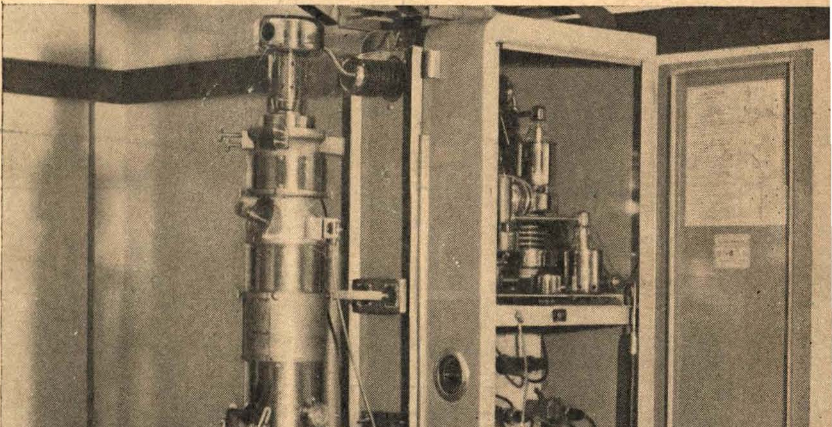
Journal of Scientific & Industrial Research

V. 9, No. 8, AUGUST 1950

IN THIS ISSUE :

- Chelation & Isomeric Change
- Diamond & Carbide Dies
- Gypsum Deposit in Saurashtra
- A New Scale-of-two Unit
- Stability of Oil Varnish Emulsions
- Viscose & Cellulose Acetate from Bamboo & Bagasse
- Pulse Amplifiers for Electrical Counters



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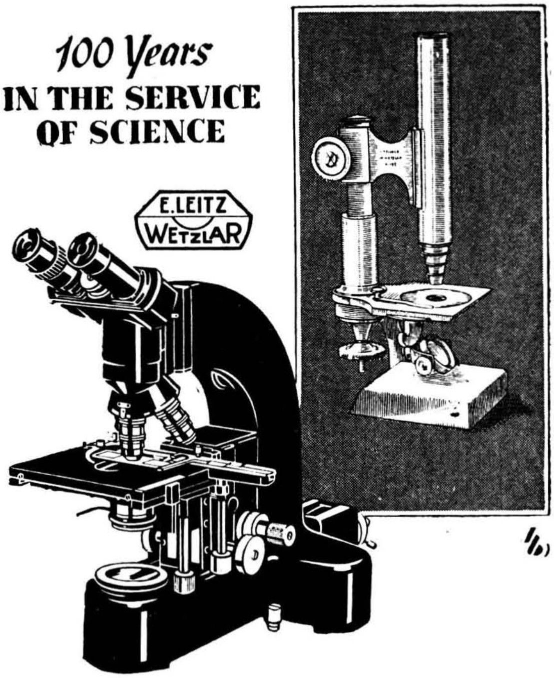
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Journal of Scientific & Industrial Research

V. 9A, No. 8, AUGUST 1950

CONTENTS

COVER PICTURE

Picture on the cover shows the electron microscope which has been recently set up at the National Physical Laboratory, India. A brief description of the microscope appears on page 288.

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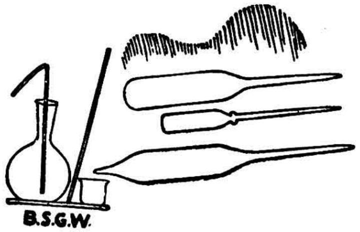
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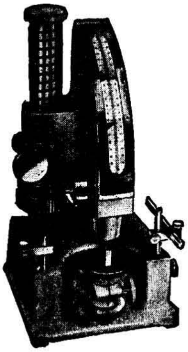

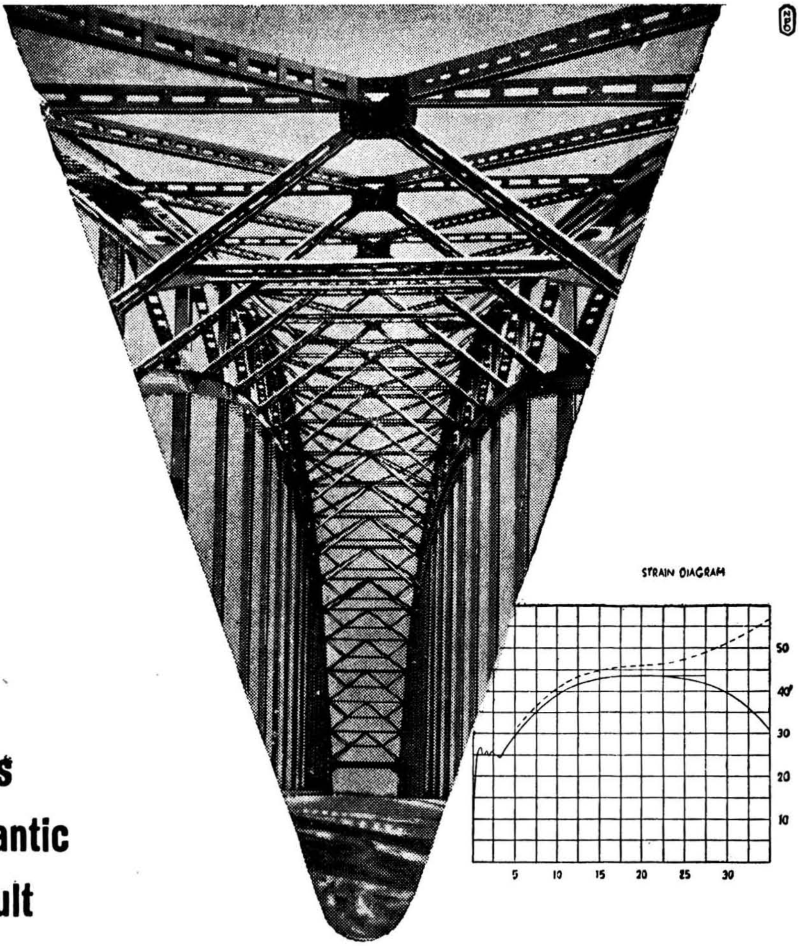
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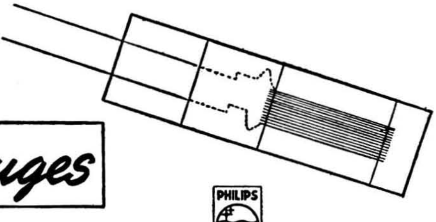

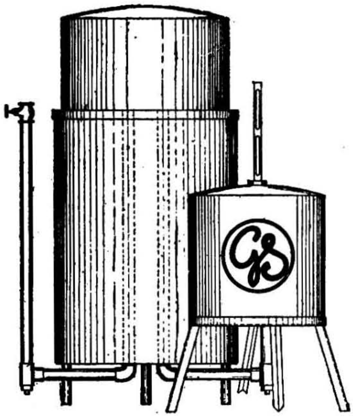
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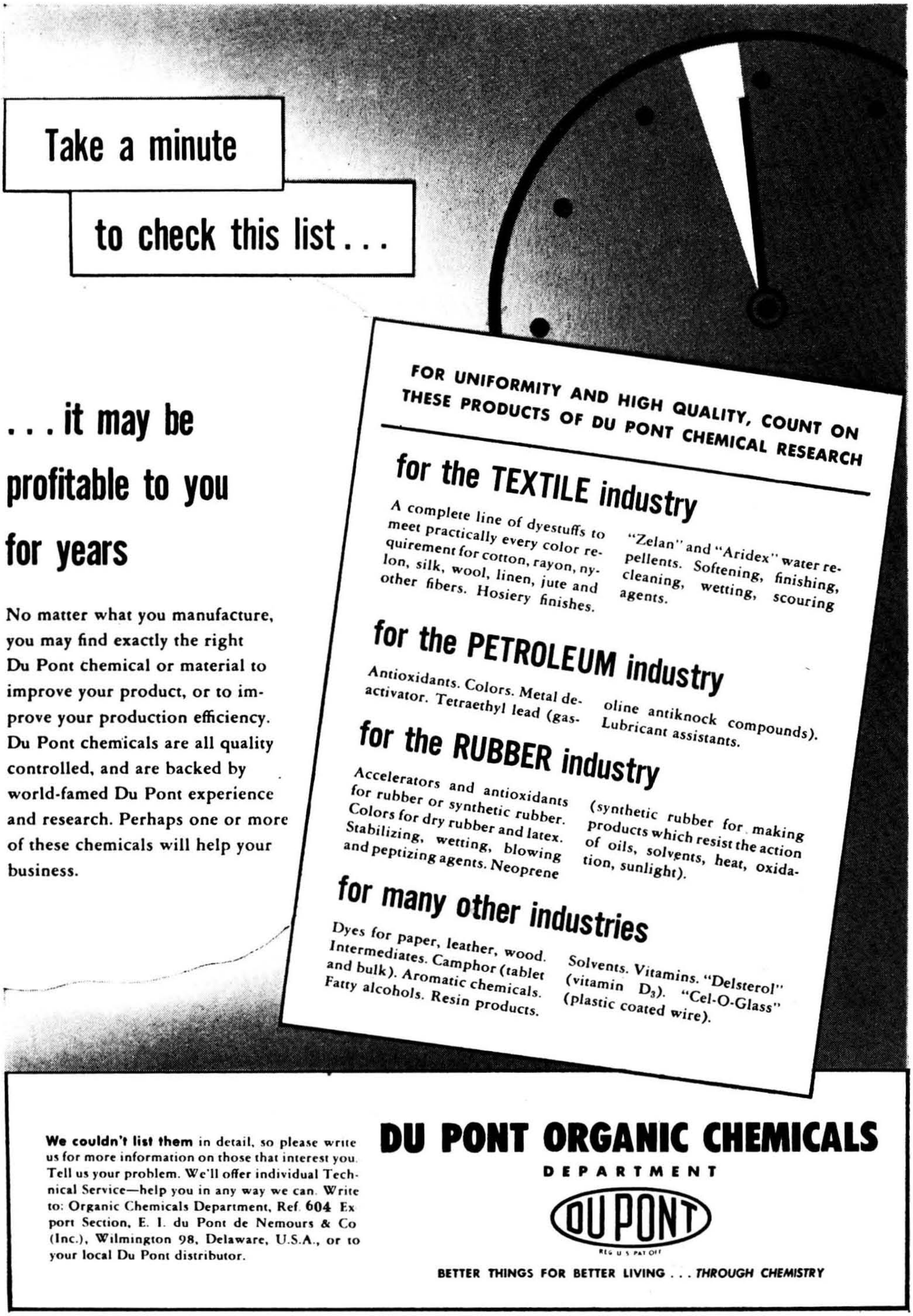

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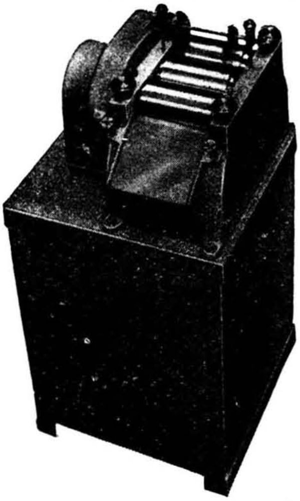
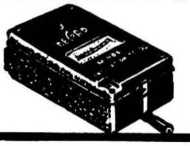
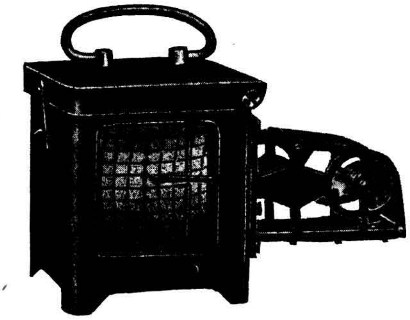




INDEX TO ADVERTISERS




Electrothermal
HEATING
MANTLES

Learned Societies & Science Progress

THE encouragement given to the development of scientific societies in India to which reference is made in the Report of the Department of Scientific Research for 1949-50, constitutes an enlightened recognition of the rôle of learned societies in the promotion of science in this country. In the continuing growth of science non-official academies and specialist societies have played a notable part directly by facilitating the meeting of specialists to discuss research problems and by serving as centres for collecting and disseminating scientific information, and indirectly by linking the efforts of universities and research institutions, fostering creative thought and checking the trend towards isolation and exclusiveness among scientists consequent on increasing specialization.

The development of modern science in India runs parallel to the growth in the number and activity of the learned societies of the country. Disinterested and objective inquiry into the realms of natural knowledge — which is science — is facilitated as much by experiment as by discussion among those engaged in similar pursuits. Indeed, the importance of discussion as a desideratum for scientific progress was brought home to the natural philosophers of Europe in the seventeenth century, as a study of the history of the foundation of the Royal Society, London, would show. Learned societies provide an index of the vitality of the scientific movement in any country, and their activities faithfully reflect the qualitative and quantitative features of scientific research and development.

History records that science began with comprehensive inquiry into natural phenomena, and progressed when particular problems were isolated, defined and inquired into. Even so, in the evolution of scientific societies, the first phase was the foundation of learned bodies which comprehended the whole realm of Nature. This was followed by the foundation of specialist societies with restricted fields of inquiry, which, in turn, gave rise to others with still narrower and more restricted fields. History also reveals that the absorbing and penetrating inquiries into specialized branches of knowledge, invaluable as they are for the understanding of Nature, have in them the germs of isolation, and at some stage the urge for collaboration with allied bodies becomes assertive. The foundation of societies designed to co-ordinate the activities of specialist organizations and, at the same time, to initiate studies into " border " sciences and neglected fields so that the ever-widening frontiers of science may be uniformly cultivated, becomes a necessity. These phases are clearly discernible in the evolution of learned societies in India.

The first learned society organized to stimulate interest in science was the Asiatik Society of Bengal founded in 1784 by Sir William Jones. Its objectives were the study of " Man and Nature, whatever is performed by the one or produced by the other ". Invested with so expansive a field for its labours, the Society did yeoman service to the cause of science in India. Within a century after its establishment, it had fulfilled its ideals by providing " a commodious house for scholars, the making of a library, of a collection of ancient coins and moulds, of a collection of pictures and busts, and the formation of Archaeological, Ethnological, Geological and Zoological collections, or Museums. In addition, the Asiatik Society published 354 volumes of works of various kinds."

During the early years of the revival period, as investigation and discovery were gaining momentum, other societies came into existence. Among them were the Madras Literary Society, an auxiliary of the Royal Asiatic Society of Great Britain & Ireland (1833), the Royal Agri-Horticultural Society of India with its beginnings in 1820, and The Bombay Natural History Society, established in 1833. The last-named society, through its well-known journal, has made distinguished contributions to the progress of science in India. Medical science was represented by the Medical & Physical Society. The Indian Association for the Cultivation of Science was established at Calcutta in 1876, and the Anthropological Society of Bombay in 1886.

With the beginning of the twentieth century, progress of scientific research in India was greatly stimulated by the establishment of a large number of research institutions all over the country. Increasing numbers of young men and women took to the study of science, and visits to foreign countries for under-graduate and post-graduate studies in science became frequent. Research under the Scientific Services and in the departments of the Government made rapid progress. The universities founded in the earlier century established post-graduate studies in science. Research in all the departments of science was intensified and a large number of scientific societies came into existence. In the words of Sir Lewis Fermor : " In the twentieth century, we have entered on a new stage in the development of scientific research in India — a period characterized by the formation of numerous specialist scientific societies and numerous Government research institutes ". Among the societies may be mentioned the Mining & Geological Institute of India (1906) ; the Indian Mathematical Society (1907) ; the Institution of Engineers, India (1920) ; the Indian Botanical Society, with peripatetic headquarters (1921) ; the Psycho-Analytical Society, Calcutta (1922) ; the Indian Chemical Society, Calcutta ; and the Geological, Mining & Metallurgical Society (1924) ; the Indian Psychological Association (1925) ; the Indian Physical Society, Calcutta ; and the Biochemical Society (1934) ; the Indian Ceramic Society (1928) ; the Indian Statistical Institute (1931) ; the Indian Society of Social Science and the Indian Physiological Society (1936) ; the Entomological Society of India (1938) ; the Zoological Society of India (1939) ; Indian Society of Genetics & Plant Breeding (1941) ; Horticultural Society of India (1942) ; the Phytopathological Society (1947) ; the Association of Psychiatry (1947) ; the Association of Indian Geographers (1947) ; the Indian Institute of Metals (1947) ; the Aeronautical Society of India (1948) ; and the Indian Dairy Association (1948). Among the societies with more restricted geographical scope may be mentioned the Bihar & Orissa Research Society, Patna (1915) ; Banaras Mathematical Society, Banaras (1918) ; the Anthropological Society (1933) ; the Botanical Society of Calcutta (1935) ; the Botanical Society of Bengal ; and the Gujarat Research Society (1936). All these societies had more or less similar objectives, viz. the promotion of a particular branch of knowledge in all its aspects, the publication of a journal relating to its special field, diffusion of knowledge among the public, facilitating contacts among members and encouraging original investigations.

The coming into existence of many centres of scientific research, separated by long distances over the vast sub-continent of India, created an " isolation " among scientists which was sought to be removed by organizing a common forum. Impressed by the " great lack of scientific intercourse in India " and realizing that " scientific research in the country might be stimulated if an annual meeting of the workers on the lines of the British Association for the Advancement of Science could be arranged ", Professors P. S. McMohan and J. L. Simonsen took the initiative in organizing the Indian Science Congress Association in 1914, with headquarters at Calcutta. They foresaw that " not only would the direct personal contact and association of actual workers be of great value, but also that the general public would be brought to realize the importance and value of scientific research ". The Association was to hold an annual meeting, sectional or otherwise, in the more populous Indian towns, where papers might be read and discussed and the proceedings be published in the form of an annual report. Their expectations have been fully realized and, during the four decades of its existence, the Association has developed into a mighty organization under whose auspices Indian and foreign scientists now meet to discuss scientific problems and exchange ideas. It also brings scientists into contact with others who, following administrative or other careers or belonging to some other learned professions, seek opportunities to imbibe new ideas and knowledge, and to make their own contributions in some department or other. The Indian Science Congress Association has established international scientific collaboration not only with similar societies within the Commonwealth, but also with many European and American societies.

Important as the advent of the Science Congress Association was, there still remained the need for bringing specialist associations together and to counteract fissiparous tendencies " so as again to bring men of science and other branches of learning back to a common fold, providing for a free exchange of views,— a result that can be secured either on a comprehensive basis enabling the co-operation of all branches of learning or at least of all branches of science, or upon a compartmental plan in which allied groups of scientists are brought together ". There was also the need for a central body to represent the learned societies and act as their spokesman at conferences and international gatherings.

During the quinquennium 1930-35, several Academies came into existence. The United Provinces Academy of Sciences was founded at Allahabad and was re-named the National Academy of Sciences (India) in 1936. The Indian Academy of Sciences was started with headquarters at Bangalore in 1934. The National Institute of Sciences of India was established in 1935, and had for its objects, among others, the co-ordination between scientific academies, societies, institutions and Government scientific departments and services. The National Institute of Sciences received Government recognition in 1945 as the premier scientific organization in the country. It occupies a position relative to academic science on the one hand and Government organizations on the other, corresponding to that of the Royal Society of London or the National Academy of Washington. The Institute acts as adviser to the Government on all scientific matters, secures and manages funds and endowments for the promotion of science, and publishes transactions, proceedings and Indian science abstracts.

This brief survey of scientific societies in India lays no claim to be exhaustive. Many new societies continue to be founded to meet specific requirements as they arise. As the bounds of knowledge expand, new fields come into prominence, drawing teams of workers to cultivate them. Science in India is on the march ; stimulated by freedom and encouraged by an enlightened National Government, significant developments are expected in scientific research, both in its fundamental and applied aspects, which will profoundly influence the activities of learned societies in India.

Characteristics of the Ionosphere over Calcutta (May 1950)

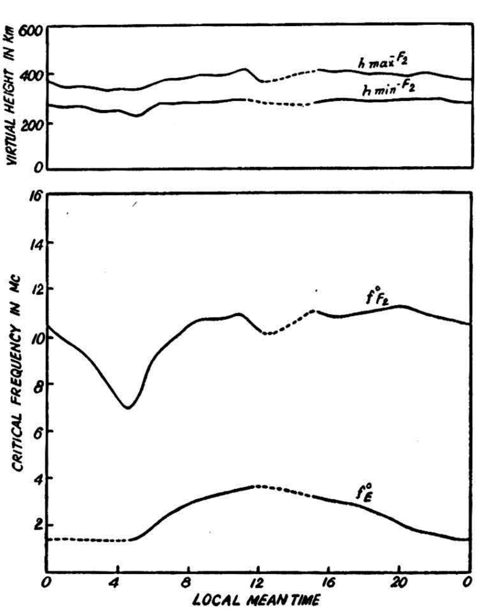
S. S. BARAL, R. K. MITRA, D. C. CHOUDHURY, R. B. BANERJEE & A. P. MITRA

Ionosphere Laboratory, Institute of Radio Physics & Electronics, Calcutta

THE following are the ionospheric data observed at Calcutta for the month of May 1950.

Fig. 1 represents the mean hourly values of the penetration frequency of region E and the penetration frequencies and virtual heights of region F_2 in graphical form. The figures are obtained from average values of the data taken for each hour of the day for 5 days a week. Fig. 2 gives the prediction of the maximum usable frequencies which can be used for different distances of transmission by reflection at the F region over Calcutta for the month of August 1950. Table I gives the different occasions during routine observations when sporadic E ionization was observed and the values of the corresponding penetration frequencies and heights.

Sporadic E ionization was found to occur frequently during the afternoon and night and the frequency was found to be greater in this month than in the previous one. It may be noted that thunder-clouds were more frequent in the evening hours in this month. Echoes from both regions E and F_2 suffered high absorption from 10 a.m. to 3 p.m. during almost every day in this month.



(5 HOURS 54 MINUTES AHEAD OF G.M.T.)
FIG. 1 — MAY 1950.

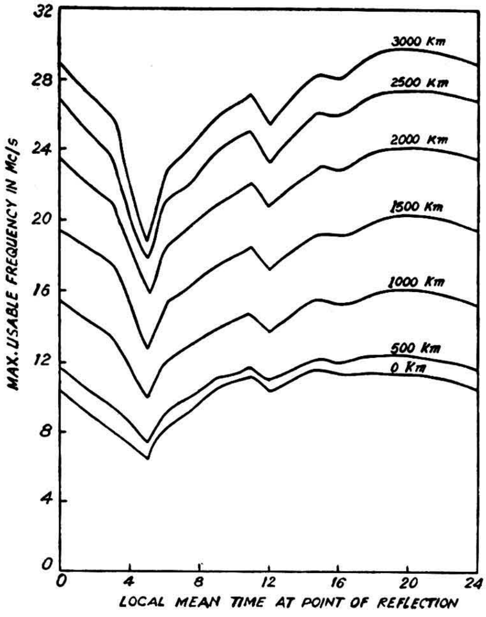


FIG. 2 — PREDICTED M.U.F. VIA F_2 LAYER AUGUST 1950.

TABLE I

Month & year	Date	Hours L.M.T.	$f^{\circ}E_s$ Mc.	$^{h}E_s$ Km.
May 1950	1	18.00	3·30	120
		19.00	4·00	120
		20.00	5·00	120
		21.00	2·50	105
		22.00	2·60	105
	3	21.00	3·50	105
		23.00	3·50	90
	4	00.00	3·60	90
		01.00	3·80	90
		02.00	3·20	90
		20.00	7·00	120
		22.00	4·00	120
	5	23.00	3·90	105
	6	00.00	4·20	105
	8	16.00	4·00	120
		18.00	2·70	120
		20.00	3·20	120
		21.00	4·00	120
	9	07.00	4·00	120
		20.00	3·40	120
	10	00.00	4·00	105
		06.00	3·50	105
		07.00	3·00	105
		09.00	5·00	120
	12	00.00	4·00	105
		01.00	3·25	90
		05.00	3·00	90
		18.00	3·65	120
		19.00	4·60	120
		20.00	3·60	120
		21.00	3·50	105
	13	01.00	3·50	90
		02.00	3·00	90
		03.00	3·00	90
	16	15.00	6·50	135
		16.00	6·50	135
		17.00	6·00	135
		18.00	7·20	135
		19.00	6·40	120
		20.00	3·50	105
		21.00	3·30	105
	17	02.00	3·65	90
		03.00	4·05	90
		04.00	4·25	105
		20.00	6·40	105
		21.00	7·50	135

TABLE I — *contd.*

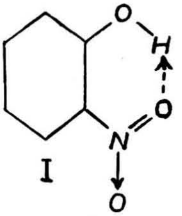
Month & year	Date	Hours L.M.T.	$f^{\circ}E_s$ Mc.	$^{h}E_s$ Km.
May 1950	17	22.00	7·50	135
		22.00	7·50	120
		23.00	7·10	100
	18	00.00	6·25	105
		01.00	4·00	90
		16.00	4·95	120
		17.00	4·95	120
		19.00	6·00	120
		20.00	3·25	120
	19	08.00	8·20	135
		09.00	9·35	135
	23	20.00	3·90	105
		21.00	6·00	120
	24	04.00	5·05	120
		19.00	5·40	135
		20.00	5·40	120
		21.00	4·80	120
		22.00	4·00	120
	25	11.00	8·00	150
		17.00	5·00	135
		19.00	3·80	120
		21.00	3·20	105
	26	21.00	3·70	105
		22.00	4·00	105
		23.00	3·50	105
	27	00.00	3·20	90
	29	16.00	4·70	120
		17.00	4·40	120
		18.00	3·20	105
		22 00	3·30	105
		23.00	3·85	90
	30	00.00	4·20	90
		01.00	4·95	105
		02.00	4·70	105
		03.00	3·85	90
		17.00	5·20	120
		19.00	4·90	120
		20·00	5·00	120
	31	00.00	9·30	105
		02.00	3·45	90
		03.00	4·50	90
		04.00	3·45	105
		19.00	6·80	120
		20.00	6·80	120
		21.00	4·65	105
		22.00	4·50	105
		23.00	6·10	105

Chelation & Isomeric Change*

T. R. SESHADRI
Department of Chemistry, Delhi University

CHELATION in aromatic hydroxy compounds has been known to have marked effect on the properties of the compounds. For example, *ortho*-nitro phenol (I) which is chelated has a markedly lower melting point, higher steam volatility and greater solubility in anhydrous solvents than the *para* isomer (II). Further, the *ortho* compound is unassociated whereas the *para* is associated. Besides these properties, in the case of *ortho*-hydroxy carbonyl compounds like methyl salicylate (III), a marked colour is produced by alcoholic ferric chloride which is not given by the *para*-hydroxy compounds (IV). Further, the *ortho* hydroxyl is resistant to methylation unlike the *para*-hydroxyl group. The behaviour of a number of derivatives (V) of resacetophenone, resorcylic acid and aldehyde in several reactions lends support to the suggestion of Baker that chelation gives rise to a fixation of aromatic double bonds (see *Fixation of Aromatic Double Bonds* by Rangaswami and Seshadri[1]). The present discussion relates to the discovery of the important part played by chelation on the stability of the molecular structures of flavanones and chalkones and their interconversion and the light it throws on the constitution of a few typical compounds.

In the course of the study of the flavanone glycosides, naringin (VI) and butrin (VIII), a remarkable difference was noticed in their behaviour when subjected to acid hydrolysis; whereas the former yields a single aglucone, naringenin (VII), which gives all the reactions of a flavanone, the latter, under the same conditions, forms a mixture of aglucones consisting of the flavanone, butin (IX) and the chalkone, butein(X). A similar difference in behaviour is exhibited by the two isomeric flavanones, butin and naringenin, when heated with mineral acids or dissolved in alkali and reprecipitated with acids. The first undergoes partial change into the chalkone butein whereas the second is unaffected, The difference could be attributed to the presence of a 5-hydroxyl in naringin and naringenin and its absence in butrin and butin. This explanation was fully supported by a study (1) of the methylation products of the above four compounds obtained by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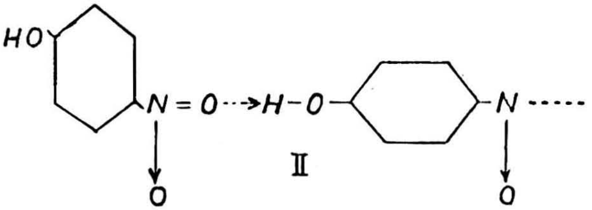
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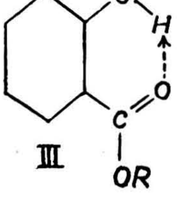
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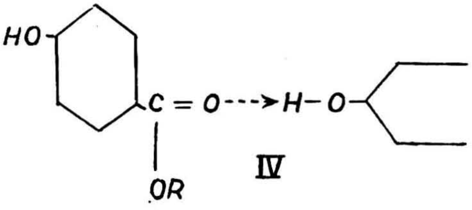
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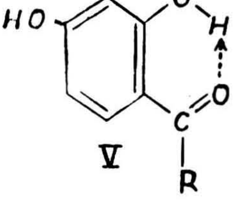
V

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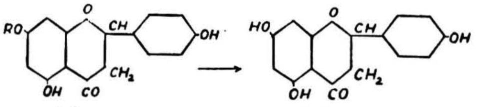
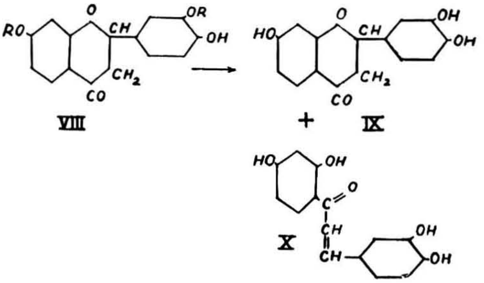
* A contribution to a symposium held during the Indian Science Congress at Poona in January 1950.

using varying molar proportions of dimethyl sulphate and (2) of a number of simpler flavanone derivatives[2]. The flavanone structure is not stable when the 5-hydroxyl is non-existent or is methylated.



VI VII

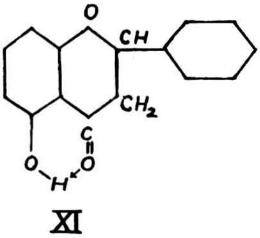


VIII IX X

The above-mentioned significant influence of the 5-hydroxyl group is attributed to the existence of chelation involving this hydroxyl and the neighbouring carbonyl group of the flavanone molecules as shown in (XI). When it is absent the flavanones and the corresponding chalkones exist in equilibrium in an acid or alkaline medium and are capable of undergoing interconversion (XII to XIV). That chalkones are largely chelated is amply borne out by their properties and thus structure (XII) will correctly represent them. The existence of the non-chelate form (XIII), though in small amounts, is indicated by the study of the Raman effect of *ortho*-hydroxy carbonyl compounds[3]. This was originally explained by giving the trans structure to the hydroxyl alone. It seems to be more correct to consider that the reorientation of the CO group is also involved as shown in (XIII). The presence of a 5-hydroxyl adds more stability to the flavanone structure by the formation of an additional chelate ring as shown in (XI). Even if the flavanone ring opens, for instance, in an alkaline medium, the concerned groups are not able to move far enough to yield a stable chalkone. On the other hand, whatever alternative constitution the chalkone form takes in this case, it is favourable for quick conversion into the flavanone.

A consequence of the above considerations is that chalkones with hydroxyls in the 2- and 6-positions should be extremely unstable and should have very little chance of existence particularly in the presence of acids and only the corresponding flavanones should be obtainable. Such chalkones have not been found to occur in nature though the flavanones are fairly common. On the other hand, butein in which this structural feature does not exist, occurs free[4]. An interesting verification of the above conclusion was provided by the study of despedicellin and dihydropedicinin which are important derivatives of the chemical components of *Didvmocarpus pedicellata.*

Despedicellin was obtained by the action of hydriodic acid on the chalkones pedicellin, pedicin and pedicinin. It was, therefore, given the chalkone structure (XV). A substance of this constitution would normally be expected to have a bright red colour, but despedicellin is only pale straw yellow. Its colour would suggest that it is a flavanone (XVI), a structure which is in accordance with the conclusions recorded in the above paragraph. The position is quite similar in the case of dihydropedicinin obtained by the reduction of the chalkone, pedicinin using stannous chloride



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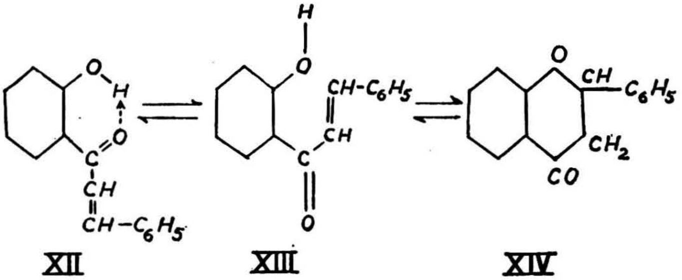

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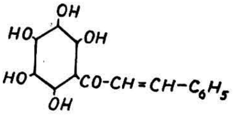

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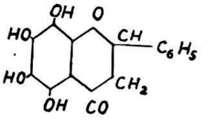

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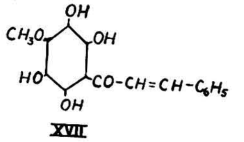

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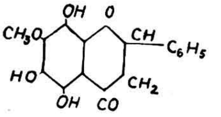

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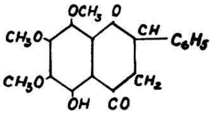

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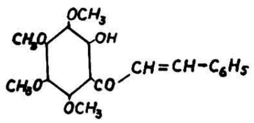
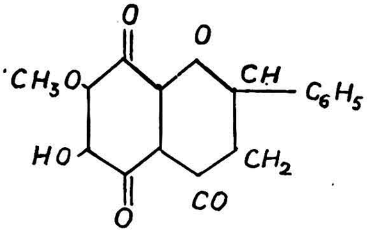


XX

and hydrochloric acid. Though it was originally given the chalkone formula (XVII), the lack of prominent colour even here would indicate that dihydropedicinin is also a flavanone (XVIII). That these two compounds have the flavanone structure was established by the detailed study carried out by Rao, Rao and Seshadri[5]. They undergo partial methylation with excess of diazomethane yielding 5-hydroxy-6 : 7 : 8-trimethoxy flavanone (XIX) whose constitution was definitely established. If they were chalkones, a tetramethyl ether (XX) would have resulted since only one phenolic hydroxyl could be protected in this reaction by the neighbouring carbonyl group. Dihydropedicinin undergoes oxidation with *p*-benzoquinone to form allopedicinin (XXI) which is definitely different from pedicinin (XXII) and whose constitution was also definitely established.

Yet another unequivocal evidence was provided by the determination of active hydrogen atoms using magnesium methyl iodide. Despedicellin gave evidence for the presence of only four hydroxyl groups in its molecule and dihydropedicinin for only three. These independent proofs of the constitutions of despedicellin and dihydropedicinin add support to the original theory that chelation provides stability to the flavanone structures.

Based on the same principle is the recent preparation by Narasimhachari and Seshadri[6] of sakuranetin (XXIII) by the partial demethylation of 2-hydroxy-4 : 6 : 4′-trimethoxy chalkone (XXIV) using hydrobromic acid. The stability of the resulting flavanone is an important consideration in the preparation of this substance in a pure condition.



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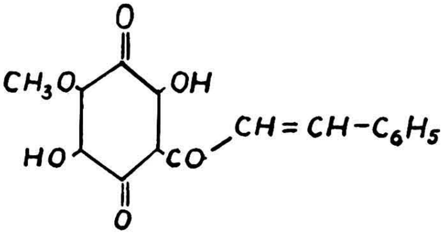

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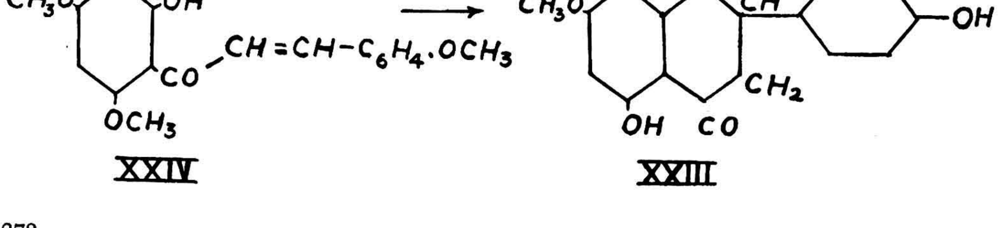
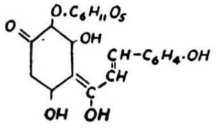


XXIV XXIII

It may be appropriate to refer here to the constitution of carthamin and *iso*carthamin, the glucosidic pigments of safflower. Miss Kuroda[7] gave them the structures (XXV) and (XXVI) based on the absence of certain colour reactions. If they are chalkones, as most probably they are, in view of the general principles established in the foregoing paragraphs, these formulations may not be correct and may require revision with regard to the position of the sugar unit. One of the two *ortho* positions, either 2 or 6, is more likely, thus giving greater stability to the chalkone form. This also agrees with the observation that as soon as the glucose unit is removed by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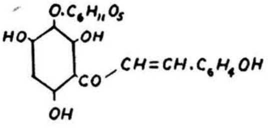
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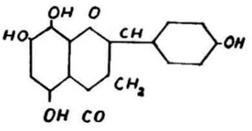
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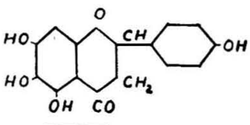
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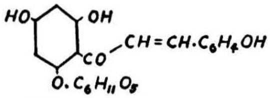
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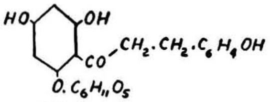
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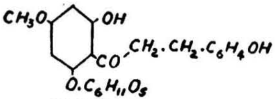
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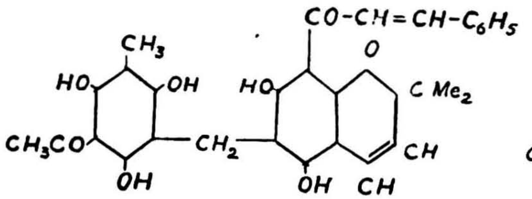
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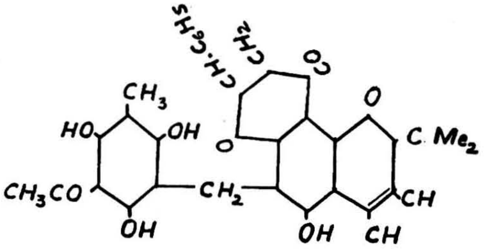
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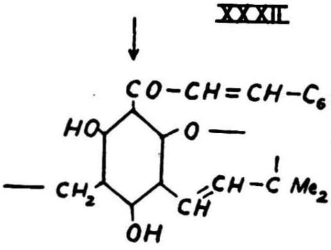
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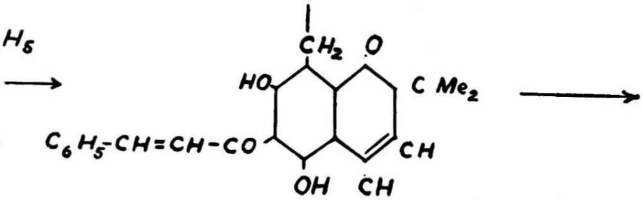
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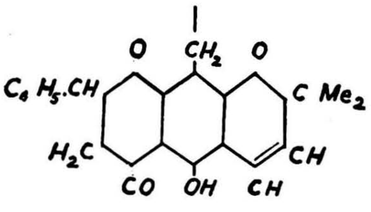
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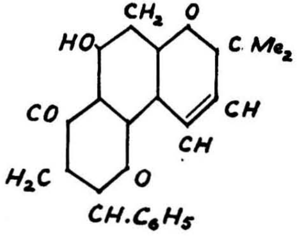
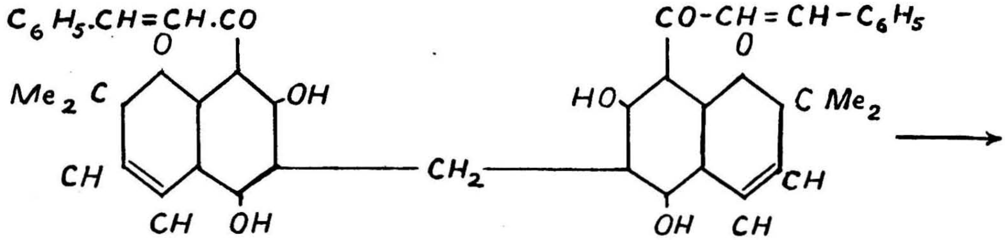
or


XXXV

hydrolysis, the two isomeric flavanones, carthamidin (XXVII) and *iso*carthamidin (XXVIII), are produced. Analogous 2-glucosides are found in *iso*salipurposide (XXIX)[8], phloridzin (XXX)[9] and asebotin (XXXI)[10].

Another interesting application of the above discovery of the effect of chelation is in connection with the rottlerin-*iso*rottlerin change[11]. Rottlerin (XXXII) is the important colouring and anthelmintic principle of the *kamala* dye. Its isomerization into *iso*rottlerin (*iso*allorottlerin) was observed by a number of workers. Brockmann and Maier[12] considered that it consisted in the cyclization of the chalkone form (XXXII) into the corresponding flavanone (XXXIII). McGookin, Robertson and Tittensor[13] later showed that it was not a simple ring closure but involved further an interchange of the position of the cinnamoyl and substituted phloroglucinol residues (formula XXXIV or XXXV). They expressed the view that the first stage of the reaction is the conversion of rottlerin into the intermediate (XXXVI) by the opening of the chromene ring and this is followed by the reformation of the latter to produce (XXXVII) which is strictly analogous to rottlerin and is termed allorottlerin. At the same time the chalkone is cyclized to the flavanone system with the production of either (XXXIV) or (XXXV) which was appropriately designated *iso*allorottlerin.

The important point that is definitely established by the work of McGookin *et al.* is the shift of the chromene ring. But it was not clear as to why it happened and when. As a result of the discovery of the effect of chelation on the stability of flavanones, it is now possible to explain these and also make a choice of the alternatives for the constitution of the final product. If there were no shift of the chromene ring and only the flavanone ring closure took place, a 7-hydroxy flavanone derivative (XXXIII) would have resulted. But on account of the rearrangement, a 5-hydroxy flavanone derivative is obtained and this represents a more stable structure. The reason for the *iso*allorottlerin change would, therefore, appear to be that thereby the molecule reaches greater stability. If this perfectly reasonable position is accepted, it then follows that the chromene ring shift takes place only after the initial flavanone ring closure to (XXXIII) and



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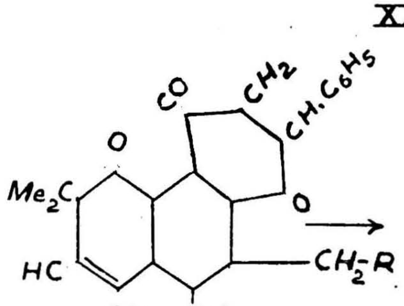
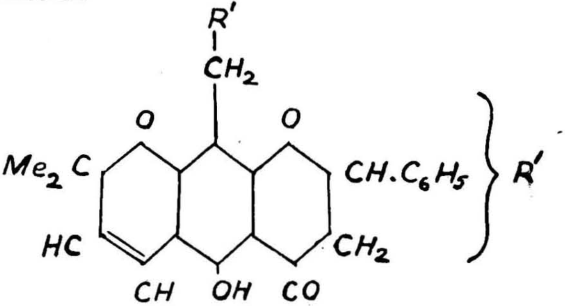


XXXIX



XL

hence the constitution of the final product, *iso*allorottlerin, should be represented by (XXXIV).

A closely analogous substance suitable for this study of isomeric change is rottlerone (XXXVIII), the main degradation product of rottlerin. Its constitution was established by Robertson and co-workers and it has all the structural features required for this test. It undergoes isomeric change almost completely by boiling in acetic acid solution for 1 hr. The deep-red colour of rottlerone disappears and a pale-yellow product is obtained in good yield. For it the name *iso*allorottlerone is suggested (Rao and Seshadri[11]). Its properties agree with the 5-hydroxy flavanone structure (XL), the intermediate produced by simple flavanone ring closure being represented by (XXXIX).

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Obituary — Dr. Roland Victor Norris (1888-1950)

DR. ROLAND VICTOR NORRIS DIED AT PORT Shepstone, South Africa, on 28th April 1950, at the age of 62.

Dr. Norris went to South Africa in November 1949 on a holiday and was due to return to the Tea Research Institute of Ceylon of which he had been the Director since 1929. His death is a sad loss to the Institute he served so well, and a personal misfortune to his many friends.

After graduating from Manchester University, Dr. Norris became private assistant to Professor W. H. Perkin. Moving to the Lister Institute of Preventive Medicine, London, in 1910, he joined Professor Arthur Harden's School and took part in the classical researches on the mechanism of alcoholic fermentation by yeast enzymes, for which work he was eventually awarded the D.Sc. degree of the London University. In 1912, during his career at the " Lister ", he was elected to a Beit Memorial Fellowship.

Dr. Norris's long career in the East began in 1914 when he accepted the post of Physiological Chemist at the Imperial Bacteriological Laboratory in India. His first administrative experience was gained in the Indian Army in which his administrative abilities were soon recognized after a brief period of active service in 1915.

From 1918 onwards, Dr. Norris gradually turned towards agricultural research, first becoming Agricultural Chemist to the Government of Madras. As Professor of Biochemistry in the Indian Institute of Science, Bangalore, from 1924 to 1929, he and his research students were largely occupied with biochemical problems relating to agricultural subjects such as soils, plants, manures, the lac industry and the spike disease of sandalwood.

In 1929 Dr. Norris was appointed to the Directorship of the Tea Research Institute, Ceylon, when the construction of the permanent quarters at St. Coombs had just started. The Institute has grown from its foundation on St. Coombs Estate to its present status under his guidance and will be a living memorial to his industry so long as it exists.

" R.V. ", as he was known to his colleagues, was by no means a pedant. He was a widely travelled and well-read man of varied interests. European, Indian and Ceylonese colleagues of two generations will remember R.V. with affection. Many members of the tea industry will remember Roland Norris either as a personal friend or as a personality.

J.L.

Diamond & Carbide Dies — Literature Report No. 6

B. S. SRIKANTIAH & B. R. NIJHAWAN
National Metallurgical Laboratory, C.S.I.R., Jamshedpur

MANY fundamental changes and considerable improvements in methods and equipment for drawing wires have taken place in the past three decades. The use of diamond dies for drawing very fine wire has notably increased and the introduction of synthetic carbide and hard metal dies is a significant feature of recent years. The finish and quality of the wire produced has been improved. Increased drawing speeds are possible now and most important of all is the successful introduction of the heavy multiple die-drawing bench and the continuous wire drawing mill. These developments have been possible because of the long life and reliable performance of the carbide composition die. However, these advances have created special problems, particularly in regard to the making, maintenance and servicing of dies.

Diamond Dies

Until very recently, the making of diamond dies of very fine bore was a closely guarded secret. The outbreak of last war stopped the export of the dies from Europe and the large demand created by the war effort led to their manufacture in the U.K. and the U.S.A.[1].

The diamonds used for wire-drawing dies are what are known as industrial diamonds. Three kinds are generally used : (1) carbons, (2) Bortz and (3) Ballas. Of these the carbons, being porous, are not suitable. The Bortz are impure diamonds of white, brown or black colour and possess high shock resistance. They are obtained from Brazil and South Africa and are the most useful stones for industrial purposes. Ballas are composed of radial clusters of minute diamond crystals. Amongst the Bortz the well known are the Cape Round Bortz and the Brazilian Bortz.

The Ballas are priced high and fetch the same price as the black diamonds from Brazil. The better grades of carbonades and Ballas sell for $ 20 to $ 100 a carat. Good quality Bortz diamonds sell for about $ 5 to $ 10 a carat while diamond powder sells at about $ 2 per carat.

The diamonds must be free from imperfections such as spots, feathers, inclusions, bubbles, cracks, etc., as these seriously reduce the life of a die especially appearing in the taper hole region.

For producing fine bore dies a rhombic dodecahedral stone is preferred. An octahedron is used for large bore dies. Stones exhibiting twinning are not used for dies as the bond between the twins is weak and invariably leads to early die failure through cracking.

The first rough selection of the stones is usually made with the aid of a hand lens in strong daylight and the final selection is done after a microscopic examination. Many stones exhibit internal stresses when examined under polarized light and it is desirable that only stones which are substantially free from stress should be used.

The weights of diamond required for making dies for a given diameter of wire are given in Table I[2].

TABLE I

WIRE DIA. TO BE DRAWN, mm.	WT. OF DIAMOND, carats
0·05 to 0·16	¼
0·16 to 0·19	⅜
0·19 to 0·23	½
0·23 to 0·27	⅝
0·27 to 0·31	¾
0·31 to 0·41	1
0·41 to 0·45	1¼
0·45 to 0·50	1½
0·50 to 0·55	1¾
0·55 to 0·61	2
0·61 to 0·65	2¼
0·65 to 0·70	2½
0·70 to 0·75	2¾
0·75 to 0 80	3
0·80 to 0·90	3½
0·90 to 1·00	4
1·00 to 1·10	4½
1·10 to 1·20	5
1·20 to 1·30	6
1·30 to 1·40	7
1·40 to 1·50	8
1·50 to 1·60	9

The holders for the stones are made of metal. Low-temperature alloys have been developed for fastening the diamond in the holder. Brass and steel are commonly used. Monel metal[3] has also been used and it is reported to be ideal for this purpose. Taylor[4] has described the various methods of mounting diamonds in metal holders. The earlier methods, viz. mechanically tightening the diamond in a steel block with a strip of copper foil, casting, etc., are not quite satisfactory.

Investigations carried out at the *General Electric Company Research Laboratories*, U.S.A., have shown that employing a carbide-cement composition such as carboloy manufactured by the *Carboloy Co. Inc.* (similar to a composition known as *Widia* in Europe) provides intimate contact between the carboloy and the diamond. In wire-drawing dies[3], where a single stone is set, the use of carboloy in preference to any other alloy is recommended for the following reasons: (1) coefficients of expansion of diamond and of carboloy are very nearly the same and carboloy does not undergo plastic deformation ; and (2) good thermal contact is obtained between carboloy and diamond which helps to dissipate the heat generated during wire-drawing operation.

Manufacture of the Die

The appearance of a typical diamond die can be seen in perspective in Fig. 1. The die can be divided into several zones and the profile of the die varies according to the metal to be drawn. Typical profiles for dies for drawing copper, bronze, steel and tungsten wires are given in the British Standard Specification, War Emergency British Standard 1168 (1944).

The most important zone in the die is the reduction zone and is so designed as to avoid excessive wear.

The various processes employed in producing a die and the different parts of the prepared stone are described with reference to Fig. 1.

1. *Drilling Faces* — The two flat parallel surfaces ground on the diamond at right angles to the drilling axis of the die aperture and referred to as drilling faces.

2. *Two other flat surfaces* (*viewing windows*) are ground on the diamond at right angles to the first two so that the progress of drilling can be continuously observed.

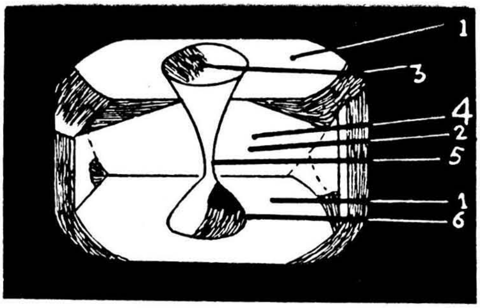

FIG. 1 — PERSPECTIVE VIEW OF A PREPARED DIAMOND SHOWING THE PROFILE OF THE DRILLED HOLE : (1) DRILLING FACES, (2) VIEWING FACES, (3) ENTRANCE TO THE DIE, (4) APPROACH TO THE BEARING OF THE DIE, (5) BEARING OF THE DIE AND (6) EXIT OF THE DIE.

3. *The entrance to the die* is referred to as the lubricating cone.

4. *The approach to the bearing of the die* is conical in shape and is varied according to the type of the metal drawn.

5. *The bearing of the die* determines the size of the wire drawn through it. The length of the bearing is varied according to the wire-drawing requirements of different types of metal.

6. *The Exit of the Die* — The drilling of the diamond calls for exceedingly accurate and careful work. The various appliances such as polishing machine, drilling lathe, etc., have been fully described by Dudding and others[5-6]. High speed precision methods have also been described by Wall[6] and Zahour[7].

The operations in die production are: (1) preparation of diamond powder ; (2) preparation of diamond for drilling ; (3) centring and starting the entrance ; (4) drilling ; (5) completing the exit ; (6) mounting and (7) polishing.

1. *Preparation of the Diamond Powder* — The lowest quality of diamonds unsuitable for dies are used in the preparation of diamond powder. Mechanical methods of crushing are employed to obtain the desired mean particle size. The powder is chemically treated to remove impurities and graded up to 300 meshes per linear inch. After this the powder is further graded by means of an elutriator (sizes up to 20×10^{-6} metre). For extremely fine sizes ($0{\cdot}5 \times 10^{-6}$ metre), centrifugal methods are employed.

Fig. 2 shows the size-quality relationship of 5 grades of diamond powder.

2. *Preparation of Diamond for Drilling* — The selected stones are polished and working faces and viewing windows are cut and polished.

For polishing, the diamond is set in a lead matrix and mounted over a revolving disc driven by an electric motor at *c.* 2,500 r.p.m. The disc is of cast iron and impregnated with diamond dust. Great care is taken to see that the two working faces are polished exactly parallel to one another.

3. *Centring & Starting the Entrance* — The exact position where the diamond is to be pierced is marked on one of the working faces. The diamond is then cemented to the chuck on the specially shaped rotating steel head by means of shellac. The stage containing the steel head is capable of being rotated through 90°. It is first set so that the face of the diamond may be viewed through a vertically aligned microscope. The mark made on the face is centred by means of adjusting screws, the stage is then turned to a horizontal position and coupled to a fractional horse-power motor with foot-operated speed control. A small lamp is arranged to illuminate the diamond during boring. The apparatus (*G.E.C. British Patent Specification No.* 544381) is described by Patterson and Leeds. On the marked spot an indenture is made by pressing a diamond splinter while the diamond is rotating. This first indenture serves as a guide for piercing. The depth and shape of drilling are observed through a second microscope.

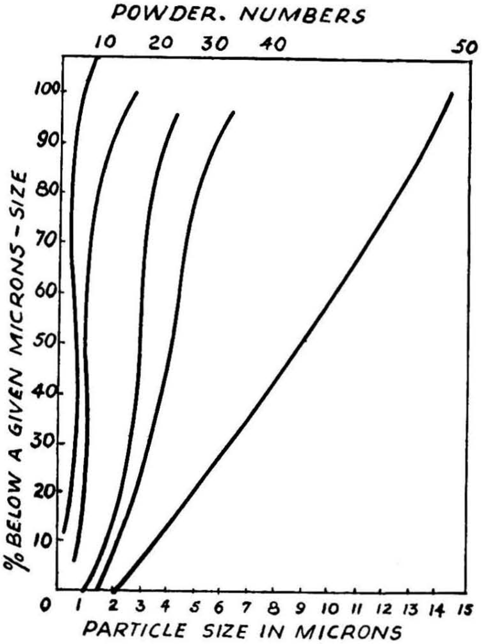

FIG. 2 — SIZE QUALITY OF FIVE GRADES OF DIAMOND POWDER.

4. *Drilling* — The diamond is pierced for approximately two-thirds its thickness on a lathe[8] in which the spindle carries a gramophone needle ground to the requisite size. Penetration of the diamond is effected by means of a paste of fine diamond dust and olive oil applied to the end of the needle. At the tail-stock end two trunnions are provided and on these rests the rod to which the diamond is fixed. The diamond is retained in position by the needle entering the hole and is only lightly attached to the rod by vaseline. The needle is periodically withdrawn and returned to the hole by the motion of the rod on which the diamond is fixed. This horizontal motion of the rod is on the same axis as that of the piercing needle. Patterson and Leeds[1] report that for very fine dies it is necessary to control the ratio of the time during which the needle is in contact with the stone to the interval for which it is withdrawn. The diamond is then turned round and is drilled to produce the exit.

5. *The Exit* — The exit is drilled from the back of the die as before under the microscope with the side already drilled facing downwards. The centring is done by means of screws. If the faces are not accurately parallel, the die will be wedge shaped and an appreciable error is introduced in the axiality of the entrance and exit of the die. Lack of co-axiality is a common defect in dies and may lead to the drawing of curly wire.

A cup-shaped hole is made until it meets the channel drilled on the other side. At this stage drilling must be made with sufficient care to avoid splintering at the junction.

The successive stages in the drilling operation are diagrammatically represented in Fig. 3.

Electrical drilling methods for superfine wire dies have been developed at the National Bureau of Standards, U.S.A.[9].

It is claimed that a good quality fine diamond die from 0·0004 in. to 0·00015 in. in diameter can be produced with a considerable saving of time and cost over the established mechanical methods.

6. *Mounting* — After the drilling operation the die is mounted in a metal casing before it is polished. A precision mounting method is described by Patterson and others[5,1]. The casing is a disc, approximately one inch in diameter and a quarter to three-eighths of an inch in thickness. For use in drawing wires at elevated temperatures, steel casing appears to be the best. The material employed must be capable of holding the diamond securely for long periods at temperatures as high as 700°C. The die must be so mounted in its casing that the drawing hole is placed centrally and its axis oriented at right angles to the plane of the casing.

In mounting, the casing is rested on a heat insulator and the diamond placed in the recess of the casing by means of two tungsten needles, one at the top and the other at the bottom of the hole. On the top of the diamond is placed a pellet of suitably shaped brass alloy and by the application of heat from a ring burner and two side burners, the case, the diamond and the alloy are heated until the alloy becomes plastic. It is then pressed by means of a plunger until it fills the space between the diamond and the case. Care must be taken to see that the alloy fills the surrounding space perfectly. A method[8] of mounting the die in a monel metal casing is given below.

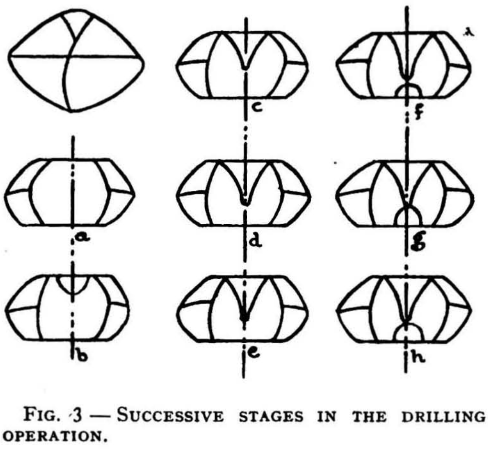

FIG. 3 — SUCCESSIVE STAGES IN THE DRILLING OPERATION.

A monel metal die casing, which has been recessed, countersunk and drilled, is placed in a metal jig and clamped in position by a molybdenum wire pin locating the drilled hole. Steel blocks are used to clamp the casing in position in the jig and the pin is then removed. The diamond is then placed in the casing and accurately centred over the aperture by locating the hole in the diamond by the molybdenum pin. When viewed through a magnifying glass, the point of the pin appears through the die aperture as a small black dot in the centre of the diamond. The pin is then firmly fixed in position to keep the solder away from the aperture. The usual practice is to set the jig between two electrodes until the correct heat is reached; then the solder is cast in to fill the recess around the stone. The solder used is either silver or bronze and must have a melting point above that of the wire to be drawn. Care has to be taken to ensure that no blow holes are left around the stone or around the countersink formed by the pin.

When the die has cooled, the outer surfaces are turned and finished so that the entrance and the exit of the casing are opened out to form a continuous contour with the corresponding portions of the die.

7. *Polishing* — For polishing dies of diameter greater than 0·002 in., fine steel needles may be used in combination with diamond powder. In one method the dies are placed in a vertical polishing machine revolving at a high speed while a finely ground non-rotating needle is mechanically oscillated from left to right. The swaying action results in producing a smooth entrance by blending the cone at the entrance and the drilled inner cone. Sometimes the dies are polished in a horizontal polishing machine where both the die and needle revolve. For extremely fine dies tungsten or copper wire impregnated with diamond dust may be employed for polishing.

Close grading of the diamond powder plays a very important part in the degree of polish obtaining in the die.

It is necessary to give a high polish to the die to make it perfectly smooth. A badly drilled, poorly polished die will produce unevenly drawn, out of round wire and will wear out rapidly. Such dies can seldom be recut.

Carbide or Hard Metal Dies — The development of this die has eliminated much of the skill required by the operator. However, it has given rise to problems in their maintenance. The quality and finish of the wire produced by these dies are better and the dies have long life.

Swinn[10] and Sandford[11] have described the development of sintered tungsten carbide die. The difficulties in the casting of tungsten carbide products were overcome by the application of powder metallurgy. The tungsten carbide powder is cemented together with an auxiliary metal like cobalt, pressed and sintered. The British-made product of this type is known as Wimet.

Preparation of Tungsten Carbide — The raw material is pure tungstic acid or tungstic oxide. Tungsten metal powder, obtained by reducing the oxide in an electric furnace, is mixed to a homogeneous mixture with 6 per cent lamp black, packed into graphite containers and heated in an atmosphere of hydrogen to 1500°C. for several hours. Tungsten carbide so obtained contains 6·12 per cent carbon.

Cobalt powder is obtained similarly. Accurately weighed charges of tungsten carbide and cobalt are then mixed in a ball mill. The amount of cobalt employed in the mixture varies from 6 to 12 per cent.

Sintered tungsten carbide is quite hard and shaping and rough sizing of the article must, therefore, be carried out prior to sintering.

The tungsten, carbide and cobalt mixture is pressed in steel dies in a hydraulic press to give die nibs of required size. The powder is mixed with a lubricant to prevent the formation of cracks. Paraffin wax dissolved in carbon tetrachloride or camphor dissolved in petrol is usually used.

Pre-sintering before machining is necessary. The casting is heated in an atmosphere of hydrogen to a temperature of 750°C. to 1,000°C. for about 30 min. when it attains greater strength and is chalk-like in consistency. It can then be safely handled in a chuck or a vice and turned or ground with ease.

The die nib is machined prior to sintering so that a minimum amount of metal has to be removed after sintering. Machining of the die nib is carried out on non-automatic lathes using carbide-tipped or diamond-tipped single point tools.

During sintering considerable shrinkage occurs (*e.* 20 to 30 per cent) and this must be allowed for during machining by allowing sufficient amount of over size in the nib.

The machined nibs are placed in graphite trays or " boats " embedded in crystalline alumina and heated in an atmosphere of hydrogen to a temperature of 1,400°C. to 1,500°C. for several hours.

Sintered tungsten carbide has great hardness, uniform and fine grain size, is free from pores and impurities, has high transverse and compressive strength and high resistance to abrasion and corrosion.

Necessary precautions must be taken against fracture of the die on account of over stresses or shock. This is done by giving the die a very rigid steel support.

For cutting and polishing cemented carbide dies, a machine has been devised by *H. J. Reusch & Co.* It is claimed that in making a finished die from an encased rough nib, this machine will perform all necessary operations eliminating manual labour. The dies obtained are said to have high polish, long life and low power consumption.

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Gypsum Deposit near Ran, District Halar, Saurashtra

D. R. S. MEHTA
Geological Survey of India

A GENERAL survey of the gypsum deposits in Saurashtra was undertaken during the field season 1947-48 by the Geological Survey of India and a report was prepared by the author. As the deposit near Ran in Navanagar State (now district Halar) proved to be promising, it was decided to investigate the same in detail with the help of bore holes. The drilling operations were commenced in the area by the end of March 1949 and completed during the third week of July of the same year. Hand-driven calyx drills (2″ core) were used to sink 30 bore holes in the area.

The gypsum deposits in Kathiawar occur in the form of selenite veins and as segregations in the bluish plastic clay and marl, usually encountered near the base of Gaj limestone beds (Upper Miocene of the Tertiary system). Selenite is a crystalline variety of gypsum which, excepting for a small percentage of clayey matter, is pure.

Bore holes were sunk at intervals of 32 chains of 66′ each. The deposit, as finally demarcated by the bore holes, has been mapped with tape and prismatic compass. Details of bore hole records of the deposit are given in Fig. 1.

The average yield of selenite per cu. ft. of the core has been recorded. The nature of the selenite clay and marl bed is such that complete cores are not obtained to arrive at a correct figure for the selenite in the core. This difficulty is overcome by comparing the amount of selenite recovered

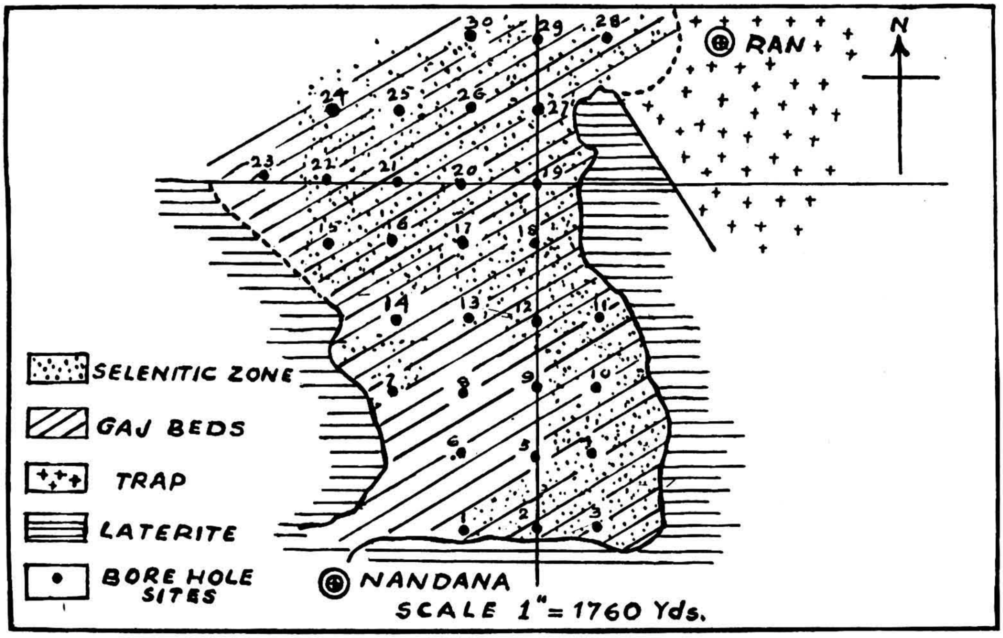

FIG. 1 — GYPSUM DEPOSIT NEAR RAN (SAURASHTRA) SHOWING BORE HOLE SITES.

from some of the bore holes and pits located in close vicinity. The pits were made during 1949 and the recovery of selenite per 1,000 cu. ft. were recorded. The ratio between the amount of selenite recovered from the pits and from the bore holes has been taken as a constant for estimating from the bore hole data the percentage of selenite available in the clay and marl bed.

General Description

The selenitic clay and marl patches occur south-west of the village Ran (22°10′ : 69°20′ ; ref. Sheet 41F) and is approximately 3 miles in length and a mile and a half in width. The thickness of the Gaj beds encountered in the bore holes is of the order of 26′ to 70′. They are underlain by trap with or without a zone of laterite in between. In-liers of the laterite and occasional trap in the Gaj beds are quite common. The Gaj beds are throughout almost horizontally disposed but there is a slight increase in the thickness of the formation due westwards suggesting a low dip in that direction.

The average yield of selenite for the whole deposit can be taken as 2 tons per 1,000 cu. ft. of the selenite clay and marl.

Reserves

The area covered by the selenitic clay and marl bed, as revealed by bore holes, is about 11,24,02,200 sq. ft. Taking the average thickness of the selenitic zone as 21′, the total reserve of selenitic clay and marl in the area can be estimated at 2,36,04,46,700 cu. ft. As the concentration of selenite in the selenitic clay and marl zone is about 2 tons per 1,000 cu. ft., the reserves of selenite in this area will be about 47,20,900 tons. Assuming that 20 per cent of the material has already been worked out or has been rendered unavailable, the reserves of selenite available in the area can be estimated at 38,00,000 tons.

The nature of the gypsum deposit near Ran as well as the reserves of gypsum in the area are now more or less fully known and the next problem is to work out a suitable method for working the deposits on a commercial scale. Dredging, hydraulic working or ground sluicing are perhaps the best possible methods of working this type of deposit. The problem of water supply and line communication are important factors to be considered in this area. The technical feasibility and the cost of working the deposit can only be judged by actual field work.

The Electron Microscope at the National Physical Laboratory, India

THE ELECTRON MICROSCOPE WHICH HAS BEEN assembled in the National Physical Laboratory is the E.M.U. model of the *Radio Corporation* of America. It is capable of giving a maximum magnification of 30,000 diameters which can be optically magnified to 1,50,000. It is capable of giving a resolution of 30Å which can resolve particles of molecular dimensions.

Unlike the older models, it is a vertical column design which minimizes interference from earth's magnetic field and has arrangements for five exposures of varying focuses or varying intensities on the same plate.

Its high voltage supply is purely radio frequency which is the most modern application of electronic feed-back control system and keeps the accelerating voltage (50 kV.) constant to about 1,00,000 volts, thus ensuring freedom from chromatic aberration in the electron beam. Another special feature is the high speed pumping device which reduces the pumping time to two minutes, thus enabling the worker to take pictures at intervals of five minutes.

Finally, it has arrangements for taking stereo and transmission and reflection diffraction pictures of the same specimen on the same plate, which is a great advantage in studying the particle size and structure of crystalline materials.

REVIEWS

Photoelasticity—Principles and Methods, by H. T. Jessop & F. C. Harris (Cleaver-Hume Press Ltd., London, W. 1), 1949, pp. viii + 184. Price 28*s*.

THIS BOOK, WRITTEN MAINLY FOR THE practical worker, deals with the recently developed subject of photoelasticity from its basic principles. It goes on to give a comprehensive survey of the rapid developments in technique in recent years, with particular reference to the use of newly developed plastics and the frozen stress method for the investigation of three-dimensional stresses.

The first two chapters briefly outline the principles involved and the methods followed in the mathematical analysis of stresses in two dimensions. The next two chapters are an introduction to the optical side of the subject and deal with the principles of geometrical optics, wave motion, interference and polarization. Chapter V discusses the production of isoclinics and isochromatics, as well as the use of circularly polarized light to eliminate isoclinics and the use of compensators to evaluate the fringe orders. These five chapters are written *ab initio* and five appendices contain examples of more difficult mathematical analysis separated from them.

The next chapter contains a clear account of the methods used in the reduction and interpretation of observations including the determination of the lines of principal stress and the isotropic points, the calculation of the separate stresses at a point and the application of these results to the prototype. Consideration of stresses in three dimensions is taken up in chapter VII, which also deals with the frozen stress methods. The limitations of the frozen stress method, especially near points of stress concentration, are discussed, as well as its use with slices cut from the model in planes of symmetry.

The next two chapters contain an excellent description of the experimental technique of photoelasticity, based largely on the author's own practical experience, which will probably save the serious worker much preliminary investigation. Chapter VIII deals with the optical arrangements of the photoelastic bench and different types of straining frames. Of particular interest is the pneumatic straining frame designed by C. Mylonas. The use of sheets of cellophane, or C.R. 39, as a substitute for mica quarter-wave plates is also discussed in some detail. Chapter IX opens with a survey of photoelastic materials used in modern practice and a discussion of time creep and time edge effects. The preparation of models and the techniques of annealing and loading, as well as of frozen stress procedure, are described.

The last chapter rounds off the whole book with five practical examples which illustrate the methods of interpretation and reduction of observations outlined earlier.

The whole book is written in a clear and vigorous style and the treatment is essentially practical. An attractive feature is the number of excellent diagrams. In view of the wide recognition of photoelasticity as a powerful tool in the investigation of stress problems, this book will be found invaluable by engineers and designers, as well as by technical students.

P. HARIHARAN

Electronics : Experimental Techniques, (National Nuclear Energy Series, Manhattan Project Technical Section), by W. C. Elmore & I. Sands Matthew (McGraw-Hill Book Co. Inc., New York, Toronto, London), 1st Edition, pp. 417. Price $ 3.75

ELECTRONICS IS PLAYING AN EVER INCREASINGLY important rôle in detection, study and measurement of nuclear and other physical phenomena. Electronic circuits are being used effectively for making nuclear and other physical measurements and for counting transient acts of active atomic nuclei. From the time of the earliest developments of the science of electronics, many ingenious methods for application have been devised and many electronic circuits for detection, measurement and multifarious types of counting have been designed and constructed by many workers in the field. The literature regarding the theory, development and performance of these electronic circuits has been widespread. But there have been only very meagre expositions of the theory, design and construction of electronic circuits used for atomic, nuclear and other physical measurements, and a great need for a thorough exposition of the subject has long been felt by workers in the field.

The publication of the work under review fulfils this need. It deals very ably with the fundamentals of electronic circuit components and circuit elements. It explains the fundamentals and basic principles of electronic circuits which would prove useful in giving an excellent background for the design of new circuits. The authors of this book, as members of the electronic group of the Los Almos Laboratory, were responsible for the development of electronic instrumentation and electronic circuits of various types especially intended for nuclear and atomic energy research work. They have made an extensive survey of all types of important and efficient electronic circuits available with various electronic groups who were working for the atomic energy development schemes. Of these, the authors have selected the most useful and efficient types of circuits for description in the chapters of this book. As such the work should prove extremely useful for those who are engaged in making nuclear and other physical measurements.

The book contains seven chapters. The first deals with circuit components and construction practice, the second with circuit elements, the third with voltage amplifiers, the fourth with electronic counters, the fifth with oscillographs and associated equipment, the sixth with test and calibration equipment and the last with power supply and control circuits.

In the first chapter, the authors deal, in general, with the circuit components of every type and their individual characteristics. They also explain with diagrams the outlay and mounting of various types of counter circuits as arranged in chassis and the necessary rack arrangements for final assemblage of the circuits. The second chapter deals with all types of circuit elements: their principles, arrangements, performance and individual characteristics. This chapter no doubt is very useful for all those who want to devise new types of electronic circuits for different purposes. The third chapter describes mainly the theory, design and characteristics of voltage amplifiers. The fourth chapter describes very ably many types of electronic counters including single counters, co-incident counters, scalers and mechanical counter-operating circuits. The fifth chapter deals with the general principles of cathode ray tubes and describes some important circuits suitable for oscillographs. This chapter also describes a number of time-marker generators such as pip generators, blanking generators, etc. It further deals with trigger delay circuits and trace-brightening circuits. The sixth chapter deals, in general, with test and calibration equipment such as laboratory oscillographs, general purpose sweep circuits, voltage pulse generators, pulse generators for accurate amplitude calibrations, trapezoidal voltage pulse generators and a number of other allied instruments with their respective characteristics and uses for different purposes. The last chapter deals with the fundamental principles of power supply and control circuits and describes diagrammatically a number of them which would, no doubt, be of immense value to all the workers in the field of electronic technology as applied to nuclear and other physical measurements.

This volume should be a welcome work to students and workers in the field of nuclear and atomic power energy research. It will be a very valuable addition to libraries and research laboratories engaged in nuclear and other physical measurements.

SWAMI JNANANANDA

Experimental Physical Chemistry, by F. Daniels, J. H. Mathews, J. W. Williams, P. Bender, G. W. Murphy & R. A. Alberty, 4th Edition, 1949, pp. xiii + 568. Price $ 4.5.

THIS BOOK, WHICH IS ALREADY VERY POPULAR in many universities, has been revised so as to increase its usefulness. Apparatus has been re-designed and procedures have been simplified so as to reduce the incidence of equipment failure in crowded laboratory sections. New commercial instruments such as the Beckmann and Coleman photoelectric spectrophotometers have been described. Almost every chapter reflects the recent advances in the past decade. The book has undoubtedly improved in its usefulness and is very suitable as a text-book of practical physical chemistry for university students, as well as a reference book for research workers.

K.S.G.D.

Organic Chemistry, by G. Bryant Bachmann (International Chemical Series, McGraw-Hill Book Co. Inc.), pp. 432. Price $ 4.25.

THIS TEXT-BOOK IS PRIMARILY INTENDED FOR students of organic chemistry at the degree class stage and not for those who have taken up an advanced course. Still the book is sufficiently broad in scope and contains detailed information to serve as a reference book for advanced students.

The author has adopted rules of the International Union of Chemistry from the outset and systematic naming of organic compounds is introduced early in the book. This has helped to avoid a lot of confusion to the beginning student. The electronic concept of valence is made the basis for study of structures and properties not readily understandable in the light of other theories. A simple and new method for the student to use in predicting the products of organic reactions and in selecting suitable starting materials for the synthesis of various types of compounds is a noteworthy feature of the book.

The author has presented those applications and generalizations of the subject which form the basis for a study and understanding of organic chemistry in such a way that they are easily learnt and remembered. The book does not restrict itself to a limited survey of certain specific topics but supplies concisely a wealth of information on a large variety of subjects. Up-to-date and brief accounts on electronic resonance in organic molecule, chemical constitution and colour, chemical constitution and physiological action and synthetic polymers are given. Modern developments such as synthetic rubbers, paludrine, silicones and antibiotics are also dealt with. In addition, a chapter on definitions, a list of reference books, both for elementary and for advanced study, and model exercises at the end of each chapter are included in the book.

The volume falls in line with the excellent text-books on organic chemistry now in use in various universities in India and may be read with benefit by students as well as by teachers.

A.K.

Modern Methods for the Analysis of Aluminium Alloys, by G. H. Osborn & W. Stross (Chapman & Hall Ltd., 37 Essex Street, London, W.C. 2), 1949, pp. 144. Price 13*s.* 6*d.* net.

THE BOOK UNDER REVIEW IS THE CONCERTED effort of the Committee of Chemists formed by a group of firms engaged in aluminium light alloy refining known as Alar. The book is confined to elements related directly to aluminium alloys and the methods described are those that have been thoroughly tested in the laboratories of the member firms. The great demand for aluminium alloys accentuated by the war and the need for conforming to exact standards have necessitated the development of newer methods and the introduction of physico-chemical instruments, the polarograph and the photometer. Some of the methods employed in the control laboratories are very different from those as yet published in the general text-books. The publishers have done a distinct service by bringing out this book. Although the appeal is mainly to the practical analyst seeking the latest procedure for rapid and accurate analysis of the elements, sufficient theoretical explanations have been given wherever necessary. The book is neatly printed and well bound. The reviewer feels that the price of 13*s.* 6*d.* is prohibitive for a book of 144 pages.

G. GOPALA RAO

Aluminium and Aluminium Alloys Extruded Sections (DESIGN AND TOLERANCES) (The Aluminium Development Association, 33 Grosvenor Street, London, W. 1), 1949, pp. 45. Price 1*s.*

THE INFORMATION BULLETIN PUBLISHED BY the Aluminium Development Association under the title *Aluminium and Aluminium Alloys Extruded Sections* is undoubtedly a valuable pamphlet for all those connected with the use of aluminium. This bulletin gives a clear picture of the potentialities of aluminium and its alloys. Two decades ago aluminium was widely used for making ordinary utensils and only a few parts made of it were used in machinery. Now, with the advent of newer types of aluminium alloys, aluminium extrusions have found their way in many places where steel was normally used.

For the manifold applications to which aluminium is put, its remarkable behaviour under heat treatment has been the main factor, for when the metal or its alloy is subjected to heat treatment, the tensile strength increases to a considerable extent. Being a light metal, aluminium has a better strength-weight ratio compared to many other metals. During the war, aluminium extrusions were used mainly in aircraft and here they have proved very efficient under very severe conditions over a period of years. Now there is practically not a branch of engineering where aluminium and its alloys are not used in some form or the other.

In the bulletin there are 9 tables giving valuable information about mechanical properties, tolerances, available sizes, etc., of aluminium extrusions. Out of the 26 figures given there, the first 7 illustrate the process of extrusion and other details connected with it; in Figs. 8 to 26 are illustrated the various applications of aluminium extrusions in different branches of engineering and test data are given for each type of extrusion.

Though there is nothing original in this pamphlet, the reviewer feels that the vast amount of data collected should prove highly valuable to many small manufacturing industries using aluminium extrusions as the basic material in their products.

V. CADAMBE

An Introduction to the Theory and Design of Electric Wave Filters, by F. Scowen (Chapman & Hall Ltd., London), 2nd Edition, 1950, pp. xi + 188. Price 18*s*.

THIS BOOK COVERS THE TECHNIQUE AND design of wave filters which are very essential for the telephone and wireless engineers. Wave filters are widely used in many electronic circuits, carrier-wave telephony and telegraphy. A wave filter is an electrical network used for either passing through or rejecting a signal of a particular frequency or signal covering a small band of frequencies in the audio and radio frequency spectrum. In any general electrical circuit, where low and high frequency signals are being handled, the filter is an essential feature. All telephone and telegraph transmitters depend very much upon the efficiency of the filter circuits used therein.

Following a short mathematical introduction on simultaneous and quadratic equations and on hyperbolic, circular and inverse functions which are the basic requirements for the design, the author discusses the electrical networks and the evolution of filters from such network using inductance and capacitance as the components. The simple characteristics of a filter are well explained and the equations for a particular line impedance and a cut-off frequency are derived systematically from the fundamental principles using hyperbolic functions. These equations are of immense value to the engineer who wishes to design and construct a filter. M-derived filter is the modified form of the simple one and the characteristics of it give a sharp pass or rejection to any signal of particular frequency. Equations for a m-derived type filter, wherein infinite attenuation is achieved with resonance phenomena on either side of the required signal, are also derived from the simple equations obtained for low pass, high pass and band pass sections. For various values of m, the author has given types of curves that can be obtained. For further simplification, the various values to be used for a m-derived shunt and series types of band pass filters, which are widely used, are also given.

In practice, reflection and insertion loss are the two main factors that are to be considered when designing wave filters. Impedance matching, phase shift and attenuation factor are also important to get the filter characteristics. These are discussed in detail by the author with reference to some practical problems. After the design of a filter, the engineer is faced with the problems of testing and technique of quantitative measurements when the filter is put into actual circuit. These problems are also well discussed at the end.

The book is a simple and well-written treatise on the theory and design of wave filters. The design of any particular type of filter can be handled well with minimum of labour using the derived equations. The presentation of the text is so systematic that it can be well recommended as a text-book. Telecommunication engineers will find it a good companion volume to some of the earlier books on the subject by Campbell, Shea and Sterr.

C. S. RANGAN

Paper Base Laminates, by S. E. Sorrell (Cleaver-Hume Press Ltd., London), pp. 223 + 4 plates. Price 12*s*. 6*d*. net.

THIS LITTLE BOOK, WRITTEN IN CLEAR AND simple language, will serve as a very useful introductory study of the technology of paper base laminates, which have found such versatile and ingenious applications in different industries. One cannot help feeling that a more valuable monograph could have been brought out by the author if he had not limited the scope of the book to paper base laminates alone but had included products such as plywood, glass-reinforced laminates, etc.

After a too brief introductory chapter covering only 3 pages, the author proceeds to a fairly detailed consideration of the two essential components of paper base laminates, namely the paper base dealt with in chapter II and the resin binder dealt with in chapter III. The resin treatment of paper, prior to the formation of laminates, is dealt with in chapter IV. Chapters V, VI and VII deal with the different laminating procedures, special purpose laminates such as composite boards, wire-reinforced laminates, paper tubes, etc., and special techniques in the fabrication of laminates. In chapters VIII and IX the specifications, the methods of testing the mechanical and electrical characteristics of the laminates and the different factors influencing the physical properties of the laminates are described at length. In chapter X a very brief review of the different applications of paper laminates is given.

As the author himself has admitted in his preface to the book, the routine methods of paper-making have been dealt with in comparatively greater detail than the manufacture of the resins. Despite the author's attempted justification of the same on the grounds that information on resin manufacture is readily available whereas, according to him, many readers are not so familiar with the processes of paper manufacture, the book leaves a feeling in the reader's mind that the author has a purposive partiality towards the paper-making industry. There will be nothing wrong in this if the author had concentrated more on the special aspects which are involved in the manufacture of specific types of paper particularly suited to, and useful for, making plastic laminates rather than on the usual routine methods of paper-making, which are normally dealt with in any ordinary book on paper manufacture. A more detailed discussion of the ultimate properties of the resulting laminated products in terms of the physical and mechanical characteristics of the fibre, the anisotropy, the orientation of the fibres in the paper structure, the absorbent nature of the paper, etc., would have been highly relevant in this connection.

Chapters IV to VII, dealing with the treatment of the paper, the laminating procedures and the special types of fabrication of laminates, are very well written and are undoubtedly of great use to one interested in the manufacture of laminated products. In these chapters the author has collected almost all the latest techniques in use, which is difficult for an ordinary technician or a man of the trade to collect from the vast scientific literature on the subject. The technique of deep-drawing of laminates, however, seems to have escaped the author's attention in the preparation of chapter VII. A number of papers dealing with significant improvements in deep-drawing technique have been published both by workers in America and in India. Chapters VIII and IX contain valuable information on the specifications and the methods of carrying out the tests for various mechanical and electrical properties and also the different factors which have a bearing on the ultimate physical properties of the laminates. The last chapter dealing with the applications of paper base laminates is too brief and covers only 3 pages of the book. This appears to be rather inadequate in view of the diversity of interesting applications referred to in recent literature. This probably could not be helped for want of space.

One or two mistakes of a minor nature have occurred in this book. "Aniline resins" should not have been spelt as "*Analine* resins" as has been done in the book. In the subject index it is indicated that pages 33 and 208 contain references to glass fibres. It has been noticed, however, that there is no reference whatsoever to glass fibres on page 208. This is perhaps an oversight in the final preparation of the manuscript and in any case is not of much consequence since the book is wholly devoted to the subject of paper base laminates and as such the reader need not expect to find much about glass fibre-reinforced laminates in the book.

On the whole, the book is very well written. The exposition of the subject is clear and concise. There is no doubt that the book will be of great usefulness to the junior classes of research workers. It will serve as an incentive for a more detailed study by going to the original papers published in recent scientific periodicals to which very discriminating and valuable references are cited at the end of each chapter. The price of the book is perhaps a little too high for its size.

A.J.R.

Modern Workshop Technology, by M. Wright (Cleaver-Hume Press Ltd., London), 1950, viii + 514. Price 32*s*.

THIS BOOK FULFILS ADMIRABLY THE NEEDS of a practical man in the works, who requires a theoretical background for workshop technology in addition to the essential practical details pertaining to the working of his machines and tools.

Each chapter has been written by one who is an authority on the subject and, therefore, full details are provided for how and why of everything that one has to handle in the workshop. The book deals with problems of every type met with in the workshops and is recommended for those who have anything to do with the workshops either in a supervisory or an official capacity. This volume gives an up-to-date and concise survey of British tools and provides an adequate outline of the principles of measurement and inspection. The last chapter on " Human Relations in the Workshops " is of special interest to the supervisory staff and is, in the opinion of the reviewer, most valuable under the conditions obtaining at present in the country when proper handling of staff problems can go a long way towards increased production in the workshops.

D. R. MALHOTRA

Theory of Wing Sections, by Ira H. Abbott & Albert E. von Doenhoff McGraw-Hill Book Co. Inc., New York), 1949, pp. viii + 693. Price $ 15.00.

AFTER WORLD WAR II, MANY BOOKS HAVE been published on aerodynamics, both in U.S.A. and U.K. But there is hardly a book in which the aerodynamic theories that are most useful in working with the wing sections are brought together. In this book, the author and his colleague Albert E. von Doenhoff have systematically developed the theory of " wing sections " from the classical hydro-dynamics, involving simple two-dimensional flows to the effects of compressibility at subcritical speeds. The authors are well-known authorities in this field and are connected with the premier body, viz. the National Advisory Committee for Aeronautics.

This book presents all the useful aerodynamic theories of wing sections, together with a comprehensive summary of experimental results. Though the theoretical treatment progresses from elementary considerations, yet a sufficient knowledge of calculus, differential equations and complex variables is necessary for easy understanding of the text. The mathematical calculations of NACA low-drag airfoils were so far not accessible to students for classroom study. With the de-classifying of the confidential work done during the war, the authors have taken full advantage of the opportunity to treat exhaustively in this volume the theory behind these low-drag airfoils. One noteworthy point about the book is that the use of " vectorial notations " has been scrupulously avoided in the mathematical treatment.

The volume is rather unwieldy for use as a text-book in the under-graduate study; in the graduate course it can be used in the fifth and sixth years; but for practising engineers and research workers it should prove a valuable reference work.

There are 9 chapters in the book which bring together all the theories essential in working with the modern wing sections, particularly those of NACA types. A list of 160 useful references are included. The outstanding feature of the publication is comprehensive appendices on basic thickness forms, mean lines, airfoil ordinates and aerodynamic characteristics of wing sections.

The reviewer feels that the price of the book seems to be on the high side, although the vast amount of data presented may justify it.

This book is the first of its kind to be published giving valuable and exhaustive information on wing sections for the practising engineer.

V. CADAMBE

Communication Circuit Fundamentals, by Carl E. Smith (McGraw-Hill Book Co. Inc., New York), 1st Edition, 1949, pp. 401. Price $ 5.00.

THE WORK UNDER REVIEW, ENTITLED " COMMUNICATION Circuit Fundamentals ", is designed as a text-book for students of technical physics who are interested in specializing in the field of communication engineering. It meets the needs of radio operators and technicians who wish to equip themselves with the fundamental knowledge of this branch of science so as to enable them to tackle the problems of repair and improvement in communication services.

As a preliminary to a systematic treatment, after explaining the basic principles of the electron theory, the author deals with the fundamental electrical quantities which are essential for the formulation of the theory and deduction of quantitative expressions for circuit constants and alternating and direct-current circuits. These electrical quantities are presented in a form best suited for a systematic study of the subject.

The book ably deals with the physics of circuit elements and components together with the thermionic valves. It explains the fundamentals of alternating and direct-current circuits. The circuit constants are discussed in detail and are then used in a treatment of direct-current circuits. The principles of alternating circuits are also treated after explaining the relevant principles of magnetism, inductance and capacitance. Ohms and Krichhoffs's laws are explained and are used in solving simple problems of direct-current circuits. The alternating-current circuits are treated with the application of vector notation. A comprehensive treatment of the theories of some of the important networks is given so as to enable the students to apply them for various problems.

Each chapter of the book gives the theory, develops design equations and scrutinizes them in a manner so as to enable the students to understand and solve many important problems. The book, therefore, will be found very useful not only to the students of technical physics but also to the electrical and communication engineers. It will also be useful as a reference book in research laboratories.

SWAMI JNANANANDA

PUBLICATIONS RECEIVED

THE ROLLING OF METALS (Vol. I), by L. R. Underwood, Chapman & Hall, 42*s*.

PRACTICAL APPLICATIONS OF SPECTRUM ANALYSIS, by Herbert Dingle, Chapman & Hall, 40*s*.

THE PROPERTIES OF METALLIC MATERIALS OF LOW TEMPERATURE, Vol. I, by P. Litherland Teed, Chapman & Hall, 21*s*.

VEGETABLE CROPS (4th Edition), by Homer C. Thompson, McGraw-Hill, $ 6.00

THE ORGANIZATION OF INDUSTRIAL SCIENTIFIC RESEARCH (2nd Edition), by C. E. Kenneth Mees & John A. Leermakers, McGraw-Hill, $ 5.00

ESSENTIALS OF ELECTRICITY FOR RADIO AND TELEVISION, by Morris Slurzburg & William Osterheld, McGraw-Hill, $ 4.00

THRESHOLD SIGNALS, by James L. Lawson & George E. Uhlenbeck, McGraw-Hill

PRINCIPALS OF AERODYNAMICS, by James H. Dwinnell, McGraw-Hill, $ 5.50

NOTES & NEWS

Q-Enzyme

Haworth *et al.* isolated an enzyme, termed *Q*-enzyme, in potato juice, capable of converting amylose to amylopectin. The enzyme is obtained in a pure crystalline form by precipitating it, at low temperature, with ethanol from solutions of low ionic strength followed by crystallization from ammonium sulphate solution (*Nature*, 1950, **165**, 573).

Peeled and sliced potatoes are steeped in 0·7 per cent sodium hydrosulphate solution for 20 min., washed in water, minced and the juice expressed is centrifuged and brought to a concentration of 11 per cent in ethanol at −2°C. The precipitate is discarded and the ethanol concentration raised to 16 per cent at −5°C. to give a further precipitate. This is taken up in sodium citrate solution (*p*H 6·0) and ionic strength 0·01 and the solution again brought to 11 per cent in ethanol. The slight precipitate is removed and the concentration of ethanol again raised to 16 per cent, the *p*H and ionic strength being kept constant throughout. The precipitate is taken up in citrate solution and reprecipitated at 16 per cent ethanol. The final precipitate is dissolved in citrate solution and ammonium sulphate added (at 0°C.) to an ionic strength of 3·8 and *p*H of 6·2. The precipitate is dissolved in water and ammonium sulphate is added at 10°C. until a cloudiness appears at an ionic strength of about 3·2. The solution is cleared by adding a minimum amount of water and then cooled slowly to 0°C. *Q*-enzyme separates in a few hours in needle-like crystals.

A solution of amylose of initial light absorption value of 1·30 was half-converted into amylopectin in 12 min. at 20°C. in 0·2*M* sodium citrate solution of *p*H 7·0 in a digest containing $2{\cdot}2 \times 10^{-2}$ mg. of enzyme per c.c.

Vitamin B_{12}

The isolation and properties of vitamin B_{12}, the active principle of liver, are described (*Chem. Age*, 1950, **62**, 575).

Vitamin B_{12} has been isolated by exclusively physical means from liver owing to the absence of any particular chemical properties characterizing it. The methods include adsorption (charcoal or alumina) and partition chromatography (using damp silica and butanol). In the latter method three zones were obtained : brown at the top, pink in the middle and yellow at the bottom. All the activity was found to be concentrated in the pink fraction. Deep-red crystals of the pure vitamin were obtained from aqueous acetone after repeated purification by chromatography and subsequent concentration. One ton of liver was required to give 15 mg. of the pure vitamin.

Vitamin B_{12} exhibits a typical and characteristic absorption spectrum of its own. X-ray crystallography has confirmed its molecular weight of 1650·100 for the hydrated substance. The chemical formula is given as $C_{61\text{-}64}H_{86\text{-}92}N_{14}O_{13}PCo$. Its synthesis by *Streptomyces griseus* has been achieved on a commercial scale. The substance could be synthesized by certain intestinal bacteria.

Further work has resulted in the isolation by chromatographic means of another red factor vitamin $B_{12}b$, also clinically active.

Vitamin B_{12} has a phenomenal potency producing haemopoietic response in pernicious anaemia in doses of about 0·001 mg. ; folic acid of 5,000-10,000 times this amount is needed for the same response. The vitamin contains about 4 per cent of cobalt, this being the first time that the metal has been found in a pure material of biological origin.

Colour Reaction for Pyrethrins

The reaction product of carboxylic acid derivatives and hydroxylamine forms coloured complexes with ferric chloride. Similar complexes are also formed with pyrethrins and their synthetic analogues (*Nature*, 1950, **165**, 567).

6 c.c. of alkaline hydroxylamine reagent (3 c.c. 2*M* hydroxylamine hydrochloride solution and 3 c.c. 3·5 *N* sodium hydroxide solution) was added to 3 c.c. of an ethanolic solution of ester and the mixture allowed to stand for 1 min. or more, acidified with 3 c.c. of hydrochloric acid (1 vol. conc. acid, sp. gr. 1·18+2 vol. water), and finally 3 c.c. of ferric chloride solution (0·37 *M* in 0·1 *N* hydrochloric acid) was added. A blank was carried out with ethanol alone and absorption measurements were made. The absorption spectra of the complexes obtained from a mixture of the natural pyrethrins, purified by the nitromethane technique, and the synthetic pyrethrin analogue, the *DL-cis-trans* chrysanthemum monocarboxylic acid ester of 3-methyl-2 - allyl - *cyclo* - penten - 4- ol - 1-one are similar to these. The absorption by the coloured complexes at λ 540 mμ is proportional to the amount of ester used ; the reaction is also dependent upon the acidic and alcoholic components of the ester. Thus, to give the same colour intensity, the amount of synthetic pyrethrin analogue required is 3·3 times that of the natural pyrethrin mixture (pyrethrin I : pyrethrin II = 1·6 : 1). Since the naturally occurring esters of chrysanthemum dicarboxylic acid (pyrethrin II) contain two ester groupings, they may be expected to yield a more intense colouration than the esters of chrysanthemum monocarboxylic acid (pyrethrin I) which is in line with the experimental results.

The reaction which should prove useful for the detection of pyrethrins in chromatographic separation cannot, however, be applied to the estimation of pyrethrins unless (1) they can be first separated, or (2) the ratio in which pyrethrins occur is known to be constant.

Measurement of Proteolytic Activity

A new method is described for determining the activity of proteolytic enzymes by detecting the change effected in the affinity of the native albumin for simple dye anions in the presence of such enzymes. Quantitative activity measurements may be made by estimating the concentration of the native protein in the presence of the proteolytic enzyme as a function of time, using an empirical curve as is usually done in spectrophotometric analysis. In this method the quantity of native protein remaining in solution is measured, whereas the usual determination is based on an analysis of the products of hydrolysis (*Science*, 1950, **111**, 387).

The effect of a 0·1 per cent pepsin solution upon a 0·2 per cent albumin solution at *p*H 5·4 in the presence of a constant concentration of the dye, Orange I, has been studied. The addition of bovine albumin to the dye causes a depression of about 20 per cent in the absorption maximum and on adding crystalline pepsin, the optical density of the reaction mixture in the presence of the dye approaches that obtained for the dye alone.

The reason for having the concentration of pepsin as high as 0·1 per cent and the *p*H at 5·4 instead of 2 was to gather information on the nature of enzyme substrate interaction. Nevertheless, the method is generally the same if conditions of *p*H and initial concentration of enzyme and substrate are altered. Using the procedure outlined above, no particular difficulty was encountered in studying the activity of pepsin on albumin at *p*H 2 when enzyme concentration was one part per billion.

An important difference in the activity, when determined by the dye method instead of classical methods, is that the linear effect of enzyme concentration on the reaction rate can be observed not only at the beginning of the experiment, but even when 50 per cent or more of the native protein has been removed.

The use of dyes as indicators for following the course of a proteolytic reaction may offer the advantages of increased sensitivity and ease of adaptation of the method to micro-procedures.

Manganese Dioxides

SOME MANGANESE ORES ARE FAR superior in dry cell manufacture while others excel in certain chemical processes. The reasons for these differences in their properties have been investigated (*C.T.J.*, 1950, **126**, 935).

The ores examined were: African, Belgian Congo, Montana and Caucasian. The method of differential thermal analysis depends on the fact that minerals show breaks in their heating curves at points where changes in composition or physical structure take place. By comparing the temperature of a substance heated at a definite rate with that of a thermally inert substance such as alumina heated under the same conditions, a differential temperature curve is obtained which is characteristic of the material examined. The temperature at which such transformations occur serves to identify the mineral involved, while the magnitude of the transition break indicates the quantity present. Ergogene and Montana ores give small peaks, while the relatively inactive Caucasian ores give a high double peak. These observations are in line with the known relative activities exhibited by the ores. Tests conducted to explain these observations indicate that the product of decomposition of Caucasian manganese dioxide is first α-manganese oxide which is transformed by continued heating or higher temperature to bixbyite and hausmannite. X-ray diffraction and chemical analysis have indicated the existence of a whole series of compounds between the end members, ramsdellite (γ-manganese dioxide) and pyrolusite (β-manganese dioxide). Many ores contain manganese dioxides in such a complex mixture that the relative strengths of the different component patterns are difficult to determine. African Gold Coast mineral can be considered as the poorly crystallized and impure ramsdellite. Pure anhydrous manganese dioxide has been demonstrated in only two forms, namely ramsdellite and pyrolusite, which occur naturally and are limited to well-crystallized materials giving sharp X-ray patterns.

From the battery manufacture standpoint, the compositions of the African Gold Coast ores is important. The principal components of the ore have been identified to be poorly crystallized ramsdellite. The Montana ores are more impure and complex than the African ores. The major component is γ-manganese dioxide with quartz, cryptomelane, lithiophorite and pyrolusite as the main impurities. Caucasian ore is composed almost entirely of pyrolusite with more or less manganite and a trace of quartz. Ergogene and Burgess chemical ore are typical of a group of artificial chemical ores and contain as the major component γ-manganese dioxide with cryptanelane, quartz and bixbyite as principal impurities. An electrolytic product is composed of γ-manganese dioxide and contains a little graphite from the electrodes employed.

Vulcanization of Rubber

A NEW PROCESS FOR THE VULCANization of rubber makes use of mild oxidizing agents in place of sulphur (to a substantial extent) normally employed and also eliminates the use of zinc oxides (*Industr. & Engng. Chem.*, 1950, **42**, 671).

Conventional vulcanization may be considered a two-step oxidation process in which zinc oxide or zinc soap functions through its ability to form zinc mercaptides which are more easily oxidized by sulphur to disulphide cross-links than are thiol compounds. As zinc oxide or zinc soap is required in the second step of the sulphur reaction, the use of a suitable oxidizing agent eliminates the necessity of these materials.

2, 2′-dibenzothiazyl disulphide examined for this purpose readily oxidizes hydrogen sulphide to free sulphur and reacts relatively slowly with rubber. Vulcanization was carried out at 110°C. for a period selected to give the maximum physical cure as measured by stress at 200 per cent elongation. The replacement of zinc oxide and stearic acid by 2, 2′-dibenzothiazyl disulphide increased physical cure and in air absence of sulphur, but the compound itself is not a vulcanizing agent. The compound was most effective in replacing zinc oxide when it is accelerated with a metal (zinc) salt of a dithiocarbamic acid and brings about the greatest physical cure. At equivalent molecular concentrations methazate and butazate (zinc salts of dimethyl and dibutyldithiocarbamic acid) are equally effective. About 0·0035 mole is required to give maximum physical cure in a compound containing 0·02 gm. atoms of sulphur (0·64 part) and 10 parts of 2, 2′-dibenzothiazyl disulphide. Other milder oxidizing agents which proved effective include quinine dioxime, diazoaminobenzene, *bis*-(ethoxyphenyliminomethyl)-disulphide, N-nitrosodiphenylamine, quinone *bis*phenylimine, 2,2′-dibenzothiazyl disulphide and benzothiazyl-2-monocyclohexyl sulphonamide. None of the chemicals, effective in the new process, brings about any cure in the absence of sulphur. However, rubber containing hydrosulphide groups can be vulcanized by thiazyl disulphides alone.

Recent Applications of Thallium

THE COMPARATIVE SCARCITY OF thallium, the limited knowledge of its properties and the high cost of extracting it from known sources have hindered its commercial development. On account of the increasing importance of the element, in recent years, its properties have been studied in detail by the *U.S. Bureau of Mines* (*Chem. Age*, 1950, **62**, 685).

The natural sources of thallium comprise deposits of thallium minerals, rocks containing small proportions of such minerals and water or brine with traces of dissolved thallium compounds. No ores of the element that can be commercially exploited exist. The sources are industrial wastes and residues derived from metallurgical and chemical processes in which thallium from the original raw material has been somewhat concentrated.

A recent application of thallium is in the manufacture of incandescent lamps. Thallous salts, being more stable than thallic compounds, absorb traces of oxygen in such lamps and hence prolong the life of the tungsten filament.

Several new uses of thallium have been developed within the past decade. Even at the present high prices, thallium and its compounds can be employed to advantage for a number of commercial as well as scientific and military applications.

Alloyed with silver or lead, thallium greatly increases the corrosion resistance of the metals. In conjunction with other metals, thallium forms alloys that have unique and valuable properties. Examples are lead-thallium, silver-thallium and many ternary alloys. By far the largest proportion is consumed in compounds for lenses and photoelectric cells in the glass industry to impart dark, opaque, black or brown colours as well as to increase density and provide an index of refraction higher than that of lead glass.

Acrylic Resin Emulsions

ACRYLIC RESIN EMULSIONS OF the non-ionic type are becoming increasingly popular for formulation of grease-proof coatings and as binders for clays and in decorative colour coatings which must have good resistance to discolouration during ageing. Some desirable characteristics and properties of these products are described (*Chem. Age*, 1950, **62**, 569).

Acrylic resin emulsions, suitable in the formulation of paper coatings, must have a 40 per cent solids content, sp. gr. 1·08 (25°C.) and should be unaffected by acids, bases, salts and organic solvents. They must possess high mechanical stability with thickness, such as concentrated water-soluble polymers, e.g. sodium carboxy methylcellulose. They should be capable of being plasticized with other resinous compounds to increase the flexibility of the film, without affecting its ageing properties. Common additions include acrylic resin dispersions, nitrile rubber latex, natural rubber and synthetic (neoprene and GR-S) lattices. The emulsion should be without effect and indifferent to common pigments such as chrome yellow, iron oxide, cadmium red, ultramarine blue, titanium oxide, carbon black, chrome oxide and organic red. A number of variables such as the degree of porosity of paper stock, maintenance of a proper balance of coating, viscosity and solids and proper control of bubble formation (by adding compounds like caprylalcohol) give successful coating.

It is possible to obtain continuous, completely grease-proof coatings on 60 lb. patent board in one pass at coating weights as low as 1·9 to 2·4 lb./1000 sq. ft. Where a partial proofing against grease is desired, good results have been obtained at 0·9 lb./1000 sq. ft.; where the base stock is less porous, deposition of continuous grease-proof films is possible in one pass at weights of 1·5 lb./1000 sq. ft. When used as a binder for high or low grade clays in pigmented coating compositions for paper, acrylic resin emulsions improve the handling characteristics and stability of the coating dispersion. The emulsions may be modified with starch to improve flexibility and calendering and with casein to contribute superior resistance of the film to yellowing during exposure to ultra-violet light.

Travelling Wave Linear Accelerator

A NEW MACHINE (FIG. 1), WHICH can generate energies of 3·5 million electron volts and accelerate electrically charged atomic particles almost to the speed of light, has recently been set up at Britain's Atomic Energy Research Establishment at Harwell. The machine also serves as a means of providing a plentiful supply of neutrons.

A powerful radio transmitter, working at a wavelength of 10 cm., provides electrical waves which speed up the movement of electrons. Short high power bursts (each lasting two millionths of a second) emitted by the machine further accelerate

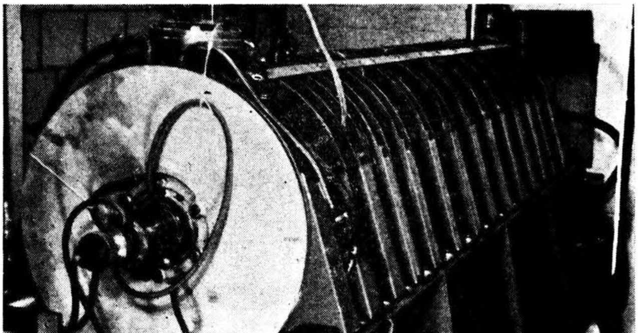

FIG. 1 — TRAVELLING WAVE LINEAR ACCELERATOR.

these electrons which are directed at a heavy metal target which, in turn, emits " hard " X-rays or γ-rays. These γ-rays enter a tank of heavy water and the heavy hydrogen nuclei in the water break up and emit the neutrons. When the machine is used at its highest capacity, in short bursts (each of which lasts only two millionths of a second), the number of neutrons released is at the rate of one million million per second. Because there is a pause between each burst of energy, the actual number of neutrons released is about 1,000 millions per second.

The new accelerator will aid the study of the effect of neutrons on nuclei of various elements which is of vital importance in the development of atomic energy for industrial purposes.

Larvicidal Action of DDT

TRIALS WITH DDT, IN POWDER and emulsion form for the control of mosquito breeding in paddy fields where cultivation is done on the common inundation irrigation methods have been carried out by the Malaria Research Institute (*Indian J. Malariol*, 1950, **3**, 165). The larva studied were *A. subpictus*, *A. annularis* and *C. fatigans*. DDT powder and Paris green diluted with soapstone were applied by hand, and DDT-toluene-terpentine emulsion diluted with water was sprayed. The approximate dosage of the insecticide applied per acre was 2 gallons of DDT emulsion in water or 24 oz. of DDT powder in soapstone or 6 oz. of Paris green with soapstone. The number of dips for larval collection (in ladles) was restricted to 15 for each plot.

Test results showed that in the plots under DDT emulsion of strengths 2·5 and 1·5 per cent, breeding was lower than in the other plots. No damage of any kind either in quality or quantity to the crop was reported from any plot under experiment.

Carbon 14

THE RADIOACTIVE ISOTOPE, CARbon 14, has been successfully prepared at Britain's Atomic Energy Research Establishment.

Carbon 14 is prepared by inserting an aluminium cylinder packed with a nitrogen compound in the atomic pile. Under the action of the bombarding neutrons, nitrogen is very slowly converted into Carbon 14. One year's exposure in the large pile at the Establishment converted only two nitrogen atoms in every million into Carbon 14. The isotope is eventually made available to research workers as radioactive carbon dioxide.

A special container which fits into the wing tip of aircraft has been designed for transporting radioactive materials by air. The container enables isotopes to be carried without the need for heavy lead sheeting. A single parcel can be reduced from 30 lb. to a few ounces, thereby effecting a corresponding decrease in transport costs.

Atomic Sieve

THE BRITISH ATOMIC ENERGY Research Establishment at Harwell has recently been equipped with an electromagnetic isotope separation plant which is capable of separating atoms of heavy elements such as uranium and dividing them according to variations in weight.

The process of separation is initiated by projecting a stream of electrically charged atoms into a magnetic field. This causes them to travel in a circle, during which the centrifugal action throws the heavy atoms on to the outer circumference from which they can be collected separately from the others. The new separator can supply as much as 1,000 mg. of separated atoms as against only one mg. supplied by the small unit in use for the last two years.

Thyroxine & Milk Yields

THYROXINE, WHEN ADMINISTERED to milch cows, has been found to increase their milk yield to a significant extent. This method is being practised, to a limited extent, in some states in U.S.A.

The use of synthetic *l*-thyroxine is recommended as it does not suffer from the disadvantages of the iodo-protein which causes undesirable effects in the animals and which is difficult to standardize.

The average increase in yield obtained was 5·5 lb. per day or 22 per cent of the initial yield of 25 lb. per day. Age of cow, productive capacity and stage of lactation are important factors affecting the amount of response. Heifers show little effect and young cows less than old cows. High-yielding cows show good response. The best time to start the treatment would be for 8-12 weeks in late lactation. Prolonged treatment results in reduced yields.

The above considerations apply to moderate doses (100 mg. per day) of thyroxine. Dosages at higher levels produce harmful effects.

Blood Meal Adhesives

IN VIEW OF THE HIGH PRICE AND shortage of casein and other raw materials used for adhesives, utilization of whole blood meal for the production of plywood adhesives has been investigated at the Forest Research Institute, Dehra Dun (*Indian Forest Leaflet, No.* 108).

Whole blood from slaughterhouse to which either 3 per cent sodium fluoride or 1 per cent sodium oxalate has been added as a preservative was used. On drying in shallow trays in a kiln at 60°C. and 60 per cent relative humidity, 600 lb. of blood yielded 12 lb. of blood meal : moisture, 16·79 per cent ; fat, 0·87 per cent ; ash, 8·9 per cent and nitrogen, 11·44 per cent. This blood meal, powdered and soaked in water for about 30 min., was used in conjunction with ingredients such as lime, borax and ammonia for making plywood boards (with $\frac{1}{16}''$ rotary cut veneers of *Cedrela toona*). The plywood specimens conformed to the specifications of commercial plywood (grade I). Tests on the susceptibility of the glue to microbial attack on the adhesive show that addition of 5 to 10 per cent " Santobrite " preserves the glue and its adhesive power is satisfactory. However, it is best to use the glue immediately after it is made. The dried blood meal can be stored up to 4 weeks without any appreciable deterioration in its quality.

Some typical formulae for satisfactory glue composition are given below. The ingredients are added in the order in which they are mentioned :

1.	Blood meal	100	parts
	Water	175	,,
	Lime	3	,,
	Water	25	,,
2.	Blood meal	100	,,
	Water	450	,,
	Lime	6	,,
	Water	50	,,
	Casein	100	,,
	Water	300	,,

	Lime	10	Parts
	Water	100	,,
3.	Blood meal	100	,,
	Water	250	,,
	Lime	6	,,
	Water	30	,,
	Casein	100	,,
	Water	250	,,
	Lime	10	,,
	Water	50	,,
4.	Blood meal	100	,,
	Water	175	,,
	Borax	7·5	,,
	Water	25	,,
	Lime	3	,,
	Water	10	,,

5. Same as 4 but with 15 parts borax.

A glue adhesion strength of 287 lb./sq. in. in dry tests and 197 lb./sq. in. in hot wet tests were observed in the case of formula 4.

Strain Gauges

FOR THE IDEAL CONSTRUCTION OF a bridge, a crane, an aeroplane or a propeller shaft, etc., the engineer must know not only the properties of the material to be used but also the distribution of the strains and stresses occurring under different conditions of load. The usual methods of measuring such stresses by mechanical and optical " extensometers " fail to answer the purpose, where the measuring points in a construction are difficult to reach. Neither are they suitable when, as is the case at practically all points of an aeroplane, strong vibrations occur in addition to the usual static load. In such cases strain gauges offer the solution.

In essence a strain gauge is just a wire which, under a tensile force or a compressive force, undergoes an elongation and a consequent change in its electrical resistance and conductivity. This change can be easily and accurately measured. The wire used for the *Philips* strain gauges (FIG. 1) is made of constantan (an alloy of 55 per cent copper and 45 per cent nickel) which is glued in a zigzag fashion on to a strip of paper. The paper and the glue have to be so stiff as to ensure that the distortions taking place in the work-piece on to which the gauge is glued are fully transmitted to the resistance wire.

Of the two types produced by *Philips*, the larger gauges are 5·5 cm. long and about 1 cm. wide, while the smaller ones are 3 cm. long. The gauge is covered with a thin layer of wax or with a sheet of rubber having inside it some moisture-absorbing material (e.g. silica gel), thus shutting out all air and moisture.

Changes in the resistance of the conductor due to variations in temperature are negligible as the wire is of constantan. A dummy gauge is applied close to the active one at a point where it is not subject to mechanical load. The two gauges undergo exactly the same variations in temperature so that the changes in resistance are equal in both and cancel out in the bridge circuit, and only the resistance variation due to the load upon the work-piece is measured.

The calibrating factor of the strain gauges, which is indicated for each individual gauge, enables the engineer to deduce the difference in stress in the work-piece from the variation measured in the resistance.

The *Philips* strain gauge has been successfully employed to measure the stresses on the standards carrying overhead power lines of electric railways when one of the conductors suddenly breaks. Another application is to measure the strains and stresses arising in the hull of a ship as it is launched into water. The distribution of strain can be deduced from the changes in resistance taking place in a set of three gauges glued on to the hull close together at an angle of 120°.

The strain gauges can also be used for measuring pressure and force. Pressure transmitted to a diaphragm on to which a strain gauge has been glued, causes the diaphragm to bend, and this brings about a change in the resistance of the strain gauge. In this way, by using special pressure boxes, the weight of an aeroplane can be very quickly determined, without such means as a very large weighbridge. They can also be employed for safeguarding costly constructions as, for instance, a crane, against overloading. When the maximum permissible load is reached, the strain gauge applied at critical points sets an alarm going or switches off the power supply.

The examples given above are only a few of a very wide variety of applications to which the instrument can be put. Special strain gauges are being used for measuring and recording the beat of the heart and respiration by means of oscillographs.

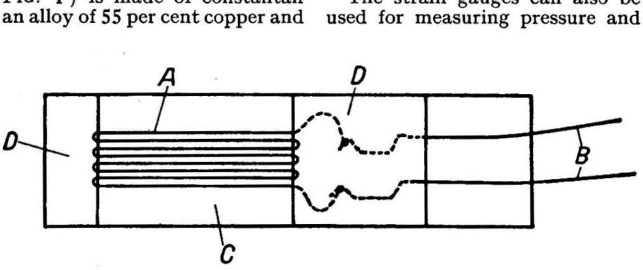

FIG. 1 — A DIAGRAMMATIC SKETCH OF A STRAIN GAUGE.

Whale Liver Extract

WHALE LIVER EXTRACTS HAVE been found to be as potent as the extracts from bovine liver. Oral administration of the simple aqueous whale liver extract filtered and concentrated (1 oz. of extract = 25 oz. of whole liver) to cases suffering from Addisonian pernicious anaemia resulted in good response. It is possible that whale liver can be used off in the preparation of pharmaceutical liver extracts (*Indian J. Pharm.*, 1950, **12**, 108).

New Cotton Cleaner

A NEW MACHINE FOR REMOVING dirt and other foreign matter from raw cotton has been developed at the Battele Memorial Institute, Ohio, U.S.A.

The machine consists of two concentric cylinders and the cotton to be cleaned is passed through the interspace. Air from a number of small pressure jets entering through the outside cylinder blows away foreign matter from the cotton. The process is repeated a number of times and the dislodged dirt is then skimmed off through special openings (*USIS*).

Fungi of Bengal

SEVEN HUNDRED AND SEVENTY species of fungi distributed over 240 genera are listed in a booklet (T. C. Roy, Botanical Society of

Bengal, Calcutta, 1949, pp. 44, price Rs. 3) recently brought out by the Department of Agriculture, Government of Bengal. This comprehensive list was compiled prior to the partition of Bengal and is the first of its kind to be published bringing together, in systematic manner, all the reported species of fungi. The booklet contains 2 indices, one relating to host plants and the other to the genera of fungi.

The booklet is a valuable adjunct to the scanty literature on the fungal flora of India and should be very useful to mycologists in devising plant protection measures and to research workers.

Indian Standards

Lubricants — A draft Indian Standard giving sampling and testing methods for lubricants has been brought out as a complement to the two recently issued draft standards relating to lubricants for various types of machinery. The standard describes the procedures for a number of routine determinations. The specialized apparatus used in the various methods is illustrated.

Textile Machinery — Eleven draft standards on methods for the determination of various properties of textiles and two draft standards defining cotton and wool terms have been released. The apparatus, procedures and evaluation of test results are also described.

Aluminium Alloy Ingots and Castings — The first in the series of specifications on aluminium base constructional material for aircraft purposes has been issued by the Engineering Division Council of the ISI and relates to aluminium alloy ingots and castings. The tentative standard has been drawn up after taking into account the resources available and technological practices obtaining in the country. The standard is priced Rs. 1/4 and may be had from the Secretary (Administration), Indian Standards Institution, 19 University Road, Delhi 8.

Soaps — The draft is a supplement to the standards for soaps already issued by the ISI and lays down a standard method of sampling and test methods for the evaluation of important characteristics of soaps. Critical reviews and comments on the draft will be received by the Director, ISI, up to September 1, 1950.

Conservation of Industrial Coal

In order to conserve coal resources in the country and to control coal distribution and production in industries, steps are being taken by the Indian Coal Commission to assess coal demands of different industries. Requirements have been classified under the following heads :

Coal for boilers ; and coal and coke for industrial furnaces. Boiler coals are again subdivided into (1) industry's boilers, (2) industrial power stations, (3) boilers in thermal power stations. A systematic study of the behaviour of different classes and sizes of coal with existing equipment is being made in the Research Department of the Ministry of Industry and Supply to improve the range of steaming capacity and the range of fuel in power plants. Suitable specifications for coals (percentage of ash, volatiles, fixed carbon to volatile ratio, etc.) are being drawn up to meet the maximum continuous rating and peak load of power-station boilers and temperature requirements of industrial furnaces. Coal requirements are also being correlated with production, the basis being power requirements per unit of production.

Microfilm Service

The Indian Council of Medical Research have set up a second Microfilm Service Unit at the Tata Memorial Hospital, Bombay, in addition to the unit at the Central Research Institute, Kasauli. The new unit also will supply microfilmed copies of articles from any scientific journal available in Indian libraries.

In order to make available the services of these microfilm service units, not only to scientific institutions and organizations, but also to individual research workers, the *I.C.M.R.* has decided to discontinue the practice of enrolling members to the scheme on payment of an annual subscription. The charges for microfilming work are now made at the following flat rates : Rs. 3 for the first 10 pages or any portion thereof ; Rs. 1/8 for every subsequent 10 pages or portion thereof plus packing and postage.

An equipment called " Reader " required to read the microfilmed articles can be obtained from *Messrs Kodak Ltd.*, Kodak House, Hornby Road, Bombay.

All requests for microfilming work should be addressed to the Officer-in-Charge, I.C.M.R. Microfilm Service Unit, Central Research Institute, Kasauli or to Dr. V. R. Khanolkar, Director of Laboratories and Research, Tata Memorial Hospital, Parel, Bombay 12.

Central Board of Forestry

The Government of India have constituted a Central Board of Forestry with the following functions : (1) Co-ordination and integration of forest policy pursued by States in the management of their forests ; (2) adoption of conservation measures affecting forest resources and soil ; (3) integration of plans for land use and national reconstruction ; (4) promotion of legislation for management of private forests in various states ; (5) regulation and development of forests in inter-state river valleys, controlled by the Central Government; (6) maintenance of adequate standards of training of officers and (7) co-ordination of forest research conducted in Central and State institutes.

Pan-Indian Ocean Science Congress, 1951

Invitations to attend the forthcoming Pan-Indian Ocean Science Congress to be held in India during the first week of January 1951 have been extended by the Government of India and the Indian Science Congress Association to Governments of various countries around the Indian Ocean. The Congress will be held side by side with the 1951 Annual Session of the Indian Science Congress Association at Calcutta and is being arranged by the Indian Science Congress Association through the Department of Scientific Research, Government of India, who will make the necessary arrangements for the delegates attending the Congress.

The following countries, which are likely to be interested in the Congress, are being invited : Australia, Indonesia, New Zealand, Iran, Kenya, Afghanistan, Tanganyika, Malaya, Uganda, Pakistan, Burma, Thailand and Ceylon.

The objects of the Congress are to discuss and promote concerted action in regard to scientific problems specially affecting industrial progress, commercial interests, health, etc., and to strengthen the bonds of peace among all the peoples around the Indian Ocean by promoting a feeling of brotherhood among scientists and the maintenance of harmonious relations between them. The Congress will have 10 sections and the topics suggested as a basis for discussion under each head are: *Agriculture*: (1) Plant Breeding, with particular reference to the production of improved varieties of wheat; (2) Soil Erosion and Soil Conservation Practices; (3) Tropical Agricultural Problems and the Use of Irrigation Waters Under Tropical Conditions. *Botany*: (1) Water Economy of Plants; (2) Plant Geography; (3) Classification of Plants. *Chemistry*: (1) Phytochemistry; (2) Forest Products. *Economics*: (1) International Trade of the Indian Ocean Area—Needs and Possibilities; (2) Comparative Consumption Standards of Populations. Policies and Measures Favourable to Removal of Disparities; (3) Factors Determining Productivity and Comparative Costs of Major Industries. *Geography & Oceanography*: (1) Nature of the Floor of the Indian Ocean, Recent Changes of Sea Level and Water Circulation in the Eastern Indian Ocean; (2) Climatology with reference to the Influence of the Asiatic Monsoon on Non-monsoonal Climates; (3) Over-Population and Migration Problems. *Geology*: (1) Origin of the Indian Ocean; (2) Pre-Cambrian Countries; (3) Economic Problems. *Physical Science*: (1) Geophysical Investigations; (2) Cosmic Rays and Solar Radiations; (3) Weather Forecasting, etc. *Public Health & Nutrition*: (1) Infectious and Quarantinable Diseases; (2) Dietary Deficiencies. *Social Sciences*: (1) Educational Standard; (2) Anthropology, Cultural Interchanges. *Zoology*: (1) Comparative Physiology; (2) Entomology and Parasitology; (3) Marine Biology; (4) Genetics.

Announcements

The First International Conference on Atomic Energy, organized by the British Atomic Energy Research Establishment, is being held in September 1950 at the Oxford University. The Conference will last for one week.

Lord Reay Maharashtra Industrial Museum, Poona — In connection with the celebrations of the birthday of J. N. Tata, an exhibition, " the Schoolboy and His Tools or the Manual Training Workshop", commencing March 3, 1951, is being organized at Poona by Lord Reay Maharashtra Industrial Museum. The exhibition is confined to small appliances and hand tools pertaining to all trades and will remain open for about six months. Further particulars are available from the Curator of the Museum.

The Andhra University has received a non-recurring grant of Rs. 3 lakhs from the Government of India for instituting a course in Geophysics (M.Sc. standard) and for conducting research in the subject. Another non-recurring grant of Rs. 2 lakhs has been sanctioned for implementing the expansion plans relating to the Departments of Chemistry, Physics and Geology.

Indian Naval College — A site measuring 138 acres has been acquired by the Government of India in the Lawsons Bay area of Vishakapatnam at a cost of Rs. 27 lakhs for the establishment of the Indian Naval College.

National Institute of Sciences of India Scholarships — The Council of the National Institute of Sciences of India made the following awards at its meeting held in May 1950: *Senior Research Fellowships*: S. P. Basu (Calcutta), Sukh Dev (Punjab) and P. B. Mathur (Banaras). *Junior Research Fellowships*: V. Chandrasekharan (Mysore), A. K. Choudhuri (Calcutta), G. S. Deshmukh (Banaras), B. D. Mundkur (Bombay), N. Sitapati (Andhra University), G. Venkatachalam (Mysore) and (Mrs.) Vidyavati (Lucknow). *Imperial Chemical Industries (India) Research Fellowships*: C. Balakrishnan (Madras), I. M. Chak (Bombay), A. G. K. Menon (Madras) and G. C. Mitra (Calcutta).

ERRATA

This Journal, 1950, **9A** (6), article entitled " Caustic Soda Industry ": *M/s Tata Chemicals Ltd.* point out that the correct production figures for soda ash (p. 185) at Dharangadhra and Mithapur Works are respectively 18,000 and 28,000 tons as estimated by the Indian Tariff Board, and not 50,000 tons as reported in the article.

1950, **9B** (6), article entitled " Investigation on Indian Radioactive Minerals — III: Monazite ": page 159, line 7, *for* F_2 (left) *read* P_2; page 159, line 33, *for* P_{11} *read* R_{11}; page 160, L.H. col., line 6, *for* $Th^{\pm V}$ *read* Th^{IV}; page 160, L.H. col., line 7, *for* P_4^{3-} *read* PO_4^{3-}; page 160, R.H. col., ref. 1 should *read*: NANDI & SEN: *J. sci. industr. Res.*, 1950, **9B**, 124.

1950, **9B** (7), article entitled " Alkaloidal Constituents of the Bark of *B. aristata* (*Rassaut*) ", page 161: Since the publication of this paper, the authors have pointed out that the correct m.p. of Native chloride 2 is 204°C. and not 235°C. as reported; page 164: the m.p. of palmatine nitrate is 239°C and not 245°C.

Progress Reports

BOTANICAL SURVEY OF INDIA

EXAMINATION AND IDENTIFICATION OF NEW COLLECTIONS, exploratory tours and reorganization of the Indian Museum, Calcutta, formed the bulk of the work carried out by the Botanical Survey of India during the year (1947-48) under review.

Over 2,500 specimens were collected during botanical excursions conducted in the Himalayan ranges of Sikkim, round about Bolepur and Santiniketan, Chota Nagpur hill tracts of the Singhbhum and Ranchi districts, Pareshnath Hills, Topchanchi Lake and hills in east Bihar, Burdwan district, Gopalpur-on-Sea, the islands in the Chilka Lake and parts of the Eastern Ghats in the Ganjam district of Orissa. The specimens included live and herbarium specimens of Rhododendrons, Primulas, Corydalis, Anemones, Abies, Juniperus and other alpines.

The examination of the collections brought from the little-explored region of the Rampa country have yielded some interesting results. Several new records of plants belonging to the Himalayas, Assam, Burma and the Andamans have also been identified.

In connection with the putting up of an exhibition of important medicinal plants of British and Indian Pharmacopoeias at the All-India Exhibition, Calcutta, an annotated list of Indian and other medicinal plants classified according to their therapeutical values was prepared. The department continued to render useful service as a bureau of information to a large clientele in India and abroad.

A review of the progress of botanical studies, conducted in India and included in the report, reveals that during the year under report over 200 scientific papers, covering such subjects as fossils, algae, fungi, ferns, embryology, cytology, ecology, anatomy, morphology, physiology, economic botany, systematic botany and tetratology and plant distribution were published. Fifty-five papers were on systematic botany alone. The new records which are additions to the published flora of Madras are the following: *Hypserpa cuspidata* (Wall.) Miers (*Limacia cuspidata* H.F. and T.). (Menisp), *Cochlospermum religiosum* Alston. *Paramignya scandens* Craib. (Assam) ; *Zizyphus glabra* Roxb. (Burma & Andaman); *Pygeisum acuminatum* Colebr. *Bupleurum mucronatum* W & A. *Pimpinella heyneanum* Wall. var typicum C.B.C. ; *Wendlandia exserta,* D.C. ; *Psychotria fulva* Ham ; *Linociera malabarica* Wall., *Balanophora indica* Wall., *Balanophora dioica* Brown, *Glochidion assamicum* Roxb., *Curculigo recurvata, Ophiopogon intermedium* D. Don, *Flagellaria indica, Luisa albens* Trin, *Microstegium monanthum* (Nees) *A. camus, Alectra indica* Benth., *A. thomsoni* H.F., *Hibiscus pungens* Roxb., *Epithema carnosum* Benth. ; *Smilax prolifera* and *Vitex penduncularis* Wall. var. Roxburghiana.

These discoveries confirm the belief that there are still vast tracts in India where even a preliminary exploration has not been conducted, and that the knowledge of the Indian flora is far from complete. A very interesting instance of extended range of distribution of a very effective medicinal plant is that of *Vitex penduncularis* var. Roxburghiana of Assam, which is an acknowledged specific for the black-water fever. This was collected from the slopes of Dumma Konda Hill (Madras). So also *Dichroa febrifuga* of the Sikkim Himalaya can very well be considered a substitute for quinine, Mahonia and Berberis species from which " Berberidin " has recently been isolated are considered to be efficacious in diabetes.

The Industrial Section of the Indian Museum has been reorganized and the restoration work has made substantial progress and classification, grouping and exhibition of certain selected exhibits have been introduced. Some of the important series are (1) drugs acting on the various systems in man, (2) tropical and sub-tropical fruits, (3) vegetables classified under root vegetables, leaf vegetables, fruit vegetables, and (4) fodder.

" Story method " of display, a new technique employed in some leading institutions abroad, has been introduced for the first time in the Indian Museum. Among the new exhibits arranged on these lines, mention may be made of the " Story of Paddy from Grower to Consumer ", " Story of Tobacco from Field to Factory ", " Story of Rubber ", " Story of Indigo " ; each story is told through specimens, photographs, coloured paintings and models. A diaroma on " paddy cultivation" consisting of 20 units of 6 models showing ploughing of the field, sowing, transplanting, harvesting, threshing, milling, par-boiling, stacking and transporting, was another exhibit prepared for the museum. Other new additions to the museum comprise of interesting and valuable collections of timber, food and fodder crops, fibres, cotton, narcotics, beverages, crude drugs, minor forest products, etc.

ROAD RESEARCH IN ENGLAND

WORK ON TRAFFIC FLOW, ROAD SURFACINGS AND plant and machinery figured most prominently in the activities of the Road Research Laboratory, Britain, reviewed in the report for the year 1948 (*Road Research,* 1948, *H.M.S.O.,* price 2*s.*).

Preliminary surveys of traffic in built-up areas, utilizing observer-cars, timed over selected stages of the route, have resulted in a technique from which the required data can be obtained with the minimum of labour. Methods of conducting " before and after " studies have been devised which should assist highway authorities to assess the value of traffic changes. Zebra pedestrian crossings, which had been developed the previous year on a model scale, were tested on a full scale at a few sites with the object of studying the effect on the behaviour of drivers and pedestrians ; and a marked improvement in the behaviour of both has been noticed. Following a survey of headlamp dazzle conducted during the year, regulations have been issued fixing a minimum height for lamps on vehicles. The work on braking tests has provided information on the best form of testing and on the condition of vehicles on the road.

The Laboratory has been successful in developing improved forms of portable automatic traffic counter and speedometer; the speedometer can be employed to divide vehicles into speed groups or, when connected to a recorder, to record data from which the speed of each individual vehicle may afterwards be deduced.

An improved method of determining the suction-moisture content relationship for soils has been developed and has been employed to examine mathematically the equilibrium of moisture distribution in saturated clays.

Research on soil stabilization has been mainly directed to improving the constructional methods used in the soil-cement process. Experimental trials have shown that the crushing strength of the soil-cement is mainly dependent on its state of compaction and the highest strength is obtained at maximum dry density, irrespective of the moisture content. During an investigation of soils from Abadan, Iran, it was found that the presence of 1 to 2 per cent of sulphates led to the disintegration of samples of the soil stabilized with cement. This was attributed to the crystallization of the salts following the evaporation of moisture from the specimen.

A property of aggregates that has so far received little attention, viz. the degree of roundness of the individual particles, has been investigated. This property, which is the main distinction between gravels and crushed rocks, is known to be of significance in road-making since it affects the workability of concrete and the stability of bituminous surfacings. It has been observed that the proportion of voids in a fully compacted aggregate of a given grading is determined largely by the roundness of the particles.

The ultrasonic method of concrete testing developed in 1946-47, involving measurement of the velocity of propagation of an ultrasonic pulse, has been found useful in testing the quality of concrete in the actual structural member.

A test has been developed to measure the susceptibility of road tar to deleterious oxidation. The test is employed to obtain data on reproducibility of tar composition. The susceptibility of tars to oxidation can be reduced if the phenolic constituents of the tar are removed.

Crystallization of hydrocarbon constituents has been found to develop in certain high aromatic tars, thereby affecting their durability on the road. The addition of 10 per cent (by weight) of a hard grade of bitumen to the tar was found to retard crystallization. It is also prevented if the fluxing oils used in the preparation of the tar were cooled and filtered to remove crystalline material.

An empirical test has been developed to determine the amount of potentially crystalline material in a tar; the method involves measurement of the amount of crystalline material in the oil distilling from the tar at temperatures below 350°C.

FOOD RESEARCH IN BRITAIN

THE REPORT OF THE FOOD INVESTIGATION BOARD, D.S.I.R., London, for the year 1948 (*H.M.S.O.*, price 9*d.*) contains many items of special interest. Notable advances have been made in the development and application of displacement chromatography by means of columns packed with ion-exchange materials and of filter-paper chromatography. These two methods greatly facilitate the quick separation and identification of substances often present in small quantities in complex mixtures and are being applied to the separation and identification of the polysaccharide components of the plant cell-wall, the isolation of organic bases and amino acids from protein hydrolysates and separation of the flavonoid and anthranoid pigments and other phenolic constituents of plants. In order to improve the quantitative analysis of amino-acid mixtures on the paper chromatogram, a continuous recording device has been developed which measures the change in conductivity at a given place on the paper while the solvent is flowing between electrodes. Amino acids do not possess an appreciable conductivity in neutral organic solvents; hence a new range of acidic solvents has been developed in which the amino acids largely function as bases. The presence of an amino acid in the solvent passing the electrodes effects a distinct change in its conductivity, the change being approximately proportional to the concentration of the amino acid.

Experiments on the refrigerated gas storage of bananas have revealed that an accumulation of carbon dioxide together with other volatile products of fruit metabolism in the atmosphere do not prolong their storage life. Ozone is now being introduced to destroy the ethylene and other volatile substances produced by the fruit, the accumulation of which, under conditions of restricted ventilation imposed in gas-storage, appears to accelerate ripening, even in the presence of carbon dioxide. In this respect apples and pears differ from the banana.

An improved method of freezing herrings in metal containers at a higher temperature than by air blast or multi-plate freezing methods has been devised. Herrings can be frozen down to −15°C. in about two and a half hours, in brine at −21°C. and may subsequently be stored at −20°C. with little change of flavour for 4 to 6 months respectively.

The study of the physiological factors affecting the ascorbic acid content of cross seedlings and potatoes has revealed that salts, which raise the *p*H of the cell sap, increase the synthesis of ascorbic acid. A relationship has been observed between the ascorbic acid and sucrose content of stored potatoes at 10°C. Storage at low temperature produces a temporary increase, which varies with the maturity of the potatoes and the length of their previous storage period.

Active invertase preparations have been obtained from young Bramley's seedling apples by the alkaline buffer extraction method followed by fractional precipitation.

The palatability, chemical composition and methods of improving whale meat were examined with a view to utilizing it for human consumption. Important relations have been established between the physical conditions of the meat, its *p*H and the state of *rigor mortis*. Based on these results, standards have been drawn up by the Ministry of Food for the inspection of whale meat.

INDIAN PATENTS

The following is a list of a few of the Patent Applications notified as accepted in the *Gazette of India*, Part II, Section 1, for June 1950.

Agricultural Chemicals

42383. Synthetic polymeric composition : *Condensing mono- or poly-hydroxy phenol and phenolsulphonic acid with an aldehyde in alkaline medium* — THE FERTILISERS & CHEMICALS, TRAVANCORE LTD.

42486. Continuous manufacture of superphosphate : *Using a mixture of phosphoric acid or sulphuric acid or both with nitric acid* — MANUFACTURES DE PRODUITS CHIMIQUES DU NORD ESTABLISSEMENTS KUHLMANN

Organic Chemicals

42433. Aromatic nitro compounds : 1-*phenyl*-1-1 : 3-*diacyloxy*-2-*acylamino-propane is nitrated with sulphuric acid-nitric acid mixture to obtain* 1-*para-nitro-phenyl*-1 : 3-*diacyloxy*-2-*acylamino-propane* — PARKE, DAVIS & CO.

41560. New dyestuffs : *Treating thiourea with compound containing at least one halogen-substituted methyl group linked to aromatic nucleus through an atom or group* — I.C.I. LTD.

Food & Kindred Products

42701. Refining vegetable and animal oils : *Neutralizing insufficiently free fatty acids, followed by precipitating pigment and colouring matter by means of strong lye* — AKTIEBOLAGET SEPARATOR

Metal & Metal Products

41831. Nodular cast iron : *Melting a carbide metal stabilizing agent to a molten condition, then graphitizing the melt and pouring a casting from the melt* — SMALLEY

41832. Desulphurization of iron and steel with metal hydrides : *Introducing a reagent comprising at least one metal hydride in a mass of molten ferrous metal to reduce sulphur content* — SMALLEY

41837. Distillation of aluminium from aluminium alloys : *Repeatedly circulating the molten metal through a low-pressure reaction chamber from two accessible reservoirs at normal pressure* — INTERNATIONAL ALLOYS LTD.

Rubber & Rubber Products

42519. Condenser rubbing aprons for textile apparatus : *Apron as an endless belt has at least operative surface formed of natural or synthetic rubber composition and grooved helically from end to end* — ANDRE RUBBER CO. LTD. & CLEMENTS

Stone, Clay & Glass Products

42215. Hydraulic cement compositions : *Containing* 0·0005 *per cent to* 0·1 *per cent, based on the weight of cement, of an alkylphenyl sulphonate containing* 9 *to* 18 *carbon atoms* — THE MASTER BUILDERS CO.

Textile & Textile Products

42144. Automatic looms for weaving : *Shuttle having a recess to be engaged by a weft-cutter when the shuttle is properly boxed but the cutter, when incorrectly positioned, is pushed to put the cop leading mechanism out of action* — SHIMWELL

41756. Breeding and rearing apparatus for silkworms : *The frame having plurality of trays and the movable trays arranged each above the fixed trays* — JARES

42728. Apparatus for dyeing yarn in package form particularly to spindles for supporting packages during the dyeing process : *A spindle assembly comprising a solid rod in threaded engagement with a tapered socket having a solid portion and a longitudinal bore for passage of dye liquor* — STIENEN

Miscellaneous

42328. Manufacture of carbon moulded bodies : *Moulding to the desired shape a mixture of powdered coal and plasticizing agents and firing the moulded shape under non-oxidizing conditions at a controlled rate of temperature* — C.D. PATENTS LTD.

42635. Sifting, sieving or sorting machines for tea or other commodity : *The sieve is actuated by a driving shaft which has a counterweight mounted thereon which keeps the machine in balanced position* — DEWAR & MCLEOD & CO. LTD.

40668. Lubricating compositions : *Consist of a lubricating oil base and a minor proportion of the salt of petroleum sulphonic acid and a polyvalent metal salt of an organic dithiophosphoric acid* — WAKEFIELD & CO. LTD.

41003. Colour correction in colour photography : *Stepping up the densities of the magenta and yellow image layers of a transparency positive or negative by an orange filter in a positive process or a cyan filter in a negative process during the exposure of the film* — HATTANDI

42257. Improved windmill : *Multiplicity of wings having concave and convex side, both lengthwise and breadthwise, wings being secured to rings on a shaft held vertically over the tower* — CHAUDARY

41688. Improved windmill : *Comprising a framework supporting a vertical driving shaft rotated by two or more pairs of wings located one above the other, each pair comprising two blades hingedly mounted at their upper edge to a frame fixed centrally to upper part of the driving shaft* — GREEN

Patented Inventions of the Council of Scientific & Industrial Research

STABILIZED DIAZO SALTS & ISODIAZOTATES

Patent No. 33261

R. J. MOUALIM & K. VENKATARAMAN

STABILIZED DIAZO SALTS AND ISODIAZOTATES ARE prepared from mono- or di-aminoanthraquinones for use in dyeing and printing. The diazotization is effected by making a fine paste of the powdered base with concentrated hydrochloric acid and adding solid sodium nitrite. One molecule of the base requires 7 to 10 molecules of hydrochloric acid. Diazotization is carried out with the theoretical amount of sodium nitrite and the end point is determined by using starch iodide as indicator. The diazo salt is precipitated either by adding anhydrous sodium sulphate or zinc chloride to the diazotized solution. The diazotized base or solution is treated with caustic soda or caustic potash for obtaining stable isodiazotates. A 50 per cent aqueous solution of the alkali is used ; a mixture of the diazotized base or solution and the alkali solution is heated to a temperature ranging from 115° to 125°C. for the separation of the isodiazotates.

Excellent yields of the diazo salts of remarkable stability to heat are obtained by employing this new method of diazotization which also avoids the use of expensive solvents. The diazo salts prepared in this manner are readily soluble in water and give a variety of shades including yellow, red, maroon, claret, brown and black when coupled on the fibre with commercial " naphthol ". The azoic dyeings are of good fastness to dry rubbing and of moderate fastness to wet rubbing. All the combinations except the blacks and yellows are of excellent fastness to bleaching. The kier-boiling fastness is good, the yellow and orange-brown shades being of inferior fastness. The fastness to light is excellent for all combinations.

2 : 4-DICHLORO-1-AMINOANTHRAQUINONE

Patent No. 34211

British Patent No. 634646

S. G. BEDEKAR & K. VENKATARAMAN

ACCORDING TO THE PRESENT INVENTION, 2 : 4-dichloro-1-aminoanthraquinone is prepared by directly chlorinating α-aminoanthraquinone in glacial acetic acid suspension by bubbling dry gaseous chlorine through the suspension at 90° to 100°C. The product thus obtained is purified by crystallization from suitable organic solvents like solvent naphtha.

Example — Ten parts of α-aminoanthraquinone are suspended in 100 parts of glacial acetic acid and, at 100°C., 8·5 parts of dry chlorine are passed in at a moderate rate. A vigorous mechanical agitation is maintained during the reaction, which is complete in 3 hr. At the end of the reaction the mixture is cooled and the product crystallizes out. The crude product so obtained may be purified by recrystallizing from solvent naphtha.

When pure, it is in the form of reddish-brown needles, m.p. 205°C. It dissolves sparingly in ether and readily in glacial acetic acid and solvent naphtha. The solution in concentrated sulphuric acid is yellow.

ANTHRAQUINONE ACID DYESTUFFS

Patent No. 34210

British Patent No. 634645

S. G. BEDEKAR & K. VENKATARAMAN

THE AUTHORS HAVE FOUND THAT THE 2 : 4-DIchloro-1-aminoanthraquinone can be conveniently employed for the manufacture of acid dyestuffs. 2 : 4-Dichloro-1-aminoanthraquinone is heated with an organic base such as aromatic amine, if desired, in the presence of a catalyst or acid-binding agent, the product being sulphonated prior to, or following, purification. Examples of organic bases used are *p*-toluidine, aniline.

Example — Three parts of 2 : 4-dichloro-1-aminoanthraquinone are dissolved in 30 parts of amyl alcohol and refluxed with 5 parts of *p*-toluidine, 1 part of anhydrous sodium acetate, $\frac{1}{20}$ part of anhydrous copper sulphate and $\frac{1}{20}$ part of copper bronze, till the reaction is complete. The solvent is then removed by steam distillation and the residue is purified by washing with 40 parts of a hot, low-boiling organic solvent like alcohol. The purified product is sulphonated by treatment with 5 parts of sulphuric acid monohydrate at 100°C. so as to obtain a product soluble in boiling water.

The products dye a beautiful blue on wool. The dyeings possess good fastness properties.

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CONTENTS

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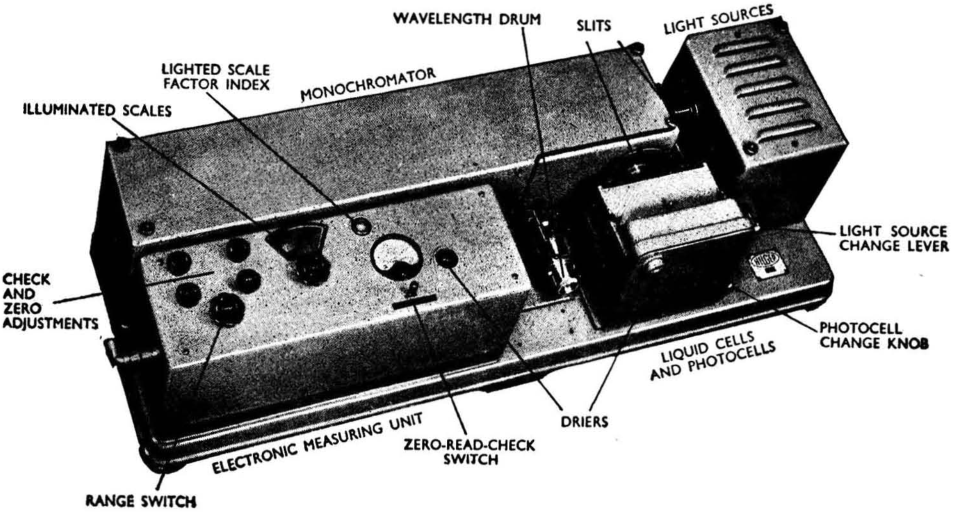
WAVELENGTH DRUM
SLITS
LIGHT SOURCES
LIGHTED SCALE FACTOR INDEX
MONOCHROMATOR
ILLUMINATED SCALES
LIGHT SOURCE CHANGE LEVER
CHECK AND ZERO ADJUSTMENTS
PHOTOCELL CHANGE KNOB
LIQUID CELLS AND PHOTOCELLS
DRIERS
ELECTRONIC MEASURING UNIT
ZERO-READ-CHECK SWITCH
RANGE SWITCH

A New Type of Scale-of-two Unit

B. RAMACHANDRA RAO

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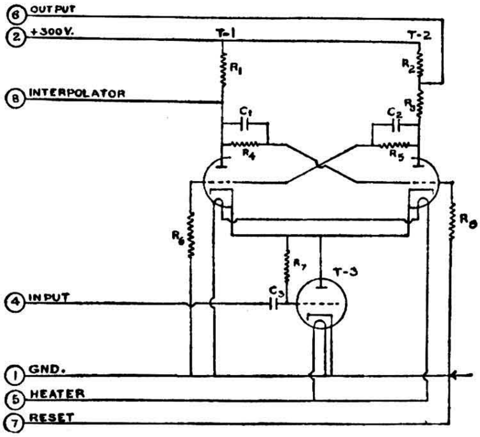
A new scale-of-two unit is described in which the triggering of scaling units is effected by the use of triodes as auto-bias as well as input. The circuit is sensitive and reliable in operation.

SCALING circuits are very widely used in nuclear counters to circumvent the limitations of the mechanical register by reducing the rate of counting. A single scale-of-two unit reduces the number of pulses to half, two such units to one-fourth and so on. In all modern types of counters these scaling circuits are constructed as replaceable plug-in units so that if any single scale-of-two unit is defective it is immediately replaced by a new one.

The well-known thyratron scaling circuit of Wynn-Williams[1] has been subsequently superseded by a number of high-speed vacuum tube circuits. Many such circuits based upon the trigger circuit of Eccles and Jordan[2] were developed by a number of workers[3-10]. Lewis[4] employed inductance coils and cuprous oxide rectifiers in the grid circuit whereas subsequent modifications employed condensers. The circuit devised by Lifschutz and Lawson[5] uses three 6C5 triodes, two of which are connected in the manner of Eccles and Jordan circuit and the third one negatively biased so as to respond to positive pulses only. Another circuit suggested by Reich[7] employs two pentodes in such a manner that the circuit has a high sensitivity to negative pulses only. A new method of triggering is employed in Don DeVault's[8] scaling circuit in which the tripping pulses are applied to the cathodes of the scaling triodes. In this circuit only positive pulses are effective because negative pulses will leak off through the conducting tube. The resolving time of this circuit is 170 microseconds. Subsequently this circuit has been simplified by Don DeVault[9] by using a double triode 6SC7 and eliminating choke coils in the plate circuit, but it requires careful adjustment of the cathode resistor for reliable operation. Further, the high resolving time of this circuit imposes a limitation on its use in the first stages of a counter employed for high rate of counting. The Higginbotham's[10] circuit is a replaceable plug-in type of unit and is one of the latest type. This circuit employs a double triode of the type 6SN7 or 6SL7 as scaling tubes connected together in the manner of the Eccles-Jordan circuit so as to assume one of the two stable states. The triggering from one state to another by an input pulse is effected by means of a double diode 6H6. It is essential in this circuit to keep the filament of the double diode at the potential of the high tension and hence a separate secondary winding is necessary for feeding the filaments of the diodes. The resolving time of this circuit using 6SN7 is about 5 microseconds. A number of these units have been constructed by the author on an open type of aluminium chassis of dimensions 3″ × 2″ × 2″ and have been in constant use in the laboratory.

A scale-of-two unit, in which a new method of triggering the scaling tubes is effected, is proposed here (FIG. 1). As in Higginbotham's circuit, a 6SN7 tube is used for scaling triodes but the auto-biasing arrangement for the scaling tubes is replaced by a miniature triode T_3 whose maximum plate potential is very



T-1 and T-2, 6SN7 ; T-3, 9002 ; R_1, 20K ; R_2, 2K ; R_3, 18K ; R_4 and R_5, 200K ; R_6 and R_8, 100K ; R_7, 0·5 meg.; C_1, C_2 and C_3, 50 pf.

FIG. 1 — CIRCUIT OF SCALE-OF-TWO.

nearly equal to the required auto-bias voltage. The characteristics of valve T_3 must be such that at the maximum plate potential and zero grid bias it is at the positive end of the I_p-E_g characteristic and draws an amount of current approximately equal to that of triode T_1 or T_2 in conducting state. Valve 9002 is very nearly found to satisfy these conditions and has got the additional advantage that it requires the same filament voltage as 6SN7. Pulses from the previous stage are applied to the grid of valve T_3 through a 50 pf. mica condenser with a grid leak of 5,00,000 ohms. That the triggering from one state to another is achieved only by negative pulses can be easily seen. As the valve T_3 is drawing almost saturation current, a positive input pulse at the grid of T_3 will not be able to change the plate current and hence the circuit will not respond to positive pulses. On the other hand, a negative pulse at the grid of T_3 will reduce the plate current of T_3 and initiate the triggering from one stable state to another in the usual manner. This method of triggering the scaling tubes by the use of a triode as auto-bias as well as input is new and quite reliable in operation. The circuit is highly sensitive because of the additional amplification obtained by the triode 9002 and a pulse of one volt or even less will be able to trigger the unit unlike the Higginbotham's circuit which requires considerably higher voltages for triggering. The high sensitivity of the unit made it possible to take a small output voltage for coupling to the next scaling unit, thereby reducing the effect of the output load on the scaling action of the first unit. The circuit has got the additional advantage that the scale-of-two unit is made extremely compact. The author has constructed the unit on an open aluminium chassis of dimensions 2¼″ × 1½″ × 1½″, the complete unit weighing only 100 gm. Further, as the filaments of both the valves can be maintained at ground potential, a single 6·3-volt secondary tap on the power transformer is sufficient whereas in Higginbotham's unit two separate 6·3-volt taps are necessary. Though the number of components used on this circuit are the same as in Higginbotham's circuit, heavy components required for auto-biasing and valve 6H6 in the latter circuit are replaced by a miniature valve 9002, 50 pf. condenser and a one-fourth watt resistance, thus enabling the circuit to be made highly compact and light. A number of these units are constructed by the author and are in regular use in this laboratory, the performance being quite satisfactory. Fig. 2 shows the new unit (b) photographed with the Higginbotham's unit (a) for comparison and shows the layout of the components. This circuit is being developed further and a detailed analysis together with the technical data will be shortly published.

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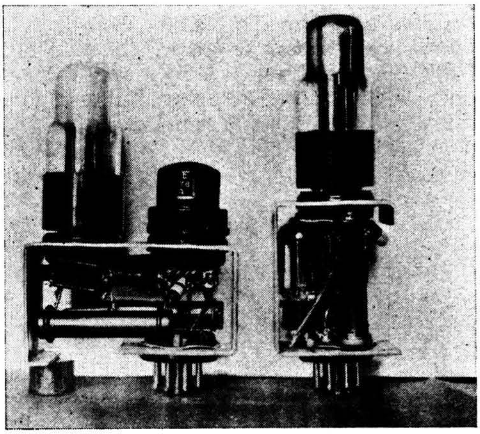
(a) (b)

FIG. 2

during this work and to the Council of Scientific & Industrial Research under whose auspices the work was carried out.

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Studies in the Syntheses of Quinolino-α-Pyrones—Part II

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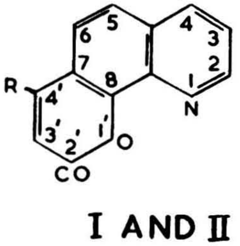
The synthesis of four new bases, quinolino-8-7-α-pyrone ($C_{12}H_9O_2N$), quinolino-8-7-α-(4′-methyl)-pyrone ($C_{13}H_9O_2N$), quinolino-8-7-α-(3′: 4′-cyclopenteno)-pyrone ($C_{15}H_{11}O_2N$) and quinolino-8-7-α-(3′ : 4′-cyclohexeno)-pyrone ($C_{10}H_{13}O_2N$), have been effected according to the method of Pechmann.

IN the preceding communication[1] the synthesis of some new quinolino-α-pyrones by the condensation of β-keto-esters with 6-aminocoumarin and subsequent cyclization after the method of Conrad and Limpach[2] was reported. The present paper describes the synthesis of some further new bases of the series by the application of Pechmann[3] reaction to 8-hydroxy-quinoline with β-keto-esters. Bobranski and Kochanska's synthesis[4] of quinolino-7 : 8-α-pyrone from 7-hydroxy-quinoline and malic acid appears to be the only earlier work in this line.

Four new bases, namely quinolino-8 : 7-α-pyrone, $C_{12}H_7O_2N$ (I), quinolino-8 : 7-α-(4′-methyl)-pyrone, $C_{13}H_9O_2N$ (II), quinolino-8 : 7-α - (3′ : 4′ - cyclopenteno) - pyrone, $C_{15}H_{11}O_2N$ (III), and quinolino-8 : 7-α-(3′ : 4′-cyclohexeno)-pyrone, $C_{16}H_{13}O_2N$ (IV), have been synthesized by the condensation of 8-hydroxy-quinoline with malic acid, ethyl acetoacetate, ethyl cyclopentanone-2-carboxylate and ethyl cyclohexanone-2-carboxylate respectively.

These bases, which are obtained in nearly theoretical yields, are sparingly soluble in common organic solvents and give all the colour tests and precipitation reactions with the usual alkaloidal reagents. Unlike the bases described in Part I of the series, these are strongly basic in character as there is no phenolic hydroxyl group in the molecule and form stable hydrochlorides which are fairly soluble in water. They are insoluble



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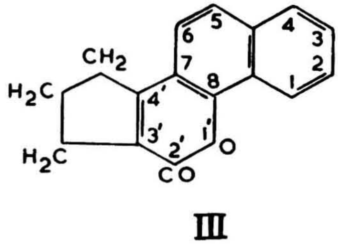

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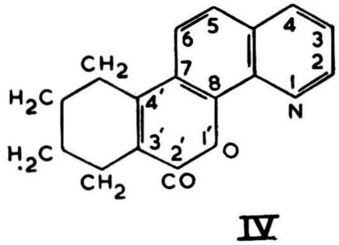

IV

in dilute alkalies but, on refluxing with alcoholic alkali, they go into solution (with a deep-yellow colour) on account of the opening up of the lactone ring.

Experimental

Quinolino-8 : 7-*α-pyrone*, $C_{12}H_7O_2N$ (*I*—) To absolute acetone (50 c.c.) was added 8-hydroxy-quinoline (1·45 gm.), malic acid (1·5 gm.) and freshly fused zinc chloride (3 gm.) and the reaction mixture was refluxed on the water bath for half an hour. After cooling, it was filtered and the residue washed with water, dilute alkali and then repeatedly with water. The base thus obtained was purified through solution in hydrochloric acid followed by precipitation with dilute sodium hydroxide solution and crystallized from cyclohexanone when greenish yellow needles, m.p. (above) 360°C. (decomp.), readily soluble in warm cyclohexanone, fairly soluble in xylene and insoluble in other organic solvents were obtained; yield 85 per cent. Found N, 7·13 per cent; $C_{12}H_7O_2N$ requires: N, 7·11 per cent.

Hydrochloride — Pale-yellow needles, m.p. 242°C. (decomp.).

Chloroplatinate — Yellow needles, m.p. 205°C. (decomp.).

Picrate — Deep yellow, rhombic crystals, m.p. 211°C.

Quinolino - 8 : 7 - *α* - (4′ - *methyl*) - *pyrone*, $C_{13}H_9O_2N$ (*II*)—8-Hydroxy-quinoline (5 gm.) was heated with an excess of ethyl acetoacetate (7·5 gm.) in the presence of freshly fused zinc chloride (5 gm.) at 140°C. in an oil bath for 5 min. The reaction mixture was cooled, the solidified product treated with a 20 per cent solution of caustic soda, filtered and washed repeatedly with water. The base thus obtained was crystallized from cyclohexanone; yellow needles, m.p. (above) 360°C. (decomp.), fairly soluble in hot xylene and cyclohexanone; yield 95 per cent. Found N, 6·66 per cent; $C_{13}H_9O_2N$ requires N, 6·63 per cent.

Hydrochloride—Yellow needles, m.p. 257°C.

Chloroplatinate — Brown-coloured needles, m.p. 282°C. (decomp.).

Picrate — Yellow rhombic crystals, m.p. 205°C.

Quinolino - 8 : 7 - *α* - (3′ - 4′ - *cyclopenteno*) - *pyrone*, $C_{15}H_{11}O_2$ N, (*III*) — A mixture of 8-hydroxy quinoline (1 gm.), cyclopentanone carboxylic ester (1·1 gm.) and freshly fused zinc chloride (2 gm.) was heated gradually in an oil bath, the temperature being allowed to rise up to 140°C., in the course of half an hour and then maintained at that point for 5 min. The cooled mass was treated with water, filtered and successively washed with water, dilute alkali (5 per cent), again with water and then acetone, dried and crystallized from cyclohexanone, when yellow needles, m.p. 360°C. (decomp.), fairly soluble in warm cyclohexanone were obtained; yield 80 per cent. Found N, 5·98 per cent; $C_{15}H_{11}O_2N$ requires N, 5·91 per cent.

Hydrochloride — Pale-yellow rectangular plates, m.p., 252°C.

Chloroplatinate — Deep-yellow needles, m.p. 207°C.

Picrate — Bright-yellow needles, m.p. 202°C.

Quinolino-8 : 7-*α*-(3′ : 4′-*cyclohexeno*)-*pyrone*, $C_{16}H_{13}O_2N$ (*IV*) — A mixture of 8-hydroxyquinoline (1·45 gm.), cyclohexanone carboxylic ester (1·8 gm.) and freshly fused zinc chloride (2 gm.) was heated in an oil bath at 140°C. for 5 min. The reaction product was worked up by following the procedure for base III and the resulting base crystallized from cyclohexanone as deep-yellow needles, m.p., 346°C. (decomp.)., highly soluble in warm cyclohexanone; yield 85 per cent. Found N, 5·62 per cent; $C_{16}H_{13}O_2N$ requires N, 5·58 per cent.

Hydrochloride — Pale-yellow rectangular plates, m.p. 259°C. (decomp.).

Chloroplatinate — Brown needles, m.p. 220°C. (decomp.).

Picrate — Deep-yellow rhombic crystals, m.p. 214°C.

Studies in the pharmacological activity of these compounds are projected and further work in this line is in progress.

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Studies in the Partially Reduced 4-Hydroxy-benzo-(h)-quinolines

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The synthesis of 2-methyl-4-hydroxy-7 : 8 : 9 : 10-tetrahydro-benzo-(h)-quinoline ($C_{14}H_{15}NO$), 2 : 3 - cyclopentano - 4 - hydroxy - 7 : 8 : 9 : 10 - tetrahydrobenzo - (h) - quinoline ($C_{16}H_{17}NO$) and 2 : 3 cyclohexano-4-hydroxy-7 : 8 : 9 : 10 - tetrahydrobenzo - (h) - quinoline ($C_{17}H_{19}NO$) has been carried out in two steps employing the Conrad-Limpach reaction.

4-HYDROXY quinolines are of interest as many of the plant alkaloids are derived from them. These include the angostura alkaloids[1] and those from some plants of the *Rutaceae* family[2]. Further, 4-hydroxy quinolines form the starting-point in the synthesis of 4-alkyl-aminoquinolines which have found considerable use in the treatment of malaria. On the other hand, 5 : 6-benzoquinolines (β-napthoquinoline) are noted for their marked physiological activity[3]. A good deal of work has been done on the synthesis of completely aromatic benzoquinolines and their derivatives[4-8] but the synthesis of benzoquinolines, reduced in the benzene ring, appears to be limited to the work of Bachman and Wetzel[9], and Lindner and Zaundauer[10]. In consideration of the facts referred to above, synthesis of partially reduced benzoquinolines, containing also, in the 4-position, a hydroxyl group, which could be replaced by an alkylamino group, was undertaken.

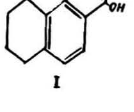
The present paper describes the synthesis of 2 - methyl - 4 - hydroxy - 7 : 8 : 9 : 10 - tetrahydro - benzo - (h) - quinoline, $C_{14}H_{15}NO$ (I), 2 : 3 - cyclopentano - 4 - hydroxy - 7 : 8 : 9 : 10 - tetrahydro-benzo-(h)-quinoline, $C_{16}H_{17}NO$ (II) and 2 : 3 - cyclohexeno - 4 - hydroxy - 7 : 8 : 9 : 10 - tetrahydro - benzo - (h) - quinoline, $C_{17}H_{19}NO$ (III). These bases have been synthesized in two steps by the application of the Conrad-Limpach reaction[11]. The general procedure followed consisted of (1) condensation of the tetrahydro-α-napthyl amine with the appropriate β-keto-ester by allowing the reaction mixture to stand overnight in the presence of a drop of hydrochloric acid (1 : 1) and (2) cyclization of the condensation product by adding it slowly to paraffin oil, preheated to 270°C., filtering off the paraffin and crystallizing the cyclized product from a suitable solvent.

The hydrochlorides and sulphates, both of which get readily hydrolysed in water, and 4-chloro-derivatives of the bases have been prepared. The weak basic character of these substances is due to the presence of a phenolic hydroxyl group which is also responsible for their solubility in dilute alkali. All the bases give precipitates with Dragendorff's reagent in acetic acid solution.

Experimental

2 - *Methyl* - 4 - *hydroxy* - 7 : 8 : 9 : 10 - *tetra-hydro-benzo-(h)-quinoline* (*I*) — 3 gm. (0·02 mol.) of tetrahydro-α-naphthylamine was added to 4 gm. (0·03 mol.) of acetoacetic ester and the mixture kept overnight adding a drop of hydrochloric acid (1 : 1). It was then taken up in ether and the ethereal solution was successively washed with water, dilute caustic soda solution and again with water, dried over anhydrous sodium sulphate and freed of the solvent. The intermediate β-arylamino acrylate was obtained as a light-red oil ; yield, 4·5 gm.

The crude intermediate (3·5 gm.) was added drop by drop to 40 gm. of paraffin oil, preheated to 270°C., and kept at this temperature for 5 min. On cooling, a crystalline product separated out which was filtered from the paraffin oil after dilution with petrol ether, thoroughly washed with



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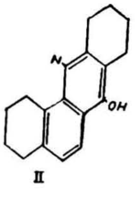

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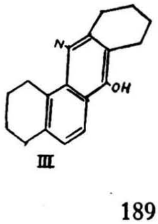

III

the same solvent and crystallized from alcohol, when colourless needles (m.p. 298°C.), insoluble in most organic solvents but soluble in alcohol and sparingly so in pyridine were obtained; yield, 2·2 gm. Found: C, 78·47; H, 7·38; N, 6·05; $C_{14}H_{15}NO$ requires: C, 78·87; H, 6·91; N, 6·58 per cent.

Hydrochloride — It came out almost immediately after initial solution of the base in conc. HCl, as colourless needles which, after filtration through a sintered funnel and washing with a little alcohol and ether, melted at 310°C. (decomp.).

Sulphate — On careful concentration of a solution of the base in 50 per cent sulphuric acid, the sulphate came out in colourless needles which, after filtration and washing with alcohol and ether, melted at 245°C. (decomp.).

2-*Methyl*-4-*chloro*-7:8:9:10-*tetrahydro-benzo-(h)-quinoline* — 0·1 gm. of (I) was refluxed on the water bath for 2 hr. with an excess of $POCl_3$ then poured on crushed ice, stirred, decomposed with 2 c.c. of conc. hydrochloric acid and filtered. On making the filtrate ammoniacal, a white precipitate was thrown down, which was washed and dried on porous tile and crystallized from alcohol; m.p. 120°C.

2:3-*Cyclopentano*-4-*hydroxy*-7:8:9:10-*tetrahydro-benzo-(h)-quinoline* (*II*) — It was prepared according to the method described for the preparation of (I), using cyclo-pentanone-carboxylic ester in place of aceto-acetic ester for the reaction with the amine. The crude cyclized product was charcoaled in boiling absolute alcohol from which it crystallized in colourless needles; m.p. 343°-45°C., insoluble in most organic solvents but soluble in pyridine and moderately in alcohol; yield of the intermediate product (theoretical) was 5·7 gm. and the yield of the cyclized product was 42 per cent on the weight of the intermediate. Found: C, 79·57; H, 7·33; N, 5·75; $C_{16}H_{17}NO$ requires: C, 80·33; H, 7·11; N, 5·85 per cent.

Hydrochloride — M.p. 300°C. (decomp.).

Sulphate — M.p. 250°C. (decomp.).

4-*Chloro derivative*—M.p. 110°C.

2:3-*Cyclohexano*-4-*hydroxy*-7:8:9:10-*tetrahydro-benzo-(h)-quinoline* (*III*) — It was prepared in a similar manner using cyclohexanone-carboxylate for the initial condensation with the amine. The crude cyclized product crystallized from boiling absolute alcohol in colourless needles; m.p. 346°-48°C. (decomp.), insoluble in most solvents but soluble in pyridine and moderately in alcohol. The yield of the intermediate (light-red oil) was 7·3 gm. and that of the cyclized product 46 per cent on the weight of the intermediate. Found: C, 79·61; H, 7·51; N, 5·80; $C_{17}H_{19}NO$ requires: C, 80·63; H, 7·51; N, 5·53 per cent.

Hydrochloride — M.p. 275°C. (decomp.).

Sulphate — M.p. 162°C. (decomp.).

4-*Chloro derivative* — M.p. 124°-25°C.

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Stability of Oil Varnish Emulsions

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The stability of an oil emulsion varnish under storage is affected by the phase volume ratio of the system as well as by the concentration of the emulsifying agent. An increase in the phase volume ratio gives more stable emulsions containing finely dispersed particles, provided the system contains a minimum concentration of the emulsifying agent.

ONE of the interesting developments in the field of paint technology during 1939-47 has been the development of emulsion paints — a new type of surface coating, using water as a diluent instead of thinners like turpentine and white spirit. This product, as prepared in the earlier years, suffered from several drawbacks, particularly that of inferior weathering properties and flatness of finish, but as a result of intensive research these defects have been overcome and now these emulsion paints have not only come to stay but are rapidly ousting out of the market the conventional oil paints by virtue of their cheapness, ease of handling and other good qualities.

While the manufacture of emulsion paints has made rapid progress, particularly in America, this has not been accompanied by a study of the fundamental principles of emulsion paint technology as applied to their manufacture. Most of what has been published on the subject during the last 12 years is in the form of patent literature, or it deals with some practical aspect of the problem and even to this day the manufacturer arrives at his final working formulae and processes more as a result of empirical experiments than on any well-understood principles. Hence, there is good scope for work on the mechanism underlying the formulation of emulsion paints.

The object of the present work was to determine the important property of storage stability of the emulsion vehicle before it was pigmented and see how far the size frequency analysis of the samples was able to throw light on the gradual degradation of the system and to find out the extent to which the stability of the system was affected by changes in the phase volume ratio and the amount of the emulsifying agent. Soap-stabilized emulsions have received more detailed study than any other type and hence were considered suitable systems for this work to start with.

Harkins and Beeman[1] carried out a series of size frequency analyses on soap-stabilized emulsions and recommended the study of the change in diameter, area and volume distribution of the emulsified particles with ageing as a method for determining stability. King and Mukherjee[2] have applied the size frequency method to compare emulsions stabilized by soaps and under different conditions. For our experiments an emulsion of a medium oil varnish stabilized by soap was chosen for investigation. Ammonium oleate was considered the best soap to be used as it contained a volatile alkali and would not give pronounced hydrophylic properties to the dried varnish film.

In this connection it may be noted that the two aspects of the problem investigated, namely the effect of phase volume ratio and that of concentration of the emulsifying agent in affecting the stability of the emulsion, are particularly significant in the case of emulsion paints. The vehicle for such a paint is a varnish emulsion which has to be stable for a length of time before it is pigmented. If the stability of the emulsion vehicle is unaffected by an increase in the phase volume ratio, a given volume of the vehicle will contain a greater quantity of the internal phase which ultimately becomes the film-forming material leading to greater economy of space and transport. Regarding the emulsifying agent, if the emulsion could be stabilized with a minimum of the emulsifying agent, the dried film would have better water resistance. The present investigation examines these two aspects of emulsion paints and in addition attempts to correlate stability and water resistance properties by means of a new factor.

Experimental

Reagents & Apparatus

Boiled linseed oil (to I.S.D. specifications).

Ester gum (Shalimar) — Acid value 8·5.

Staining dye — Sudan G — obtained as a brown powder by diazotizing aniline and coupling the same with β-naphthol. It was insoluble in water and acids and soluble in turpentine and varnish, staining the latter orange.

Medium oil varnish — Estergum (200 gm.) was melted in an enamelled pot and boiled linseed oil (200 gm.) added gradually with stirring. The contents were cooked for about 30 min., cooled and 60 c.c. turpentine added to reduce the viscosity to 8 poises at 85°F. To this the dye (2 gm.) was added.

Aqueous ammonia — 3·5 per cent solution.

Oleic acid — Technically pure.

10 per cent gelatine solution in water.

Reading graph — A transparent graph sheet to measure particle diameter up to 0·5 mm. was prepared as follows : The lines in the middle portion of a graph sheet measuring 8″ × 8″ were intensified with black ink. The paper was hung vertically and was illuminated sufficiently by diffused light. The distance of a copying camera from this graph was so adjusted that the image formed on the ground-glass screen measured exactly 8 cm. × 8 cm. After a sharp focus the exposure was made. A contact print obtained served as a transparent graph.

The emulsion varnish samples were prepared according to Table I in 20 c.c. pyrex glass tubes.

The required quantity of the varnish was taken in a test-tube, oleic acid and water added, and finally aqueous ammonia from a microburette to form the emulsifying agent *in situ*. The contents were shaken for about 10 min. One c.c. of the emulsion was pipetted out immediately, mixed with one c.c. of 10 per cent gelatine solution and a drop of the mixture placed on a microscopic slide and covered with a watch-glass. 30 min. were allowed for the emulsion to set completely in the gelatine. Meanwhile, the photomicrographic equipment was got ready. To start with, the camera was calibrated for reduction in magnification obtained in the eyepiece of the microscope. This was done by placing a piece of graph paper with a square hole of 2 mm. side in the centre, immediately below the eyepiece. The camera was brought immediately above the eyepiece and the width of the image obtained on the screen measured. This gave a value of 12·5 mm. By the naked eye the eyepiece gave a magnification 10 times, i.e. a square of 20 mm. side. For the experimental emulsion the magnification used was 400X and hence the photomicrograph obtained on the camera would have magnified the particles only 250 times. An enlarged positive print was obtained to get 1,000 magnification for the particles. Thus photomicrographs were obtained for all the samples immediately they were prepared and after a period of 3 days and 6 days. The exposure time was 2 to 3 min. Any free phase separating during this storage was removed before photographing. Figs. 1, 2 and 3 are photomicrographs of sample (6). The decrease in the fineness of dispersion with ageing is evident from the same. Figs. 4, 5 and

TABLE I — COMPOSITION OF EMULSION VARNISH

(10 *gm. prepared*)

SAMPLE No.	WT. OF VARNISH, gm.	WT. OF OLEIC ACID, gm.	AMMONIA ADDED, c.c.	WT. OF WATER, gm.	OIL PHASE, %	AQUEOUS PHASE, %	EMULSIFYING AGENT, %	EMULSIFYING AGENT BASED ON 100 GM. OIL PHASE, %
1	2	0·094	0·35	7·65	20	79	1	5
2	2	0·188	0·70	7·30	20	78	2	10
3	2	0·282	1·00	7·00	20	77	3	15
4	3	0·094	0·35	6·65	30	69	1	3·3
5	3	0·188	0·70	6·30	30	68	2	6·6
6	3	0·282	1·00	6·00	30	67	3	10
7	4	0·094	0·35	5·65	40	59	1	2·5
8	4	0·188	0·70	5·30	40	58	2	5
9	4	0·282	1·00	5·00	40	57	3	7·5

6 represent the photomicrographs of freshly prepared samples (7), (4) and (1) having a varying phase volume ratio. Comparing the same, it will be seen that a higher phase volume ratio gives rise to finer dispersions.

Size frequency analysis was done on the basis of the photomicrographs as follows: Since the emulsion particles were seen magnified 1,000 times, a particle of 1 micron diameter would occupy a square of 1 mm. on the photomicrograph. The total number of particles in the size range of 0·5μ to 10μ was determined by actual counting and the diameter of each particle measured with the help of the transparent graph. The particles were then arranged in their size order. The percentage of particles having the same diameter to the total number of particles

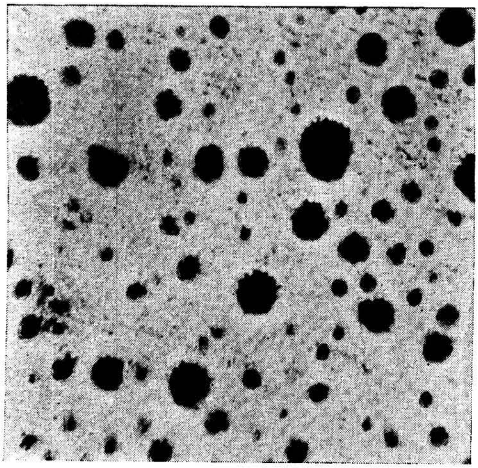


FIG. 1 — PHOTOMICROGRAPH OF EMULSION VARNISH SAMPLE (6) IMMEDIATELY AFTER ITS PREPARATION (1000X).

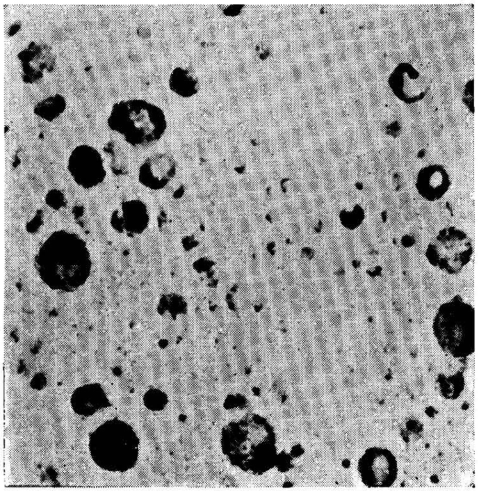


FIG. 3 — PHOTOMICROGRAPH OF EMULSION VARNISH SAMPLE (6) AFTER 6 DAYS AGEING (1000X).

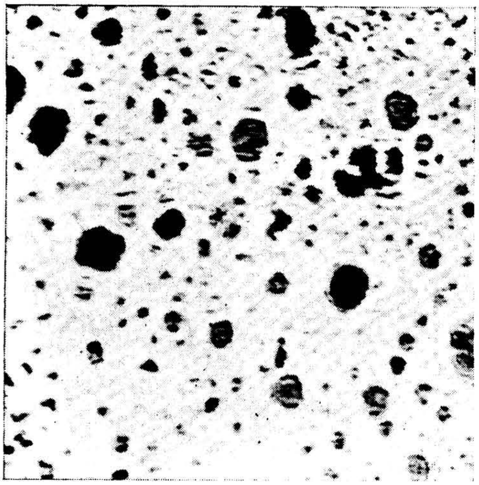


FIG. 2 — PHOTOMICROGRAPH OF EMULSION VARNISH SAMPLE (6) AFTER 3 DAYS AGEING (1000X).

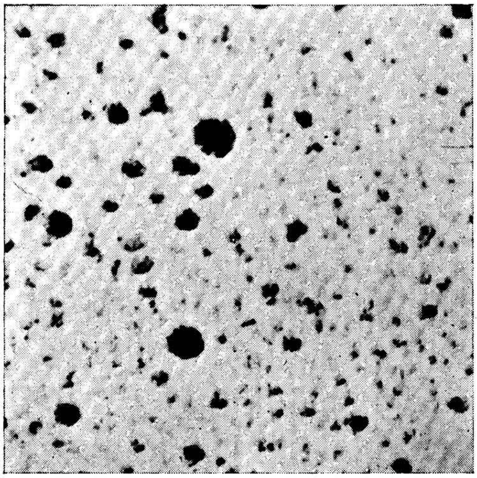


FIG. 4 — PHOTOMICROGRAPH OF EMULSION VARNISH SAMPLE (7) IMMEDIATELY AFTER ITS PREPARATION (1000X).

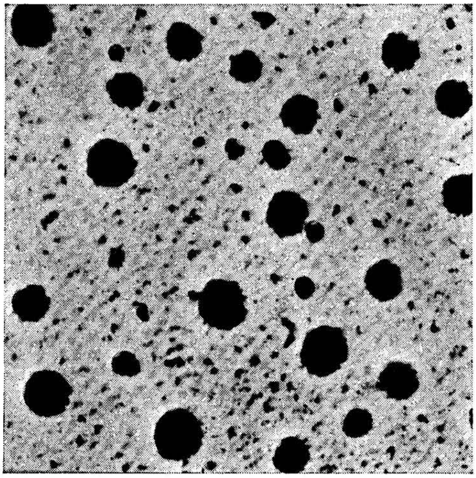


FIG. 5 — PHOTOMICROGRAPH OF EMULSION VARNISH SAMPLE (4) IMMEDIATELY AFTER ITS PREPARATION (1000X).

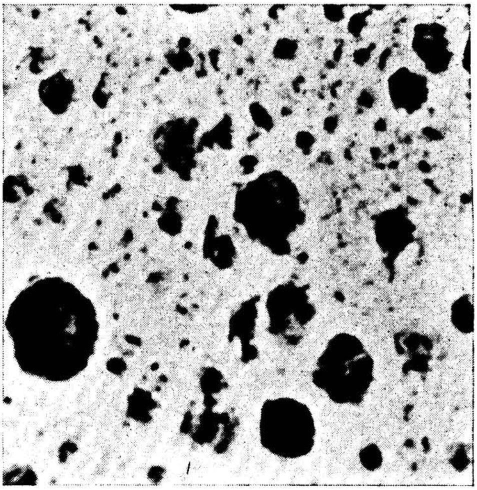


FIG. 6 — PHOTOMICROGRAPH OF EMULSION VARNISH SAMPLE (1) IMMEDIATELY AFTER ITS PREPARATION (1000X).

in the area was determined for each size in the range. Similarly, the per cent by volume occupied by particles having equal diameters to the total volume occupied by all the particles in the area was calculated for each size in the range. The results obtained in the case of sample (8) are recorded in Tables II, III and IV. The numerical distribution curves were obtained by plotting the values in column 1 against those in column 3. The volumetric distribution curves were obtained by plotting the values in column 1 against those in column 5. Figs. 7 and 8 represent the former and Figs. 9 and 10 represent the latter for the samples (1) and (3).

TABLE II — SIZE FREQUENCY ANALYSIS OF SAMPLE (8)

(*Readings taken immediately after preparation of emulsion*; *projected area*, 15·5 × 13·5 *cm.*; *magnification* 1000X)

PARTICLE DIAMETER, microns	NUMBER OF PARTICLES	TOTAL NUMBER, %	TOTAL VOLUME, c.c. × 10^6	TOTAL VOLUME, %	INTERFACIAL AREA, cm.^{2} × 10^6	SPECIFIC INTERFACE, cm.^{2}/gm.
0·5	108	39·41	0·00000707	0·27	0·8484	
1	57	20·80	0·00003225	1·232	1·935	
2	47	17·15	0·0001968	7·518	5·904	
3	29	10·58	0·0004101	15·670	8·202	$\frac{40\cdot3264}{0\cdot002618\times0\cdot982^5} = 11{,}580$
4	19	6·93	0·0006365	24·320	9·552	
5	8	2·92	0·0005240	20·020	6·288	
6	4	1·46	0·0004520	17·270	4·52	
7	2	0·73	0·0003590	13·720	3·077	
8						
9						
10						
	274	99·98	0·00261772	100·020	40·3264	

TABLE III — SIZE FREQUENCY ANALYSIS OF SAMPLE (8)

(*Readings taken after the emulsion was stored for 3 days ; projected area*, 15·5 × 13·5 *cm.* ; *magnification*, 1000*X*)

PARTICLE DIAMETER, microns	NUMBER OF PARTICLES	TOTAL NUMBER, %	TOTAL VOLUME, c.c. × 10^6	TOTAL VOLUME, %	INTERFACIAL AREA, cm.^{2} × 10^6	SPECIFIC INTERFACE, cm.^{2}/gm.
0·5	292	50·60	0·00001913	0·5363	2·2956	$\frac{50\cdot056}{0\cdot003567 \times 0\cdot9825} = 14{,}290$
1	160	27·73	0·00008384	2·351	5·0304	
2	77	13·31	0·0003226	9·044	9·678	
3	27	4·679	0·0003817	10·300	7·634	
4	4	0·693	0·000134	3·757	2·010	
5	3	0·520	0·0001965	5·509	2·358	
6	6	1·04	0·0006786	18·020	6·786	
7	5	0·866	0·0008980	25·180	7·698	
8	2	0·346	0·000536	15·030	4·020	
9	1	0·173	0·0003818	10·300	2·546	
10	0	...	...	...	...	
>10	0	...	...	...	...	
	577	99·957	0·00356747	100·0273	50·0560	

TABLE IV — SIZE FREQUENCY ANALYSIS OF SAMPLE (8)

(*Readings taken after the emulsion was stored for 6 days ; projected area* 15·5 *cm.* × 13·5 *cm.* ; *magnification* 1000*X*)

PARTICLE DIAMETER, microns	NUMBER OF PARTICLES	TOTAL NUMBER, %	TOTAL VOLUME, c.c. × 10^6	TOTAL VOLUME, %	INTERFACIAL AREA, cm.^{2} × 10^6	SPECIFIC INTERFACE, cm.^{2}/gm.
0·5	198	30·70	0·00001297	0·209	1·5564	$\frac{85\cdot3692}{0\cdot006205 \times 0\cdot9825} = 14{,}010$
1	224	34·72	0·00011738	1·892	7·044	
2	116	18·04	0·00048604	7·832	14·5812	
3	55	8·507	0·00077770	12·530	15·554	
4	22	3·41	0·00073700	11·880	11·055	
5	15	2·326	0·00098250	15·830	11·790	
6	7	1·085	0·00079210	12·760	7·921	
7	1	0·155	0·00017960	2·896	1·5396	
8	4	0·620	0·00107200	17·280	8·040	
9	0	...	...	...	...	
10	2	0·310	0·00104800	16·900	6·288	
>10	1	0·155	...	...	...	
	645	100·028	0·00620500	100·009	85·3692	

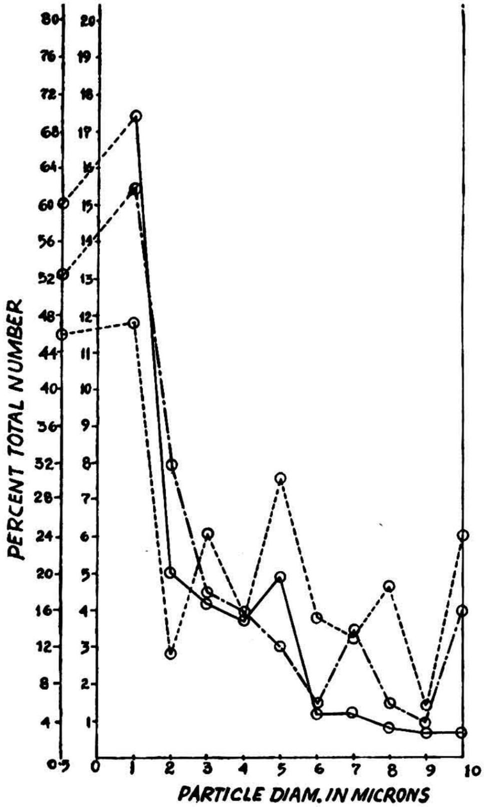
The interfacial area was then calculated for all the particles, assuming a spherical size for them. Knowing the total volume occupied by all the particles (in the projected area) and the density of the varnish, the specific interface in sq. cm./gm. was calculated. Table V gives the values for specific interface in sq. cm./gm. for the various samples when freshly prepared and after ageing.

TABLE V — SPECIFIC INTERFACE OF EMULSION VARNISHES

SAMPLE No.	OIL PHASE, %	FRESH SAMPLE	3-DAY OLD	6-DAY OLD
1	20	10190	8986	7879
2	20	10510	9223	8040
3	20	11050	9776	8363
4	30	11000	10990	10520
5	30	11800	11340	11200
6	30	12660	12390	11900
7	40	16550	12830	10300
8	40	15580	14290	14010
9	40	13740	13600	13350

On ageing there is a decrease in the interfacial area due to coalescence. A variation of specific interface with ageing provides useful information regarding the stability of the emulsion. This variation with time has been graphically represented in the case of samples (1) and (2) (FIG. 11).

King and Mukherjee[2] have defined emulsion stability quantitatively by means of the product of the initial specific interface and the reciprocal of the rate of decrease of interfacial area with time. Making use of the same relation, the stability factor for each of the samples under investigation was determined as follows : Since the variation of specific interface with time is known for each sample, the difference in the specific interface for the sample after the first part of storagy (0 to 3 days) was calculated and divided be the time lapse to get the rate of decrease of interfacial area with time. Similarly, knowing the difference in the value of specific



o——o, fresh sample ; o · — · — · o, 3-day sample ; o - - - o, 6-day sample.

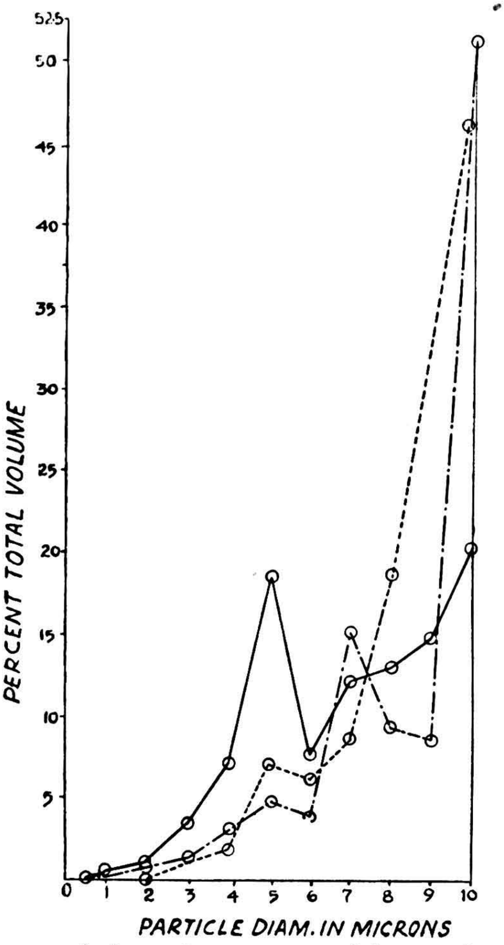
FIG. 7 — NUMERICAL DISTRIBUTION CURVE FOR SAMPLE (1).

interface after the second part of storage (3 to 6 days), the rate for the second part was calculated. From these figures the average rate was determined and its reciprocal multiplied by original specific interface to give the factor of stability. Table VI gives the factor of stability for the different samples.

It is desirable to evaluate the water resistance properties of the paint films and correlate it with the stability of the emulsion paint. A new factor has been worked out to indicate the water resistance of the ultimate film consistent with storage stability, based on the following assumptions: The adsorbed film of the emulsifying agent was mono-molecular. The length of the oriented soap molecule[3] was 25 × 10^{-8} cm. and the

TABLE VI — STABILITY FACTOR OF EMULSION VARNISH SAMPLES

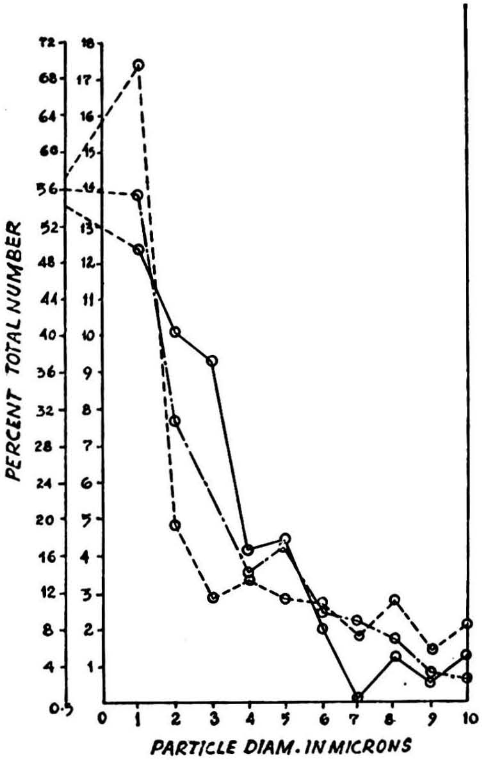
SAMPLE No.	INITIAL SPECIFIC INTERFACE, $cm.^2/gm.$ (S)	DECREASE OF INTERFACIAL AREA WITH TIME, first period	DECREASE OF INTERFACIAL AREA WITH TIME, second period	AVERAGE RATE OF DECREASE OF INTERFACIAL AREA, days	STABILITY FACTOR, $S \times do/ds$
1	10190	401·0	369	385	26·50
2	10510	429·0	394	412	25·50
3	11050	428·0	266	447	24·70
4	11000	3·3	157	80	137·50
5	11800	153·0	47	100	118·00
6	12660	90·0	167	128	100·00
7	16550	1240·0	676	958	17·28
8	15580	430·0	93	262	59·50
9	13740	47·0	83	65	211·40



o——o, fresh sample ; o · — · — · o, 3-day sample ; o - - - o, 6-day sample.

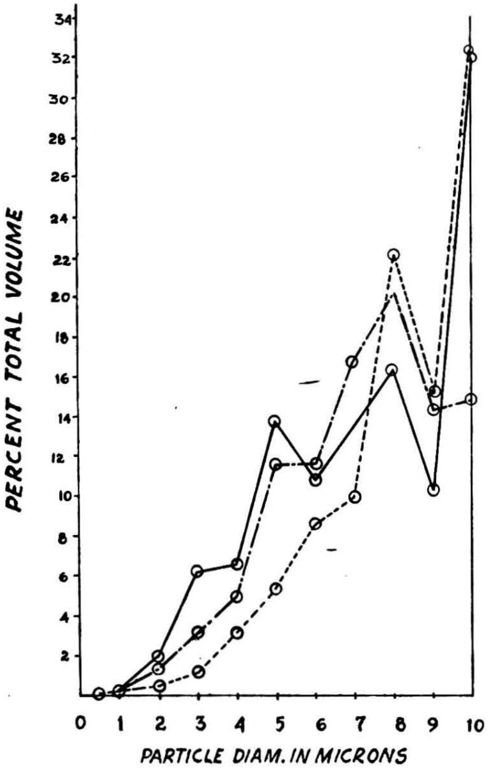
FIG. 8 — VOLUMETRIC DISTRIBUTION CURVE FOR SAMPLE (1).

weight of soap (sp. gr. 0·9) per sq. cm. of interface was $25 \times 10^{-8} \times 1 \times 0{\cdot}9 = 22{\cdot}5 \times 10^{-8}$ gm./sq. cm. Since the specific interface was known for the samples, the theoretical soap concentration to emulsify 100 parts of the oil phase was calculated as $22{\cdot}5 \times 10^{-8} \times$ sp. interface × 100 gm. soap/100 gm. of oil varnish. Assuming the absence of hydrolysis of soap, the theoretical concentration of the emulsifying agent to emulsify 100 gm. of oil varnish was calculated for the stable emulsions. This value was compared with the actual concentration and the ratio of actual concentration to the theoretical was determined. Greater the value of this ratio means greater the occlusion of the hydrophylic emulsifying agent in the ultimate varnish film. By dividing the stability factor by this ratio, λ, the new factor was obtained. Table VII indicates the results.



o——o, fresh sample ; o·—·—·o, 3-day sample ; o - - - o, 6-day sample.

FIG. 9 — NUMERICAL DISTRIBUTION CURVE FOR SAMPLE (3).



o——o, fresh sample ; o·—·—·o, 3-day sample ; o - - - o, 6-day sample.

FIG. 10 — VOLUMETRIC DISTRIBUTION CURVE FOR SAMPLE (3).

Discussion

A good deal of published literature is available on the effect of phase volume ratio

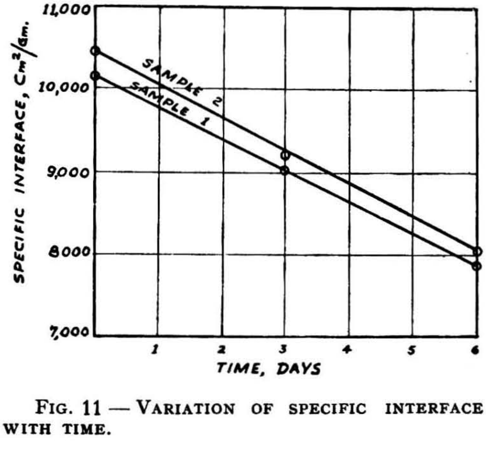


FIG. 11 — VARIATION OF SPECIFIC INTERFACE WITH TIME.

TABLE VII — RELATION BETWEEN THE STABILITY FACTOR OF THE EMULSION VARNISH TO THE RATIO OF ACTUAL & THEORETICAL CONCENTRATION OF EMULSIFYING AGENT

SAMPLE No.	SPECIFIC INTERFACE (S) cm.^{2}/gm.	MINIMUM SOAP CONCN. TO FORM MONOMOLECULAR FILM, gm.	THEORETICAL CONCN. OF SOAP BASED ON 100 GM. INT. PHASE	ACTUAL CONCN. BASED ON 100 GM. INT. PHASE	RATIO OF ACTUAL/ THEORETICAL CONCN. OF SOAP	STABILITY FACTOR	QUALITY	λ-RATIO OF STABILITY FACTOR TO THE RATIO OF ACTUAL/THEORETICAL CONCN. OF EMULSIFYING AGENT
1	10190	0·002293	0·2293	5·0	21·8	26·5	Unstable	...
2	10510	0·002368	0·2368	10·0	42·2	25·5	Unstable	...
3	11050	0·002486	0·2486	15·0	60·3	24·7	Unstable	...
4	11000	0·002475	0·2475	3·3	13·3	137·5	Unstable	...
5	11800	0·002655	0·2665	6·6	24·8	118·0	Stable	118·0/24·8=4·8
6	12660	0·002849	0·2849	10·0	35·1	110·0	Stable	100·0/35·1=2·9
7	16550	0·003724	0·3724	2·5	6·7	17·3	Unstable	...
8	15580	0·003506	0·3506	5·0	14·3	59·5	Stable	59·5/14·3=4·2
9	13740	0·003092	0·3092	7·5	24·2	211·4	Stable	211·4/24·2=8·7

on the stability of emulsions. Hatschek[4] is of the opinion that the stability of an emulsion is generally not complete until the figure corresponding to closest packing, namely a phase volume ratio of 74·06 is reached. Zhukov and Buschmakin[5], on the other hand, believe that an optimum relation corresponding to 1 : 1 exists for the formation of stable emulsions and that any divergence from this ratio results in a decrease of stability. This view is supported by the work of Mattiello[6]. Then again, as an increase in phase volume ratio increases the internal viscosity, this latter indirectly makes for better stability. Whatever be the optimum phase volume ratio, our experiments confirm that within the range studied, an increase in phase volume ratio improves stability of emulsion varnishes. It also gives rise to finer emulsions, which is in agreement with the results obtained by Marshall[7].

According to the oriented adsorption theory, the emulsifying agent gets adsorbed at the interface and serves as a protective film which resists the impact of the emulsified molecules in motion, if the quantity of emulsifier added to the system is insufficient to protect the interface completely, the system would obviously show signs of coalescence and instability. Hence there is a theoretical minimum for the quantity of emulsifier required for securing stability. In order to arrive at this figure, however, it is very necessary to take into account all the important factors that come into play, namely:

1. The interfacial area of the disperse phase.
2. The concentration of the emulsifying agent required to reduce the interfacial tension sufficiently to ensure emulsification.
3. Structural compatibility of the non-polar ends of the emulsifier and oil.
4. Extent of hydrolysis of the emulsifying agent.
5. The extent to which it goes into colloidal solution and its function in stabilizing the emulsion.
6. The thickness of the interfacial film.

The value of interfacial area solely depends on the degree of dispersion. The interfacial area or, more precisely, the specific interface can be easily calculated from a size frequency analysis based on photomicrographic examination of the emulsion with reference to the values in Table VI.

As regards the second factor, the work of Quincke and Plateau[8] and that of Bancroft[9] has already shown how the lowering of the surface tension is intimately connected with emulsification and maintenance of stability. The work of Harkins, Brown and Davies[10] has shown that sodium oleate in a concentration of 0·03 N gives excellent emulsions with a reduction of interfacial tension between benzene and water from 35·0 ergs/sq. cm. to 2·2 ergs/sq. cm. Harkins and Zollman[11] have also shown that reduction of interfacial tension between water and benzene to below 10 dynes/sq. cm. permits easy emulsification, and that 0·1 N sodium oleate is effective in reducing the same to 2·64 dynes/sq. cm. From all this data it is safe to assume that 0·1 N solution of soap will suffice to reduce tension to facilitate emulsification. In our experiments a 3 per cent solution of ammonium oleate was used.

As regards structural compatibility, if the emulsifying agent is to remain at the interface, it is very necessary that the polar and non-polar portions of the molecule are of approximately equal strength[12]. Ammonium oleate is more suitable as an emulsifying agent than sodium oleate by virtue of its weaker polar group giving it lesser tendency to be pulled into the aqueous phase and a non-polar end consisting of a fatty acid similar to that existing in the oil phase. Hence, from the point of view of compatibility, it should be a satisfactory emulsifying agent.

The hydrolysis of the soap would ordinarily be an important factor to be taken into account without which any estimation of the quantity of emulsifier required would be wide off the mark. Unfortunately no data appears to have been published on the hydrolysis range for ammonium salts of the fatty acids though work has been done on the sodium and potassium salts[13]. Though there is no published data for ammonium oleate, in view of the fact that it is a salt of a weak base, we would be justified in assuming that it would hydrolyse still less as compared with its corresponding sodium or potassium salt ; hence in our experiments the effect of hydrolysis of the emulsifying agent may be taken to be negligible.

The effect of the colloidal nature of soap solutions is of no importance in this particular set of experiments under consideration as colloidal solutions are not likely to form at the concentrations used.

It is when we come to the question of the thickness of the interfacial film that we meet with a considerable divergence of views.

Griffin and Rienmann[14,15] have shown that interfacial films are essentially monomolecular. The investigations of Harkins and Beeman[16] support this view. On the other hand, the work of Nanoka[17], Seymour, Tartar and Wright[18] and Ramsden and Seifriz[19,20] is against this view. Thus, as far as our present knowledge goes, there is a good deal of divergence of opinion as to whether the interfacial film is monomolecular or polymolecular. In actual industrial practice, the quantity of emulsifier used is rarely less than 6 times or more than 20 times the theoretical quantity required to form a monomolecular layer at the interface. But if we remember that a good part of the emulsifier remains ineffective by remaining in solution in the outer phase and thus is not brought into action at the interface, and besides if we take into consideration the well-known tendency in industrial practice to err on the safe side, for purposes of evaluation of the minimum quantity of emulsifying agent required, we could assume that the interfacial layer is monomolecular.

Thus, to sum up, in the particular state of emulsions we are concerned with, the main factors which determine the minimum quantity of emulsifying agent required to stabilize emulsions would appear to be the specific interface, lowering of the surface tension, extent of hydrolysis of the emulsifying agent, the thickness of the interfacial film and the extent to which the emulsifying agent remains in aqueous solution.

Assuming 0·1 N as a suitable concentration of the emulsifying agent for optimum reduction of interfacial tension, and presuming that hydrolysis is negligible, the theoretical quantity of the soap necessary can be calculated on the basis that the interfacial layer is one molecule thick. Table VII gives this figure in column 4 together with the actual concentration used in column 5. From this it will be seen that while samples (5) and (6) are stable, containing 6·6 per cent and 10·0 per cent of emulsifying agent based on 100 gm. of the internal phase, samples (2) and (3) are unstable in spite of a higher concentration of the emulsifier. This is very likely due to the fact that though stability is dependent to a great extent on the concentration of the emulsifying agent, it is also governed by the internal agitation of the droplets. With a reduction in the phase volume ratio (20 per cent internal phase), the internal kinetic effect comes more into play overcoming the resistance of the interfacial film, resulting in a rupture of the same and coalescence of the particles. The stability of samples (4) and (7) is poor because of insufficient emulsifying agent.

Sample (8) is a stable emulsion. This represents a phase volume ratio of 40 per cent and an actual concentration of 5 per cent of emulsifying agent based on 100 of the internal phase as against a theoretical figure of 0·3506, i.e. a ratio of actual to theoretical of 14·3.

The excess indicated may be necessary for the formation of polymolecular films and to allow for the emulsifying agent not used up but remaining in the aqueous phase in solution without undergoing hydrolysis.

While stability is an all-important property in the case of emulsions, in the case of emulsion varnishes or paints, the resistance of the ultimate film to water, which is governed to a great extent by the hydrophilic nature of the emulsifying agent, is also an important consideration. Coupling these two considerations a new factor "λ" has been tentatively put forward to account for both stability and film character. From the values for "λ" for the different samples (TABLE VII) it will be seen that sample (9) with a value of 8·7 appears to be the best vehicle for subsequent pigmentation.

The work also throws light on the distribution of particles in terms of particle size. Fischer and Harkins[21] report that in the case of paraffin oil emulsions the majority of particles had a diameter of about 1μ while in the case of benzene it was smaller. King and Mukherjee[2], examining olive oil emulsions, found that the maximum number of particles had a diameter of about 1μ and that the greatest contribution to the area was given by particles between 6 and 7μ. In the case of our emulsions the maximum number of particles have been found distributed in the size range 0·5μ to 1·5μ and that the greatest volume of oil is dispersed in the range 6μ to 8μ.

Thermodynamically, emulsion instability can be defined as the rate of decrease of its interfacial area with time; hence measurement of the extent of interface at various periods of time in the life of an emulsion should provide a quantitative measure of its properties. Since the tendency to coalesce is more for particles having a small diameter, ageing should decrease the number of particles of a small size and increase the bigger ones. Therefore, the degree of stability will be given by the change in the numerical distribution curve with time. King and Mukherjee[2] have obtained numerical distribution curves for samples which were allowed to stand for several days. From the curves which intersect near about 1μ, it may be inferred that the tendency to coalesce is maximum for particles having a diameter of 1μ or less and minimum for larger particles. The variation of interfacial area with time plotted for the same samples gives a straight line for most of their samples. In the case of our experiments, the numerical distribution curves show that the coalescence tendency is apparent up to a diameter of 5μ. The variation of specific interfaces with time is almost a linear function for some of the samples (FIG. 11).

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Studies in the Preparation of Viscose & Cellulose Acetate from the Pulps of Indigenous Cellulosic Materials

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Pulps from bamboos, reeds and bagasse, after a preliminary treatment with alkali, are suitable for the manufacture of viscose and acetate rayons.

CERTAIN species of bamboo, e.g. Manwel (*Dendrocalamus strictus*), thorny bamboo (*Bambusa arundinacea*) and *Kamti*, and reeds, bagasse, jute fibres, etc., yield high grade pulps if suitably processed[1,2]. The pulps prepared from these approximate in chemical composition to rayon grade pulp[2]. But the cellulose isolated from the different plant tissues, though chemically identical, differ from cotton cellulose both in reactivity and physical properties. Their behaviour towards chemical reagents used in the viscose, acetate and other processes will be largely governed by physical properties.

The present study relates to the behaviour of different cellulose preparations towards chemical reagents employed in the viscose and acetate processes and the optimum conditions for obtaining technically suitable products. Also acetic acid esters have been prepared from the pulps to ascertain their suitability as raw materials for the manufacture of cellulose products.

Experimental

Preparation of Viscose — Samples of pulps were reduced to the fibrous condition and cleaned by hand. Viscose preparations obtained from them were examined for degree of ripening, viscosity, free alkali content and cellulose. Finally they were converted into transparent films by Doree's method[3]. The periods of ripening and of coagulation were noted in each case.

Acetylation — The pulps were purified by steeping them in 8 per cent caustic soda solution (1 : 10) for 1·5 hr. at room temperature ; they were then washed, scoured, washed again and dried. Before acetylation they were treated with glacial acetic acid (1 part cellulose and 1 part acetic acid), the quantity of acid so used being deducted from the acetylation mixture.

The acetylation mixture consisted of glacial acetic acid, acetic anhydride and a catalyst, viz. sulphuric acid. Sulphuric acid was used as catalyst on account of its cheapness. The mixture was cooled to 10°C. before adding the pulp and maintained at that level for about 15 min. The temperature was allowed to rise gradually to 30° to 35°C. till the dissolution was complete and a transparent, acrid-smelling, semi-fluid mass was obtained. A portion of this mass when added to water gave a tough, leather-like precipitate, soluble in chloroform.

Secondary Acetates — The hydrolysis of primary acetate to secondary acetate (acetone soluble) was brought about by dilute acetic acid ; in some cases, mixtures of glacial acetic acid and 10 per cent sulphuric acid were employed. The hydrolysing agent was slowly added to the primary acetate solution under vigorous stirring, the temperature being maintained below 40°C. The mixture was stored in an incubator at 50° to 55°C., until a test portion, when coagulated by the addition of water, gave a light fibrous precipitate soluble in acetone. When the reaction was complete, the solution was poured into a large quantity of cold water. The precipitate was washed free of acid, stabilized and dried. The acetyl content of the preparation was determined by Eberstadt method[4].

Preparation of Films — The secondary acetate was dried in a vacuum desiccator and the dried material dissolved in acetone. The solution was allowed to ripen for 24 hr. and filtered through a sintered glass funnel. The clear filtrate was spread over mercury to form films. The films so obtained were dried at 100°C. to remove the last traces of solvent. After cooling them in a desiccator,

TABLE I — PREPARATION OF PULP

RAW MATERIAL	ACID EMPLOYED	PRELIMINARY TREATMENT				KIER TREATMENT				CHLORINE CONSUMED, % ON MATERIAL	YIELD OF PULP, %	ASH IN RAW MATERIAL, %	ASH IN PULP, %	ALPHA-CELLULOSE	
		Concentration		Temperature, °C.	Duration	Pressure, lb.	Duration, hr.	Alkali concentration at beginning,	Ratio of alkali to bagasse					In pulp, %	In raw material, %
		Solution %	On material %					% on material							
Bagasse	Sulphuric	1·0	10	...	...	20	2	NaOH — 15	1 : 20	...	...	...	...	...	...
	Hydrochloric	1·0	10	100	1 hr.	...	Intermediate bleach		...	3·15	32·95	3·39	0·31	87·84	28·94
Reeds	Hydrochloric	0·5	5·0	Heated to boil	Soaked overnight	20	1	NaOH — 15	1 : 20	...	...	...	...	...	...
						20	2	NaOH — 15	1 : 15	...	...	...	...	...	...
						60	6	NaOH — 15 Na_2S — 5	1 : 15	4·52	41·0	4·78	0·23	85·42	35·02
Manwel bamboo	do	0·5	5·0	do	do	20	2	NaOH — 15	1 : 15	...	...	...	...	...	...
						60	6	NaOH — 15 Na_2S — 5	1 : 15	6·00	36·08	2·06	0·28	85·82	30·96
Kamti bamboo	do	0·5	5·0	do	do	20	2	NaOH — 15	1 : 15	...	...	...	...	...	...
						60	6	NaOH — 15 Na_2S — 5	1 : 15	4·05	40·18	5·57	0·26	86·10	34·59
Thorny bamboo	do	0·5	5·0	do	do	20	2	NaOH — 15	1 : 15	...	...	...	...	...	...
						60	6	NaOH — 15 Na_2S — 5	1 : 15	4·28	38·04	2·12	0·26	87·08	33·12

strips of uniform width (15 mm.) were cut out and their tensile strength measured in a Schopper machine.

Discussion

The cooking and bleaching processes employed for preparing pulps and the compositions of the pulps are recorded in Table I. The pulps have an α-cellulose content of over 85 per cent and an ash content varying from 0·2 to 0·3 per cent.

Experimental details relating to the preparation of viscose from pulps are given in Table II. It will be seen that the weight of alkali cellulose in each case is 2 to 3 times the weight of the primary pulp. Excess of caustic soda, which would result in the formation of compounds like sodium thiocarbonate and affect the quality of viscose, was avoided. The alkali cellulose was matured for 4 days in all the cases except in the case of bagasse C viscose which was matured for 7 days.

The consumption of carbon disulphide for xanthation varies with different pulps. Bagasse pulp requires 48·81 to 73·21 per cent; reed pulp, 76·70 to 90·65 per cent; Manwel, *Kamti* and thorny bamboo pulps, 92·1 to 95·16, 90·18 to 98·50 and 96·56 to 99·00 per cent respectively. The carbon disulphide required for standard American alpha pulp is 80·19 per cent on the weight of the pulp. These figures are, however, somewhat higher than the actual requirements, as an appreciable portion of the carbon disulphide was lost during the treatment. Bagasse pulp required comparatively less carbon disulphide than either bamboo or reed pulps for complete xanthation. This characteristic gives bagasse pulp an advantage as a source of viscose rayon.

Viscose for spinning should have not only a definite viscosity but also a definite degree of ripening, and its alkali and cellulose contents should lie within specified limits. The viscose in each case was treated with 10 per cent acetic acid, and the degree of ripening, cellulose and alkali contents and viscosity were estimated (TABLE III). It will be observed that the viscose from bagasse pulp ripens within 6 to 10 days and sets within 14 to 19 days, whereas viscose from reed pulp takes 5 to 7 days for ripening and 9 to 14 days for setting. The corresponding periods for the American alpha pulp were 10 and 16 days respectively. It

TABLE II — PREPARATION OF VISCOSE

Pulp from	Treatment	Wt. of pulp, gm.	Vol. of 17·5% caustic soda for mercerization, c.c.	Wt. of alkali cellulose, gm.	Maturation period of alkali cellulose, days	Amount of carbon disulphide reqd. for xanthation, % on pulp	Vol. of the solvent (sod. hydroxide-sod. sulphite) used, c.c.
Bagasse	A	37	558	108	4	69·73	130
	B	37	558	115	4	73·21	135
	C	37	558	112	7	48·81	100
	D	37	558	105	4	62·77	145
Reeds	A	18	280	45	4	86·23	60
	B	37	558	90	4	87·17	145
	C	37	558	96	4	90·65	145
	D	37	558	85	4	83·70	145
	E	37	558	80	4	76·70	145
Manwel bamboo	A	37	558	98	4	95·16	145
	B	37	558	106	4	92·10	160
Kamti bamboo	A	37	558	96	4	96·4	145
	B	37	558	110	4	98·5	160
	C	16	237	40	4	90·18	72
Thorny bamboo	A	37	558	100	4	96·56	145
	B	37	558	112	4	99·00	160
Regular alpha-pulp (American)	A	37	558	108	4	80·19	145

TABLE III — ANALYSIS OF VISCOSE

Material	Viscose (Cf. Table II)	Ripening period, days	Gelling * time after preparation, days	Degree of ripening in c.c. of 10% NH_4Cl	Viscosity time, sec.*	Free alkali % gm. Na_4OH	Cellulose, %
Bagasse	A	7	15	8·9	29·2	7·87	7·65
	B	6	15	9·0	28·5	7·61	8·16
	C	7	14	7·7	25·8	7·98	8·10
	D	10	19	9·6	28·0	8·01	8·51
Reeds	A	5	9	...	...	...	...
	B	7	11	9·8	58·6	8·12	7·50
	C	6	11	9·2	55·9	8·00	7·10
	D	7	13	8·9	59·5	7·73	7·59
	E	7	14	8·4	61·1	7·17	7·56
Manwel bamboo	A	5	11	9·4	80·1	8·10	8·40
	B	7	14	9·2	68·8	8·65	8·25
Kamti bamboo	A	5	12	9·1	82·4	7·88	8·30
	B	7	14	8·9	72·5	8·25	8·24
	C	7	14	8·2	70·8	8·07	8·00
Thorny bamboo	A	7	12	9·1	75·0	8·30	8·46
	B	6	11	9·65	79·2	9·01	8·10
Alpha-pulp (American)	A	10	16	7·92	30·4	8·19	8·70

* Mean of 6 readings.

TABLE IV — CHANGES IN VISCOSITY OF VISCOSE DURING RIPENING

Bagasse 'D'	Age of viscose, hr.	18·0	66·0	90	138·0	186·0	210	234·0	258	306	354
	Viscosity, sec.*	15·3	16·6	18·2	19·4	23·8	26·20	28·0	29·6	33·9	38·7
Reeds 'E'	Age of viscose, hr.	18·0	45·0	69	117·0	141·0	168	216·0	...	...	...
	Viscosity, sec.*	30·4	29·6	35·3	44·7	51·1	61·07	68·5	...	...	...
Manwel bamboo 'A'	Age of viscose, hr.	18·0	44·0	92	120	162·0	186	210·0	...	...	...
	Viscosity, sec.*	55·2	54·0	68·5	80·1	91·0	99·5	108·1	...	...	...
Kamti bamboo 'A'	Age of viscose, hr.	16·0	40·0	72	98	125·0	183·0	208·0	...	...	...
	Viscosity, sec.*	58·4	55·0	66·2	72·0	82·4	98·0	110·4	...	...	...
Thorny bamboo 'A'	Age of viscose, hr.	20·0	44·0	68	95	144·0	170	194·0	220	...	...
	Viscosity, sec.*	52·1	50·6	55·2	61·4	70·0	75·0	81·1	86·8	...	...

* Mean of 6-7 readings.

may be further seen that with the same quantity, viz. 145 c.c. of the solvent used to dissolve cellulose xanthate, bamboo pulps yield viscose of high viscosity expressed in sec., 68·80 to 82·40, while the viscose from reed pulp has a viscosity of 55·9 to 61·10. The viscose from bagasse pulp has a low viscosity, viz. 25·80 to 29·20.

The rates of the changes of viscosity during the ripening of viscose were measured, and the results obtained are recorded in Table IV and are graphically represented in Fig. 1. It will be observed that the viscosity of bagasse viscose increases slowly, while those of reed and bamboo viscose are fairly rapid. Bagasse viscose has a longer coagulation period.

The cellulose sheets prepared from the different viscoses were strong and transparent. A slight milkiness was observed in the sheets and this is probably due to the presence of carbon disulphide vapour which could not be completely removed from the container in our experiments.

The primary acetates were prepared under different experimental conditions. In some cases, pulps were pre-swollen with glacial acetic acid with a view to increase the reactivity of cellulose and so minimize the time required for acetylation as in Mile's process[5]. A preliminary treatment with sodium hydroxide was given in some cases to remove the pentosans, etc. The experimental conditions and the nature of polyacetates obtained are recorded in Table V.

It was observed during these experiments that the time required for the formation of triacetate soluble in chloroform is about

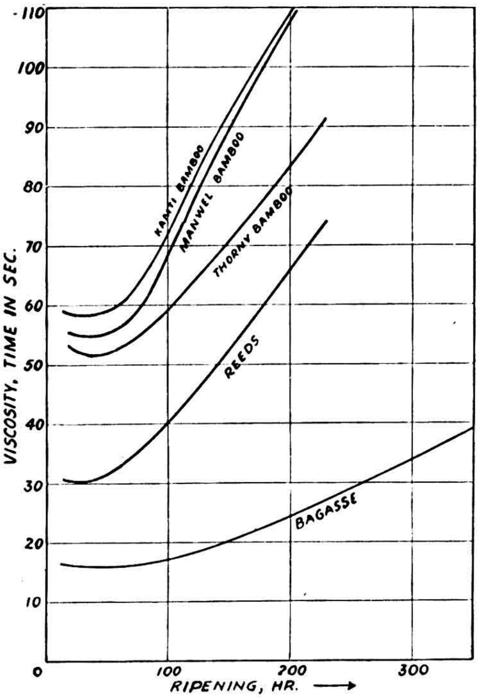

FIG. 1—CHANGES IN THE VISCOSITY OF VISCOSE DURING RIPENING.

TABLE V — PREPARATION OF PRIMARY ACETATES

PULP FROM	EXPERIMENT No.	ACETYLATION MIXTURE PER GM. OF CELLULOSE			TEMPERATURE OF THE REACTION, °C.	PERIOD OF REACTION, hr.	NATURE OF THE POLYACETATE FORMED
		Acetic acid, glacial, c.c.	Acetic anhydride, c.c.	Catalyst, viz. sulphuric acid (com.), c.c.			
Reeds	1	3·75	3·75	0·025	10 30	0·25 6·00	Very viscous, somewhat transparent mass, pulp not completely dissolved
	2	3·75	3·75	0·05	10 30	0·25 6·00	Less viscous, more transparent with few undigested fibres, slightly coloured. Tough ppt. soluble in chloroform with little alcohol.
	3	3·75	3·75	0·075	10 30	0·25 6·00	Pulp was completely soluble giving transparent, viscous, slightly coloured mass, fairly tough ppt. soluble in chloroform with little alcohol
	4	3·75	3·75	0·10	10 30	0·25 5·00	Syrupy solution, slightly coloured, weak ppt. soluble in chloroform with little alcohol
	5	3·75	3·75	0·025	10 30	0·25 20·00	Pulp completely soluble. Fairly tough ppt. soluble in chloroform with little alcohol
	6	2·75 (Pre-treated with 1 c.c. of gl. acetic acid)	3·75	0·05	10 30	0·25 4·00	Viscous, transparent mass. Pulp completely soluble, slightly coloured, very tough ppt. readily soluble in chloroform with little alcohol
	7	2·75	3·75	0·05	18	20·00	Viscous, transparent mass with very few fibres unacted, tough ppt. soluble in chloroform with little alcohol

TABLE V — PREPARATION OF PRIMARY ACETATES — *contd.*

PULP FROM	EXPERIMENT No.	ACETYLATION MIXTURE PER GM. OF CELLULOSE			TEMPERATURE OF THE REACTION, °C.	PERIOD OF REACTION, hr.	NATURE OF THE POLYACETATE FORMED
		Acetic acid, glacial, c.c.	Acetic anhydride, c.c.	Catalyst, viz. sulphuric acid (com.), c.c.			
Reeds	8	2·75 (Mild bleach and pre-treated with 1 c.c. of gl. acetic acid)	3·75	0·05	10 30	0·25 4·50	Viscous, transparent, colourless mass. Tough ppt. soluble in chloroform with little alcohol
Pulp purified to remove hemicelluloses as described	9	3·75	3·75	0·05	10 30	0·25 8·00	Colourless, transparent, viscous mass with few undigested fibres. Tough ppt. soluble in chloroform; more easily in presence of little alcohol
	10	2·75 (Pre-swollen with 1 c.c. of gl. acetic acid)	3·75	0·10	10 30	0·25 4·00	Colourless, transparent, viscous mass, pulp completely soluble, ppt. not quite tough, soluble in chloroform with little alcohol
	11	2·75	3·75	0·05	10 30 35	0·25 4·00 1·00	Colourless, transparent, syrupy solution with all the fibres dissolved. Tough leather-like ppt. soluble in chloroform, more easily in presence of little alcohol
Kamti **bamboo**	1	3·75	3·75	0·05	10 30	0·25 6·00	Very viscous, somewhat transparent, slightly coloured mass with few fibres undissolved
	2	3·75	3·75	0·05	10 30	0·25 8·00	Pulp completely soluble, viscous, transparent but slightly coloured mass. Tough ppt. soluble in chloroform with little alcohol
	3	2·75 (Pre-treated with 1 c.c. of gl. acetic acid)	3·75	0·05	10 30	0·25 5·00	Slightly coloured syrupy solution, very tough ppt. soluble in chloroform with little alcohol
	4	2·75	3·75	0·10	10 30	0·25 4·00	Slightly coloured syrupy solution. Ppt. weak, soluble in chloroform with little alcohol
Pulp purified	5	3·75	3·75	0·05	10 30	0·25 6·00	Viscous, transparent mass with few fibres undissolved. Tough ppt. soluble in chloroform but not very freely
	6	2·75 (Pre-swollen with 1 c.c. of gl. acetic acid)	3·75	0·05	10 30 35	0·25 4·00 1·00	Colourless, transparent, syrupy solution. Tough leather-like ppt. soluble freely in chloroform with little alcohol
Bagasse	1	3·75	3·75	0·025	10 30	0·25 4·00	Pasty mass with few fibres unacted
	2	3·75	3·75	0·05	10 30	0·25 6·00	Pulp completely dissolved. Viscous, transparent mass with slight colouration. Tough ppt. soluble in chloroform in presence of alcohol
	3	3·75	3·75	0·10	10 30	0·25 4·00	Syrupy solution. Ppt. very weak, soluble in chloroform in presence of little alcohol
	4	2·75 (Pre-treated with 1 c.c. of gl. acetic acid)	3·75	0·05	10 30	0·25 4·00	Viscous solution, pulp completely dissolved, tough ppt. soluble in chloroform with little alcohol
	5	2·75	3·75	0·05	10 30 35	0·25 4·00 1·00	Almost colourless, transparent, viscous solution. Tough ppt. soluble in chloroform more easily in presence of little alcohol
Alpha pulp (American)	1	2·75 (Pre-treated with 1 c.c. of gl. acetic acid)	3·75	0·05	10 30	0·25 4·00	Viscous, quite transparent clear solution. Ppt. tough, leather-like, soluble in chloroform with little alcohol
	2	2·75	3·75	0·05	10 30 35	0·25 4·00 1·00	Clear, transparent, syrupy solution. Tough ppt. soluble in chloroform, more easily in presence of little alcohol

TABLE VI — HYDROLYSIS OF THE PRIMARY ACETATES

Primary acetate (from Table II)	Experiment No.	Hydrolysing agent per gm. of cellulose	Temperature, °C.	Period of hydrolysis, hr.	Percentage yield of secondary acetate	Acetyl content expressed as acetic acid, %	Tensile strength of the films, kg./mm.²	Nature of the secondary acetate
Reeds	1	25 c.c. gl. acetic acid + 8·8 c.c. distilled water	55	12	...	...	...	White fibrous ppt. hardens on drying, not completely soluble in acetone. Films — somewhat brittle and not quite clear
	2	6 c.c. gl. acetic acid + 6 c.c. distilled water	55	12	...	...	...	White fibrous ppt. not freely soluble in acetone. Films — fairly strong but not quite clear and transparent
	3	do	30	18	...	...	...	White powdery ppt. soluble in acetone. Films — clear but brittle
	4	do	30	14	...	...	...	White powdery ppt. soluble in acetone. Films — very brittle
	5	3 c.c. gl. acetic acid + 3 c.c. of 10% sulphuric acid	55	14	...	...	...	White fibrous ppt. soluble in acetone. Films — not very strong
	6	do	30	18	120·6	54·60	5·8	Light fibrous ppt. easily soluble in acetone. Films — quite clear, strong, transparent
	7	do	30	18	110·0	51·60	5·2	White fibrous ppt. soluble in acetone. Films — strong but not clear
	8	do	30	18	118·7	54·88	5·6	The fibrous precipitate easily soluble in acetone. Films — quite clear, transparent and strong
	9	3 c.c. of gl. acetic acid + 3 c.c. of 10% H_2SO_4	50	12	128·4	50·82	5·6	Ppt. fibrous but hard, not very freely soluble in acetone. Films — quite strong but not quite clear and transparent
	10	1 c.c. of gl. acetic acid + 1 c.c. of distilled water	50	12	130·8	54·60	5·8	Ppt. fibrous and light, soluble in acetone. Films — clear, transparent but somewhat brittle
	11	do	50	12	131·5	55·12	6·1	Ppt. fibrous, light, freely soluble in acetone. Films — very clear, transparent and strong
Kamti **bamboo**	1	3 c.c. of gl. acetic acid + 3 c.c. of 10% sulphuric acid	30	24	...	...	...	White fibrous ppt. hardens on drying. Not easily soluble in acetone. Films — brittle
	2	do	30	18	118·8	52·78	5·1	White fibrous ppt. freely soluble in acetone. Films — quite clear, strong, transparent
	3	do	30	18	126·3	55·20	5·6	do
	4	do	30	18	...	...	...	White fibrous ppt. soluble in acetone. Films — quite clear but brittle
	5	1 c.c. of gl. acetic acid + 1 c.c. of distilled water	50	12	130·80	49·92	5·0	Ppt. fibrous but not quite light and not freely soluble in acetone. Films — fairly strong but not clear
	6	do	50	12	134·10	55·45	5·8	Ppt. quite light and fibrous, easily soluble in acetone. Films — strong and transparent
Bagasse	1	12 c.c. of gl. acetic acid + 12 c.c. of distilled water	55	12	...	...	...	Fibrous ppt. which became powdery on drying. Not freely soluble in acetone. Films — brittle
	2	3 c.c. of gl. acetic acid + 3 c.c. of 10% sulphuric acid	30	17	120·50	54·16	5·4	White fibrous ppt. soluble in acetone. Films — transparent, clear and strong

TABLE VI—HYDROLYSIS OF THE PRIMARY ACETATES—*contd.*

PRIMARY ACETATE (FROM TABLE II)	EXPERIMENT NO.	HYDROLYSING AGENT PER GM. OF CELLULOSE	TEMPERATURE, °C.	PERIOD OF HYDROLYSIS, hr.	PERCENTAGE YIELD OF SECONDARY ACETATE	ACETYL CONTENT EXPRESSED AS ACETIC ACID, %	TENSILE STRENGTH OF THE FILMS, kg./mm.^{2}	NATURE OF THE SECONDARY ACETATE
Bagasse	3	3 c.c. of gl. acetic acid + 3 c.c. of 10% sulphuric acid	30	17	...	...	...	White powdery ppt. soluble in acetone. Films — very brittle
	4	do	30	17	122·0	53·88	5·4	White fibrous ppt. freely soluble in acetone. Films — glossy, transparent and strong
	5	1 c.c. of gl. acetic acid + 1 c.c. of distilled water	50	14	128·6	54·18	5·6	Light, fibrous ppt. soluble in acetone. Films — strong and transparent
Alpha pulp (American)	1	3 c.c. of gl. acetic acid + 3 c.c. of 10% sulphuric acid	30	18	142·7	55·20	6·4	White fibrous ppt. freely soluble in acetone, transparent and strong films
	2	1 c.c. of gl. acetic acid + 1 c.c. of distilled water	50	12	143·5	55·25	6·5	Light fibrous ppt. readily soluble in acetone. Films — very clear, transparent and strong

20 hr. at 18°C. and 6 to 8 hr. at 30°C. The period could be reduced to about 4 hr. by swelling the cellulose with acetic acid before actual acetylation. The reaction period decreases with increase in the amount of sulphuric acid; quantities exceeding 10 per cent of the weight of the pulp had a detrimental effect on the final product.

The triacetate was slightly coloured except in the case of reed pulp (treatment 8, TABLE V) which was given a mild bleach prior to acetylation. Transparent and colourless masses were obtained also by treatments 9, 10 and 11 (TABLE V).

The results of experiments on the hydrolysis of triacetate are recorded in Table VI. Acetone-soluble products were obtained by hydrolysing the triacetate with 50 per cent acetic acid at 50°C. for 12 to 16 hr. The secondary acetates were obtained as light fibrous precipitates (TABLE VI, treatments 10 and 11). The percentage yield of secondary acetate from reed pulp is 131·5 per cent; from *Kamti* bamboo, 134·1 per cent; from bagasse 128·6 per cent. The yield in the case of alpha pulp is 143·5 per cent. The acetyl content of all the acetates is 55·0 per cent. The tensile strengths of films prepared from the acetates are as follows: reed pulp, 6·1 kg./sq. mm.; *Kamti* bamboo, 5·8 kg./sq. mm.; bagasse pulp, 5·6 kg./sq. mm.; alpha pulp, 6·5 kg./sq. mm.

These data clearly indicate that pulps from reeds, bamboo and bagasse, after a preliminary treatment with caustic soda, are suitable for use in the rayon industry.

The investigations were conducted with equipment ordinarily available in a laboratory. Better results could be obtained with specialized equipment for stirring and beating pulps, for de-aeration and filtration of viscose and for casting films. The data recorded here should be regarded as indicative of the possibilities. Trials on a pilot-plant scale are necessary to enable definite conclusions to be drawn on the suitability of these raw materials for large-scale exploitation.

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Long Chain Aliphatic Nitriles from Methyl Esters of Fatty Acids

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A method is described for the preparation of nitriles of long chain fatty acids by the action of gaseous ammonia on the methyl esters. Good yields (60-65 per cent) of the nitriles are obtained without employing a catalyst. A preferential saponification method for the estimation of the esters in the presence of nitriles has been standardized.

LONG chain fatty acid nitriles of the type of R-CN are used as plasticizers, insect repellents and as intermediates in the preparation of a host of cationic detergents. They are prepared by the ammonolysis of fats and fatty acids. Two procedures are described in literature. In the first, liquid ammonia is made to react with fatty acids or oils in the presence of a catalyst like ammonium chloride in a Carius tube or a steel autoclave[1-2]. The pressures developed by liquid ammonia at temperatures which sometimes range up to 165°C. are so high (at 132°C. the pressure is 1635 lb./sq. in.) that it requires specially constructed vessels and careful handling. The amides so formed (reported to have been obtained in 90 per cent yield) can then be thermally decomposed to yield the nitriles. This two-stage preparation has now been superseded by one-stage simpler methods[3] wherein ammonia gas reacts with fats or fatty acids at temperatures ranging from 330° to 360°C.

By passing gaseous ammonia through liquid stearic acid at 330°C., Ralston *et al.*[4-5] obtained the nitriles in 84-85 per cent yields. Other patents and reported procedures are essentially modifications of the methods mentioned above. Reutenauer and Paquot[6-7] prepared stearonitrile and palmitonitrile and succeeded in converting unsaturated acids like oleic and erucic to their respective nitriles (yields 75 per cent and over) by adopting a method similar to that of Ralston and co-workers. The method has also been adapted to prepare nitriles from other fats and oils[8] but the product obtained is a complex mixture, difficult to separate, and the method is not suited for the preparation of homogeneous products.

The vapour-phase reaction between fatty acid esters and ammonia in the presence of catalysts like Japanese acid clay[9,10] were confined to the preparation of nitriles from low molecular weight acids like acetic and propionic acids. Two patents[11,12] report the preparation of nitriles of fatty acids (containing more than 8 carbon atoms in the chain) by the catalytic vapour-phase reaction method.

In the present communication the possibility of converting the liquid methyl esters of fatty acids into the corresponding nitriles by direct interaction with ammonia gas has been investigated. The esters are prepared as intermediates in the purification of fatty acids by fractional distillation of fatty acid esters.

Experimental

A mixture of 94 per cent methyl stearate and 6 per cent methyl palmitate is used for ammoniation. It is a white waxy solid, m.p. 36·5°-37·5°C., free from acid and has an ester value of 187-190·5. The boiling range of the mixture at 1 mm. pressure is 152°-55°C.

30 gm. of ester mixture and the catalyst are taken in a 500 c.c. round-bottom three-necked flask, fitted with a lead-in tube for gaseous ammonia, a thermomete and a 0·5″ bore glass tube (70 cm.) bent in the form of a V to serve as a reflux. Ammonia is passed at the rate of 3-4 bubbles per second. The bubbling is started when the temperature of the contents of the flask reaches 150°C. The temperature is raised to 345°-50°C. and maintained for about 5½-6 hr., after which the product is cooled in a stream of ammonia, transferred to a 100 c.c. Claissen flask and distilled.

Analysis of the Product

The percentage of nitrile in the product is estimated by the Kjeldahl's method. The product undergoes easy digestion and the values are reproducible (experimental error 2-3 per cent). There is little chance of any amide distilling over at 340°-58°C., since the decomposition of the amide commences at temperatures as low as 250°C.

The percentage of free fatty acid in the product is determined by the estimation of acid value by the standard method and expressed as stearic acid.

Some unreacted ester may also be present in the distillate. Since both the nitrile and the ester are neutral bodies, a chemical separation and estimation of the residual unreacted ester is difficult. Fractionation under vacuum distillation can be employed, but it is time-consuming and not quite quantitative. A method of differential hydrolysis by alcoholic potash of definite strength has been successfully adopted for the analysis of such a mixture and found to give consistent results. Preliminary experiments with pure nitrile and different concentrations of alcoholic potash have shown that the lower limit of KOH concentration, at which the nitrile begins to hydrolyse, is about 1 N (TABLE I). Hydrolysis with mixtures of known compositions of nitriles and ester, for 1 hr. with 0·37 N alkali, shows that while the ester undergoes complete hydrolysis, the nitrile is unaffected (TABLE II).

TABLE I

STRENGTH OF ALKALI, N	NITRILE HYDROLYSED IN 1 HR., %
0·23	0·0
1·26	1-5
2·87	84-90
3·73	95 and above

TABLE II

ESTER IN THE ESTER-NITRILE MIXTURE, %	WEIGHT OF ESTER, gm.	WEIGHT OF ESTER CALCULATED FROM SAPONIFICATION VALUE, gm.	ERROR, %
39·5	0·2902	0·295	1·8
39·7	0·3040	0·310	2·0
41·5	0·3126	0·318	1·7
52·0	0·4380	0·435	−0·7
55·5	0·9990	0·997	−0·2
61·5	0·9450	0·943	−0·2

The results of ammoniation of the ester mixture employing different catalysts are recorded in Table III. Ammoniation in the liquid phase, under reflux, proceeds smoothly. Good overall yields (60-65 per cent) of the nitrile are obtained in 5½-6 hr. at a temperature of 345°-50°C. When ammoniation is carried out at pressures lower than the atmospheric pressure and temperatures lower than 300°C., it is found that the yield of nitrile is very small. At 250°C. and 50 cm. pressure, there is no nitrile formation.

TABLE III

(30 *gm. of ester mixture* ; *time of reaction* 5·5-6 *hr.*)

YIELD OF THE DISTILLATE, gm.	CATALYST USED	STEARONITRILE BY KJELDAHL METHOD, %	FREE STEARIC ACID FROM ACID VALUE, %	UNREACTED ESTER FROM ESTER VALUE, %
22	......	76-77	7·2	15·6
21	3 gm. B.D.H. Fullers' earth	76-77	2·5	20·4
17	3 gm. of 40 mesh Al_2O_3	67·5	3·2	26·5
18	1 gm. of tungstic acid	61·9	3·0	31·2
22	3 gm. of glass wool	56·0	3·3	36·1
20	3 gm. of silica gel	53·8	17·6	24·2
21	10 gm. of silica gel	77·3	6·3	15·8
21	Silica gel from above, re-used	78·6	6·3	14·2
20	Silica gel (3 gm.) coated with P_2O_5	60·2	1·7	34·3

Discussion

The nitrile formation apparently takes place in two stages :

$$\text{(I)}\ RCO\,OCH_3 + NH_3 \rightarrow RCO\,NH_2 + CH_3OH$$
$$\text{(II)}\ RCO\ NH_2 \rightarrow RCN + H_2O$$

The mechanism of reaction II is not very clear. If it was direct dehydration, the residue must be only nitrile and unreacted ester. There is, however, an appreciable quantity of free acid found in the product (TABLE III). This can be accounted for if the water generated in reaction II can hydrolyse some of the amide formed in reaction I. But under the conditions of reaction there is hardly any likelihood of hydrolysis of the amide in the absence of high pressures. The presence of free acid was also observed by Ralston in the decomposition products of stearamide. This can be explained on the basis of the " disproportionation " reaction (reaction III) which

Ralston has postulated as the main step in the ammoniation of fats and fatty acids.

(III) $2\ RCO\ NH_2 \rightarrow RCN + RCO\ ONH_4$

The ammonia soap formed in this reaction should decompose readily, either to RCO . OH and NH_3, as shown in reaction IV, or to $RCO.NH_2$ and H_2O as shown in reaction V. Though there is excess ammonia in the system, the reaction IV will not be retarded as it is carried out only at atmospheric pressure. Ammonia salts decompose readily except when high back-pressures are developed.

(IV) $RCO\ ONH_4 \rightleftarrows RCO.OH + NH_3$

(V) $RCO\ ONH_4 \rightleftarrows RCO\ NH_2 + H_2O$

There is an appreciable degree of dissociation taking place as per reaction IV and this accounts for the presence of free acid.

It is to be noted that when free fatty acids are used for ammoniation, the formation and volatilization of ammonia soap according to $RCO.OH + NH_3 \rightarrow RCO.ONH_4$ is generally rapid and chokes the condenser. Packed columns, heated electrically, have, therefore, been used for reflux. With fatty acid ester as the starting material, the reaction is so smooth that a 0·5″ dia. and 2′-2·5′ long glass tube serves efficiently for refluxing purposes. Also good yields of nitriles are obtained without the use of any catalyst. Since methyl esters of fatty acids are usually prepared in the process of purification of fatty acids, the possibility of direct conversion of the ester into nitriles is of interest.

My best thanks are due to Dr. M. A. Govinda Rao, Director, A. C. College of Technology, for his kind interest in the subject.

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Letters to the Editor

INTERFERENCE BY CERTAIN SUBSTANCES PRESENT IN RAGI (*ELEUCINE CORACANA*) IN THE DETERMINATION OF THIAMINE BY THE THIOCHROME METHOD

BHAGVAT AND DEVI[1] REPORTED THAT WHEN thiamine was added to suspensions of raw or autoclaved ragi in acetate buffer (*p*H 5·6) and incubated overnight at 37°C., only a small portion of the added thiamine was found in the aqueous extract as determined by the thiochrome method and biological assays. On eluting the ragi residue with various common elutrients, they could not detect any thiamine in the eluates. They also observed that the recovery of thiamine (by the thiochrome method), added to water or chloroform-water extracts of ragi, was low (10-30 per cent). On the basis of the above findings, they concluded that ragi and ragi extracts contained an anti-thiamine factor which destroyed a greater part of the added thiamine.

Ragi is one of the important cereals consumed extensively in certain parts of South India and the Deccan Plateau, particularly in Mysore State. The investigations of Bhagvat and Devi (loc. cit.) would suggest that the anti-thiamine factor present in ragi is likely to destroy not only the thiamine present in ragi but also that present in other foods consumed along with ragi. So far as is known, beriberi has not been reported to occur among poor ragi eaters, even though this disease is known to occur among poor rice eaters in Northern Circars in the Madras Province. This would suggest that the thiamine present in ragi and other foods consumed along with it is probably available *in vivo*. However, in view of the findings of Bhagvat and Devi (loc. cit.), it was felt desirable to investigate further the nature of the anti-thiamine factor in ragi.

The thiamine content of the sample of ragi (variety H. 22) used in the present investigation was determined by the thiochrome method described previously by one of the authors (Swaminathan[2]) with slight modifications and also by the rat-growth method according to Bhagvat and Devi[1]. The results were as follows : by thiochrome method, 3·8 μgm./gm. ; by rat-growth method, 3·6 μgm./gm., thus showing that there was close agreement between the values obtained by the two methods. When thiamine (100 μgm.) was added to ragi (10 gm.), the recovery of added thiamine by the thiochrome method was about 80 per cent, the percentage of recovery obtained being higher than that (20 to 30 per cent) reported by Bhagvat[3].

Next a chloroform-water (C.W.) extract of ragi was prepared according to Bhagvat and Devi (loc. cit.). The recovery of thiamine added to the C.W. extract was found to be low, ranging from 20 to 25 per cent. Bhagvat and Devi (loc. cit.) also reported very low recoveries (5·7 per cent). It was found, however, that on clarification of the extract with basic lead acetate according to Swaminathan[2], the recoveries were 93 to 95 per cent (TABLE I).

The results showed that there was no destruction of the added thiamine and that almost the entire quantity could be recovered after clarification of the mixture with basic lead acetate which apparently removed the interfering substances present in the extract.

TABLE I — THE EFFECT OF CLARIFYING THE CHLOROFORM-WATER EXTRACT OF RAGI WITH BASIC LEAD ACETATE ON THE RECOVERY OF ADDED THIAMINE

SERIAL No.	TREATMENT	RECOVERY OF THIAMINE ADDED TO THE CHLOROFORM-WATER EXTRACT OF RAGI, %
1	25 μgm. of thiamine added to 25 c.c. of C.W. extract of ragi	25
2	25 μgm. of thiamine added to 25 c.c. of C.W. extract of ragi and the mixture clarified by treatment with basic lead acetate, excess of lead being removed as lead sulphate	95
3	25 μ gm. of thiamine added to 25 c.c. of C.W. extract of ragi, the mixture allowed to stand for 2 hr. at room temperature and then clarified by the addition of basic lead acetate	93

TABLE II — THE EFFECT OF ADDING VARYING QUANTITIES OF A SOLUTION CONTAINING THE INTERFERING SUBSTANCES ON THE THIOCHROME REACTION

SERIAL No.	TREATMENT	RECOVERY OF ADDED THIAMINE, %
1	5 μgm. thiamine plus 10·0 c.c. of water (control)	100
2	5 μgm. thiamine plus 0·25 c.c. of sol. A (0·05 gm. ragi) plus 9·75 c.c. of water	80
3	5 μgm. thiamine plus 0·5 c.c. of sol. A (0·1 gm. ragi) plus 9·5 c.c. of water	60
4	5 μgm. thiamine plus 1·0 c.c. of sol. A (0·2 gm. ragi) plus 9·0 c.c. of water	50
5	5 μgm. thiamine plus 2·0 c.c. of sol. A (0·4 gm. ragi) plus 8·0 c.c. of water	38
6	5 μgm. thiamine plus 5·0 c.c. of sol. A (1·0 gm. of ragi) plus 5 c.c. of water	26
7	5 μgm. thiamine plus 10·0 c.c. of sol. A (2·0 gm. ragi)	19
8	10·0 c.c. of sol. A oxidized with alkaline ferricyanide and extracted with 15 c.c. of isobutyl alcohol containing thiochrome from 5 μgm. thiamine	90
9	15·0 c.c. of sol. A plus 15 c.c. of acetate buffer (*p*H 5·6) plus 30 μgm. thiamine (incubated at 37°C. for 24 hr.)	33
10	Same as (9) above, but after clarification of the mixture by addition of basic lead acetate and removing excess of lead as lead sulphate	86

The interfering materials were separated from the lead precipitate and their effect on the thiochrome reaction was further studied. To 200 c.c. of C.W. extract of ragi, 40 c.c. of 10 per cent basic lead acetate solution were added. The precipitate was separated on the centrifuge and suspended in 98 c.c. of water. It was then decomposed by the addition of 2 c.c. of $10.N.H_2SO_4$. The precipitated lead sulphate was removed on the centrifuge. The clear supernatant liquid was adjusted to *p*H 5·6. Varying quantities of this liquid (A) were then added to known quantities of thiamine and the estimations carried out in the usual manner (TABLE II).

The results showed that (1) the addition of a solution containing the interfering materials in increasing quantities progressively decreased the percentage recovery of added thiamine ; and (2) the interfering substances did not destroy the thiamine added even when kept in contact for 24 hr. at 37°C. as shown by the high recovery of added thiamine obtained, after removal of the interfering materials by treatment with basic lead acetate.

Bhagvat and Devi (loc. cit.) reported that the recovery of thiamine added to suspensions of autoclaved or raw ragi in acetate buffer was low (5 to 10 per cent). In view of the foregoing observations and with a view to determine whether the added thiamine was actually destroyed under such conditions, the experiments were repeated according to Bhagvat and Devi (loc. cit.) with the following modifications : (1) the aqueous extracts of ragi were clarified by treatment with basic lead acetate according to Swaminathan[2] before estimating the thiamine present by the thiochrome method ; and (2) the residue of ragi left after separating the aqueous extracts was digested with pepsin for 24 hr. and the peptic digests were analysed for thiamine content after being clarified with basic lead acetate. The results obtained are given in Table III.

TABLE III — RECOVERY OF THIAMINE ADDED TO A SUSPENSION OF AUTOCLAVED OR RAW RAGI IN ACETATE BUFFER

	THIAMINE ADDED TO SUSPENSION OF AUTOCLAVED RAGI (5 GM.) IN ACETATE BUFFER, µgm.	THIAMINE GROUND UP WITH 2·5 GM. RAGI POWDER & SUSPENDED IN ACETATE BUFFER, µgm.
(1) Thiamine added to the sample	1000	1000
(2) Thiamine found in the extracts obtained after incubating the mixture in acetate buffer at 37°C. for 18 hr.	50	266
(3) Thiamine found in the residue from (2) above after digestion with pepsin at 37°C. for 24 hr.	720	550
(4) Thiamine found in the residue from (3) above after further digestion with pepsin at 37°C. for 24 hr.	50	not determined
Total thiamine recovered	820 µgm. (82%)	816 µgm. (82%)

The present investigation has shown that (1) aqueous or chloroform-water extract of ragi contains interfering substances which can be removed by treatment with basic lead acetate ; and (2) the solid material of ragi retains tenaciously a greater part of the added thiamine. The above findings may explain the apparent loss of thiamine added to ragi reported by Bhagvat and Devi (loc. cit.). The thiamine retained by the solid material of ragi can be recovered by digesting the material with pepsin. The recovery of thiamine added to ragi was about 82 per cent. Considering that the error by the thiochrome method (using the fluorimeter) is usually of the order of 5 per cent and that the recovery of thiamine added to most common biological materials ranges from 70 to 95 per cent, it may be inferred that almost the whole of the thiamine added to ragi was recovered by following the above procedure. The above results would indicate that there is no appreciable destruction of thiamine added to ragi. This is further supported by biological assay, the results of which are in close agreement with those obtained by the modified thiochrome method[2].

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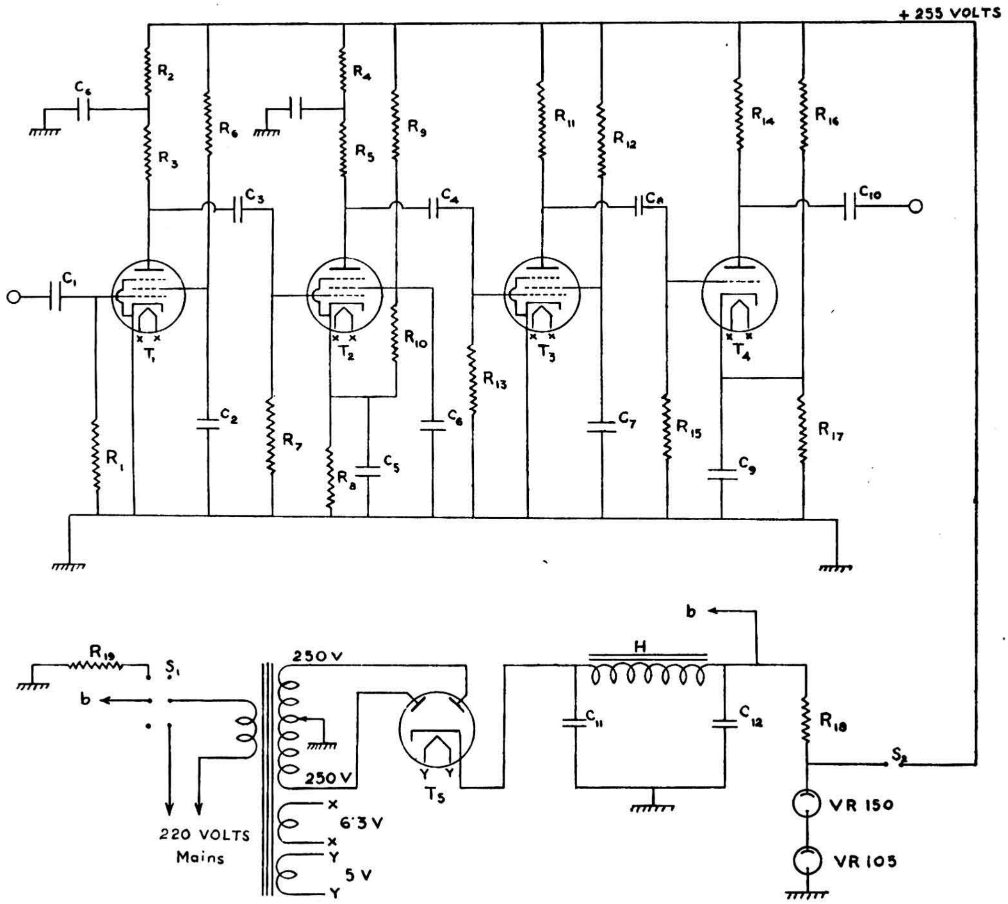
AMPLIFIERS OF PULSES FROM ELECTRICAL COUNTERS OR IONIZATION CHAMBERS OR ELECTRON MULTIPLIERS

THE OUTPUT PULSES OF ELECTRICAL COUNTERS or electron multipliers which are usually of the order of 10^{-2} to 10^{-3} volts are not adequately effective so as to render the electronically operated mechanical counter or recorder operative. Hence these pulses with such a low amplitude are incapable of being either detected effectively or recorded or counted. It is, therefore, essential to provide electrical counters or electron multipliers or ionization chambers with suitable amplifiers to amplify and equalize the amplitude of the pulses so as to secure the registration of the impulse frequency with high degree of accuracy. The operational principle of this pulse amplifier, shown in Fig. 1, like that of the linear amplifier of Wynn-Williams and Ward[1], is in a way similar to that of an audio frequency amplifier.

The amplifier (FIG. 1) employs three stages of resistance-capacity coupling. It accomplishes the greater part of the amplification with the first two pentode tubes. The highest resolution is obtained between the second and the third tubes and in the output of the third tube.

The grid of the second tube is kept positive. The impulses coming from the first stage of the amplifier are of sufficient amplitude and positive in nature above the level of the positive grid bias. The output of the second tube will then be only the genuine negative impulses without spurious signals such as those arising out of the thermal noise in the resistance of the grid circuit, short noise from grid current in the R-C network and the zero noise of the tube.

In this circuit, shown in Fig. 1, resistance-capacity coupling of a fairly large time constant has been employed between the



$T_1 = T_2 = T_3 = 6SJ7$; $T_4 = 6C5$; $T_5 = 5Y3$; $R_1 = 1M\Omega$; $R_2 = R_3 = R_4 = R_5 = R_{11} = R_{14} = 50K$; $R_6 = R_{12} = 40K$; $R_7 = 20K$; $R_8 = R_{13} = R_{15} = 10K$; $R_9 = R_{16} = R_{17} = \cdot 1M\Omega$; $R_{10} = 75K$; $R_{18} = 2500\Omega$ (10W); $R_{19} = 25000\Omega$ (10W); $C_1 = \cdot 0001\mu F$; $C_2 = C_6 = C_7 = \cdot 1\mu F$; $C_4 = \cdot 00001\mu F$; $C_5 = C_9 = 50\mu F$; $C_8 = C_{10} = \cdot 001\mu F$; $C_{11} = C_{12} = 16\mu F$ (Electrolytic); $H = 25$ Henry.

FIG. 1 — PULSE AMPLIFIER.

first and the second tubes so as to obtain equalization of the pulses in the second stage which is important from the point of view of the short time constant of the resistance-capacity coupling between the second and the third tubes and between the third tube to the output stage. The levelling of the impulses is very advantageous for either effecting reliable operation of the electronically operating mechanical counter or for easily bringing the accompanying scaling system into working order so as to accomplish a very reliable scaling of the impulse frequency.

The output of an electrical tube-counter, whose electrode is at positive potential and the tube at ground potential, when applied to the amplifier, the amplifier at the end of its third stage of R-C coupling, transmits pulses of positive potential. These positive pulses may directly be transmitted to a thyratron operated mechanical counter for recording the counter impulse frequency. The mechanical counter, however, is unable to cope with the high rate of impulse frequency. To surmount this difficulty, the impulses are scaled down by means of a scaler to a rate that is capable of being recorded without appreciable error by electronically operated mechanical counter.

The scaler which is designed for incorporating in this circuit, however, is ineffective to the pulses of positive potential transmitted from the third stage of the amplifier. Hence a suitable triode circuit is incorporated and the output pulses of the third stage of the amplifier are applied to this triode tube circuit in order to amplify and change the pulses to those of negative potential for transmitting them to the scaler for operation. With proper selection of the time constant of the coupling between the second and third stages of the amplifier, and the amplification and the resolution of the triode tube circuit, the amplitude, form and the time constant of the input pulses transmitted to the scaling system can be moulded with greater flexibility and degree of freedom to a magnitude and form necessary for easily accomplishing scaling action.

The amplifier is simple in construction and easy to operate. It requires only one stabilized power supply for its operation. It needs no batteries or additional power supply for grid bias. It has been in use for the last six months and has been found stable, reliable and efficient with adequate resolution not far exceeding the dead time of the counter.

In concluding this note the authors express their deep gratitude to Dr. Swami Jnanananda for kindly suggesting the development of this unit and guiding them throughout the course of the work.

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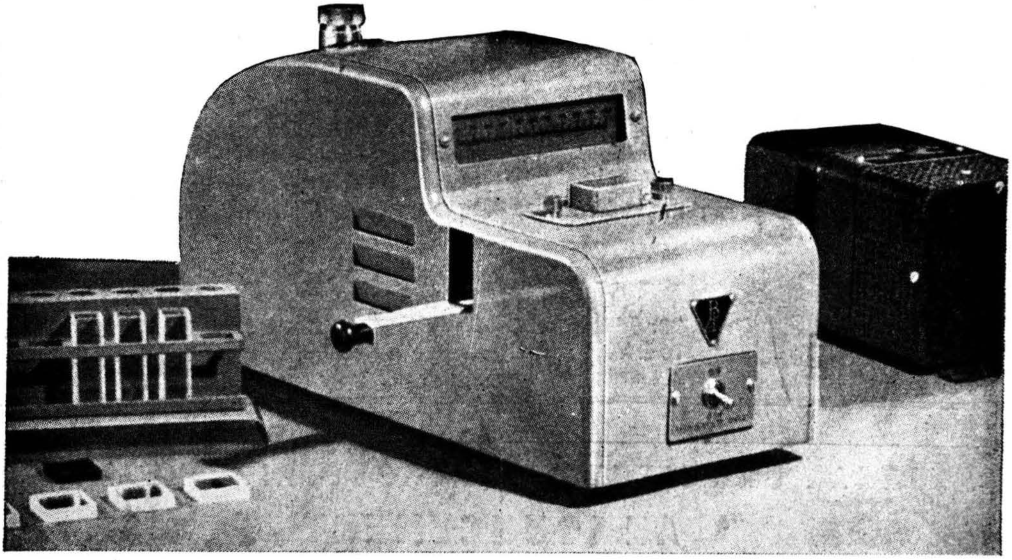

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