitter, weaker flavour and less acidic	—	—	—	—	do
Ascorbic acid in bottled juice, mg./100 g.	7·45*†	14·92†	—	—	25·57‡	23·79§	—	—	—	—	43·97¶

* Fermented and mouldy due to faulty corking. †, ‡, § and ¶, examined at the end of 15 days, 2, 6 and 8 months respectively.

The juice of the Sathgudi orange, which is a highly prized orange in the Madras State, has a Brix value higher than that of the loose jacket orange and also nearly twice the amount of ascorbic acid. Further, it does not develop any bitterness on processing, and this accounts for the superiority of this orange.

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G. S. SIDDAPPA
B. S. BHATIA

Central Food Technological Research Institute
Mysore
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A NOTE ON THE ISOLATION OF A CRYSTALLINE GLYCOSIDE FROM COMMERCIAL INDIAN SQUILL

CHOPRA, DE AND MUKERJI[1] SHOWED THAT Indian squill may be considered as equivalent to European squill in therapeutic value. Seshadri and Subramanian[2] succeeded in getting crystalline substances from commercial Indian squill (*Urginea indica* Kunth. with a slight admixture with *Scilla indica* Roxb.) after hydrolysing amorphous glycosidic fractions obtained by them. They failed, however, to obtain any crystalline glycoside as such. Based on the isolation of scillaridin A and the preparation of glucosazone and rhamnosazone, they concluded that scillaren A may be present in the water-insoluble glycosidic fraction. They further reported the occurrence of another minor aglycone, m.p. 265°-67°C. in this fraction, as also an aglycone, m.p. 227°-30°C. in the water-soluble glycoside fraction. We have now been successful in isolating a crystalline glycoside from commercial Indian squill.

Coarsely powdered drug was exhausted with 90 per cent alcohol in the cold. The partially concentrated solution was treated with freshly precipitated lead hydroxide and filtered. After removing all the alcohol from the filtrate, the residue was separated into three fractions: (i) chloroform extract, (ii) chloroform : ethanol (9: 1) extract and (iii) chloroform : ethanol (2: 1) extract. Fraction (iii) was acetylated using acetic anhydride and pyridine, and the crude acetate chromatographed on alumina. The eluates obtained with benzene, benzene: chloroform (49 : 1) and benzene : chloroform (19 : 1) yielded colourless needles, m.p. 155°-56°/255°-56°C., giving with 80 per cent sulphuric acid a deep violet red colour changing to violet, indigo, blue and bluish green in the course of 20 min. In 95 per cent ethanol solution, it showed absorption in the ultraviolet with maximum at 300 mμ. The Legal test was negative.

The substance was deacetylated with potassium bicarbonate in aqueous methyl alcohol solution in the cold. Subsequent working up yielded colourless rhombic plates from 90 per cent methanol, melting at 196°-98°/255°-65°C. (decomp.). With 80 per cent sulphuric acid the substance gave the same colour reaction as described above, but the colour changes were more rapid. It gave positive Molisch reaction and Legal test was negative. Its ultraviolet absorption showed a maximum at 299·5 μ. It was intensely bitter to taste. It does not seem to be identical with any of the crystalline glycosides reported by Stoll and co-workers[3,4] from European squill or by Louw[5] from South African squill.

Further work is in progress and details will be published elsewhere.

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S. RANGASWAMI
S. SANKARA SUBRAMANIAN

Pharmacy Department
Andhra University
Waltair
12 *Dec.* 1953

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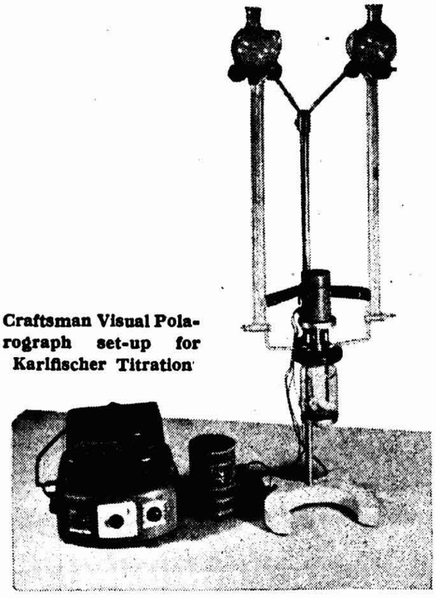

Craftsman Visual Polarograph set-up for Karlfischer Titration

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