Journal of Scientific & Industrial Research

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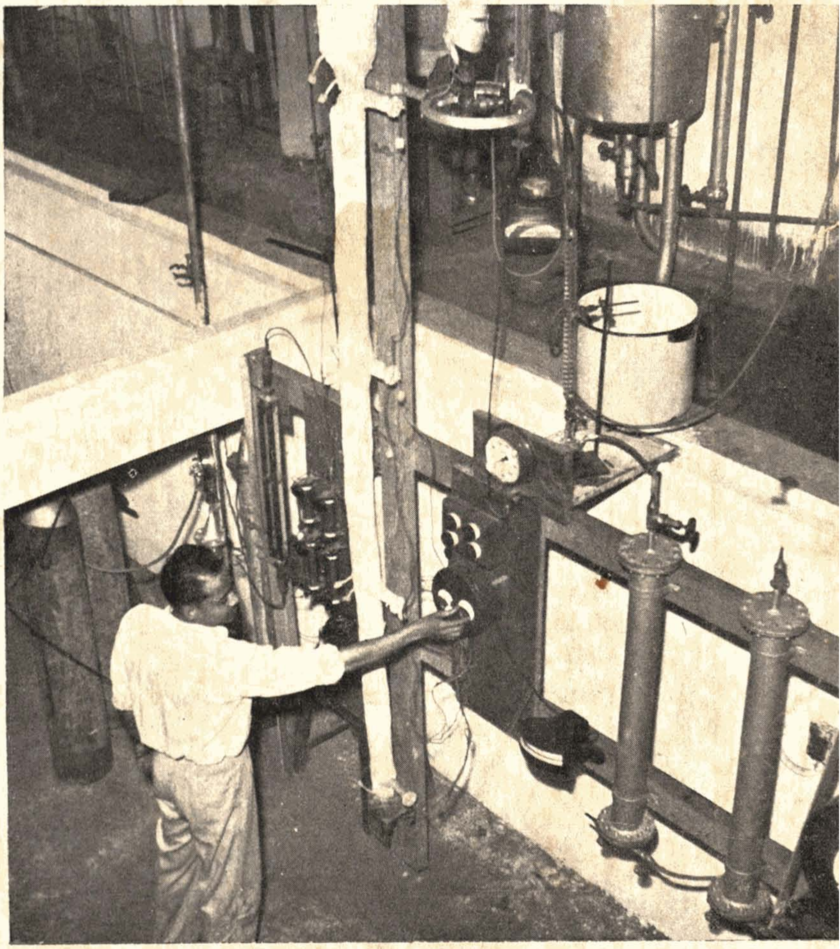
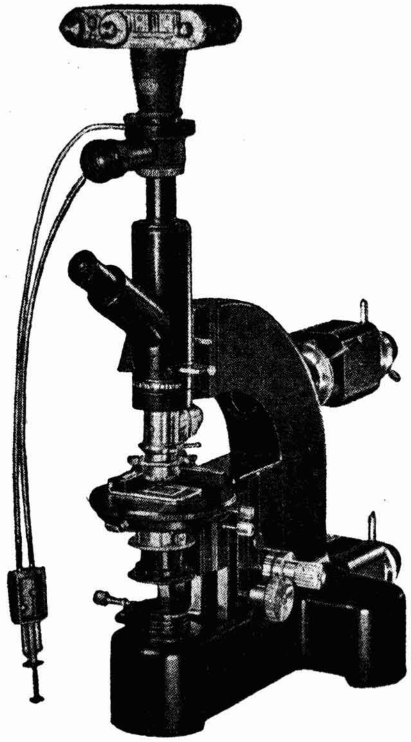


BLISHED BY THE COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, INDIA
NEW DELHI

J. sci. industr. Res., Vol. 13A, No. 7, Pp. 309-354; & Vol. 13B, No. 7, Pp. 455-526. July 1954



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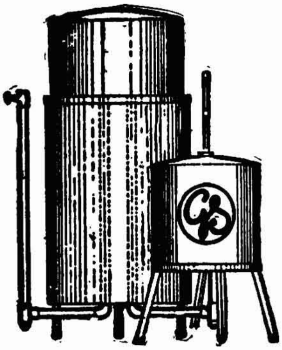

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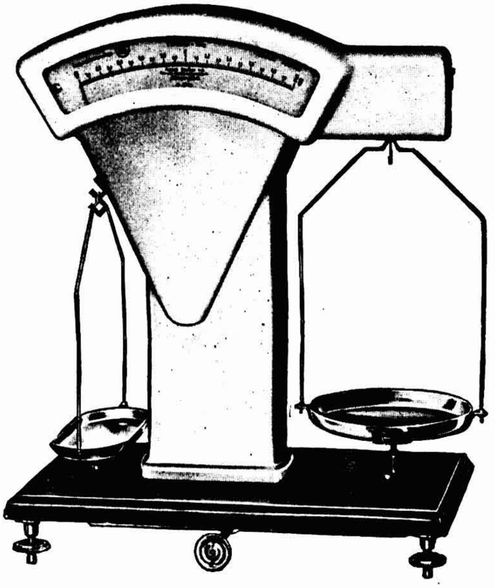

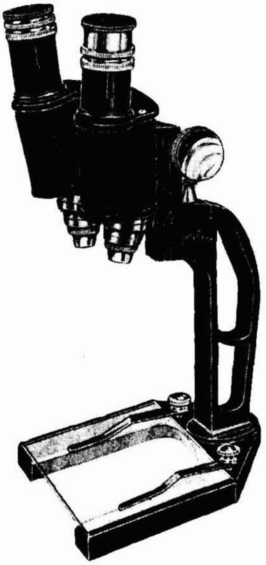

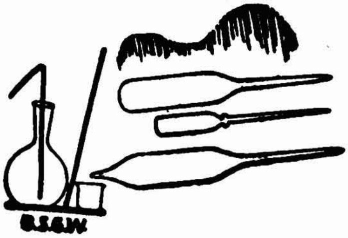
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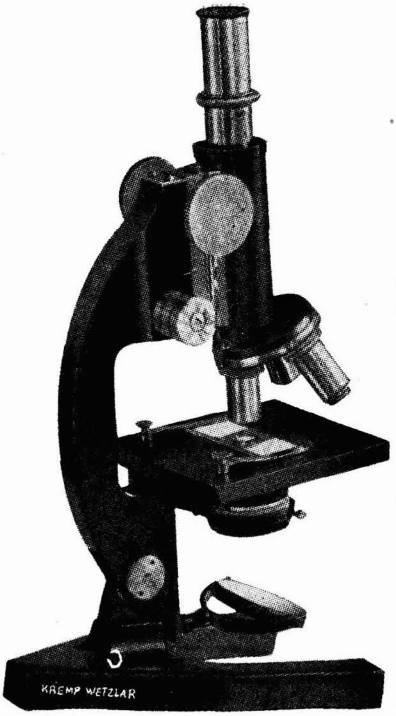
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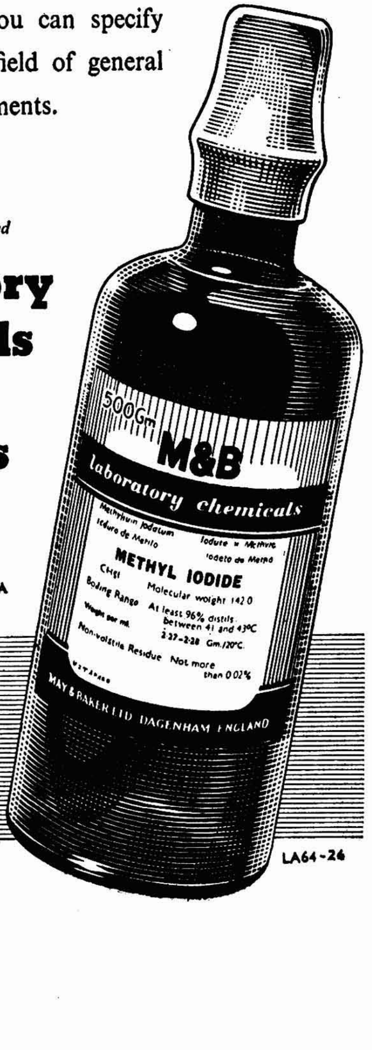
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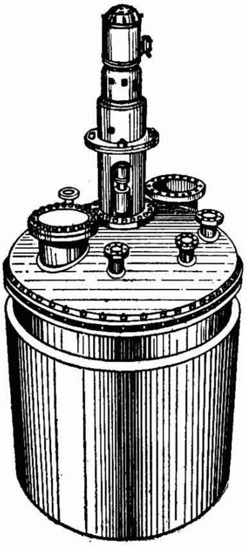

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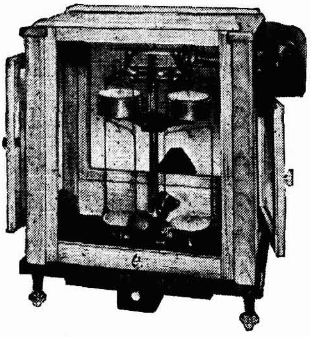

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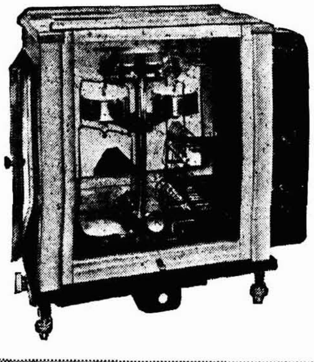

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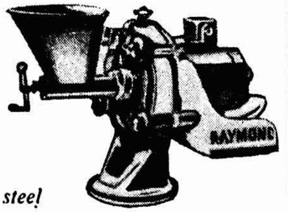

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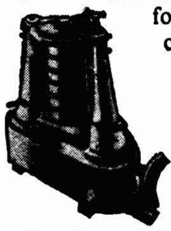

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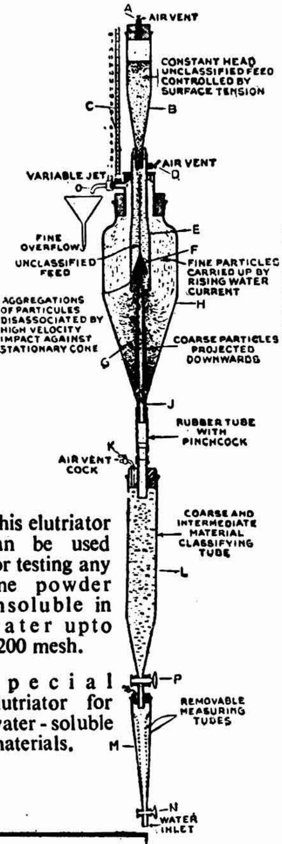

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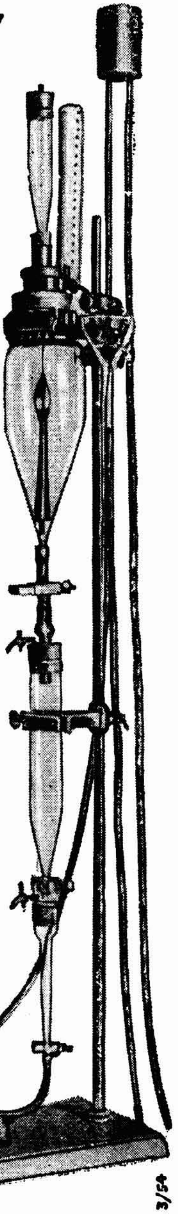

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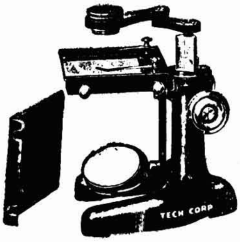
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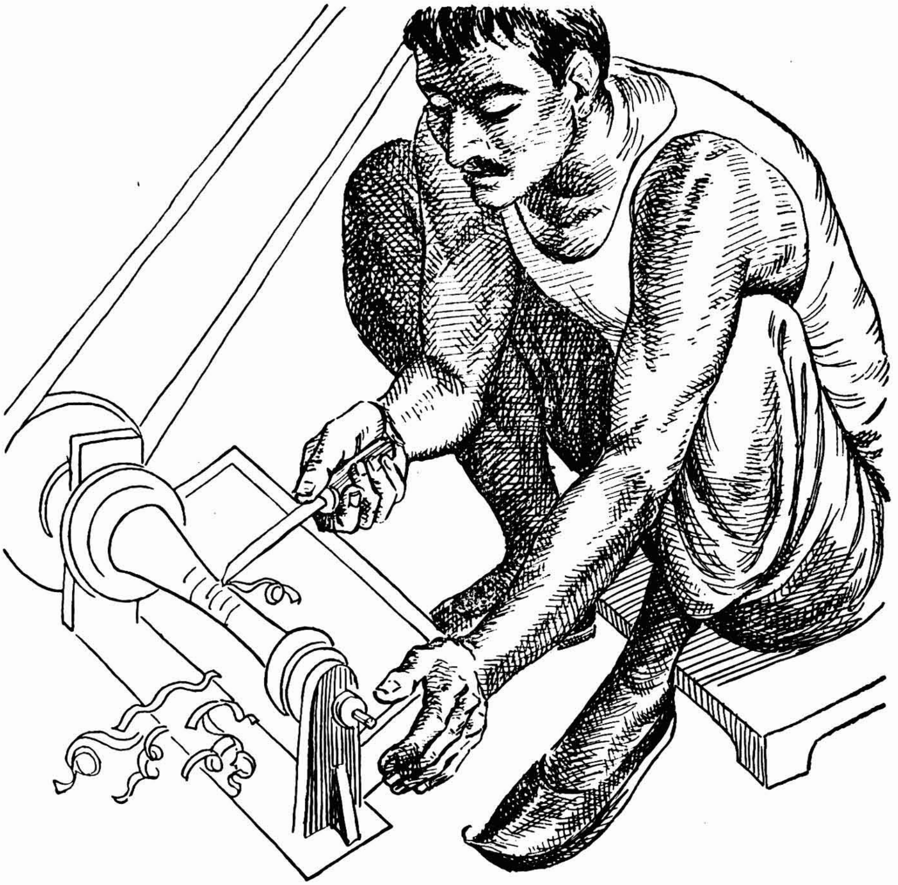

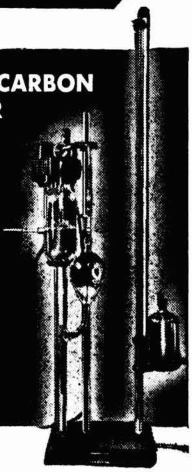

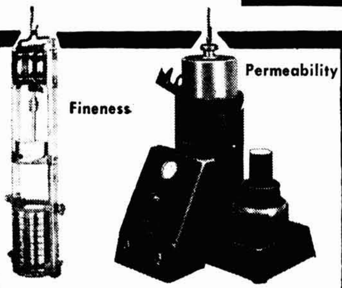
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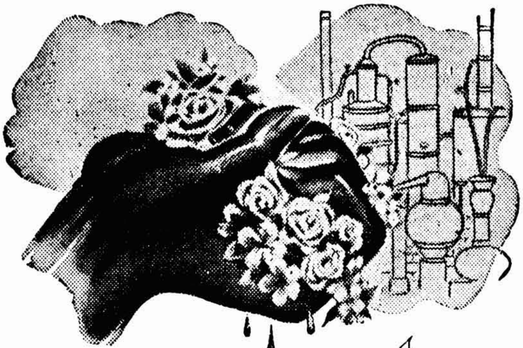


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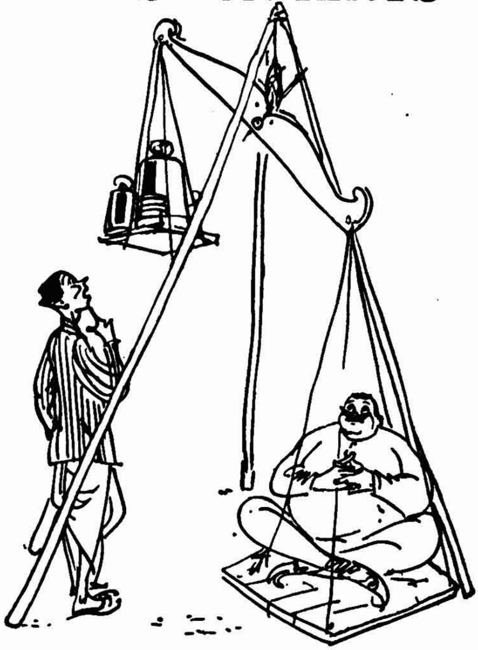

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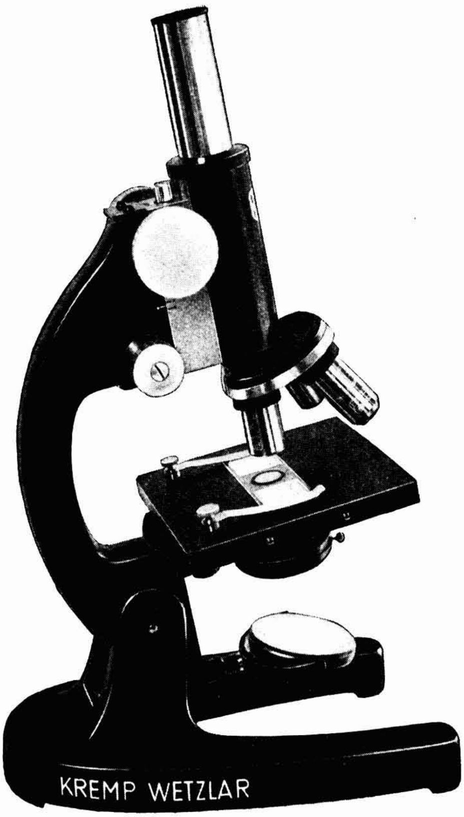
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INDEX TO ADVERTISERS

Scientific Journals & Editorial Problems

THE increasing volume of original scientific papers and increasing publishing costs have created critical financial and other problems for most scientific journals. That these problems merit serious and urgent consideration is evident from the attention they are receiving in recent years from learned societies, individual scientists and editors of scientific periodicals.

The National Research Council, U.S.A., called in 1950 a Conference on Primary Publication attended by representatives of scientific journals, learned societies, publishing houses and government agencies to discuss measures for reducing costs and increasing revenues. A Conference on Scientific Editorial Problems was organized for the 1952 meeting of the American Association for the Advancement of Science (AAAS) to discuss some of the important problems that confront those who prepare scientific manuscripts and technical reports and those who edit and produce scientific publications. The second Conference was held in December 1953 and multiple sessions are being planned for the 1954 Conference on Scientific Editorial Problems.

The National Science Foundation, Washington, recently carried out a survey on the current status of American scientific periodicals and interesting data have been collected [*Science*, **119** (1954), 357-59].

Some of the problems have been discussed in the recent issues of *Science*. Mention may be made of the six papers presented before the 1953 AAAS Conference on Scientific Editorial Problems [*Science*, **119** (1954), 529-39]. More recently, Mr. L. J. F. Brimble, Joint Editor of *Nature*, discussed the problems confronting scientific journals in an address to the Royal Society of Edinburgh.

Volume and quality

The problems of the editor today "are not entirely financial", observes W. Albert Noyes, Editor, *Journal of the American Chemical Society*; "they arise to some extent merely from the bulk of the things he has to handle." The volume of scientific periodicals have been increasing continuously. "Part of this rising flood of words can be considered normal in that the number of scientists today is larger than ever before and hence a greater output can be expected. Of still more significance is the fact that a larger proportion of man-years is being drawn into research and development work because of the unprecedented amount of support for such work." But what about the nature of the manuscripts received by the editors? Dr. W. Albert Noyes has pointed out that "there is more fragmentary publication". As the number of scientists increases, the competitive spirit is bound to become greater and greater "and authors feel that they must have rapid publication. Since presidents of universities base promotions not on the quality of work but on the avoirdupois of the reprints, it behoves scientists to get out small articles rather than one big one."

There has been a large increase in the number of routine articles received for publication since the war, and editors, particularly of large journals, have begun to consider whether they should accept material which has primarily only archival value. An examination of the quality of research work presented in the manuscripts received for publication in the *Journal of the American Chemical Society* revealed interesting facts. An attempt to choose those in which there was an "honest" attempt at interpretation of data and correlation of facts, in other words, something more than mere description of a routine synthesis or a routine set of physical measurements, showed that "only 12 per cent of the papers received had really some meat in the way of scientific discussion; the rest were merely either recordings or routine observations, synthesis of compounds, or measurements ".

Mr. L. J. F. Brimble, in his address to the Royal Society of Edinburgh, has drawn attention to the tendency of authors to send " half-baked " papers for publication. Further, much of the details published in many research papers is of limited interest and value and men of science may well consider publishing only the main points of their research and filing the rest for possible reference.

The National Science Foundation Survey also has revealed interesting facts regarding the quality of manuscripts received for publication. It is stated that "several editors called attention to the large number of articles that are badly written, repetitious, over long, and in which the presentation of scientific material was confused even where reported results and techniques appear to be sound. This creates difficult editorial problems and contributes to the cost and delay in publication."

Delays in publication

According to the data collected by the National Science Foundation during its survey, the backlog of accepted but unpublished articles varied from 1·9 months to one year or more; 70 out of 100 journals covered by the survey reported a backlog of about six months. There is much that can be done by the authors themselves in obviating delays in publication. Reference has already been made to the quality of articles received for publication and the process of revising articles to meet space limitations in journals is time-consuming. It was pointed out by George S. Tulloch, Editor, *Bulletin of the Brooklyn Entomological Society*, that only 20 per cent of the manuscripts received by him was " perfectly typed, punctuated and arranged in the style of the journal and required a minimum of routine attention. The remaining 80 per cent ranged from nearly satisfactory documents to those that require complete overhauling and in some cases retyping ". Submission of carefully prepared and cautiously written papers will go a long way in obviating delays in publication and will also help in accommodating more papers.

Cost of publication

Many research papers are documented with detailed or extensive tables of data, illustrations, derivations of mathematical equations, protocols, appendices, detailed description of methods, long bibliographies or other materials which are of use only to workers in specific fields and which are expensive to compose and print. To the majority of readers of the published paper the detailed documentation is neither necessary nor desirable and if easy availability of the material to those who need it is assured, as for instance by depositing it in a central documentation centre, the cost of its publication can be saved.

" The editors of journals can do considerably more than their printers in reducing costs. They can insist on reduction of the amount of verbiage in which many authors conceal their contributions; they can insist on the simplification of tables and on these being prepared to fit the format of the journal, on simplification of mathematical derivations, and on restriction of bibliographic citations to those specifically pertinent to each paper."

The views expressed by the editors who participated in the 1953 AAAS Conference have in some measure been anticipated by the recommendations of the Royal Society Scientific Conference on the Preparation of Scientific Communications held in 1948 in London. It may be recalled that the Conference came to the conclusion that: " Many defects of scientific articles and delays in publication are due to inadequate preparation of manuscripts submitted to publishing bodies ". The Conference recommended that manuscripts submitted by authors should be written clearly and concisely and that they should be prepared in accordance with rules of the journals for which they are intended. The Conference also recommended that heads of departments in universities and technical colleges and directors of government laboratories, research associations and industrial laboratories should ensure that " to the best of their knowledge and belief, any contribution passed through their hands, whether as communicators or referees, is worthy of publication on its merits as scientific information alone ". The adoption of these recommendations will minimize editorial problems and promote the objects of publication.

CHARACTERISTICS OF THE IONOSPHERE OVER CALCUTTA

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FIG. 1 shows the monthly average diurnal variations of the ordinary ray critical frequencies of regions E and F_2 (f°E and f°F_2) and also similar variations of the heights of maximum ionization (hpF_2) and the bottom (h'F_2) of the F_2 layer during April 1954. The f°F_2 variation curve has been compared to that predicted three months before. The percentage of the total number of occasions during routine observations when the critical frequency for the

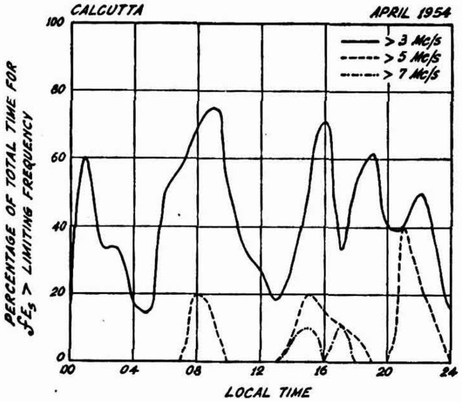

FIG. 2 — PERCENTAGE OF TOTAL NUMBER OF OCCASIONS WHEN fE_S WAS GREATER THAN 3, 5 AND 7 MC./S. DURING APRIL 1954

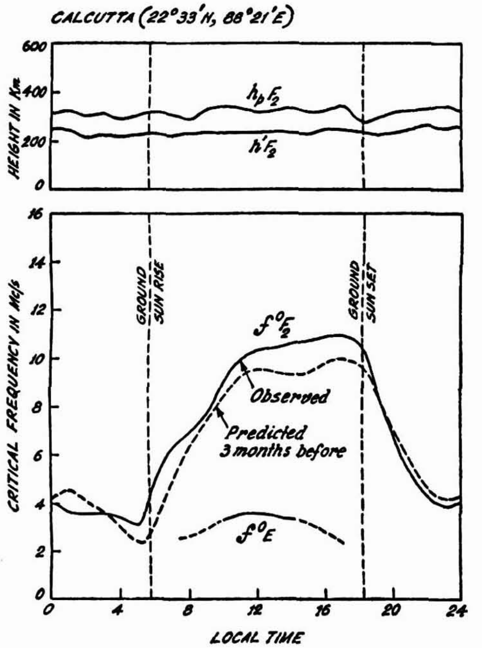

FIG. 1 — MONTHLY MEAN IONOSPHERIC CHARACTERISTICS FOR APRIL 1954

TABLE 1 — MONTHLY MEDIAN HOURLY VALUES

(*April* 1954)

TIME*	f°F_2	hpF_2	h'F_2	f°E	fE_S	(M3000)F_2
	Mc./s.	km.	km.	Mc./s.	Mc./s.	
00	3·85	300	240			3·10
01	3·55	300	240		3·00	
02	3·60	300	210			
03	3·50	300	210			3·05
04	3·25	300	210			
05	3·05	300	210			
06	4·90	300	240		3·45	3·05
07	6·45	300	225	—	3·00	
08	7·30	300	225	2·55	3·50	
09	7·10	315	240	2·85	3·95	2·85
10	9·00	330	210	3·25	3·85	
11	9·90	345	240	3·50		
12	10·55	300	240	3·60		3·10
13	10·85	315	240	3·45		
14	11·00	330	240	3·40		
15	11·00	315	225	3·20	3·05	2·95
16	11·00	315	240	2·45	3·90	
17	11·00	345	240	—	2·55	
18	11·00	278	233		31·50	3·25
19	8·70	285	210		3·45	
20	7·45	300	210		2·80	
21	5·20	300	240			3·05
22	4·05	330	270		4·90	
23	3·80	330	240		2·80	

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

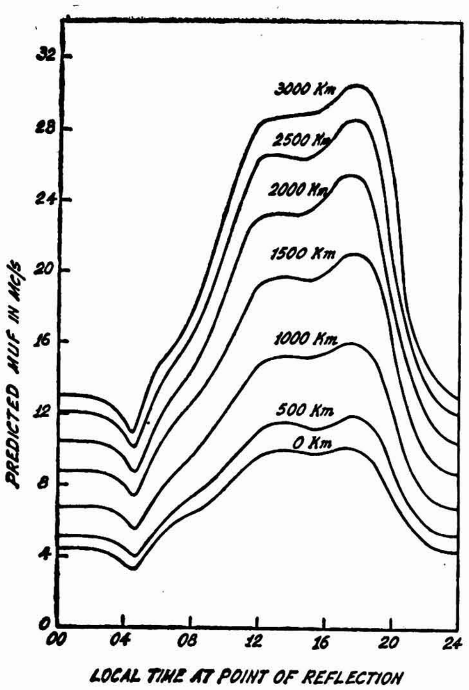

FIG. 3 — PREDICTED M.U.F. FOR TRANSMISSION VIA F_2 REGION OVER CALCUTTA DURING JULY 1954

sporadic E layer (fE_s) was greater than 3, 5 and 7 Mc./s. have been plotted for the different hours in Fig. 2. Table 1 gives the meridian values for the different ionospheric parameters for April 1954.

Fig. 3 gives the mean M.U.F. predictions for transmissions to different distances via F_2 region over Calcutta during July 1954. In conformity with previous year's observations, the intensity and frequency of occurrence of sporadic E ionization were found to be very high, particularly in the afternoon hours.

CHARACTERISTICS OF THE IONOSPHERE OVER AHMEDABAD

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FIG. 1 shows the diurnal variations of the monthly median critical frequencies of the ordinary waves reflected from E, F_1 and F_2; Fig. 2 shows the variations of the height of maximum electron density and of the minimum virtual heights of the different regions; Table 1 gives the monthly median values of the various parameters for E, E_s, F_1 and F_2 regions and the frequencies of occurrences of E_s during routine observations when fE_s was higher than 3, 5 and 7 Mc./s.

The median critical frequencies of F_2 in this month were higher during daytime than in the previous month, but they were lower (noon $f°F_2$ lower by 1·7 Mc./s.) than those found in April 1953. The intensities and

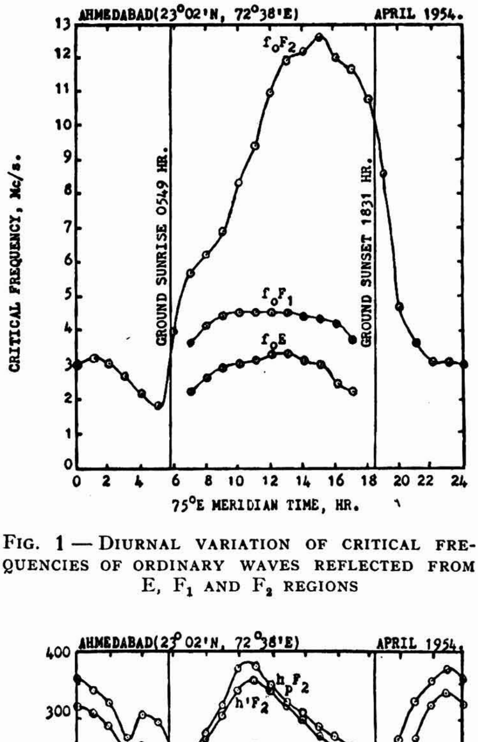

FIG. 1 — DIURNAL VARIATION OF CRITICAL FREQUENCIES OF ORDINARY WAVES REFLECTED FROM E, F_1 AND F_2 REGIONS

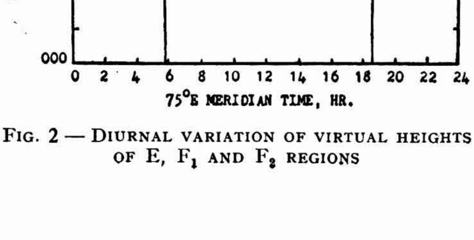

FIG. 2 — DIURNAL VARIATION OF VIRTUAL HEIGHTS OF E, F_1 AND F_2 REGIONS

frequencies of E_s occurrences showed appreciable increase over those in the previous month, being intense during day hours and frequent round sunrise and sunset hours. Strong E_s activity was observed on 4 and 26 April, day and night.

TABLE 1 — IONOSPHERIC DATA — AHMEDABAD, APRIL 1954

(Tabulated hours, 75°E. Meridian Time)

TIME hr.	MEDIAN VALUES								NO. OF OCCURRENCES OF E_s WITH			TOTAL NO. OF DAYS FOR WHICH E_s DATA ARE AVAILABLE
	f^oF_2 Mc./s.	h_pF_2 km.	$h'F_2$ km.	f^oF_1 Mc./s.	$h'F_1$ km.	f^oE Mc./s.	h_pE km.	fE_s Mc./s.	$fE_s >$ 3 Mc./s.	$fE_s >$ 5 Mc./s.	$fE_s >$ 7 Mc./s.	
00	3·0	360	320	—	—	—	—	4·0	14	3	1	29
01	3·2	345	310	—	—	—	—	3·7	15	2	1	27
02	3·1	325	290	—	—	—	—	3·4	12	1	1	27
03	2·7	275	255	—	—	—	—	(3·8)	10	1	1	27
04	2·2	310	260	—	—	—	—	3·2	10	1	—	26
05	1·8	295	255	—	—	—	—	3·3	9	2	—	25
06	4·0	255	240	—	—	—	—	3·3	10	2	2	26
07	5·7	250	245	3·6	230	2·2	115	3·9	15	2	—	26
08	6·2	280	270	4·1	220	2·6	110	4·0	12	1	—	27
09	6·9	320	305	4·4	215	2·9	110	4·0	17	7	4	30
10	8·3	375	340	4·5	210	3·0	110	5·1	11	6	2	28
11	9·4	380	355	4·5	225	3·1	110	5·6	11	7	1	28
12	11·0	350	340	4·5	240	3·3	110	5·8	12	7	4	27
13	11·9	325	320	4·5	235	3·3	110	4·9*	9	4	2	26
14	12·2	310	300	4·4	225	3·1	110	4·8*	8	4	3	26
15	12·6	290	275	4·3	230	3·0	110	3·8*	4	1	—	26
16	12·0	275	260	4·2	230	2·4	110	6·3*	5	4	3	26
17	11·7	260	250	3·7	235	2·2	115	3·5*	8	3	2	26
18	10·8	255	230	—	—	—	—	3·9	16	5	4	28
19	8·6	245	215	—	—	—	—	3·6	18	7	3	29
20	4·7	270	210	—	—	—	—	4·2	17	6	2	29
21	3·7	325	270	—	—	—	—	3·3	18	2	1	29
22	3·1	355	320	—	—	—	—	3·2	13	4	1	27
23	3·1	375	340	—	—	—	—	3·8	19	—	—	29

*Median based on observations less than ten.

Distribution of Thunderstorm Days on the Land Mass of India

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NOISE due to atmospherics is the principal source of interference to the reception of radio signals at frequencies below 20 Mc./s. Atmospherics are due to thunderstorms. Utilizing the known physical facts about the nature of electric discharges associated with thunderstorms, the distribution of thunderstorm days over the globe, and the laws of propagation, the noise level at a place can be estimated. Such estimates have actually been made and noise grade maps of the world, and .nomograms giving the strength of satisfactory signals in the presence of noise corresponding to different noise grades for different frequencies have been prepared[1]. These data constitute, at present, the basis for calculations in communication engineering. Experimental investigation in the laboratory revealed significant differences between the observed and estimated noise levels. When the question was examined in detail, it was found that this discrepancy was largely due partly to the scanty data on the distribution of thunderstorm days and partly to the way in which such data were analysed and utilized.

Restricting the scope of the work to estimations of noise levels in India only, the available thunderstorm data were examined with a view to presenting them in a manner most suitable to communication engineers. The data for the oceans are given for " lightning seen ". These are, at present, being converted into " number of thunderstorm days " by the World Meteorological Organization by a statistical procedure. Data for some countries from which atmospherics may arise in India appeared to require further scrutiny. Hence, it was decided to analyse and present the available data for the land mass of India only. Even this limited information can prove very useful for estimating the noise levels for a wide variety of communication services within the country. The country is divided into regions and, in each region, average values are calculated by utilizing the available data for all the stations in the region. A feature of the work is the attempt to present on one single map all the information required by a communication engineer for noise estimations.

Method of Brooks

The first complete picture of the thunderstorm activity over the globe was published by Brooks[2]. He presents the data by the use of isobronts, i.e. lines of equal frequency of thunder; the figures associated with such isobronts being the percentage of the total number of days in the particular period when thunder was actually heard by an observer located at any point on the isobront line. While this method is most useful for general purposes, its adoption for purposes of noise estimations is not very convenient. Thunderstorm data for four seasons of the year and for the year are required. This will require drawing five sets of isobronts and can only be undertaken on five different maps. Interpolation between isobronts will have to be carried out for each set of longitude limits as the time factor has also to be taken into account. Avoiding the difficulties will be a distinct advantage. The maps require a revision anyway in view of the more recent and more diverse information available.

Available data and their utilization

The World Meteorological Organization[3] has just published the world distribution of thunderstorm days over land in the form of tables. These tables give the latitude, longitude and altitude of a place, the number of years for which observations have been taken and the number of thunderstorm days for each month, each quarter and year. The values have been obtained by arithmetical averaging. With the limited material available and having regard to uniformity of procedure for all stations, this was probably the best approach. The data are based on 10, 15 and 30 years of observations for Pakistan, India and Ceylon respectively. A thunderstorm day is defined as a local calendar day on which thunder is heard. This requirement limits the area covered by each observing point to a circle with a radius of about 20 km. Further, it makes it extremely improbable for the same thunderstorm to be recorded by more than one station. These facts can prove most helpful in arriving at noise estimates. The tables

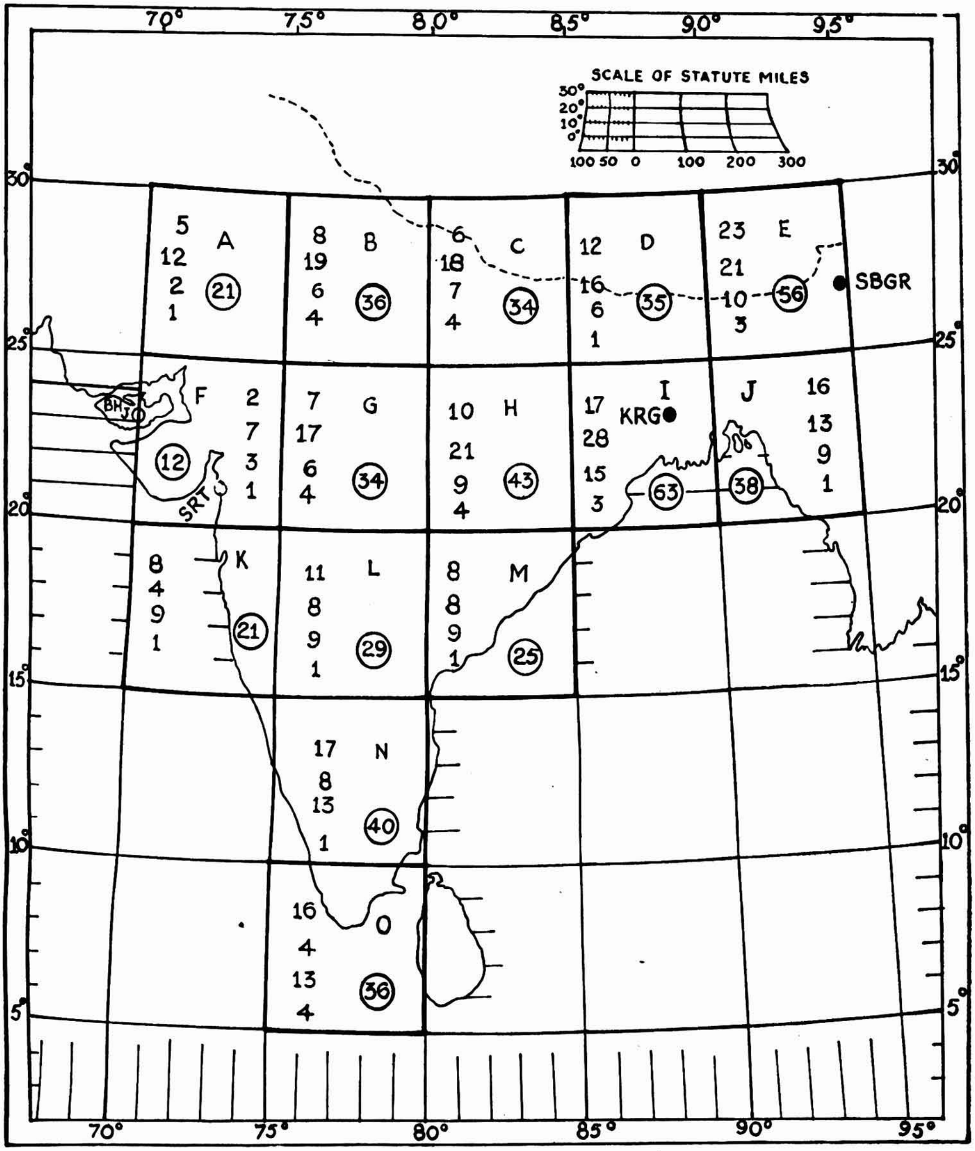

FIG. 1 — DISTRIBUTION OF THUNDERSTORM DAYS OVER THE LAND MASS OF INDIA [Figures vertically below one another refer respectively to the periods March-April-May, June-July-August, September-October-November and December-January-February and the figure in circle is the average value for the year]

have been prepared on the basis of the recommendations approved at a joint meeting of the World Meteorological Organization and Comitè Consultatif International de Radio-Communication (ITU) held at Geneva in 1951. In view of these facts, the data as provided in the tables will be utilized without modification.

The map

The land mass of India is divided into fifteen regions as shown in the map (Fig. 1). Each division extends over 5° of latitude and 5° of longitude. The resulting convenience, when latitudes and longitudes are utilized as the basis of division, needs no elaboration. Division of India into smaller units was not possible as the number of stations for which observations are available is reduced to very small figures like one or two in some cases. With this division, it is possible to have at least six stations for each region. In a large number of cases, these stations are fairly uniformly distributed over the whole region. The values for thunderstorm days for a particular period for all the stations in the region are added together and divided by the number of stations to get the average value for the region. For noise estimation purposes, such values are required for the following four seasons and the year:

I — March, April and May
II — June, July and August
III — September, October and November
IV — December, January and February

The values are given in the map.

The number of thunderstorm days during different seasons at most thundery regions in India (black dots on the map) are given in Table 1.

The number of thunderstorm days during the different seasons in the least thundery regions in India (circles on the map) are given in Table 2. All figures have been rounded off to the nearest whole numbers.

Limitations of the map

The limitations of the map are due entirely to the limitations of the available data. For region A the data for stations in Pakistan which fall in the region have been utilized. The same applies for region J. For regions C, D and E, no data were available for places to the north of the dotted line which consist of the mountains, etc. Hence, the results are based on observations at places to the south of the dotted line. For the region M the results are based on observations made mainly at coastal stations. It is, therefore, probable that the actual values should be higher. For all regions which consist of partly of sea and partly of land like K, M and O, data from land stations only have been utilized and the figures are applicable to land mass in the region only.

TABLE 1

Station	Lat.	Long.	Thunderstorm days during the year				
			I	II	III	IV	Total
Sibsagar	26° 59′	94° 38′	35	48	18	6	107
Krishnagar	23° 24′	88° 31′	31	51	23	3	108

TABLE 2

Station	Lat.	Long.	Thunderstorm days during the year				
			I	II	III	IV	Total
Surat	21° 12′	72° 50′	1	2	2	0	4
Bhuj	23° 15′	69° 48′	×	3	1	×	4

"×" indicates less than half a day.

TABLE 3

Season	I	II	III	IV
Range of noise grade for India	3·0-3·5	3·0-3·5	2·5-3·5	2·5-3·0

Conclusion

The map shows clearly that 10 per cent of the days in the year are days of local storm for all parts of India east of longitude 75°. For regions I and E (parts of Bengal, Bihar and Assam), about 20 per cent of the days are days of local storm. During March, April and May about 20 per cent of the days are days of local storm for regions N, O, I and E. During June, July and August about 20 per cent of the days are days of local storm for all places in India north of 20° latitude and east of 75° longitude.

It is not the purpose of this communication to enter into the details of noise level estimations, but it is useful to point out a very significant fact. According to the world noise grade maps[2], the *limits* of noise grade assigned to different parts of India during the four different seasons mentioned earlier are given in Table 3.

A glance at the map is enough to show that these figures require a revision and, in many cases in the upward direction by 0·5-1·0 or even 1·5 in some cases. Such a revision will result in increasing the noise level estimate by a factor of 2 even for the most noisy hours of the day. The necessity for higher powers and a larger number of frequencies becomes obvious.

Acknowledgement

The author's thanks are due to Dr. L. A. Ramdas and Mr. K. N. Rao for permission to use the library of the India Meteorological Department and to Mr. V. N. Athalye of this college for tracing out the original drawing of the map.

References

1. BROOKS, C. E. P., *Geophys. Mem. No.* 24 (Meteorological Office, London), 1925.
2. *Ionospheric Radio Propagation*, U.S. Department of Commerce, National Bureau of Standards, Washington, 1949.
3. *World Distribution of Thunderstorm Days, Part I — Tables* (World Meteorological Organization, Geneva), 1953.

Principles of Armour Penetration

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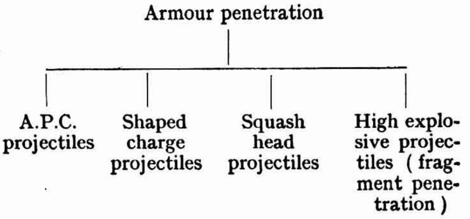
DURING the World War I, armour was used as a protection against machine-gun fire, fragments from artillery shells and so on. In 1916, Col. Ernest Swinton, an officer in the British Army, proposed that a track-laying vehicle protected by iron plates could advance over " no man's land " and in 1918 such vehicles, known as tanks, succeeded in breaking the German lines in an offensive at Amiens. The introduction of tanks and armoured fighting vehicles in the battlefield, which may be defined as moving fortresses giving armour protection and fire power to the crew, gave an impetus to the fundamental research into the mechanism of armour penetration and applied research, i.e. the development of new types of projectiles for armour penetration. The conventional method of armour penetration is an armour penetrating shot having a hardened cap (known as A.P.C. projectile). Early in the World War II, new types of projectiles based on the principle of " hollow or shaped charge " appeared almost simultaneously in the armed forces of the major combatants. Recently " squash head " projectiles have also been introduced in the family of anti-armour weapons.

Armour penetration is a subject of great importance to the services for two reasons: they want to penetrate the armour of the enemy and they also want their own armour not to be penetrated. The armour penetrating projectiles, on the basis of services jargon, are classified as follows:



A.P.C. projectiles

The primary function of this type of projectiles is to penetrate the armour and do as much damage as possible at the rear end of the armour. This consists of a solid shot, a penetrative cap and with or without a ballistic cap. The shot is made of heat treated alloy steel having a blunt nose. The nose or the ogival head is very hard and the hardness decreases from the ogival head towards the body. The entire portion of the shot ogive is covered by a penetrative cap, which is made of hardened heat treated alloy steel, either soldered or sweated to the ogive. The ballistic cap or the wind shield is made of mild steel or aluminium which reduces the air resistance in its flight. The extent of penetration obtained against armour plate depends upon the relationship between the quality of the shot and the plate. The American type of A.P.C. shell has got a small cavity which is filled with high explosives. The cavity of A.P.C. shell is closed at the rear by a heavy screwed-in base plug which is fitted to receive the base fuse. Such a shell penetrates the armour and explodes inside.

Theory of penetration — The approach to the problem is a semi-empirical one. When such a projectile strikes a metallic target, it exerts huge pressures — of the order of 20,000 atm. The ductility, which is defined as the resistance to fracture, increases at a rapid rate when the pressures reach the neighbourhood of the pressures one is concerned with here. That is why, under the impact, the armour does not fracture but the shot merely penetrates. There is ample experimental evidence that penetration in a given target depends on the kinetic energy of the projectile at the time it strikes the target. This energy is taken up by the target and the result is a deep hole. Elementary considerations indicate that the penetration should depend on the strength of the target, which may be taken as proportional to the dynamic yield stress or static yield stress E. Let D represent the calibre of the projectile, m its weight, V the striking velocity and P the penetration in the armour plate. The resistance of the target or the retarding force per unit area is equal to EP/D. The principle of dimensional analysis indicates that EP/D, i.e. the force per unit area, must be equal to mV^2/D^3, i.e. the energy per unit volume. This may be written as

$$\frac{mV^2}{D^3} = KE\left(\frac{P}{D}\right)^n \quad \ldots\ldots\ldots (1a)$$

where K and n are some constants. Experimentally n has been found to be equal to 2. Evans and Ubbelohde[1] have stated that for a shell penetrating an armour plate

$$cmV^2 = DP^n \quad \ldots\ldots\ldots (1b)$$

where n is an exponent lying between 1·6 and 2 and c is a constant depending on the type of the armour plate. The equation (1a) is the same as equation (1b). From the design point of view m/D^3 for a projectile is approximately constant. Rewriting the equation (1a) as

$$P = \sqrt{\frac{mV^2}{D^3}\,\frac{D^2}{KE}}$$

Putting $K' = \sqrt{\dfrac{m}{D^3KE}}$ in the above equation,

$$P = K'VD \quad \ldots\ldots\ldots\ldots (2)$$

As a matter of interest to a gunner, a 90 mm. A.P.C. projectile[2] with a muzzle velocity of 2,800 ft./sec. will penetrate 4·8 in. of armour at 1,000 yards.

The performance of an A.P.C. projectile depends on the energy at the time when it is about to strike a target and the weight and calibre of a projectile are governed by the design considerations, so that to have more penetration by a given projectile, the research is focussed to increase the muzzle velocity. The hyper velocity armour piercing projectiles consist of an extremely hard core of tungsten carbide steel. The 90 mm. hyper velocity A.P.C. projectile[2] (muzzle velocity 3,350 ft./sec.) at 1,000 yards range (terminal velocity 2,910 ft./sec.) can be expected to penetrate about 7·8 in. of armour.

Shaped charge projectiles

In World War II, weapons based on this principle (known as hollow charge effect or shaped charge effect or cavity effect or Munroe effect or Neumann effect) appeared almost simultaneously in the armed forces of the major combatants. The Germans developed Panzerschreck, Panzerfaust, etc., the Britishers P.I.A.T. and the U.S.A. 2·36 in. Bazooka. Shaped charges have also been fired from recoilless guns, e.g. 57 mm. and 75 mm. In recent years the 3·5 in. Super Bazooka has been introduced in the services.

The principle on which these weapons are designed is to have a metal-lined cavity in the war-head towards the target to be fired. A cross-section of 3·5 in. Bazooka war-head is shown in Fig. 1. When such a war-head strikes a target, the inertia-fuse functions and detonates the main explosive filling. This gives a high velocity jet (8,000 m./sec.), which is about $\frac{1}{10}$ in. in diameter and composed of gas and minute particles of the metal liner, which on striking a target causes a deep penetration.

Theory of jet formation — A fairly complete mathematical theory of this new phenomenon

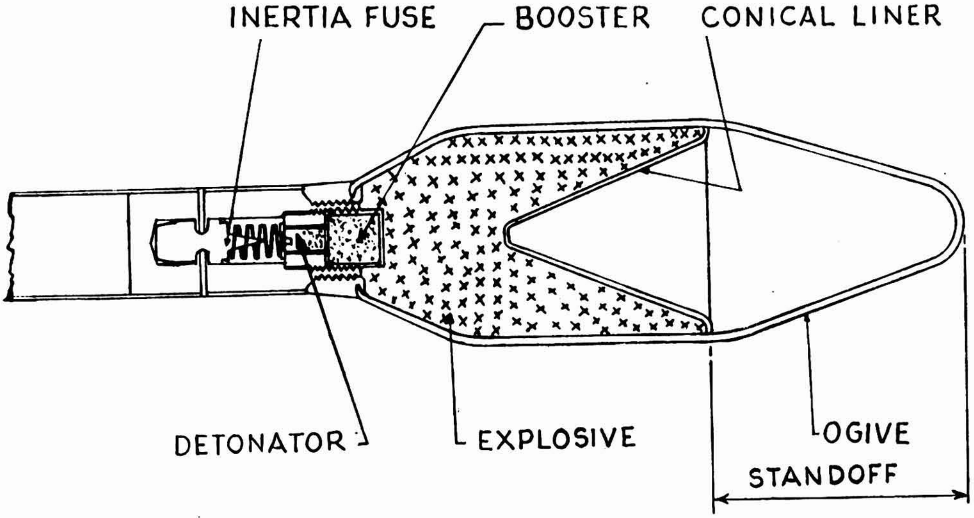


FIG. 1 — CROSS-SECTION OF THE WAR-HEAD OF A U.S. ARMY BAZOOKA

has been published by Birkhoff, MacDougall, Pugh and Taylor[3]. When a detonation wave sweeps from apex to base of a conical liner, it exerts enormous pressures on the surface of the liner, and the authors assume that under these conditions the strength of the liner is negligible and the metal behaves as a perfect fluid. The effect of the detonation wave at any element of the liner is to impart a velocity V_o which bisects the angle between the perpendiculars to the original liner surface and to the collapsing liner surface. They have assumed V_o to be constant from the apex to the base of a conical liner. An element m in the collapsing planes upon reaching the axis divides into two elements of masses m_j (going into the jet) and m_s (going into the slug), which proceed along the axis at the constant velocities V_j (velocity of the jet) and V_s (velocity of the slug) respectively. On the basis of four independent relations, the equations of the conservation of mass, energy, momentum and Bernoulli equation, the authors have derived mathematical expressions for V_j, V_s, m_j and m_s. The velocity of the head of the jet is of the order of 5,000 to 10,000 m./sec. (i.e. 17 to 33 times the velocity of sound in air); while that of the tail end of the jet is about 2,000 m./sec. The hydrodynamic theory of collapse does not explain satisfactorily the velocity gradient in the jet, issuing of the jet from the slug long after the collapse of the conical liner is complete (known as "after jet" effect) and dependence of penetration on standoff. The collapse of the liner at different stages has been actually observed by X-ray flash photography[4]. The jet has been photographed[5] by synchronizing a Kerr cell shutter and exploding a wire light source with the phenomenon. The jet appears to consist of a large number of high speed particles travelling nearly parallel to the jet and vaporizing continuously by their rapid passage through air.

Recently Pugh, Eichelberger and Rostoker[6] have extended the above steady state hydrodynamic theory by assuming that the impulse per unit mass given by the detonation wave to the liner is not constant, so the collapse velocities V_o decreases continuously from the apex to the base. The rate of decrease is very gradual near the apex but becomes much more rapid near the base. This change in V_o results in increase of β from apex to base, where β represents the angle which the collapsing surface makes with the axis of the conical liner. An increase in β results in the decrease of jet velocity and increase in the proportion of the liner going into the jet. They have modified the mathematical expressions of velocities of jet V_j and slug V_s and masses of metal going into jet dm_j and slug dm_s

and have also derived another expression connecting the half angle of collapse β with other parameters. The jet velocity decreases both when the collapse velocity decreases and the angle β increases, hence a small gradient in V_o produces a large gradient in V_j. The last formed jet element and slug element travel with the same velocity and due to the velocity gradient there is lengthening of jet, hence the illusion of " after jet ". Eichelberger and Pugh[7] have also shown that in the jet formed from a 44° mild steel conical liner, there is a uniform distribution of mass and a linear gradient of velocity.

The plug in the case of a conical liner[8] has the lowest velocity and is at the rear of the jet, whereas with a hemispherical liner[9], it travels at the head of the jet with momentum obtained at the expense of the smaller fragments. The hydrodynamic theory of the collapse of a hemispherical liner or other shapes has not been developed so far.

Recently Koski, Lucy, Shreffler and Willig[10] obtained fast jets from the collapse of cylindrical liners. As the weight of metal in the jet was too less, so these were produced in an evacuated space to prevent slowing down by air. The jet exhibited two different components — fast light jet (called fast jet having velocity 21,000 m./sec.) which was unable to break the end of the glass tube, and a more massive jet (called penetrating jet having velocity 16,000 m./sec.) which broke the glass tube quite readily. The hydrodynamic theory of jet formation by a plane detonation wave was extended by the authors so as to take into account a plane converging detonation wave. This modified theory did not explain the velocity of the fast jet but explained satisfactorily the velocity of the penetrating jet. Various experiments, including time-resolved spectrographic observations, showed the jet to be, at least in part, of a gaseous nature. A beryllium cylinder on collapse gave a jet (obtained in an evacuated system) which had a velocity of 90,000 m./sec. A correlation of the maximum observed jet velocity versus atomic weight for a number of materials was suggested.

More recently Walsh, Shreffler and Willig[11] proposed a jetless model for collisions in which the angle between the colliding surfaces is smaller than a certain critical angle. Jetless and jet-forming collisions in case of dural (94 per cent Al), mild steel, brass (67 per cent Cu + 33 per cent Zn) and lead plates were observed by firing these with high explosives and recording their impact with a high speed smear camera.

Theory of penetration — When a high velocity jet impinges upon a target it exerts a pressure of a quarter million atmospheres. The target material acts as a plastic mass and moves radially. Birkhoff *et al.*[3] have assumed the strength of the target to be negligible as compared to the pressures exerted by the jet and have derived a mathematical relation connecting the penetration P to the jet characteristics.

$$P = L\sqrt{\lambda\rho_j/\rho_T} \, . \, . \, . \, . \, . \, . \, . \, . \, . \quad (3)$$

where L represents the constant length of the jet, $\lambda\rho_j$ its mass per unit volume and ρ_T the density of the target. λ is a parameter which depends upon the nature of the jet and equals one for a fluid jet and two for a fragment jet. The depth of penetration into a given target is independent of the velocity of the jet. The theory does not explain some experimental observations, e.g. the difference of penetration in armour and mild steel, penetration in lead and dependence of penetration on standoff.

Pack and Evans[12,13] have taken the strength of the target into consideration and have concluded that

$$P = L\sqrt{\lambda\rho_j/\rho_T}\,(1 - kR) + r \; . \, . \, . \quad (4)$$

where k is some empirical factor depending on the properties of the jet and the density of the target, and R is proportional to the initial yield stress of the target material. When the whole of the jet is used up by the target, even then the crater continues to deepen until the residual energy of the target is used up, and the authors have denoted it as secondary penetration r and have assumed it to be equal to the radius of the crater (measured near the bottom of the crater). They have defined P as the total penetration, the quantity $L\sqrt{\lambda\rho_j/\rho_T}$ as the elementary penetration and $L\sqrt{\lambda\rho_j/\rho_T}\,(1-kR)$ as the primary penetration.

The velocity gradient along the jet is responsible for its lengthening and the change of its effective density as it travels. Recently Singh[14] has given an explicit expression for the length of jet. Very recently Singh[15] has also discussed the target penetration by a jet when account is taken of the velocity gradient, the elongation of the jet and also the strength of the target. The increase in penetration with increase of standoff (say, below four times the calibre) has been quantitatively explained. When the head of the jet is penetrating, the primary penetration depends only on the jet characteristics; on the other hand, when the tail end is penetrating, the primary penetration depends on the jet characteristics and the target strength. The kinetic energy of the jet, increment in volume of the hole as it penetrates a target and its momentum have also been discussed. Recently Kothari and Singh[16] have described the fragmentation of an " inverted " conical liner and the possible bearing of the result on Pugh's theory of jet formation is also discussed. By firing an " inverted " conical liner, fragmentation pattern on a mild steel " witness plate " has been obtained. From the dimensions of the pattern, the values of the velocities of collapse have been calculated which agree (to order of magnitude) with those of Eichelberger and Pugh[7].

It is well known that spinning of a shaped charge reduces its penetration considerably. Basset and Basset[17] have attributed this loss of penetration to the pressures produced by centrifugal forces. Recently Singh[18] has explained the loss of penetration by a rotating shaped charge on the basis that when such an equipment rotates, it imparts an angular velocity to the jet resulting in the increase of its cross-sectional area. A relation is given connecting penetration and speed of rotation taking into account the velocity gradient in the jet, the standoff distance and the strength of the target. The effect of standoff distance on the performance of rotating shaped charge and the profiles of holes at different rotations are also discussed.

The small size rifle grenade M9A1 penetrates 3 in. of homogeneous armour. The 3·5 in. Super Bazooka penetrates about 11 in. of armour. The M9A1 rifle grenade and the Bazooka rocket are fin stabilized in flight. The spin stabilized 57 mm. rifle HE, AT projectile penetrates about 3·5 in. of armour.

Recently Singh[19] has shown that the penetration and the calibre are linearly related. The penetration increases with the decrease of the angle of the copper and mild steel liners. Copper liner gives more penetration and less entry diameter than that of mild steel.

Squash head projectiles

When a squash head projectile strikes the armour at right angles, the explosive is spread or squashed over an area on the outside of the armour and then it detonates. A chunk of metal from the other side of the armour flies at a tremendous speed, which does damage inside the tank without any apparent damage to the interior of the armour. This fracturing of metal near one of its free surfaces which is far removed from the area of the application of pressure is called scabbing or spalling.

Mechanism of scabbing — The travel of pressure (or stress) impulse in metals which are produced on detonating an explosive in contact with the metal has been discussed by Hopkinson[20]. The principle underlying the damage to a target by such a pressure impulse has been published by Rinehart[21].

When a small explosive charge which is in contact with a mild steel or armour plate detonates, it sets up a transient compressional stress wave in the plate (FIG. 2). This wave travels without change of type so long as elasticity is perfect and at any other instant the same curve will be shifted to the right by a distance proportional to the time elapsed. When the stress wave strikes the free (right) boundary of the plate, it will be reflected as a tension wave. This comes back with the same velocity as the pressure wave and the state of strain in the rod subsequently is to be determined by adding

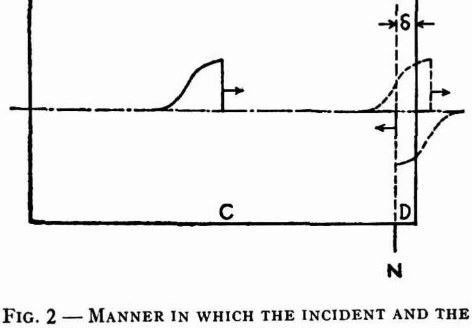


FIG. 2 — MANNER IN WHICH THE INCIDENT AND THE REFLECTED WAVES INTERFERE

the effects of the direct and the reflected wave.

Now suppose that the rod or the plate is divided at MN near the free end and both faces are in firm contact. The rod or plate at MN has no strength in tension but will transmit a compressional stress wave without change. Suppose now that a transient compressional stress wave is moving towards the right through C. It will enter unchanged into D but on reaching the free (right) surface of D, will be reflected as a tension wave. When the thickness of D is greater than one-half the wavelength λ' of the stress wave, it is apparent that, when the return wave reaches the interface between C and D, plate D will fly off to the right with all the momentum trapped in it. Plate C will remain at rest.

The velocity of the stress wave in steel is 217,000 in./sec. So 1 in. of the rod will represent 1/217,000 sec. The momentum of the rod is a measure of the stress-time curve. In case the thickness of D is greater than one-half the wavelength of the stress wave, the momentum possessed by D will be the total area under the stress-time curve. When the thickness of D is made less than $\frac{1}{2}\lambda'$, only a part of the momentum will be trapped in D, the remainder will not get out of C provided the wave has a sharp front. The momentum M_D trapped in D will be given by

$$M_D = \int_0^T \sigma(t)\, dt \quad \ldots\ldots\ldots (5)$$

where T is length of time it takes the wave to travel across D and back again and σ (t) is the stress as a function of time. Experimentally D is made initially very thin, and then its thickness is increased by steps, up to and beyond the point where its momentum reaches a constant value. By measuring the momentum of the plate D in each case the stress-time curve can be deduced. This is the principle underlying the Hopkinson pressure bar test.

Rinehart[21] has measured the velocities of the flying pieces instead of measuring momentum. Let l_1, l_2, etc., be the thickness of the pellets used. In Fig. 3, $OL_1 = 2l_1$, $OL_2 = 2l_2$, etc., and the other ordinate represents the measured velocities V_1, V_2, etc. Let v_1, v_2, etc., represent the increments of velocity and the ordinate v_i for a particular increment is

$$v_i = \frac{V_iL_i - V_{i-1}\, L_{i-1}}{L_i - L_{i-1}} \quad \ldots\ldots (6)$$

where $i = 1, 2, 3$, etc.

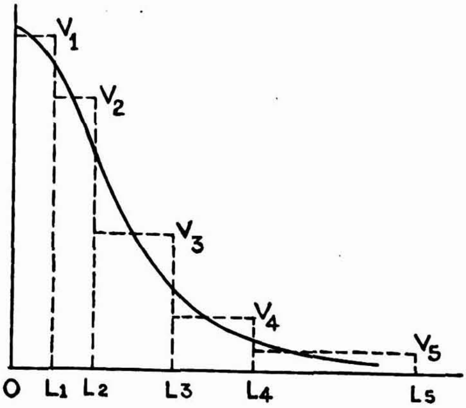


FIG. 3 — METHOD OF CALCULATING PARTICLE VELOCITY DISTRIBUTION

This curve represents the change in velocity and the length of the plate. It can be easily transformed into a stress-time curve by change of scale.

Ordinate $\sigma = \rho\, C\, v$
Abscissa $t = L/C$

where σ represents the pressure (or stress), v the particle velocity, ρ the density of the material and C the velocity of the wave. Thus the pressure-time curve on the surface of a plate due to the application of pressure of high intensity at the other end can be drawn by fixing small pellets to one side of the plate and measuring their velocities. This σ t curve can be assumed to be substantially the same within the material between the two faces of the plate.

In the light of the above discussions, let us examine how scabbing occurs on the face of a plate which is subjected to a very high pressure by detonating a small quantity of explosive touching one face of the plate. The tension is seen to increase as the reflected wave moves to the left. At some particular point, the metal may no longer be able to support the tension. It then fractures, and a scab of thickness δ flies off. The tension under which the material fractures will be referred to as the critical normal stress σ_c of the material. Scabbing should occur: (a) when the maximum value of the stress within the wave exceeds σ_c and should never occur when this is not the case; (b) the thickness of the scab ought to be equal to one-half the distance within the wave that corresponds to a decrease in stress equal to σ_c.

Let σ_o be the maximum stress and $\sigma(x_1)$ be the stress at a distance x_1 in the stress distance curve. If $\sigma_o - \sigma(x_1) = \sigma_c$, then the plate will scab and the thickness of the scab δ is equal to $x_1/2$.

Rinehart[22] has also discussed that when an explosive cartridge detonates on the surface of a steel plate, there is a depression or crater whose area corresponds roughly to the area of the base of the explosive charge. The crater is nearly conical with almost straight sides.

Recently Rinehart[23] has shown " multiple scabbing ", i.e. several parallel scabs generated within a single plate. The first scab of thickness $\delta_1 (\delta_1 = x_1/2)$ is formed when $\sigma_o - \sigma(x_1) = \sigma_c$. After the removal of the first scab, the remainder of the wave will find itself impinging on a freshly created boundary surface and the plate will scab again when $\sigma(x_1) - \sigma(x_2) = \sigma_c$. The thickness of the second scab δ_2 will be $(x_2 - x_1)/2$. The foregoing process will repeat itself until the stress level of the wave falls to a value less than σ_c. The number of scabs that will be formed will be equal to the first whole number smaller than the quotient σ_o/σ_c. The relative thicknesses of the several scabs is found to be governed by the shape of the stress wave.

Penetration by fragments

When a shell or a bomb strikes a target, the fuse functions and the filling detonates. The case is subjected initially to an extremely high pressure from the gaseous products of detonation, the peak pressure is in the neighbourhood of 4,000,000 lb./sq. in. and the duration of pressure is believed to be of the order of a few milliseconds[24]. If the case is made up of ductile materials such as steel, there is plastic expansion[24,25], to the extent of 50 per cent (i.e. the cylinder expands radially and the inside diameter increases by 50 per cent) and then fractures into long thin fragments by a combination of shear and cleavage type fracture. The energy required to break the bomb case is a negligible part of total energy of the explosive. The velocity with which the cylindrical body moves outwards is nearly equal to the final velocity with which the fragments are projected. Mott[25] has defined the fragmentation of a shell body as " the tearing apart of a rapidly expanding tube when the material of the tube reaches the limit of its ductility ". Conical surfaces of fracture generated in thick-walled cylinders have been discussed by Rinehart and Pearson[26].

These fragments travel on all sides and strike a target. The initial velocity of bomb fragments varies from 1,200 to 2,100 m./sec.[27]. After a distance of 15 m., the velocity of fragments is of the order of 750 to 1,500 m./sec. Evans and Ubbelohde[1] have stated that the penetration by a fragment is a function of the momentum per unit area, i.e.

$$P = C' \frac{mV}{D^2} \quad \ldots\ldots\ldots\ldots \quad (7)$$

where P is the penetration, m the weight of fragment, V the velocity at the time of striking the target, D the calibre and C′ is a constant depending on the target material. Shape and size of fragments also determine the depth of penetration in a given medium.

The chances of a fragment penetrating thick armour of a tank is very remote and as such high explosive projectiles are used as anti-personal.

Acknowledgement

I am grateful to Prof. D. S. Kothari, Scientific Adviser to the Ministry of Defence, for permission to publish this paper.

References

1. EVANS, W. M. & UBBELOHDE, A. R., *Research*, **3** (1950), 331, 376.
2. IVES, R. N., *Military Dig.*, **9** (1951), 41.
3. BIRKHOFF, G., MACDOUGALL, D. P., PUGH, E. M. & TAYLOR, G., *J. appl. Phys.*, **19** (1948), 563.
4. CLARK, J. C., *J. appl. Phys.*, **20** (1949), 369.
5. PUGH, E. M., HEINE-GELDERN, R. V., FONER, S. & MUTSCHLER, E. C., *J. appl. Phys.*, **22** (1951), 487.
6. PUGH, E. M., EICHELBERGER, R. J. & ROSTOKER, N., *J. appl. Phys.*, **23** (1952), 532.
7. EICHELBERGER, R. J. & PUGH, E. M., *J. appl. Phys.*, **23** (1952), 537.
8. KOLSKY, H., SNOW, C. I. & SHEARMAN, A. C., *Research*, **2** (1949), 89.
9. KOLSKY, H., *Research*, **2** (1949), 96.
10. KOSKI, W. S., LUCY, F. A., SHREFFLER, R. G. & WILLIG, F. J., *J. appl. Phys.*, **23** (1952), 1300.

11. Walsh, J. M., Shreffler, R. G. & Willig, F. J., *J. appl. Phys.*, **24** (1953), 349.
12. Pack, D. C. & Evans, W. M., *Proc. phys. Soc.*, **64B** (1951), 298.
13. Evans, W. M. & Pack, D. C., *Proc. phys. Soc.*, **64B** (1951), 303.
14. Singh, S., *Proc. nat. Inst. Sci.*, **19** (1953), 357.
15. Singh, S., *Proc. nat. Inst. Sci.*, **19** (1953), 583.
16. Kothari, D. S. & Singh, S., *Proc. nat. Inst. Sci.*, **19** (1953), 507.
17. Basset, J. & Basset, J., *C.R. Acad. Sci. Paris*, **231** (1950), 1440.
18. Singh, S., *Proc. nat. Inst. Sci.*, **19** (1953), 665.
19. Singh, S., *Proc. nat. Inst. Sci.*, **20** (1954), 274.
20. Hopkinson, B., *Proc. roy. Soc. Lond.*, **213A** (1914), 437.
21. Rinehart, J. S., *J. appl. Phys.*, **22** (1951), 555.
22. Rinehart, J. S., *J. appl. Phys.*, **22** (1951), 1178.
23. Rinehart, J. S., *J. appl. Phys.*, **23** (1952), 1229.
24. Pearson, J. & Rinehart, J. S., *J. appl. Phys.*, **23** (1952), 434.
25. Mott, N. F., *Proc. roy. Soc. Lond.*, **189A** (1947), 300.
26. Rinehart, J. S. & Pearson, J., *J. appl. Phys.*, **23** (1952), 685.
27. Wessman, H. E. & Rose, W. A., *Aerial Bombardment Protection* (Wiley, New York), 1942.

Aluminium Industry in India

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AMONG the non-ferrous metal industries, aluminium is now fairly well established in India. The industry has made some significant advance in the last decade. Production has been on the increase since 1947 as indicated by the figures* given below:

Year	*Tons*
1946	3,236
1947	3,215
1948	3,362
1949	3,490
1950	3,596
1951	3,849
1952	3,566
1953	3,758

The country as a whole, however, still remains deficient in the metal. At present the greater part of India's domestic consumption of 12,000 tons a year (in all forms) has to be imported. The main drawback in the way of increasing production has been the limited supply of cheap power.

In view of the expanding market for aluminium in the domestic and industrial spheres, the Government of India have formulated an expansion programme for the industry. On the eve of the First Five-Year Plan period (1951), the installed capacity of the two reduction works in India, the Alupuram Works of the Indian Aluminium Co. Ltd. and Jaykaynagar Works of Aluminium Corporation was 2,500 and 1,500 tons respectively. The Planning Commission has recommended that the production capacity of primary aluminium be raised to 20,000 tons per annum. This is to be achieved by expanding each of the existing plants to 5,000 tons and putting up a third 10,000 ton smelter at Hirakud in Orissa. The expansion of the existing plants is in progress and by the end of the current year it is expected that the capacities of the Alupuram and Jaykaynagar Works will have increased to 5,000 and 2,500 tons respectively.

In a previous article† it was stated that an aluminium works was under construction on a site at Muri Junction in Bihar. This plant has since been completed and went into production in 1948. The Indian Aluminium Co. Ltd., which owns and operates this plant, also started regular mining operations at Lohardaga in Bihar in 1948, thus achieving integrated production of aluminium at all its stages.

J. Industry & Trade*, **5 (1954), 672.

†*J. sci. industr. Res.*, **4** (1946), 678.

With the increase in the production of primary metal, the rolling capacity in the country is also expected to increase. Before the end of 1954 the capacity of the Belur rolling mills of the Indian Aluminium Co. Ltd. will have increased to 7,000 tons per annum. The mill will also be capable of rolling certain sizes and gauges not hitherto produced in India, as well as almost all types of alloy sheets including heat-treatable alloys. The Aluminium Corporation has also plans to increase its rolling capacity during the year to 3,000 tons per annum.

During the period under review, an aluminium foil rolling plant was started by Venesta Ltd. at Kamarhatty near Calcutta and considerable progress was made. Venesta Ltd., formerly rollers of lead, converted their machinery into that for rolling of aluminium foil for tea chest linings and general packaging. At the beginning of 1953 they brought into operation a modern 4 ft. high, light-gauge, foil rolling mill together with sufficient reeling and interleafing capacity to manufacture cigarette and other types of foil. Further expansion of this mill is under consideration and India will, in the near future, be more or less self-sufficient in the production of this important commodity.

In addition to the above rolling mills there is a large number of small rolling mills in India, with a total estimated capacity of 6,000 tons, manufacturing semi-fabricated products almost entirely from scrap which is freely available. These products, though of inferior quality, offer serious competition to the organized industry because of their low price.

The Indian Aluminium Co. Ltd. put into commission at the end of 1951 a modern powder and paste plant at Kalwa (Bombay). The plant has an annual capacity of 500 tons of aluminium powder and 250 tons of paste, which is sufficient to meet the country's current demand. The paste constitutes the pigment for aluminium paint which is widely used for its protective, heat-resisting and decorative qualities.

Another significant development is the production of extrusions which, at the present time, are entirely imported. The Indian Aluminium Company has been licensed to install a modern high-speed extrusion press adjacent to the smelter at Alwaye (Travancore-Cochin). The plant is expected to be commissioned by the end of 1954. The annual capacity of the extrusion plant will be 1,000 tons.

The previous article referred to plans for the installation of a plant in South India for the production of aluminium cable for electric transmission lines. This plant, owned by Aluminium Industries Ltd., Kundara (Travancore-Cochin), has achieved remarkable results in furthering the use of aluminium conductors in place of solid copper conductors. At present Aluminium Industries Ltd. are importing aluminium rods for their requirements. They are now expanding their plant by installing a rod mill so that in future they will require only ingots. The Indian Cable Co. at Tatanagar have also decided to make aluminium cables and are installing a rod mill to supplement their stranding capacity. The total capacity of these two companies will be 8,000 tons per annum, which will, for the first time, cover the country's entire requirements of cables. The Indian Aluminium Co. Ltd. will be producing conductor grade metal when their Alwaye plant is expanded and will be able to meet, in part, requirements of this important industry.

As mentioned earlier, the Planning Commission has recommended the establishment of a new smelter with an initial capacity to manufacture 10,000 tons of virgin aluminium per year and capable of easy expansion to 20,000 tons, in the Hirakud area. This is to be done under the aegis of Indian Aluminium Co. Ltd. The Hirakud plant is intended to make the country self-sufficient in aluminium, at least for the next few years.

The above review will show that during the last seven years there has been a substantial development in both primary and semi-fabricating stages of the aluminium industry in India. This progress is all the more remarkable in view of the serious setbacks that the industry had to face in the last few years. In the first place, the main market for aluminium in the country, i.e. the utensil industry, was faced with a tremendous slump. Consumers reduced their requirements considerably and also reduced their stocks which were never large. This reduced the demand for aluminium on the primary producers to a mere trickle. At the same time, imports from abroad and competition from country rollers using scrap added to the burden of the primary producers, who were obliged to locate new markets at very short notice. A certain amount of conservatism on the part of potentially important consumers of the metal in several fields, notably transportation, had delayed this accomplishment. However, the present difficulties are of a transitionary character and while the major portion of aluminium is still destined for the utensil market, an increasing proportion is finding new industrial applications. The future of the aluminium industry in India, therefore, remains optimistic.

Preparation of Concentrated Pyrethrum Extract

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THE cultivation of pyrethrum in Kashmir State was started by the Forest Department about ten years ago and during World War II the whole produce was supplied to the Government of India. Considerable amount of work to establish this exotic in the State and to produce a crop of standard quality has been done during these years. Such important aspects as proper time of collection, the optimum altitude for its cultivation, methods of drying and effect of storage on the pyrethrine content of the flowers have all been carefully worked out[1,2].

As a result of tribal raids on the State in 1947 and later on due to acute food shortage, most of the pyrethrum plantations were entirely neglected and the land under them was brought under food crops. This practically put an end to the pyrethrum cultivation. On account of its great utility as an insecticide its cultivation on large scale has been revived recently and it is hoped that in the near future large quantities of pyrethrum flowers will be made available for the preparation of a large variety of insecticidal preparations for agricultural and veterinary use as well as household sprays and powders.

Investigations were undertaken in this laboratory to evolve a process for the preparation of concentrated extracts of pyrethrum flowers from which ordinary commercial preparations for ready use could be prepared for the market. As a result of these investigations a process has been evolved which is based on the use of a petroleum fraction called " solvent oil " (boiling range 60°-145°C.). This solvent is being produced in India at present and is available in sufficient quantities. Extracts containing 15-20 per cent of pyrethrines have been prepared with this solvent.

Siddiqui and co-workers[3] also evolved a process for the manufacture of concentrated pyrethrum extracts using a mixture of kerosene, alcohol and acetone as solvent for extraction. The process was tried in our laboratory but it was observed that it gave extracts which contained large quantities of chlorophyll and inert material, and did not contain more than 5-6 per cent of pyrethrines.

It is well known that different solvents remove different quantities of extractive material from pyrethrum flowers. For the preparation of concentrated extracts of pyrethrum, it is essential to use a solvent which removes pyrethrines completely and at the same time extracts less of the inactive material. It was, therefore, thought desirable to determine the amount of extractives obtained with different solvents from local flowers. A number of solvents were tried and flowers containing 0·91 per cent of pyrethrines were used for this purpose. After extraction the solvent was evaporated and the residue weighed to a constant weight. The percentage of pyrethrines in the extracts employing different solvents are given in Table 1.

TABLE 1

SOLVENT	EXTRACTION AT ROOM TEMP. %	PYRETHRINE CONTENT %	EXTRACTION AT BOILING POINT %	PYRETHRINE CONTENT %
Ethyl alcohol	23·0	4·3	25·0	3·6
Acetone	9·9	9·1	10·4	8·6
Benzene	5·7	15·7	6·8	13·2
Chloroform	7·4	12·1	10·0	9·0
Carbon tetrachloride	5·6	16·1	5·8	15·5
Petroleum ether	4·0	22·5	5·7	15·7
Ether	5·9	15·2	6·1	14·7
Ethylene dichloride	6·1	14·7	7·1	12·7
Solvent oil (boiling range, 60°-145°)	4·3	20·9	—	—

From the results given in Table 1, it appears that benzene, carbon tetrachloride, petroleum ether, ethylene dichloride and solvent oil extract less of inactive material and can be considered for the large-scale extraction of pyrethrum. Of these solvents, carbon tetrachloride, ethylene dichloride, ether and petroleum ether cannot be used for large-scale extraction because of their high cost and non-availability in India in sufficient quantities. Benzene can be considered but its use is not advisable because of its toxic effects on the workers. Solvent oil appears to be the most suitable solvent for large-scale commercial extraction in this country.

Powdered pyrethrum flowers containing 0·91 per cent pyrethrines were percolated (3 times) with solvent oil. The first percolate was kept separately; the second and third percolates were used for percolating further quantities of flowers. In three percolations 92-95 per cent of pyrethrines were extracted.

The solvent from the first percolate was distilled off, first at ordinary pressure and then under vacuum. The concentrated extract thus obtained was found to contain 10-12 per cent of pyrethrines. It was observed that this extract on standing deposited resinous material and was, therefore, further processed to yield an extract containing 15-20 per cent of pyrethrines. The extract obtained is a yellow-coloured mobile liquid which is easily miscible with kerosene oil. Fifteen, 10 and 2 per cent extracts were prepared by the above method and kept under observation for one year. The stored samples were analysed at intervals of two months. It was observed that the extracts containing 15 and 10 per cent pyrethrines showed deterioration during storage while the 2 per cent extract showed no appreciable deterioration. A stable non-greasy and anti-mosquito cream containing 0·2 per cent pyrethrines was also prepared from this extract. This cream, when applied as a thin film to exposed skin surfaces, affords almost complete protection against mosquito bites for 4-5 hr.

Acknowledgement

We are grateful to Col. Sir R. N. Chopra for his valuable advice during the course of this investigation.

References

1. CHOPRA, I. C., DHAR, M. L., HANDA, K. L., HABIBULLAH, M. & ASA NAND, P., *Curr. Sci.*, **17** (1945), 104.
2. CHOPRA, R. N., KAPOOR, L. D., HANDA, K. L. & CHOPRA, I. C., *Indian Farm*, **8** (1947), 78.
3. SIDDIQUI, S., SUBHARATTANAM, A. K. & BAGCHEE, S. D., *Indian Pat.* 35338 (1948).

Electrochemical Processes & Their Applications to Indian Industry—A Symposium

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A SYMPOSIUM on "Electrochemical Processes & Their Applications to Indian Industry" was held under the auspices of the Council of Scientific & Industrial Research in the Central Electro-Chemical Research Institute, Karaikudi (C.E.R.I.), on 27-28 March 1954. Forty delegates from different parts of the country, drawn both from industry and research laboratories, participated in the symposium. The symposium was inaugurated by Sir S. V. Ramamurthi. Dr. B. B. Dey, Director, C.E.R.I., welcomed the delegates.

Four technical sessions were held: (1) Electrometallurgy and Electrothermal Processes; (2) Electrolytic Processes, Inorganic and Organic; (3) Batteries, Electrodeposition and Electropolishing; (4) Miscellaneous, including papers on analytical methods and electric discharges. Fifty-one papers were presented.

The papers presented at the symposium bring out the importance that is being given to electrochemical research in various research institutions in the country, and the useful work that is being carried out in different national laboratories, research institutions and industrial establishments. The Central Electro-Chemical Research Institute should be congratulated in bringing together research workers from various laboratories and industrial establishments and providing an opportunity to discuss problems of common interest and plan future lines of research.

Electrometallurgy and electrothermal processes — Mr. E. H. Bucknall, Director, National Metallurgical Laboratory, presented a paper reviewing the present position and the future of electrometallurgy in India. A critical survey of India's ore resources was made and the possibilities of their exploitation and export were discussed. Following this, four papers from the Central Electro-Chemical Research Institute were presented: (1) on the electrolytic production of manganese from low grade ores, (2) extraction of titanium by the electrolysis of fused salts, (3) electrolytic recovery of lead and antimony from battery wastes and (4) reclamation of aluminium from scrap. Two papers were presented on the manufacture of calcium carbide; one was a review of electrothermic processes in general with special reference to the production of calcium carbide (S. L. CHAWLA) and the other on the utilization of the lignite deposits of Neiveli (South Arcot) for the production of calcium carbide (A. JOGARAO and A. SREENIVAS). The session concluded with the presentation of papers on the electric smelting of pig iron at Bhadravathi (C. MUNIKRISHNA), applications of electricity to heating and continuous production type tunnel furnaces (B. BYSAKH), and the manufacture of ferrochrome for the direct preparation of chrome liquors (S. K. BARAT).

Electrolytic processes — Six papers were presented on the use of rotating electrodes in electrolytic reactions by workers in the C.E.R.I. H. V. K. Udupa and B. B. Dey discussed the general aspects and explained the practical implications of the use of rotating electrodes. With rotating electrodes, the application of higher current densities becomes possible without the risk of undesired side reactions, and, therefore, high capacity cell units can be used resulting in the saving of floor space and initial investments. The remaining papers described the successful use of rotating electrodes in the electrolytic preparation of chlorates, cuprous oxide, ammonium persulphate, calcium gluconate and *p*-aminophenol.

A paper on the electrolytic oxidation of organic compounds on the surface of porous carbon tubes as electrodes was contributed by J. C. Ghosh and S. K. Bhattacharyya, followed by papers on the electrochemical preparation of hydroxylamine from nitric acid (D. RAMASWAMI) and the electrochemical preparation of sodium hydrosulphite (C. C. PATEL and M. R. A. RAO). Two papers on the manufacture and the stabilization and marketing of hydrogen peroxide were read by K. Seshadri. Work done in the C.E.R.I. on the production of heavy water and the electrolysis of sodium sulphate was described in the next two papers, and the session concluded with papers on the operation of Hooker type "S" caustic-chlorine cells (N. KALYANAM) and the factors affecting power efficiency in diaphragm alkali-chlorine cells (N. S. SHIVARAMAN).

Batteries, electrodeposition and electroplating — J. P. Mehrotra of the Indian Standards Institution explained the organization of the Indian Standards Institution and the progress made in the formulation of national standards in two of the industries in which electrochemical processes are involved, namely the batteries industry and the electroplating industry. In the next paper S. Ghosh made a survey of the battery manufacturing industry in India and compared the standards adopted in India with those in other countries. A simple and cheap H.T. battery for radiosonde work was described by B. B. Huddar. V. Aravamuthan and B. B. Dey described a new primary wet cell giving continuous current drains of the order of 0·65 amp. at 1·2-0·8 V., developed in C.E.R.I. T. Banerjee of the National Metallurgical Laboratory then read two papers on electrolytic alloys, one on the structure of alloys electrodeposited at constant potential and the other on alloy plating on an industrial scale. T. L. Ramachar and V. Mathur of the Indian Institute of Science, Bangalore, described a sulphate bath for cadmium-zinc alloy plating and workers from C.E.R.I. described a bath containing copper sulphate, glycerine and sodium zincate for the deposition of brass. Electroplating on light metals was reviewed in a paper by D. S. Tandon and T. Banerjee who also read a paper describing some experiments on plating on aluminium using an iron interlayer. A paper by J. Vaid and T. L. Ramachar on the use of the pyrophosphate bath for tin plating followed next and S. Ramachandran and co-workers described the work on the hard chromium plating of internal combustion engine piston rings carried out in C.E.R.I. A paper on the production of anodic insoluble higher oxides with special reference to manganese dioxide was presented by H. K. Chakravarti and T. Banerjee. The anodization of aluminium formed the subject of two papers. A. C. Dutt and B. K. Choudhuri discussed some of the operation variables in the anodizing process for reflector grade aluminium. A. Jogarao and B. A. Shenoy described the production of anodized films on aluminium for photoprinting. The last paper presented was on the electropolishing of brass by D. R. Dhingra, M. G. Gupta and G. C. Joshi.

Miscellaneous — A paper by G. D. Joglekar and Daneswar Sen (National Physical Laboratory) dealt with the various industries using carbon products, the imports of carbon electrodes in the country, the raw materials and equipment required and the process of manufacture of carbon electrodes and its economics.

K. Chakraborty and T. Banerjee described an electrolytic method for the removal of zinc from silver refinery waste liquor and its subsequent utilization for nickel plating.

The estimation of boric acid in the presence of nickel salts using potassium oxalate as complexing agent was described in a paper by M. R. Verma and K. C. Agarwal.

Recent work on the behaviour of polyelectrolytes was reviewed in a paper by Dr. S. R. Palit. Some interesting new findings in the electrochemistry of aqueous solutions and interfaces were described in a paper by K. S. G. Doss and the inhibition of corrosion of metals was discussed in another by S. C. Shome. The two papers that followed concerned studies on electric discharge in gases; dielectric breakdown in ozonizer discharge was considered in a paper from A. Ramiah. A. Jogarao and A. R. Papa reported studies on the influence of electric discharge on formaldehyde vapour. The last paper presented described work done in C.E.R.I. on the electrodeposition of rubber.

REVIEWS

THE ELEMENTS OF NUCLEAR REACTOR THEORY, by Samuel Glasstone & Milton C. Edlund (Macmillan & Co. Ltd., London), 1953, pp. vii + 416. Price 35*s*.

The present book provides the first comprehensive account of one of the most important fields in nuclear theory and application. The book has been prepared under the auspices of the U.S. Atomic Energy Commission. Gordon Dean, the then Chairman of the A.E.C., says in his foreword: " The text prepared by these men (Glasstone and Edlund) has been reviewed by a number of scientists and engineers within the atomic energy program. . . . The Atomic Energy Commission takes pride in offering this book as an aid to further education and training in the field of nuclear science."

The book is intended to serve as an introduction to nuclear reactor theory, and is an enlarged and revised version of the lectures given by Dr. Edlund at the Oak Ridge School of Reactor Technology. The early chapters deal with such fundamentals of nuclear physics as are essential to an understanding of the working of reactors.

The first chapter is concerned with stability and structure of nuclei. The second deals with nuclear reactions. The production and reaction of neutrons are considered in the third chapter. This chapter also gives a descriptive account of Breit Wigner theory. Chapter IV deals with fission process. The proper nuclear reactor theory begins with chapter V. It is concerned with the diffusion of nucleons. The fundamental diffusion equation is established, and its solution and applications are discussed. This chapter would also be of interest to astrophysicists interested in the study and the flow of radiation in stellar interiors. The problem of slowing down of neutrons due to collisions with the nuclei of moderator is taken up in chapter VI. Chapters VII and VIII deal respectively with the bare homogeneous thermal reactor and the homogeneous reactor with reflector. The theory of heterogeneous (natural uranium) reactors is taken up in chapter IX, and the next chapter describes the time behaviour of a bare thermal reactor. The remaining four chapters deal with reactor control, the theory of homogeneous multiplying systems, perturbation theory and transport theory of neutron diffusion.

The book would be of considerable interest and usefulness not only to one particularly interested in reactor theory, but also to physicists and engineers having a general interest in nuclear physics. (Incidentally it may be mentioned that the book does not deal with the theory of breeder-type reactors.) The treatment in the book is very often mathematical, but the exposition is always lucid and most readable. This is as one would expect from an author of Dr. Glasstone's authority and eminence. The book is a most welcome and valuable addition to the literature in nuclear theory.

D. S. KOTHARI

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

As a result of long experience in the manufacture of electronic instruments, the Philips have taken another step forward in bringing out this volume in an effort to popularize the methods of application of the several types of Philips electrical instruments which have found use in many scientific laboratories and industries all over the world.

This book presents the basic theory and experimental analysis of mechanical vibrations in a manner that is neither too elementary nor too advanced. The fundamental principles explained can be applied with ease to vibration problems which are commonly encountered by engineers and scientists.

Divided into 22 chapters, the book first deals with the definitions and other fundamental conceptions such as steady state vibration of systems of one degree of freedom, which are essential for an analytical approach to any problem in vibration engineering. Analogies between mechanical and electrical oscillations have been given bringing out their physical concepts and the consequent advantage of using such models for vibration analysis.

After dealing with the application of the theory to the system of several degrees of freedom vibration, the author has discussed the theory of isolation and absorption, and damping with examples. The chapters on propagation of vibrations, some special vibration phenomena and detrimental effects of vibration give the reader a clear idea of mechanical vibrations, why they are dangerous and how they can be avoided.

In many vibration problems it is normally difficult to arrive at the correct practical approach and to suggest remedies. Even if a course is decided upon, it would be difficult to choose proper instruments for analysis, as each problem in vibration engineering requires a separate line of approach, elaborate instrumentation and finally a good amount of mathematical computation. The chapter giving some practical hints on vibration measurement is very useful for the technician and the research worker for it suggests the general lines of approach to the solution of many problems and for selection of proper instruments. As a prelude to this most important and useful chapter the author has briefly explained the theory behind a variety of vibration pick-ups and accessories built by Philips.

While dealing with sound and other wave phenomena subjects like sound proofing, seismology, gas vibrations, etc., have been explained briefly. In modern times, these aspects are gaining more importance and, therefore, require to be dealt with at length. Besides, the problems of ground vibrations and structural and foundation vibrations due to blasts, traffic, working of industrial plants are not discussed in the book. A chapter on calibration of vibration instruments would have been useful. No reference is made to the analysis of transients and recent methods of analysis such as mobility, method, etc.

V. CADAMBE

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

It is difficult to review a book of this type for a journal in India. Television is yet to come and there is no accumulated experience to go by. The reviewer claims no first-hand experience in the field of television and has approached the book with the object of finding out how useful it would be to a person well trained in radio engineering to start building and trying out circuits for television receivers. Examined from this standpoint, the book is most valuable.

Valves used for television receivers are reviewed as a whole and classified according to their functions in a television receiver. This is followed by complete data and characteristic curves for these valves and two picture tubes. For each valve, as usual in this series, typical circuits are also described. Inter-carrier sound and flywheel synchronization of the line deflection is next discussed. A description of complete television receiver circuit is then given.

The printing and get-up are excellent and the circuits, characteristics, etc., are extremely well drawn and reproduced. The presentation of the material and the language used are both simple and easy to follow. A feature of the tube data is a discussion of signal to noise ratio. The book is extremely useful to any one who wants to follow the building of a television receiver from the practical point of view. If the reviewer were asked to advise a person who wanted to build a television receiver, he will have no hesitation in recommending this valuable book and the tubes described therein and ask the person to go ahead!

The book can be recommended with confidence to every reader of this type and all degree and diploma students in communication engineering. It should be a valuable addition to science libraries of colleges.

S. C. CHANDRASHEKHAR AIYA

INDUSTRIAL ELECTRONICS, by R. Kretzmann (Philips Technical Library, N. V. Philips Gloeilampenfabrieken, Eindhoven), 1953, pp. 236. Price Rs. 14

This book forms an introduction to the modern practice of industrial electronics. The general principles of engineering electronics have been presented in two parts in a simple and practical way, mostly from the beginner's point of view. The mathematical treatment is elementary and has been introduced only in a few cases dealing with basic circuits.

The first part of the book has been devoted to the general construction, working principles and properties of the various types of electronic tubes. A brief description of the main varieties of electronic tubes with their basic static and dynamic characteristics and the immediate fundamental application has been given in 9 chapters, comprising about 85 pages. This section has been illustrated with as many as 108 figures inclusive of photographs of sections of valves and tube characteristic graphs.

During the last few years, the potentialities of electronic techniques have gained so much recognition that in industry almost every kind of process is accurately controlled and regulated to a great extent by electronic devices. And this has been amply justified in the second part of the book. In this section 11 chapters have been included, each being devoted to one particular type of application. Each application has been described with the basic circuit and the schematic diagram of a practical unit. Even though most of the circuits employ Philips tubes, the principle has been explained in a simple manner and there should not be any difficulty in adopting the circuits for British and American types of tubes. Even the latest applications such as ultrasonic soldering iron, speed and temperature control, etc., have been included. This section is also profusely illustrated with as many as 160 figures, a good many of them being actual photographs.

The book aims at indicating the wide field of application of electronic devices in industry and describes the principles upon which a large number of typical equipment operate. The subject being so vast, it is obvious that all cannot be fully treated in such a small volume. The mathematical treatment is not quite adequate for degree classes. The book will be found invaluable to technicians and engineers engaged in the installation, supervision and maintenance of industrial equipment, to those who desire of acquainting themselves with the technique of electronic control. The fundamental basic circuits have been explained in such a simple way in the book that it can be confidently recommended as a text-book on industrial electronics. A good bibliography is provided for reference and advanced study. The valve characteristics of many tubes manufactured by Philips included at the end of the book are useful.

The printing and get-up of the book are of a high order.

C. S. RANGAN

THE DIAMOND TOOL INDUSTRY IN 1953 (Issued by the Industrial Diamond Information Bureau, 32-34 Holborn Viaduct, London E.C. 1)

This report, the ninth in succession, summarizes the main developments during the year 1953. The following fields are reviewed: diamond as a material, properties of diamond, synthesis of diamond, hardness and microhardness, surface finish, fine boring and fine turning, truing of grinding wheels, diamond powders, impregnated diamond tools, sintered carbide grinding, glass grinding and stone working, rock drilling, wire drawing, diamond use and salvage, new machining methods, and jewel bearing production. With each section references are given to literature, a total of 155 references being quoted. This year's report refers in particular to new developments in hardness and microhardness testing, diamond powders, impregnated diamond tools, and diamond use and salvage. The report will be of interest to all those engaged in the use and production of diamond tools. Copies of this bibliography can be obtained, free of charge, by those interested in the diamond and diamond tools.

SIDE EFFECT OF DRUGS, by L. Meyler, translated by Ph. Vuijsje & W. Mulhall Corbet (Elsevier Publishing Co., Amsterdam), 1952, pp. xii + 268

The future medical historian will record the last two decades as the era which witnessed some of the most notable advances in the field of drug therapy. The development of sulphonamide chemotherapy was the first major event of this era which perhaps gave a fillip to the discovery of an array of wonder drugs like the antibiotics, cortisone and ACTH. This tempo of progress is steadily maintained which serves to enrich the armamentarium of the present-day physician on an unprecedented scale. So much so that it becomes almost an uphill task for the physician in his day-to-day practice of medicine to keep pace not only with the usefulness but also with the untoward side effects of a newly discovered drug. Besides, the current tendency to prepare and market synthetic drugs with possible harmful side effects adds more to the confusion. In view of these it is imperative that the information regarding the side effects of drugs hitherto scattered in various scientific and medical journals should be brought within the purview of a single treatise which could be used as a ready reference. The present volume is a commendable effort in this direction.

The aim of the book has been to embrace all the drugs used in the treatment and cure of diseases. Dr. Meyler has brought together in this volume a wealth of information on the unexpected and untoward effects of drugs and has presented the material in a methodical manner designed for quick and easy reference. The arrangement of the drugs has been based upon the physiologic system of the body — an approach which is of practical importance in therapeutics.

Every effort has been made to make the book up to date by incorporating the results of all recent observations. Each chapter contains a bibliography carefully selected and listing a number of references to original literature.

A volume with such an excellent collection of data is very welcome. The printing and get-up of the book are excellent and it can be heartily recommended as a thoroughly reliable book of reference for the clinician.

N. N. De

A New Periodic Table of the Elements Based on the Structure of the Atom, by S. I. Tomkeieff (Chapman & Hall Ltd., London), 1954, pp. 32. Price 10*s*.

Everybody would agree with Dr. Tomkeieff when he says that " the Periodic System is the most perfect and most comprehensive system of classification — because it embraces all the building bricks which compose the universe . . .".

Beginning with a short history of the origin of periodic classification, the author goes on to discuss the elementary principles of distribution of electrons in the various shells and sub-shells of the atoms and the types of the atoms as deduced from the structure and manner of filling up the atoms. A separate chapter is devoted to the properties of elements, e.g. isotopic abundance, electronic structure, valency, etc. A final chapter is devoted to a discussion of the spiral and conical arrangements of periodic classification.

The oval-shaped distorted spiral has been previously described in a number of places and the attention of the author may be drawn to beautiful pictures appearing in *Life* (May 16, 1949, p. 82) and *Science* [**111** (1950), 662]. In these articles a definite position has been given to rare earths (lanthanides and actinides) for which no provision has been made in Dr. Tomkeieff's arrangements. The periodic table is supposed to be based on the " electronic configuration of the elements ", but the fan-shaped or conical arrangement of the author has ignored the basis of expanded forms of periodic classification of elements in use today. In fact, on closer scrutiny, the Tomkeieff arrangement looks like an adaptation of Bohr arrangement enunciated in 1924, in which the transitional blocks extended from scandium to nickel, yttrium to palladium, and lanthanum to platinum. Considering the properties of the elements one would include copper and zinc, silver and cadmium, and gold and mercury in the respective transitional groups, for in essence the last element in each of the pairs, viz. zinc, cadmium and mercury, is stated to represent the limiting state to be reached by the completion of the d sub-shell. Further, there is a distinct discontinuity in the value of ionization potential of the elements in passing from zinc to gallium, cadmium to indium and mercury to thallium (Hubbard and Meggers, *Key to the Periodic Chart of Atoms*). The six elements, viz. copper and zinc, silver and cadmium, and gold and mercury, are included in the transitional block in any expanded form of the periodic table (Syrkin and Dyatkina, *Structure of Molecules*, p. 34-35; Luder, Vernon and Zuffanti, *General Chemistry*, p. 122). Recently the original Bohr arrangement has also been modified and transitional blocks have been extended to include the members of IB and IIB groups (Mellor's *Modern Inorganic Chemistry*, p. 120).

A small error has also crept in, probably inadvertently, in Tomkeieff's charts regarding the group position of sulphur (charts at the end of the book). The designation of " outer shell " (p. 8) under " transition type " is also misleading as it refers to the penultimate shell.

Tomkeieff's formula adopted by the present author for calculating the length of the period in the table does give an answer to the number of elements in a period, but has perhaps no physical significance. The author's attention may be drawn to the formula given by Kapustinskii [*Dok. Ak Nauk S.S.S.R.*, **80**(3), 365, 1951], $S = 2(n_1 + n_2)^2$ where n_1 and n^2 are the even and odd ordinal numbers of periods from the beginning of the system. This equation leads to what may be called the periodicity of periods of the Mendelejeff's system and is intimately related to even and odd series originally proposed and gives an accurate answer to the number of elements in each period. This may be adopted by the present author in preference to the Keystone formula.

The get-up and printing of the book are excellent.

M. R. VERMA

AN ATLAS OF END-GRAIN PHOTOMICROGRAPHS FOR THE IDENTIFICATION OF HARDWOODS — Forest Products Research Bulletin No. 26 (Department of Scientific & Industrial Research, London), 1953, pp. iv + 87. Price 12*s.* 6*d.*

It is well known that for efficient and economic utilization of timber, one must know that the materials used are of the right type. People who regularly handle timbers recognize them usually by their look, feel, behaviour with tools and so on. But in a country like England, which has to import timbers from other countries, new timbers are often introduced into the market and thus the common practice of recognizing imported as well as home-grown timbers no longer meets the situation. The need for identifying timber in the field more scientifically becomes all the more imperative. The Forest Products Laboratory, Princes Risborough, has, therefore, removed a long-felt want by publishing this atlas for the benefit of the trade, industry and timber technologist.

The publication under review contains end-grain photomicrographs of a wide range of timbers of broad-leaved species (hardwoods) that usually enter the market in the United Kingdom. In all 390 timbers have been dealt with and in each case their scientific and trade names have been indicated. Actually this atlas forms an important adjunct to the previous Bulletin No. 25, entitled *Identification of Hardwoods: A Lens Key*, where a scheme for identifying timbers based on perforated card system is provided. For a rapid check up or comparison of timbers, this atlas will provide sufficient visual aid for practical purposes. For the benefit of the users of this atlas, characteristic anatomical features visible on the end surface of logs have been listed. The photomicrographs would further facilitate the diagnosis and comparison of timbers.

The illustrations are, on the whole, good, as all photomicrographs have been taken directly from the wood after making the end surface smooth with the help of a microtome knife. This technique has certain disadvantages as will be evident from some of the photomicrographs. Timbers with smaller vessels have not usually come out satisfactorily as compared with the large-pored ones. Again, in the case of *Juglans regia* and *Mansonia altissima*, the outstanding anatomical feature — " net-like " parenchyma — is scarcely noticeable, and for the purpose of identification such photographs are of little value.

The get-up of the book and the reproduction of the plates are of a high standard. The publication will be useful not only to those dealing in timber but also to advanced students of botany.

S. S. GHOSH

ANALYSIS OF DEFORMATION — VOL. I — MATHEMATICAL THEORY, by Keith Swainger (Chapman & Hall Ltd., London), 1954, pp. xix + 285. Price 63*s.*

This volume is the outcome of the work done by the author during the years 1945-50 when he was an Imperial Chemical Industries Research Fellow in the University of London, and constitutes one of the few modern comprehensive works on deformation theory. The classical elastic theory developed by Cauchy, Navier, St. Venant and others in the nineteenth century led to differential equations of the quadratic form. There has been little change in the theory of elasticity since then and many recent workers like B. R. Seth, F. D. Murnaghan, R. S. Rivlin and a few others have used the classical quadratic form to analyse finite elastic strain. The author has obviated this difficulty by evolving mathematically linear differential equations for analysing finite strain and has developed a comprehensive linear theory for analysis of finite deformation of all solids.

In this volume the author has formulated the mathematical theory and has tried to draw inferences without solving the equations for specific cases leaving the application of the theory and its experimental verification to the next volume. The general theory in three dimensions has been formulated in the first four chapters. Displacement of a point in an amorphous continuous body, stress and strain are considered in the first three chapters. In the fourth the problem of relating force with displacement is dealt with in a general way. Substances with specific properties, viz. isotropic elastic substances, vizco-elastic isotropic substances and elasto-plastic isotropic substances are taken up in chapters VI, VII and IX. Thermal effect is considered in chapter V, and the theory of yield in chapter VIII. Since vector analysis has been extensively used the appendix in which the subject of vector analysis is treated briefly and yet clearly is a very useful addition to the book, particularly from the point of view of a general reader or an engineer. The author is to be commended for having made a valuable contribution to the field of deformation theory.

C. N. LAKSHMINARAYANA

A TEXT-BOOK OF PHARMACOGNOSY, by George Edward Trease (Bailliere, Tindall & Cox, London), Sixth Edition, 1952, pp. viii + 821, 276 illustrations. Price 37*s*. 6*d*.

The advances in the field of synthetic organic chemistry have been so rapid in recent years that one may be led to believe that in the not too distant a future synthetic drugs may take the place of natural products. But, considering the vast resources of drugs available from the vegetable and animal kingdom, only a small proportion of which has been chemically and pharmacologically investigated so far, there is no doubt that drugs derived from natural products would continue to be in demand for a long time to come.

Dealing with the history, commerce, cultivation, collection, preparation for the market, storage, constituents, uses, identification, standards and evaluation of drugs, textbooks of pharmacognosy require frequent revision so that obsolete matter can be deleted and fresh information incorporated.

Everyone interested in pharmacognosy should, therefore, welcome the sixth edition of the standard text-book by Trease which has appeared three years after the previous edition in 1949. Certain portions from the fifth edition have been revised, condensed or deleted, and new matter has been added on. Three chapters have been added on: The Classification of Drugs for Study; The Literature of Pharmacognosy; Bacteria and Antibiotics. Fluorescence and chromatographic analysis included in one chapter in the fifth edition have been dealt with in two separate chapters to include additional information on partition chromatography.

Some mistakes in printing have, however, crept in. They are: The page reference to *Cassia fistulae fructus* in the index is given as 426 whereas it should be 420. Some mistakes which have occurred in the previous edition have been carried over: Thus, a, b, c and d referred to in the caption for Fig. 229 on page 446 occur in capital letters in the figures. In the key to Map I on page 781, item No. 27, Eriodictyon . . . p. 487 has to be included.

In giving the geographical distribution of drugs the author could have taken into account the partition of India and indicated Pakistan separately. Suitable revision of the maps should have been made on the basis of the political boundaries of the various countries of the world.

The information given on *Belae fructus* (p. 353) is not up to date. Nigella seeds, *Ajowan* and lemongrass are sufficiently important drugs and could have been included in the book.

The get-up of the book leaves nothing to be desired. The book is of great value to students of pharmacognosy, research workers and dealers in crude drugs.

S. A. CHARI

PUBLICATIONS RECEIVED

UTILIZATION OF MOLASSES IN INDIA, by M. N. Mitra (B. L. Sarkar, Calcutta), 1954, pp. vi + 38, price Rs. 2/8

SURVEY OF INDIA TECHNICAL REPORT, 1951 (The Surveyor General of India, Dehra Dun), 1953, pp. v + 47 + 2 index maps, price Rs. 5 or 8*s*.

METHUEN'S MONOGRAPHS ON CHEMICAL SUBJECTS: CHEMISTRY OF THE DEFECT SOLID STATE, by A. L. G. Rees (Methuen & Co. Ltd., London), 1954, pp. viii + 136, price 8*s*. 6*d*.

THE INSULATION OF ELECTRICAL EQUIPMENT, by Willis Jackson (Chapman & Hall Ltd., London), 1954, pp. ix + 340, price 42*s*.

THE AMPLIFICATION AND DISTRIBUTION OF SOUND, by A. E. Greenlees (Chapman & Hall Ltd., London), 3rd ed., revised, 1954, pp. x + 300, price 35*s*.

INDUSTRIAL ORGANIZATION: PART I — GENERAL PROBLEMS, by Bimal C. Ghose (Oxford University Press, Bombay), 1954, pp. 250, price Rs. 8

NOTES & NEWS

Solar battery

An electric battery run on sunlight has been developed by the Bell Telephone Laboratories, U.S.A. The experimental solar battery uses strips of wafer-thin silicon about the size of common razor blades. These strips are extremely sensitive to light. They can be linked together electrically and can deliver power from the sun at the rate of 50 watts per square yard of surface. The solar battery thus delivers 50,000,000 times the power of the recently announced atomic battery which delivers one-millionth of a watt.

An efficiency of 6 per cent has been achieved in converting sunlight directly into electricity. This compares favourably with the efficiency of steam and petrol engines, in contrast with other photoelectric devices, which have a rating of not more than 1 per cent [*Science Newsletter*, No. 157 (1954), Item No. 2035, Indian Scientific Liaison Office, London].

The " condensing enzyme " in *Aspergillus niger*

The occurrence and purification of the " condensing enzyme " in *Aspergillus niger* is reported. The enzyme, which catalyses the reaction

$$\text{acety coenzyme A} + \text{oxalacetate} \rightleftharpoons \text{citrate} + \text{coenzyme A}$$

has previously been reported in animal tissues, yeast and bacteria.

The enzyme was obtained from *A. niger*, N.R.C. 233. The mould was grown in shake culture at 26° in a medium containing malt extract, yeast extract and glucose. After 18-20 hr. incubation, it was removed, washed with water and pressed dry. The mycelium was ground in a ball mill for 30 min. at 1° with an equal weight of alumina and four times its volume of 0·02M phosphate buffer, *p*H 7·2, and then centrifuged at 35,000 r.p.m. for 15 min. The supernatant was used either directly or after fractionation with ammonium sulphate. The fraction precipitating between 35 and 50 per cent saturation was used after dialysis for 14 hr. against 0·02M phosphate buffer, *p*H 7·2, at 1°. *Escherichia coli*, N.R.C. 428, was used as the source of transacetylase.

Both the supernatant and the ammonium sulphate fractions (35-50) of the *A. niger* extract readily catalysed the synthesis of citrate from acetyl phosphate, coenzyme A, and oxalacetate, in the presence of a source of transacetylase. The presence of the " condensing enzyme " in *A. niger* lends support to the hypothesis that citric acid is synthesized, in part at least, through condensation of acetate and oxalacetate [*Chem. Ind.*, No. 6 (1954), 160].

Quality of tea

Extensive morphological studies on a large number of tea plants have confirmed an earlier hypothesis that the amount of hair on the lower epidermis of the fresh leaf is a reliable index of the quality of manufactured tea. This pubescence of the tea leaf has been found to be genetically conditioned, and plants which are categorized in respect of hair on one occasion can be expected from experience to remain in substantially the same order. This discovery provides a useful guide to the selection of plant material for breeding.

Another characteristic studied is the occurrence of a red anthocyanin pigment in the petiole and leaf. Plant types in which this characteristic is strongly marked are of no value for tea production and are not cultivated. However, where a slightly pigmented plant of low quality is crossed with a comparatively non-pigmented plant of good quality, the tea made from the progeny is as good as that made from the high quality parent, and may be better. Vigour is also improved by the cross. The amount of pigmentation, however, is critical, and if the pigment is present in the progeny to an extent that would be noticed by an untrained eye, the quality of the tea is likely to be low [*Nature*, **173** (1954), 630].

A new protective colloid

Lustrex X 820, a carboxyl containing polyelectrolyte resin, developed by Monsanto Chemical Co., is a water insoluble stabilizer or protective colloid possessing all the desirable properties of casein as a stabilizer, at the same time it is free from the disadvantages of susceptibility to bacterial attack and changes in viscosity on standing. It is normally dissolved by adding 3 parts of 0·88N ammonia with continuous stirring to 10 parts of Lustrex X 820 which has been allowed to swell with continuous stirring for about 15-20 min. in 87 parts of water. Lustrex solutions, unlike casein solutions, deposit a water insoluble film immediately on drying. The inclusion of Lustrex X 820 increases the total insoluble content of a film and adds materially to its water resistance.

The most important application of Lustrex X 820 is its use as a protective colloid in emulsion paints, but it has other important uses in the preparation of pigment dispersions, wax emulsions, adhesives, heat sealing compounds, leather finishes, printing inks and high gloss and grease resistant coatings [*Chem. Age*, **70** (1954), 692].

Potassium from sea water

An experimental plant for extraction of potash from sea water by the Kjelland process has been set up at Ijmuiden, Holland. In this process, potash is recovered from sea water in the form of potassium nitrate, *c.* 2,000-3,000 cu. m. of water being processed for the production of one ton of K_2O. The sea water is first subjected to sand filtration and the potash precipitated as an insoluble organic compound (dipicrylamine salt). This compound is separated as a moist crystalline mass which is decomposed with nitric acid to give potassium nitrate, the organic precipitant being recovered for re-use [*Chem. Tr. J.*, **134** (1954), 704].

Vitamins in margarine

The Ministry of Food (Britain) has approved the following recommendations of the Food Standards Committee regarding the addition of vitamins A and D to margarine: (1) (a) The vitamin A content of margarine should be between 27 and 33 I.U./g. and that of vitamin D between 2·9 and 3·5 I.U./g.; (b) for this purpose the vitamin A content should be calculated as the sum of the vitamin A present as such or as its esters plus 0·8 times the β-carotene equivalent of any carotenes present, α-carotene being considered as equivalent to half its weight of β-carotene; (c) when red palm oil is used as a source of carotenes, the β-carotene equivalent should be taken as 53·5 per cent of the total carotenes. (2) The vitamins should be added in the form of an approved master-mix containing vitamin A and D in known proportions. (3) A statement of the vitamin contents in I.U. per oz. should appear on the wrappers of all domestic margarine packed for retail sale [*Chem. Age*, **70** (1954), 564].

Zinc in foods

The Food Standards Committee of the Ministry of Food (Britain) has adopted the Report of the Metallic Contamination Subcommittee in respect of the limits of zinc in foods. The limits recommended are: (1) Beverages, ready-to-drink, 5 p.p.m.; (2) other foods, 50 p.p.m.; and (3) edible gelatin, 100 p.p.m. [*Chem. Tr. J.*, **134** (1954), 448].

New wood preservative

A new preservative, Premasan 116, which will not only protect timber against fungal and insect attack, but also reduce warping, splitting and other changes due to rapid variation in moisture content, has been developed by Monsanto Chemicals Ltd. The preservative consists of pentachlorophenol formulated with water-repellent substances in suitable organic solvents. It penetrates readily into seasoned timber which, after the evaporation of the volatile solvent, regains its natural appearance and may be primed, painted and puttied [*Chem. Tr. J.*, **134** (1954), 730].

Analysis of reducing sugars

A rapid gasometric method for analysis of reducing sugars has been described in which the reduction of reducing sugars to the corresponding polyols is carried out with aqueous solutions of sodium borohydride at *p*H 7. From the amount of hydrogen used up, the concentration of sugar in the solution can be calculated.

Sodium borohydride solution is standardized by measuring the volume of hydrogen gas evolved when the solution is made acid. The sugar solution is treated with an aliquot of the sodium borohydride reagent, and after completion of the reduction, the excess of reagent is determined by acidification, etc., as in the standardization procedure. The difference in volume of hydrogen evolved is equivalent to the amount of reducing sugar. It has been found that one mole of hydrogen is utilized for the reduction of one mole of glucose, fructose, galactose, lactose or glucosamine with an accuracy of better than 1 per cent. Complete reduction is achieved in 20-30 min. at room temperature, or in less than 1 min. at the boiling point [*Nature*, **173** (1954) 401].

Estimation of metallic bismuth

The standard method of estimating bismuth volumetrically is to dissolve the freshly precipitated metal in an acidic ferric solution and titrate the ferrous iron produced with potassium permanganate. When the metal is mixed with oxide, which is required to be determined separately, this method is not suitable as the oxide also dissolves in the acidified ferric solution.

A new method has been developed for the estimation of bismuth in the presence of bismuth oxide. In this method, which takes advantage of the relative positions of bismuth and silver in the electrochemical series ($Bi/Bi^{3+}+0·226v$, $Ag/Ag^{+}+0·798v$), silver is displaced from a neutral silver nitrate solution by precipitated bismuth. Silver is volumetrically determined by titration against standard sodium chloride solution using potassium chromate as indicator. The weight of bismuth as calculated from the silver lost agreed to within a fraction of 1 per cent of the weight of bismuth taken [*Research* (*Supplement*), **7** (1954), S17].

HF as solvent for proteins

Anhydrous hydrogen fluoride (m.p. −83°C.; b.p. 19·5°C.) has been found to be a powerful solvent for a wide variety of proteins. Among proteins which are readily soluble in hydrogen fluoride at 0°C. are ribonuclease, lysozyme, pepsin, trypsin, crystallized egg albumin, bovine plasma albumin, bovine plasma globulin, edestin, peanut protein, globulin, casein, zein, silk fibroin, hide collagen, insulin and adrenocorticotrophic hormone. These are all soluble at least to the extent of 20 mg./cc., and much more concentrated solutions can be easily prepared. The solutions are clear, colourless to faint amber, and are very much less viscous than corresponding aqueous solutions. The globular proteins dissolve rapidly even at −78°C., whereas silk fibroin and hide collagen undergo strong swelling and require many hours at room temperature for complete solution. A considerable variety of metal-complex compounds, e.g. iron-containing proteins cytochrome *c*, catalase and haemoglobin, metal phthalocyanines, and cobalt (III) amine complex, dissolve in hydrogen fluoride without precipitation of metal fluoride.

Proteins were recovered by evaporation of the solutions on the vacuum line. Films of recovered silk fibroin and collagen gave characteristic polypeptide infra-red spectra. Ribonuclease, lysozyme, trypsin, cytochrome *c*, haemoglobin, hide collagen, insulin and adrenocorticotrophic hormone were recovered in a water-soluble state after remaining in hydrogen fluoride solution for 2 hr. at 0°C. Recovered insulin was found by bioassay on mice to have retained 80 per cent of its initial activity, and similarly adrenocorticotrophic hormone was recovered intact with full retention of its original biological activity. This retention of biological activity of the substances after dissolution and recovery from hydrogen fluoride solution suggests that this solvent may have real significance in protein studies. Because of its low freezing point, liquid hydrogen fluoride may be an interesting medium for carrying out chemical reactions on proteins at very low temperatures [*Nature*, **173** (1954), 265].

Preparation of phenyl acetic acid

Investigation of the use of finely dispersed sodium in the preparation of organosodium compounds has resulted in the development of low cost sodium routes to phenyl acetic acid and dimethyl phenyl malonate. The process is based on the formation of phenyl sodium by the rapid quantitative reaction of chlorobenzene with freshly dispersed sodium in toluene at 25°C. These new routes to phenyl acetic acid and dimethyl phenyl malonate appear to be more economical than existing synthesis and do not require the isolation of any intermediates.

Phenyl sodium is used to form benzyl sodium by metalation of an equimolar portion of the toluene reaction medium at reflux temperature. Carbonation of benzyl sodium on solid carbon dioxide or by addition to ether saturated with gaseous carbon dioxide at -20°C. gives nearly theoretical yields of phenyl acetic acid. A slow gaseous carbonation of benzyl sodium at 30°-40°C. gives a 70 per cent yield of phenyl malonic acid and a 25 per cent yield of phenyl acetic acid. Treatment of the reaction mixture, resulting from the gaseous carbonation, with methanol and hydrogen chloride at 60°C. for 5 hr., gives dimethyl phenyl malonate and methyl phenyl acetate which are easily separated by distillation. It is possible to separate the free acids before esterification and subsequently prepare dimethyl phenyl malonate from pure phenyl malonic acid in 94 per cent yield. The overall yield of dimethyl phenyl malonate, based on chlorobenzene, is 65 per cent [*Industr. Engng. Chem.*, **46** (1945), 539].

Moisture-set inks

OIL INKS USED FOR PRINTING labels of food packages develop rancid odours in the drying process. Food products seem to soak up these unpleasant smells, concentrating them to the point where the food is unpalatable. Hence, moisture-set inks are replacing oil inks in printing labels for food packages. Moisture-set inks dry instantaneously, are free from odour, stand extremes of temperature and are tough.

The vehicle in the moisture-set inks contains a high-boiling, hygroscopic solvent and a water-insoluble resin with a relatively high acid under (300 or more). The resin is soluble in the hygroscopic solvent. As the ink system absorbs water, the viscosity of the vehicle decreases, and when the critical point is reached at which the resin is insoluble in the water-solvent mixture, resin and pigment precipitate and the liquids diffuse into the paper stock. A tough, hard, pigmented film is left on the surface. Inks used with plastic wraps are usually solvent formulations which have a slight solution effect on the plastic, or are baked or react with the plastic to achieve binding. For greatest drying speed the ink should have a minimum water tolerance and a high absorption rate. A moderately water-tolerant resin plus a moderately hygroscopic solvent is preferred.

Glycols are used as the solvents in this ink system. Combinations of several glycols are used to ensure the best combination of fast setting, press stability and other factors. Ethylene glycol is regarded as a fast dryer, commercial grade diethylene glycol is rated as medium fast and triethylene glycol, which is medium slow and very stable, is recommended in inks for use on presses where high temperatures resulting from friction might be encountered. Dipropylene, hexylene, and octylene glycols are valuable where their particular combination of properties can be utilized to adjust stability, drying speed, body and tack. A strong co-solvent may be included to increase the water tolerance by increasing the solubility of the resin.

Most moisture-set varnishes (resin plus solvent) are made with maleic or fumaic modified resins. Modified phenolics or alkyds, urea- or melamine-formaldehyde resins, and others are used for specific purposes, and to modify specific qualities. Other modifiers — waxes, wetting agents, high molecular weight polyglycols — are added to control flow and water resistance. Mazein, a vegetable protein, is often included to improve the binding of the film. For the best combination of qualities, between 40 and 60 per cent of resin is necessary in the vehicle.

Since the ink contains a polar solvent, a highly acid resin and water, it presents many problems in printing operations. Since the solvent combination will attack the glue-glycerol composition and natural rubber printing press rollers, it is necessary to use glue-glycol or synthetic rubber rollers. To combat corrosion of metal printing plates, additives are included in the formulation. Colour change in moisture-set inks, another vexing problem, can be corrected by adding salts such as calcium metaphosphate.

Moisture present in most paper stocks and in the air is adequate to bring about fairly fast setting of moisture-set inks. With the use of auxiliary sources of moisture (steam, water sprays), press speeds of over 1,000 ft. per min. become possible. For printing on non-absorbent stocks, temperatures over 700°F. are sometimes used [*Industr. Engng. Chem.*, **46** (1954), No. 3, 15A].

Silicon carbide insulation

FINELY DIVIDED SILICON CARBIDE (SiC) has been found to be a very satisfactory insulation material when substituted for carbon black in a high frequency induction furnace. The relative insulating effectiveness of the various powders showed that a decrease in the particle size of SiC powders results in an increase in their total pore volumes, which in turn enhances their thermal insulating ability. From a study of the stability of the power input to the induction furnace, SiC was found to have superior electrical inertness than carbon black. Under the conditions of the experiment, the power input to the furnace when using all types of powdered SiC tested, increased only 5 to 8 per cent when heated from room temperature to 2,000°C. In comparison, the power input increased approximately 50 per cent when the furnace was heated from room temperature to 1,750°C. using carbon black insulation.

The advantages of using SiC powder are: (1) it acts as a dielectric in the presence of high-frequency magnetic fields; (2) it does not adsorb gases readily; (3) it tends to pack around the susceptor so that when the susceptor is withdrawn the cavity for the susceptor is preserved; (4) its use does not present a major housekeeping problem; (5) it is not readily consumed by oxidation, but will oxidize sufficiently to inhibit the oxidation of the graphite susceptor; (6) it is economical to use. Its disadvantages include: (1) the need for a greater amount of energy to heat the furnace insulation; (2) the maximum furnace temperature is limited to the dissociation temperature of the SiC, but runs up to 2,300°C. have been made with no adverse effects [*Amer. Ceram. Soc. Bull.*, **33** (1954), 43].

Sulphuric acid from phosphogypsum

Phosphogypsum, byproduct calcium sulphate from wet process phosphoric acid production, has little commercial value and its sulphur content is wasted. With a view to conserving natural resources and improving the economics of the wet process, methods of regenerating sulphuric acid from phosphogypsum have been investigated and two promising methods have been developed. Both methods involve the desulphurization of a mixture of phosphogypsum and silica by thermal dissociation and the subsequent conversion of the sulphur dioxide to the sulphuric acid. The desulphurization step may be carried out at temperatures below fusion (calcination process) or at fusion temperature (fusion process). Calcination of agglomerated mixtures of partially dehydrated phosphogypsum and silica (SiO_2 : S mole ratio of 1 and iron-aluminium oxide contents of 3 per cent) at 1,300°C. resulted in complete disulphurization in 15-30 min. As the size of the agglomerate was decreased and the intimacy of mixing was increased, the time required for complete desulphurization decreased. In the fusion process, incorporation of raw phosphate matrix in the charge resulted in a byproduct phosphate slag (10 per cent phosphorus pentoxide) of potential fertilizer value, which should return a significant credit to the process.

The sulphur dioxide concentration in the off-gases from large-scale calcination or fusion plants would be at least 5 per cent which is believed to be high enough for the production of sulphuric acid by a standard process [*Industr. Engng. Chem.*, **46** (1954), 453].

Saccharic acid production

The possibilities of manufacturing potassium acid saccharate on a commercial scale by the oxidation of dextrose with nitric acid are indicated. The oxidation is conducted as a batch process. Commercial grades of granular dextrose hydrate and 40°Bé. nitric acid are used. The mole ratio of nitric acid to dextrose is 3·0.

Nitric acid (40°Bé.) is heated to 130°F., and dextrose is added over a period of 1½ hr. The temperature is raised to 158°F., and the oxidation is continued for an additional 1½ hr. The oxidized liquor is vacuum distilled to recover the residual nitric acid.

Recovery of potassium acid saccharate is accomplished by precipitation in two steps. Potassium hydroxide solution is added to the oxidation liquor while the temperature is maintained at 85°F. by cooling. The first crop is precipitated at *p*H 3·8, filtered, washed and dried. Combined mother liquor and washings are concentrated to one-half volume and then adjusted to *p*H 9·0 with potassium hydroxide. The temperature is allowed to rise to 158°F. and is held there for 20 min. after which it is cooled and adjusted to *p*H 3·4 with 40°Bé. nitric acid. The resulting crystals are filtered, washed and dried. The purity of the first crop of crystals is 99-100 per cent, while that of the second crop is 98 per cent.

Potassium nitrate recovery is accomplished by acidifying the mother liquor to *p*H 2·0 with nitric acid and removing two successive crops of crystals by concentration, crystallization and centrifugation. The second crop of crystals is recycled with the first mother liquor to be concentrated.

The cost of potassium acid saccharate employing a plant having a daily capacity of 9,600 lb. is estimated to be 35·2 cents per pound [*Industr. Engng. Chem.*, **46** (1954), 427].

Acetylene from methane

A new method for the manufacture of acetylene developed by the Badische Anilin und Soda Fabrik A.-G. is based on the partial combustion of hydrocarbons, usually methane, with oxygen. It was worked out on a laboratory scale in 1935-36 and the first full-scale plant was built at Oppau in 1942. The main problems of the process are to eliminate the danger of explosion, to maintain the proper burning condition and to develop burners capable of withstanding thermal stresses. The thermal expansion of burner at the Oppau plant was controlled by special ceramic materials. The capacity of the burner was more than 4,000 cu. m./hr. of methane. The high speed of the gas was required to counter the effect of the rust particles introduced from the methane pipelines. Under these conditions the rust particles are reduced to pyrophoric metallic iron and removed before they could pre-ignite the gas mixture.

Although the burner gases, which contain about 10 per cent of acetylene, can be used directly for chemical processing, in cases where it is necessary to separate the acetylene in pure form, a method has been worked out based on the use of a selective water miscible solvent, the gas being eventually separated into three streams, an acetylene-free poor gas, an acetylene stream and a gas containing the higher acetylene homologues. The acetylene fraction contains not more than 0·2 per cent by volume of propadiene, 0·02 per cent of diacetylene and 0·005 per cent by volume of benzene. This is sufficiently pure for most uses.

Data obtained from large technical plants show that for the production of one kilo of pure acetylene, the following materials are needed: hydrocarbons, 4·3 kg.; oxygen, 4·9 kg.; solvent, 0·005 kg.; steam, 4 kg.; and electric power, 1·5 kW. [*Chem. Tr. J.*, **134** (1954), 447].

Benzole refining

A catalytic pressure process for refining crude benzole is now being operated on a large scale in W. Germany. In the modified process, hydrogen, or water gas, is compressed to 60 or 150 atm. respectively and mixed with the vapours of the crude benzole introduced into the common pipeline under the same pressure as the gas. The mixture passes through a heat exchanger where its temperature is raised to *c.* 200°C. In the following pressure vessel the readily resinifiable constituents of crude benzole polymerize. The mixture then passes to an evaporation vessel in which superheated (400°-450°C.) water gas is introduced. The bulk of the benzole is distilled and the resins separate as a sludge which is subsequently distilled to pitch. The vapours of the de-resinified crude benzole pass through another heat exchanger where their temperature is raised to about 350°C. and then pass through the contact furnace where sulphur is converted to hydrogen sulphide, hydrogen to water and nitrogen to ammonia while any residual olefines are hydrogenated.

In a heat exchanger and cooler, the reaction gases are cooled and pass to a separator where the purified liquid benzole is separated, still under pressure from the water gas. The pressure is then reduced from 150 atm. to 1 atm. in two stages, the liberated hydrogen sulphide and ammonia being removed by alkali and water washes. The yield of purified benzole is stated to be 98 per cent of the crude employed [*Chem. Tr. J.*, **134** (1954), 719].

Continuous caustic finishing

A MAJOR ADVANCE IN CAUSTIC alkali technology is the development of a continuous caustic finishing by the Dowtherm vapour process developed by the Dow Chemical Co., U.S.A. The process has the following advantages over batch evaporation in open, direct-fired cast iron pots: (1) A Dowtherm-heated evaporator installation costs only one-fifth as much as a new pot installation of the same capacity; (2) it uses only half as much fuel; (3) maintenance cost is lower; and (4) the process is automatic. The modified unit is built along the lines of the usual long-tube vertical evaporator, with a vapour head some 8 ft. in diameter mounted directly above the tubes.

Dilute caustic soda solution (0·2 per cent) from the diaphragm-type electrolytic cell contains a little sodium chlorate which is a source of trouble in the Dowtherm-heated high concentrator. Its decomposition liberates nascent oxygen, which rapidly attacks nickel. Sucrose has been found to be one of the most effective reducing agents for chlorates. About 1 lb. of sucrose per ton of mercury-cell liquor is found necessary. The sucrose is usually added as a solution of 23° to 24°Bé., the solution being fed continuously just as close to the inlet of the evaporator as possible.

One disadvantage in the use of sucrose is that it raises the carbonate content of the product, and in cases where carbonate specifications are strict, reduction has to be carried out with metallic iron. The excess of iron is then removed as ferrate or ferrite by adsorption on finely ground strontium sulphate or carbonate.

With diaphragm cell caustic containing the usual amounts of chloride and sulphate and with 2 to 3 per cent carbonate, it is not difficult to reach 75 per cent Na_2O with mercury cell caustic. A set of tubes will finish about 17,000 tons of solid before replacements become necessary [*Chem. Tr. J.*, **134** (1954), 445].

Large-scale production of oxygen

" OXYTON ", A TONNAGE OXYGEN unit for producing large quantities of oxygen required for the direct flash smelting of copper concentrates, has been put into operation by the International Nickel Co. of Canada Ltd. Inco's new oxygen flash smelting process eliminates the fuel normally required for smelting and makes economical the large-scale production of sulphur dioxide from furnace exhaust gases. The air is first liquefied under pressure, and then the oxygen is separated from the other constituents of the atmosphere by distillation and carried as a gas through a 16 in. diameter elevated pipeline from the Oxyton to the smelter.

The important regenerator-heat exchanger system consists of two nitrogen regenerators, each 8 ft. in diameter and 17 ft. long, and two oxygen regenerators, each 4 ft. in diameter and 14¾ ft. long. While one pair of regenerators chills the incoming air, the other pair is being chilled by the separator gases. Working temperatures range from 26° to −170°C. Since most ferrous metals suffer a marked increase in brittleness at sub-zero temperatures, the regenerators were made from special 8½ per cent nickel steel [*Chem. Age*, **70** (1954), 577].

High-pressure ultra-filter

AN ULTRA-FILTER FOR RAPID CONcentration of bacterial toxins is described. The filter may be useful in other fields where highly concentrated solutions of proteins are required.

Filtration through a collodion membrane is carried out under nitrogen at a pressure of 300 lb./sq. in. The membrane is supported on a flat smooth porous tile, which in turn rests on a perforated steel plate. The ultra-filtrate is collected in a flask beneath the filter. The apparatus has a total capacity of 15 l. and a filter area of 400 sq. cm.

The membrane is prepared by stretching a sheet of " cellophane " over a square of plate glass, fixing it to the underside of the glass with " cellotape ". An 8 per cent solution of collodion in glacial acetic acid is poured over the cellophane surface. When the surface has been covered, the glass is picked up and excess of collodion drained from each corner. It is then plunged into cold water. After a few minutes the cellophane sheet is cut away from the glass and the collodion membrane separated from it. It is allowed to harden in running water overnight. After hardening the membrane is found to have one smooth surface and the other slightly uneven. It is placed on tile smooth side upwards and trimmed to fit. Two litres of 0·5 per cent solution of sodium bicarbonate are then forced through the membrane under a pressure of 100 lb. per sq. in. to remove any traces of acid.

Under a pressure of 300 lb. per sq. in., 2 l. of a solution of horse haemoglobin in distilled water (40 mg. per 100 ml.) were reduced practically to dryness in 2½ hr. The haemoglobin remained on the surface of the membrane as a thick film, too dry to flow. The ultra-filtrate passing through gave no reaction to the benzidine test [*Nature*, **173** (1954), 254].

Gyrotron

A NEW INSTRUMENT KNOWN AS the " Gyrotron ", made by the Sperry Gyroscope Co. (Britain), has been developed from observation of the flight-control methods of the fly Diptera. Halteres, the club-shaped lateral projections from the fly's thorax vibrate in a vertical plane through an angle of some 150° during horizontal flight, the motion having a constant amplitude and being maintained at the natural frequency of the system. The end knob of the haltere has a lateral in-and-out motion at twice the frequency of the oscillation of the haltere, and by reason of this in-and-out component of the motion, the fly is able to detect a yawing turn. The Gyrotron developed is sensitive enough to measure rotation as slow as that of the earth and has a speed indication up to about a 100 r.p.m.

The basic detector unit of the Gyrotron consists of a tuning fork which is maintained in vibration with constant amplitude by an electromagnetic drive. This is used to detect a rotation about the axis of the " handle " of the fork. The tines oscillate inwards and outwards in a way that corresponds to the essential part of the motion of the halteres of a fly.

This device, which is more robust and sensitive than the gyroscopic type currently in use, has an immediate possibility as a normal rate-of-turn meter for aircraft [*Nature*, **173** (1954), 572].

Improved infra-red lamp

AN IMPROVED INFRA-RED LAMP, which gives twice the heat energy on the same current as ordinary bulbs, and takes up much less space, is announced by the General Electric Co. (Britain). The new tubular shaped lamps are from 5 to 10 in. long and not much thicker than a cigarette. The tubes are made of fused translucent quartz. The 500-watt models weigh only three-quarters of an ounce, compared with 4 oz. for the bulb types, and withstand both high temperatures and violent changes of temperature. The lamps produce full radiation immediately, without a warm-up period, and produce some visible light as well as infra-red radiation. The life of the tube is expected to be 5,000 hr. [*Science Newsletter*, No. 157 (1954), Item No. 3034, Indian Scientific Liaison Office, London].

New tablet coating method

A PRACTICAL METHOD OF PRESS coating tablets has been evolved by the Evans Medical Laboratories, England. The process consists of the application of a suitable coating material by compressing it in the dry state on to a ready formed " core tablet " of the active ingredient. The process is rapid and automatic. A special device for the correct centring of the core tablet in the machine has also been designed. " Prescoted " tablets can be made to disintegrate more readily than tablets prepared by the conventional pan-coating process, since they need not be compressed so hard, nor is a protective coating required for hygroscopic ingredients [*Chem. Age*, **70** (1954), 428].

High Polymers — A Symposium

THE INDIAN ASSOCIATION FOR THE Cultivation of Science organized a symposium on High Polymers on 29-30 March 1954 in Calcutta. The symposium was attended by scientific workers from research institutions and industrial firms from all parts of the country. The opening session was presided over by Prof. Santi R. Palit. Dr. M. N. Saha delivered the inaugural address.

Eighteen papers were presented to the symposium.

Dr. A. Lahiri (Fuel Research Institute, Dhanbad) initiated the discussion with a paper on polymeric constitution of coal. Dr. Lahiri observed that coal is a naturally occurring polymer similar in structure to cellulose or rubber, the repeat unit tending to be in one plane only. He emphasized the need for further studies on the structure of coal, particularly its solution by the established techniques of high polymer chemistry. The reaction and properties of coal are markedly influenced by their colloid structure and cross-linking may take place in high oxygen containing non-coking coals. The study of the adsorption isotherm of water vapour on coal indicates the presence of a pronounced hysterisis loop between sorption-desorption cycles which is an indication of micro-capillary structure of coal. The surface area values lie in the range of 20-200 sq. m. per g. of coal, depending on rank. X-ray diffraction studies indicate the presence of incipient layer plane structure present in coal. Studies on bituminous coal, viz. pyrolysis in a molecular still, action of solvents, mild hydrogenation and mild oxidation, have shown that the nucleus of this coal is a condensed C_6 ring structure with occasional heterocyclic rings containing oxygen, nitrogen and sulphur. Infra-red spectroscopy shows that coal is a gel and that in the course of metamorphosis from the stage of peat to high rank coal with 90 per cent carbon, the change is from a lyophilic to a lyophobic colloid.

Dr. D. Banerjee (National Rubber Works, Calcutta) spoke on the rubber industry in India. About 22,000 tons of raw rubber are annually processed by the industry. Of this quantity, Indian plantations provide 20,000 tons, the balance being imported. Among the rubber goods manufactured in the country, tyres account for nearly 67 per cent of the total consumption of raw rubber.

Dr. D. B. Das (Jardine Henderson Research Laboratories, Calcutta) gave an account of the structure and various new uses of fibres, and discussed various problems relating to cotton, cellulose and jute fibres.

Six papers were on plastics.

Dr. S. Mukherjee (Indian Institute of Sugar Technology, Kanpur) discussed the possibility of manufacturing low cost thermosetting plastic from sugarcane molasses containing about 50 per cent of sugar. On condensation with phenol obtained from wood tar, molasses yields a resin insoluble in water, which on mixing with requisite quantity of filler, hardening agent and lubricant gives insoluble and infusible thermosetting plastic. The physical and electrical properties of the finished product compare favourably with those of phenol-formaldehyde plastics.

Plastics from protein and lignin was the subject of another paper by Shri T. V. Subba Rao (Tata Oil Mills Co. Ltd., Bombay) who briefly reviewed the existing knowledge on proteins and lignin with special reference to the various processes suggested for their utilization as plastic compositions.

Dr. P. K. Chaudhuri, in his paper on thermosetting moulding powder from agricultural wastes, described a simple method for the preparation of a plastic composition from groundnut shell and sawdust without the use of formaldehyde. A small percentage of a phenolic substance is necessary to bring about the conversion of the shell or sawdust into the moulding powder. No special equipment is necessary for the reaction. The method of fabrication is almost similar to that of the phenolic resin. The moulding conditions, the curing time, temperature, etc., are also practically the same. The cured product is unaffected by water and acetone and has a high resistance to temperatures up to 230°C. which it can withstand without any sign of distortion or decomposition.

The other three papers dealt with Plastics Industry in India

(Shri N. Srinivasan, New Delhi); Standardization in the Field of Plastics (Shri V. B. Mainkar, Indian Standards Institution, Delhi) and Future Possibilities of Plastic Industry (Shri T. V. Subba Rao, Tata Oil Mills Ltd., Bombay).

Five papers were presented on the fundamentals of polymerization. Shri K. C. Mazumdar (Indian Institute of Sugar Technology, Kanpur) put forward new equations to explain the distribution of molecular weight of high polymers as affected by chain transfer.

The second paper on determination of kinetic constants of polymerization of vinyl monomers using various peroxides and azobisnitriles by (late) Shri Nani Gopal Saha (Indian Association for the Cultivation of Science, Calcutta) was read by Shri U. S. Nandi. The author studied the kinetics of addition polymerization with nine substituted peroxides and seven azobisnitriles both in bulk and in solution. Most of the catalysts were found to be ideal in behaviour and follow the square root law. Substituents were found to have marked effect on the initiation and transfer reactions. The nitro substituted dibenzyl peroxides were found to behave abnormally.

Prof. Santi R. Palit read out the last two papers, " Studies on Chain Transfer " by R. N. Chadha and G. S. Misra (Lucknow University, Lucknow) and " Studies on Macromolecules " by N. H. Shibaramakrishnan and M. R. A. Rao (Indian Institute of Science, Bangalore). The first paper presents a study on the chain transfer reaction between growing styrene (M) polymer radical and toluene (S), when catalysed by phenylazotriphenyl methane (B). It has been shown that the transfer constant from the slope of I/P against S/M plots at constant B/M values is not appreciably affected by the presence of low concentrations of the catalyst and the initiation reaction was found to be bimolecular. The paper on macromolecules dealt with a study of spreading properties of rubber and its derivatives. The effect of protein content and solvent on the spreading of rubber was studied and it was found that the double bond of the isoprene group was responsible for the spreading property of rubber. The rate of oxidation of rubber films as influenced by the *p*H and halogens in the aqueous substrate was discussed and a comparative study of the spreading and other physicochemical properties of chlorinated rubber samples had been carried out.

Studies carried out on the use of polyvinyl pyrrolidone as plasma expander and its chemical and biological examination were described in a paper on high polymer therapy by Shri S. K. Ganguli (Bengal Immunity Research Institute, Calcutta). The product was made isotonic with blood with the addition of electrolytes and tested biologically for maintenance of blood pressure by intravenous transfusion in artificially bled experimental animals.

Dr. S. Mukherjee (Indian Institute of Sugar Technology, Kanpur) in his paper on ion exchange resins from sugars described the preparation of a number of cation exchange resins from sugar using different proportions of sucrose and phenolsulphonic acids at different temperatures of condensation.

Dr. S. K. Mukherjee (Science College, Calcutta) presented a paper on the use of ion exchange membranes as electrodes in the determination of the activities of alkali metals. This is an improvement on the old clay membranes in which Dr. Mukherjee substituted ion exchange clay by synthetic resins thereby improving the accuracy and sensitivity of the method. Some possible developments on the preparation of these membranes in which mixture of ions could be determined by proper choice of some fixing components on the resin molecule were suggested.

In a comprehensive survey of ion exchange resins, Dr. S. L. Bafna (National Chemical Laboratory, Poona) dealt with various aspects of the subject with special reference to the modern uses of anion and cation exchange resins and the application of the basic principles for synthesis of cross-linked polymers to the synthesis of ion exchangers.

The concluding paper dealing with gums as polyelectrolytes was read by Dr. Sadhan Basu (Indian Association for the Cultivation of Science, Calcutta). Dr. Basu observed that natural gum acid salts like sodium arabate and sodium salt of agar acid have been found to behave like synthetic polyelectrolytes, e.g. polyvinyl pyridinium methyl bromide. The results which have been corroborated by viscometric and osmometric methods, point to the conclusion that gum acids are linear chain polymers with some branching.

International Conference on Low Temperature Physics

THE THIRD INTERNATIONAL CONference on Low Temperature Physics and Chemistry was held in Houston, Texas, on 17-22 Dec. 1953. Delegates from leading laboratories in England, Holland, Belgium, France, Switzerland, Germany, Canada, Australia and the U.S.A. attended the conference. Over one hundred papers were presented and the sessions covered a wide field of studies at liquid helium temperatures. The properties of liquid helium isotope three and the new theory on superfluid liquid helium by Prof. Feynman of California Institute of Technology were much discussed. A new magnetic cycle refrigerator capable of maintaining a constant temperature of 0·2°K. was described by Dr. C. Heer and Dr. J. Daunt of Ohio State University.

Prof. Pippard reported experiments on the residual flux trapped in superconducting tin-indium alloys. The experiments consisted of measuring the flux in a tin-indium cylinder after the superconducting transition has been effected by removing a transverse magnetic field. For tin with less than 1·8 per cent indium, it is found that the percentage of flux trapped (defined as $8\pi M/H_c$, where M is the magnetic moment of the rod and H_c the critical field for the temperature at which the transition is made) is constant at low temperatures and decreases near the critical temperature. For 2 per cent indium content, the behaviour is quite different. The percentage of flux frozen in is constant at low temperatures but increases very sharply near the critical temperature. These results are taken as evidence that the indium impurity can lower the interphase surface energy between normal and superconducting regions.

Results of high pressure research at low temperatures were presented by several authors. C. A. Swenson of M.I.T. described an apparatus capable of producing 10,000 atmospheres pressure with which he is studying Young's modulus of selected materials at temperatures from 300° to 4°K. M. D. Fiske of General Electric reported an ingenious " hot wire " technique by which he is able to obtain hydrostatic pressures with solid helium. G. O. Jones of Queen Mary College, University of London, presented his recent investigations on the effects of pressures up to 40,000 atmospheres (obtained at the apex of a double cone clamped tightly before cooling) on the phenomenon of superconductivity. Jones found that this extreme pressure reduces the temperature at which tin, lead and thallium become superconducting. For tin and lead the results are in accord with previous work at much lower pressures, but in the case of thallium, Jones's results are opposite in sign and thus contradict early low pressure work and recent high pressure work by Fiske, who used the same technique as Jones. The most spectacular result of Jones's work was that he has caused bismuth, which at extremely low temperatures has remained a normal conductor, to become superconducting at 7°K. under 40,000 atmospheres.

There were a number of interesting papers on magnetism at low temperatures. Dr. N. Kurti of Oxford University reported the work on nuclear orientation — the nuclei, in particular the spin assignment of the various levels, the multipole character and parity changes of the transitions and finally the nuclear magnetic moment of the radioactive nucleus. The measurement consisted in the determination of the polar diagram of the gamma-ray emission and of the directions of the polarization of the gamma rays.

The theory of liquid helium was a subject of considerable discussion. Prof. Feynman presented a paper on the nature of the elementary excitations in the liquid. At very low temperatures, near the absolute zero, the excitations consist of phonons, as has already been suggested by Landau and supported by the results of experiments on second sound. At temperatures above 0·6°K., other excitations are important. These excitations are similar to the " rotons " proposed by Landau and consist of the rotational motion of small groups of atoms. The Bose-Einstein character of He^4 is important for the existence of these excitations. Approaching the condensation from the high temperature side, the picture is somewhat different. Prof. Feynman ascribes the lambda transition to the Bose-Einstein condensation, but has described the properties below the lambda temperature only in terms of the excitations described above.

Dr. Temperly also reported work on the theory of helium isotopes three and four and described the structure of He^4 in terms of small aggregates of atoms, a picture somewhat similar to that presented by Prof. Feynman. The theory has the advantage that both helium transitions can be treated in one model. Dr. Temperly also described how the introduction of Van der Waals forces in an ideal Fermi gas could describe roughly the melting and evaporation of helium three.

Several experiments of fundamental importance for the theory of helium isotope three were reported. Vapour pressure measurements down to 0·47°K., reported by S. G. Sydoriak and T. R. Roberts of Los Alamos Scientific Laboratory, are in agreement with the calculations of Chen and London, who have predicted that there is no excess of entropy at higher temperatures. These measurements indicate that there is no transition in He^3 at some lower temperature similar to the lambda transformation in He^4. The measurement of G. de Vries and J. G. Daunt of Ohio State and of Osborne, Abraham and Weinstock of Argonne National Laboratories on the specific heat of He^3 also indicates that there is no excess entropy at the temperatures investigated. These measurements also seem to show that the specific heat of He^3 is not linear with temperature, as would be expected for an ideal Fermi gas. The nuclear susceptibility measurements of W. Fairbank, W. Ard, H. Dehmelt, and W. Gordy of Duke University also show that He^3 does not behave as an ideal Fermi gas down to 1°, since the susceptibility does not become independent of the temperature, as would be expected, but is still proportional to the reciprocal of the temperature. To support the importance of the Bose-Einstein condensation in the theory of liquid helium, Drs. Guttman and Arnold of the University of Chicago reported experiments demonstrating the nonparticipation of He^6 in the superfluidity of He^4.

A number of other papers reported experiments on the properties of helium isotope four. Measurements at the National Bureau of Standards, U.S.A., by R. Hudon and W. Hanson on the attenuation of second sound and similar measurements by K. Atkins at Toronto indicate that the normal thermal conductivity as well as the viscosity must be taken into account, as predicted by Khalaunikov. Measurements on the helium film reported by K. Mendelssohn and by L. C. Jackson indicate that the mechanism of the formation of the film is still not well understood. The thickness of the film seems to depend on the method of measurement and the relation of the thick saturated film to the unsaturated film is still something of a mystery.

G. Hercus and J. Wilks of Oxford reported measurements on the specific heat of helium. They report results that are about 10 per cent higher than those found by previous workers. Their results seem to be in agreement with some of the already available thermodynamic data.

Measurements of the susceptibility of a paramagnetic salt between 1·2° and 4·2° by R. Ericksen and L. Roberts of the University of Tennessee and Oak Ridge National Laboratories indicate that the present vapour pressure temperature scale for He^4 may be in error by as much as 12 millideg. at the lambda point. These conclusions are confirmed by comparison with other thermodynamic data.

Development of pepper and cashew-nut industries in India

THE CREATION OF A SEPARATE fund of Rs. 1·25 crores at the Centre for the development of pepper and cashew-nut industries is the main recommendation made by the Spices Inquiry Committee in its report to the Government of India. Pepper and cashew-nuts are the most important dollar-earning commodities of South India, pepper earning nearly Rs. 13·13 crores and cashew kernels about 7 crores per annum. The Committee has, therefore, recommended that their scientific development should be undertaken for the benefit both of the producing States and the Central Government.

In addition to pepper and cashew-nut, the Committee has separately dealt with the problems of cardamom, ginger, turmeric and lemongrass oil and the recommendations are given below.

Black pepper — Nearly half of the world supply of 43,500 tons is produced in India, the bulk of the indigenous production being exported to overseas market. The average annual exports from India during the triennium ended 1952-53 amounted to 14,000 tons, valued at Rs. 21·17 crores.

In order to reduce the cost of production and offer more competitive prices to foreign consumers, the Committee has recommended that two regional research stations should be started in the important producing areas of Travancore-Cochin and Malabar and two sub-stations at Sirsi in North Kanara and some suitable hill area in Assam. In order to increase internal production, it has urged encouragement being given to: (1) intensive methods of cultivation, (2) replacement of old and uneconomic vines and (3) extension of cultivation wherever possible. To provide the necessary inducement, the Committee has recommended that the Government of India should create a Pepper Development Fund and earmark from the export duty levied on this article a sum of not less than Rs. 1 crore for developing the production and marketing of these crops according to an integrated ten-year plan.

Cashew-nut — India is the principal source of supply of cashew-nut in the world markets and accounts for more than 95 per cent of the international trade in this product. The raw cashew-nut, however, is in short supply in India and out of the 26,012 tons of kernels processed in India during 1951-52, nearly half the quantity was extracted from raw cashew-nut imported from East Africa.

The Committee urges encouragement of extensive cultivation of the crop on a plantation basis on the east coast of Madras, the coastal districts of Ratnagiri and North Kanara in Bombay State and parts of Coorg and Mysore. The Committee recommends the creation of a development fund of Rs. 25 lakhs for a period of 10 years for extending cashew-nut cultivation and other developmental measures concerned with the industry. An important byproduct of the cashew-nut processing industry is the cashew-shell liquid. As the industrial utilization of this byproduct presupposes a uniform quality, the Committee has recommended the adoption of standard specifications for its manufacture.

Cardamom — India is the principal supplier of cardamom in the world. The normal crop is expected to be 1,800 tons, while the average demand for this spice in the world markets is reckoned at hardly 1,200 tons annually. The Committee has recommended that research should be carried out by the National Chemical Laboratory, Poona, and the Council of Scientific & Industrial Research to find out alternative uses of cardamom and cardamom oil, and for greater utilization of this spice in India itself. It has also suggested the opening of two additional research stations for conducting agronomic and botanical researches on the crop, one in the Saklespur area (Mysore State) and the other in the Cardamom Hills of Travancore-Cochin.

Ginger — In India, the preparation of commercial dry ginger is largely confined to Travancore-Cochin and Malabar on the west coast, and the average annual supply from these sources is reckoned at 10,000 tons, as against 1,500-2,500 tons available from Sierra Leone and 1,000-1,500 tons from Jamaica. Indian varieties are, however, not much preferred because of their higher fibre contents as well as relatively higher price. Since the export trade is largely dependent on improvement in the quality of indigenous varieties, the Committee has recommended the opening of research stations in all typical producing areas.

Turmeric — The total annual out-turn of dry cured turmeric is 1,20,000 tons, out of which 10,000 tons are exported. As the Committee was unable to obtain adequate evidence concerning the problems of the industry, it has recommended a detailed survey of the industry by the Central Government.

Lemongrass oil — India is the largest supplier of the oil in the world markets, the main producing areas being Travancore-Cochin and Malabar. The annual supply of the oil is at 700 tons at present, but the demand for it has declined since last year.

Preliminary investigations carried out by the Government of Travancore-Cochin have indicated the possibility of utilizing Indian lemongrass oil for synthesizing ionones and vitamin A. The Committee has, therefore, recommended that a pilot plant should be set up in the State for the commercial manufacture of these synthetic products and that the Central Government should subsidize this project and encourage the use of these products by Indian industries.

Indian Standards

THE ISI HAVE RECENTLY ISSUED a standard (IS : 456) entitled " Code of Practice for Plain and Reinforced Concrete for General Building Construction ". The publication is intended chiefly to cover the technical provisions relating to the use of cement concrete and reinforced cement concrete in general building construction. In such structures as tanks, reservoirs, chimneys, bridges, shell structures, etc., where the speciality of the structure relates principally to the mechanics of design, the general provisions of this code may be applied with such modifications as found necessary to suit the special conditions of the case under consideration. This code does not apply to special types of concrete constructions such as pre-stressed concrete construction. In addition to sections explaining Terminology and Symbols used in the code, other sections deal with Materials, Concrete mix, Design, Workmanship, and Inspection and Testing. The 10 appendices included in the code are: Specification for cold twisted steel bars for concrete reinforcement; Preliminary test for compression strength of concrete; Field method of determining the necessary adjustment for bulking of fine aggregates; Method for determining surface moisture in fine aggregates; Works test for compression strength of concrete; Works test for transverse strength of concrete; Test for consistency of concrete (slump test); Live loads and wind loads in buildings; Specification for welding of reinforcement in reinforced concrete work; and Equivalent designations of IS, BS, ASTM and Tyler test sieves.

The following are some of the other standards issued by the Indian Standards Institution: (1) benzole, industrial grade; xylol, industrial solvent grade; amyl alcohol, industrial solvent grade; butyl alcohol, normal, industrial solvent grade; (2) methods of test for dissolved acetylene; (3) hard coke; (4) glass making sands;

(5) cotton-covered copper wire and enamelled copper wire; (6) expanded metal made from steel; (7) general lighting service electric lamps; (8) reels for electrical winding wire.

The British Welding Journal

THIS NEW MONTHLY HAS BEEN started with the co-operation of the Institute of Welding and of the British Welding Research Association. The journal is intended to provide a unified avenue of publication for all aspects of welding, and amongst the papers contained in the first issue are: welding as a career; the welded structure in a pump-house foundation; the effect of steel quality on spot-welding properties; and the use of self-adjusting arc equipment for welding a light-alloy deckhouse. The journal is published from 2 Buckingham Palace Gardens, London S.W. 1 (members, free; non-members, 10*s*.).

Announcements

Lady Tata Memorial Trust Awards, 1954-55 — International awards of varying amounts (totalling £6,275) for research in diseases of the blood with special reference to Leucaemias are made to Doctors J. F. Kieler (Denmark), Astric Fagraeus and Bo. Thorell (jointly) (Sweden), R. Rask-Nielsen (Denmark), R. Robineaux (France), J. Nordmann (France), N. A. Stenderup and F. Kissmeyer-Nielsen (on a joint research project) (Denmark), J. Ringsted (Denmark), J. Rygaard (Denmark), M. Seligmann (France), G. Negroni (Italy) and A. Sreenivasan (Bombay).

Indian scholarships of Rs. 250 per month each for one year for scientific investigations having a bearing on the alleviation of human suffering from disease are awarded to Dr. (Mrs.) M. Aikat (Gwalior), Miss K. S. Laul (Bombay), Mr. P. R. J. Gangadharam (Bangalore), Mr. N. V. Bringi (Bombay), Dr. R. S. Grewal (Lucknow), Mr. N. A. Nityananda Rao (Bangalore) and Mr. T. K. Sundaram (Madras).

Science Research Scholarships — Shri K. Aghoramurthy of the University of Delhi and Shri S. Chandrasekhar of the Indian Academy of Science, Bangalore, have been awarded the 1954 Science Research Scholarships by the Royal Commission for the London Exhibition of 1851 and the Rutherford Scholarship of the Royal Society, London.

A symposium on " The Vegetation Types of India " will be held at Baroda by the Indian Botanical Society on 31 Dec. 1954. The topics covered are: forests, grasslands, aquatic vegetation, mangrove, desert vegetation, vegetation of other habitats such as sand dunes, silted banks, eroded and barren areas, etc. Workers in the field are requested to send their manuscripts together with brief abstracts so as to reach the Convener, Steering Committee, Department of Botany, University of Saugar, Saugar, by 1 Sept. 1954.

The XXVII International Congress of Industrial Chemistry is to be held in Brussels from 11 to 19 Sept. 1954. The Congress will include 29 sections grouped under the following main headings: (1) general problems of the chemical industry; (2) fuels; (3) nuclear science; (4) metallurgy; (5) industrial inorganic chemistry; (6) cements, building materials, glassware, ceramics, enamels; (7) industrial organic chemistry; (8) foodstuffs and agricultural industries; (9) colonial problems; (10) organization: industrial, commercial and professional. Full particulars of the Congress may be obtained either from the Secretariat du Comite d'Organization, XXVII Congress International de Chimie Industrielle, 32 Rue Joseph II, Brussels, or from the Commission Permanente d'Organization des Congres de Chimie Industrielle, 28 Rue Saint Dominique, Paris 7.

INSTRUMENTS & APPLIANCES

MODIFIED INFRA-RED GAS ANALYSER

The following advantages are claimed for a new infra-red gas analyser, the type S.B.I.: greater compactness and flexibility, saving in cost, reduced effect of vibration, maximum sensitivity, and a simple electrical circuit.

The instrument can be used either with a spot galvanometer such as that manufactured by the Cambridge Instrument Co. Ltd., or with a Philips valve voltmeter. An internal battery provides the high voltage, 90 V., for the single amplifying valve; since the anode current is only 0·3 ma. the battery has a long life. If desired the high voltage supply can be taken from the Philips valve voltmeter when this is used. Low voltage supplies are obtained from a.c. mains and are stabilized with a constant voltage transformer.

An inexpensive recorder such as the Elliott, type 230, can be connected directly to the output circuit of the valve voltmeter. This recorder is available with high and low relay contacts so that alarms or controllers can be operated without difficulty. The output from the gas analyser can be applied to a C.R. oscilloscope when the fastest possible response is required.

When the highest sensitivity is required, two 20 cm. tubes are used. A sensitivity of full scale for 0·01 per cent by volume of such gases as carbon dioxide and nitrous oxide can be achieved. Normally the sample tube is fitted with mica windows, but fluorite can be substituted at an extra cost if, for example, the tube is to be evacuated.

The multi-cell arrangement provides three paths in the ratios 1: 20: 100, so that with most gases the ranges 0-1, 0-10 and 0-100 per cent can be covered. A tap system is incorporated so that the range is changed by setting the taps. No other adjustment is required in operation.

An important advantage of this arrangement is that the calibration of the instrument can easily be checked by setting to the 100 per cent range and passing in the pure gas. Four fluorite windows are used in the multi-cell to ensure accurate path lengths. The cell is demountable for cleaning. Dry carbon dioxide-free air or other non-absorbing gas is passed through the tubes not in use. The instrument is manufactured by C. A. Parsons & Co. Ltd., England.

ELECTRONIC RECORDING DEVICE

The new Philips electronic apparatus consists of a potentiometer which is continuously balanced with the aid of an electronic amplifier and a servomotor system. Direct reading is obtained on an indicator dial and the voltage can be recorded at any instant by a pen, connected with the servomotor dial drive, on a paper roll continuously driven by a synchronous motor. Special features claimed are its high precision currentless measuring, high sensitivity, high speed balance, remote measuring possibility, etc.

TEMPERATURE TRANSMITTER

A new air-operated transmitter for distant indication, recording and control of temperature incorporates a mercury-in-steel system and is suitable for temperatures up to 650°C. It employs the force balance principle, requires a compressed air supply of 20 p.s.i., and has a consumption of 1/6 cu. ft. per minute.

The following advantages are claimed for the device which has been designed by Negretti & Zambra Ltd., England: no capillary is required between the sensitive bulb and receiving instrument; the force balance principle needs only a maximum movement of 0·002 in. of the Bourdon tube, thus ensuring freedom from fatigue and a long life; a small sensitive bulb is used giving a high speed of thermal response, and the sensitivity of the balance system is such that for a temperature change of 0·5 per cent of the range the air leak valve remains wide open or fully closed until balance conditions are obtained, i.e. the correct value is transmitted in minimum time. A span as small as 20°C. is normally available.

The temperature pressure relationship is linear over the whole scale to within ± 0·5 per cent; the pressure output is the standard 3-15 p.s.i. for any given range, and no external booster or relay is required on piping runs up to 200 ft. Higher speed of response can be obtained, for example when required for air conditioning control, by using a capillary type bulb; the system is not affected by changes in barometric pressure.

The pressure output is not influenced by ambient temperature variations up to 30°C. at the transmitter head. For high temperature ranges a stem extension is introduced.

In addition to the measurement transmitter an alternative type is available incorporating a control mechanism which can be directly connected to a control value.

RADIOPAQUES

Iodinated organic compounds such as chloriodized oil, iodoxyl and diodone are now being manufactured by Bengal Immunity Co. Ltd., Calcutta, for use as X-ray visualization diagnostics. The compounds are claimed to satisfy the necessary requirements of radiopaques.

LIGHT-WEIGHT TUNING FORK

A light-weight Mg-Al alloy tuning fork developed by Hargolal & Sons, Ambala Cantt., is claimed to be accurate to ±1 per cent. The influence of mechanical fatigue and temperature is considerably minimized.

BIBLIOGRAPHICAL LIST OF PAPERS PUBLISHED IN SOME INDIAN SCIENTIFIC PERIODICALS, MAY 1954

CHEMISTRY

Biological

BANERJEE, R. M. & DAS, N. B., Studies on the diastatic activity of certain Indian wheats, *Indian J. agric. Sci.*, **24** (1954), 45

BANERJEE, M. & GUPTA, S. N., A quick and economical method for the determination of chromium in chrome tanned leather, *Tanner*, **8**(12) (1954), 14

BARAT, S. K., A note on the tannage with chebulinic acid, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 217

BARAT, S. K., A note on the tannage with fractionated myrobalans, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 218

BHATTACHARYA, S., CHOWDHURY, N. K. & BASU, U. P., Studies on vitamin A in solution. Part VI. Stability in relation to concentration and chemical forms of vitamin-A and solvents, *J. Indian chem. Soc.*, **31** (1954), 231

BHATTACHARYA, S. & BASU, U. P., Studies on vitamin-A in solution. Part VII. Effect of trace metals, *J. Indian chem. Soc.*, **31** (1954), 241

BOSE, B. C., GUPTA, S. S. & DE, H. N., Effect of deficiency of thiamine and pantothenic acid on the synthesis of acetylcholine in rats, *Curr. Sci.*, **23** (1954), 122

CHAUDHURI, H. N., Variation of alkaloid content due to difference in size of the leaves of *Datura metel* Linn., *Indian J. Pharm.*, **16** (1954), 34

CHOWDARY, P. S., JOSEPH, K. A. & PADMANABHAN, K., An analytical study of indigenous tanning materials, *Tanner*, **8**(12) (1954), 18

DAKSHINAMURTI, K., The amino acids in the leaf of *Azadirachta indica* (*melia*), *Curr. Sci.*, **23** (1954), 125

KLAVEREN, F. W. VAN, BANERJEE, D., SHRIVASTAVA, P. C. & PATEL, S. A., A photometric determination of vitamin B_{12}, *Indian J. Pharm.*, **16** (1954), 36

MISRA, RANI (Miss) & GYANI, B. P., Light absorption and approximate indicator constants of extracts of some Indian flowers and their indicator properties, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 167

NAIK, M. S. & NARAYANA, N., Riboflavin in gram seedlings, *Curr. Sci.*, **23** (1954), 123

RAMA RAO, P. B., BALAKRISHNAN, S. & RAJAGOPALAN, R., Supplementary value of a malted ragi food, *Sci. & Cult.*, **19** (1954), 561

RATTAN SINGH, RAFIQUE, M. & BAINS, G. S., Investigations on the preparation and use of sweet potato and groundnut cake flours in conjunction with wheat for leavened bread (*dabal roti*) and chapatis, *Indian J. agric. Sci.*, **23** (1953), 139

Inorganic

CHAUDHURI, J. C., Determination of tetraethyl lead, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 207

DAS, P. P. & CHATTERJEE, B., Iron as a catalyst in the decomposition of carbon monoxide, *Trans. Indian Inst. Metals*, **6** (1952), 279

OSMANI, RAZIA (Miss) & DATAR, D. S., Reactions of sulphates at high temperature. Part I. Thermal decomposition of the sulphates of the alkali metals in presence of aluminium oxide, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 162

PATEL, M. C., A note on periodate oxidation of starches, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 221

RAMAMURTHY, S., A note on certain disproportionation reactions of the halides of titanium, *Trans. Indian Inst. Metals*, **6** (1952), 274

SIDHANTA, S. K. & BANERJEE, S. N., *S*-methyl thiourea sulphate as an analytical reagent—Colorimetric estimation of nickel and cobalt, *Sci. & Cult.*, **19** (1954), 573

SINGH, APAR, Chloramine-B as volumetric reagent. Part I, *Res. Bull. Punjab Univ.*, No. 43 (1954), 17-20

Singh, Balwant, Singh, Apar & Kapur, S. R., Oxidation with chloramine-B: volumetric determination of metals by oxine method, *Res. Bull. East Punjab Univ.*, No. 41 (1953), 205-10

Organic

Baliah, V. & Gopalakrishnan, V., Synthesis of some 4-piperidone derivatives, *J. Indian chem. Soc.*, **31** (1954), 250

Bami, H. L., Studies in dihydrotriazines, *Curr. Sci.*, **23** (1954), 124

Bharucha, F. R. & Joshi, G. V., A note on organic acids of *Ricinus communis* Linn., *Sci. & Cult.*, **19** (1954), 565

Chatterjea, J. N., Experiments on the syntheses of furano compounds. Part IV. Synthesis of cumaran-diones, *J. Indian chem. Soc.*, **31** (1954), 194

Chatterjea, J. N. & Prasad, K., A synthesis of thioindoxyl. Condensation of some thioindoxyls with 1 : 2-diketohydrindene, *J. Indian chem. Soc.*, **31** (1954), 203

Desai, C. M. & Vaidya, B. K., Action of light on some organic colouring matters. Part I, *J. Indian chem. Soc.*, **31** (1954), 261

Desai, C. M. & Vaidya, B. K., Action of light on some organic colouring matters. Part II, *J. Indian chem. Soc.*, **31** (1954), 265

Dhingra, S. N., Dhingra, D. R. & Gupta, G. N., The essential oil of *Ocimum basilicum*, *Indian Soap J.*, **19** (1954), 251

Dhingra, D. R., Kapoor, S. N., Ganesh Chandra & Sharma, R. C., The component fatty acids of the body fat from he and she-buffalo, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 172

Joshi, G. G. & Shah, N. M., Studies in Fries migration. Part X. The Fries isomerisation of esters of 2 : 6-dibromophenol, *J. Indian chem. Soc.*, **31** (1954), 220

Joshi, G. G. & Shah, N. M., Studies in Fries migration. Part XI. The Fries migration of acyl esters of methyl 1-hydroxy-2-naphthoate and the corresponding acids, *J. Indian chem. Soc.*, **31** (1954), 223

Mahesh, V. B., Narasimhachari, N. & Seshadri, T. R., Synthetic experiments in the benzopyrone series. Part XLII. A new synthesis of 5 : 6 : 7-trihydroxy isoflavone derivatives, *Proc. Indian Acad. Sci.*, **39A** (1954), 165

Mukherji, P. C. & Raha, C. R., Experiments towards the stereospecific synthesis of hydroaromatic steroids, *Sci. & Cult.*, **19** (1954), 569

Naidu, N. B., Naidu, M. B., Ozmani, Z. H. (Mrs.) & Saletore, S. A., Studies on *Annona squamosa* (sitaphal) seed. Part II. The insecticidal fatty oil, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 179

Patel, M. C., A note on acyl derivatives of starch, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 221

Pujari, H. K. & Rout, M. K., Preparation of *n*-substituted 2-aminothiazoles. Part II. Condensation of acetone with substituted thioureas, *J. Indian chem. Soc.*, **31** (1953), 257

Roy, A. K., Use of biguanide sulphate as a reagent, *Sci. & Cult.*, **19** (1954), 568

Sen, A. B. & Mukerji, D. D., A new route for the synthesis of chloromycetin intermediates. Part I, *J. Indian chem. Soc.*, **31** (1954), 269

Sen Gupta, M. L. & Ganguly, A. K., Purification of groundnut oil. Part IV. Chromatographic separation and estimation of tocopherol in *Arachis* oil, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 175

Shah, Latika G. (Mrs.), Chemical investigation of the lichens: *Parmelia kamtschadalis* and *Parmelia arnoldii*, *J. Indian chem. Soc.*, **31** (1954), 253

Suryanarayana, B. & Tilak, B. D., Naphthoquinone series. Part V. Reaction of 2 : 3-dichloro-1 : 4-naphthoquinone with β-ketoesters, diethyl malonate, acetyl acetone and acetoacetanilide in pyridine, *Proc. Indian Acad. Sci.*, **39A** (1954), 185

Physical

Choudhury, P. K. & Khemka, K. N., Studies in ester-gum from Indian rosin. Part I. Solubility and molecular weight of ester-gum during esterification of rosin, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 153

Das Gupta, H. N. & Chatterjee, S. K., Studies on ceramic raw materials. Part IV. A comparative study of the reducing power of adsorbed bases, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 201

Doss, K. S. G. & Gupta, S. L., Effect of some surface active agents on the capacity of the dropping mercury electrode, *Bull. cent. electrochem. Res. Inst.*, **1** (1954), 9

Saha, A. N., The properties of surface active agents and soaps in solution, *Indian Soap J.*, **19** (1954), 259

Sinha, P. R. & Choudhury, A. K., Adsorption of phosphate and other anions by aluminium oxide, *J. Indian chem. Soc.*, **31** (1954), 211

ENGINEERING

Srinivasan, A. & Srinivasan, S., Induction motor as a load balancer, *J. Inst. Eng. (India)*, **34** (1954), 433

GEOLOGY

Aiyengar, N. K. N., Magnesite, *Bull. geol. Surv. India*, Ser. A, No. 6 (1953)

Gundu Rao, C., Nature of the fine bandings in the Dharwar shales, *Curr. Sci.*, **23** (1954), 121

Kailasam, L. N., Thickness of the Gangetic alluvium near Calcutta as deduced from reflection seismic measurements, *Curr. Sci.*, **23** (1954), 113

Krishnan, M. S. & Venkatram, M. S., Asbestos and barytes in Pulivendla taluk, Cuddapah district, *Bull. geol. Surv. India*, Ser. A, No. 5 (1953)

Lakshmi Narayana Rao, S. V., Manganiferous micas from Kantakapalle area, Visakhapatnam district, *Curr. Sci.*, **23** (1954), 120

Sharma, R. S., On the Nerinea beds of the Pondicherry cretaceous of S. India, *Curr. Sci.*, **23** (1954), 119

MATHEMATICS

Gupta, H., Cheema, M. S. & Gupta, O. P., On Mobius means, *Res. Bull. Punjab Univ.*, No. 42 (1954), 1-16

METALLURGY

Amin, H. S., Production of aluminium powder and paste in India, *Trans. Indian Inst. Metals*, **6** (1952), 285

Balachandra, J., Amalgam metallurgy — present trends and future possibilities, *Trans. Indian Inst. Metals*, **6** (1952), 320

Chandrasekhar, V., The structure of eutectics, *Trans. Indian Inst. Metals*, **6** (1952), 243

Chatterjee, G. P., Some studies on hardness and work-hardenabilities of metals and alloys, *Trans. Indian Inst. Metals*, **6** (1952), 219

Chatterjee, S. & Chatterjee, G. P., Studies on the relation between some static and dynamic properties of carbon steels under different thermal treatments, *Trans. Indian Inst. Metals*, **6** (1952), 193

Chatterjee, G. P., Som, K. C. & Ganguly, R., Effects of anodic surcharging on the behaviour of some plain carbon steel, *Trans. Indian Inst. Metals*, **6** (1952), 233

Chinnappa, K. V., A method for the spectrographic analysis of alloys having special compositions, *Trans. Indian Inst. Metals*, **6** (1952), 342

Das Gupta, S. C. & Eppelsheimer, D. S., End-quench hardenability and evaluation of quenching media, *Trans. Indian Inst. Metals*, **6** (1952), 96

Hossain, S. M. & Khundkar, M. H., Reaction between sodium carbonate and iron pyrites under different conditions, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 185

Mitra, H. K., Current trends in the development and uses of refractories, *Trans. Indian Inst. Metals*, **6** (1952), 327

Mitra, M. S. & Fontana, M. G., Effect of wire drawing on the true stress-strain curve, *Trans. Indian Inst. Metals*, **6** (1952), 170

Mitra, M. S. & Fontana, M. G., Some observations on the deformation in stainless steels, *Trans. Indian Inst. Metals*, **6** (1952), 137

Paranjpe, V. G., Impurities as hindrances to grain boundary migration, *Trans. Indian Inst. Metals*, **6** (1952), 203

Parthasarathi, M. N. & Nijhawan, B. R., Structure of graphite spherulite, *Trans. Indian Inst. Metals*, **6** (1952), 150

Ramachandran, E. G. & Wadia, N. J., Some micrographic investigations by etch figures on commercially pure aluminium, *Trans. Indian Inst. Metals*, **6** (1952), 344

Sarkar, S., Smelting and refining of lead, *East. Metals Rev.*, **7** (1954), 358

Schrader, H. & Bose, B. N., The solid solubility of phosphorus in iron, *Trans. Indian Inst. Metals*, **6** (1952), 104

Schrader, H. & Dhanbhoora, D. R., The isothermal heat treatment of high speed steels and its effects in the light of recent structure research, *Trans. Indian Inst. Metals*, **6** (1952), 54

Schrader, H. & Visvanathan, S., Mixer operation and its relation to slopping in the acid bessemer converter and to the opening bath sulphur in the Duplex process, *Trans. Indian Inst. Metals*, **6** (1952), 22

Som, S. C. & Chatterjee, G. P., Studies on the grain growth of alpha brass, *Trans. Indian Inst. Metals*, **6** (1952), 267

Thyagarajan, R., Ramachandran, R. S. & Cherian, K. K., Some developments in the electrolytic production of aluminium, *Trans. Indian Inst. Metals*, **6** (1952), 296

PHYSICS

Chatterjee, S., Patro, A. P., Basu, B., Bhattacharyya, R.L. & Fazle Hosain, Presence of radioactive dusts over Calcutta, *Sci. & Cult.*, **19** (1954), 570

Chinnappa, K. V., A simplified procedure for the determination of index point and index line in the step-filter technique of spectrographic analysis, *Trans. Indian Inst. Metals*, **6** (1952), 339

Murgai, M. P., Application of Lennard-Jones Devonshire equation of state to detonation of PETN, *Proc. Indian Acad. Sci.*, **39A** (1954), 176

Nigam, A. N., Fine structure of X-ray absorption spectra in homopolar crystals, *Curr. Sci.*, **23** (1954), 117

Rama, On relativistic particles in high energy showers, *Proc. Indian Acad. Sci.*, **39A** (1954), 162

Raman, C. V. & Ramdas, A. K., On the polycrystalline forms of gypsum and their optical behaviour, *Proc. Indian Acad. Sci.*, **39A** (1954), 153

Santhamma, V., The force constants for the non-planar vibrations of 1, 3, 5 trimethyl benzene, *Curr. Sci.*, **23** (1954), 118

Sen, K. R., The mechanical characters of jute, *Jute Bull.*, **17** (1954), 20

Viswanathan, K. S., The theory of elasticity and of wave-propagation in crystals from the atomistic standpoint, *Proc. Indian Acad. Sci.*, **39A** (1954), 196

TECHNOLOGY

Agarwal, H. P. & Bhargava, A. P., Electrochemical reactions in alternating fields. Effect of frequency on current efficiency, *Bull. cent. electrochem. Res. Inst.*, **1** (1954), 15

Bandyopadhyaya, N. N., Horn plastics. Part I. Plasticisation and properties, *J. Indian chem. Soc., Industr. & News Ed.*, **16** (1953), 195

Bhat, R. V. & Karnik, M. G., Indigenous cellulosic raw materials for the production of pulp, paper and board. Part XX — Chemical pulps from *Eupatorium odoratum* Linn. (*Assamlota*), *Indian For.*, **80** (1954), 277

Menon, V. S., Electrolytic preparation of gluconate, *Bull. cent. electrochem. Res. Inst.*, **1** (1954), 31

Narayanamurti, D. & Jastinder Singh, Moulding powders and boards from coconut shells, *Composite Wood*, **1** (1954), 38

Narayanamurti, D. & Jastinder Singh, Studies on adhesives: Part XVIII — Adhesives from coconut shells, *Composite Wood*, **1** (1954), 41

Narayanamurti, D. & Jastinder Singh, Studies on building boards: Part V — Utilization of tapioca stems and hoop pine bark, *Composite Wood*, **1** (1954), 10

Rajagopalan, P. R. & Dey, B. B., Electrolytic recovery of lead and antimony from battery wastes, *Bull. cent. electrochem. Res. Inst.*, **1** (1954), 26

Sekhar, A. C., Elastic constants of plywood, *Composite Wood*, **1** (1954), 32

Sen, A., Tewari, R. B. & Vyas, N. D., Production of combustible gas from cane molasses, *Sci. & Cult.*, **19** (1954), 562

Singh, K. K. & Mathur, P. B., Cold storage of guavas, *Indian J. Hort.*, **11** (1954), 1

Subramanyan, N. & Sadananda Rao, B. K., Electrochemical production of chlorates, *Bull. cent. electrochem. Res. Inst.*, **1** (1954), 29

Udupa, H. V. K. & Dey, B. B., Use of rotating electrodes in electrolytic reactions, *Bull. cent. electrochem. Res. Inst.*, **1** (1954), 20

Progress Reports

RESEARCH ON COFFEE

THE WORK OF THE TWO RESEARCH STATIONS OF THE Indian Coffee Board at Balehonnur and Chethahalli during the year 1951-52 shows that both the stations devoted considerable attention to vegetative propagation and hybridization of coffee, and to manurial trials. A notable project initiated was the commencement of a randomized layout for comparing the clonal progeny of robusta and arabica cultures selected on the basis of their yield performance during 1949-50 with a view to single out best performers for multiplication and distribution.

Botany — Special attention was devoted to work on (1) production of hybrid seeds from controlled pollination of parents that are known to produce vigorous progeny, (2) vegetative propagation of clonal material from outstanding bearers, (3) comparative trials of clonal plants from the best performers for eventual isolation of the best and (4) a search of best bearers in private estates. In addition to raising clonal progeny of selected 36 arabica and 17 robusta cultures, 1,039 clonal progeny of 40 selected Kent plants were raised and utilized for laying out manurial experiments.

The grading of coffee according to bean size and shape is of importance from the marketing point of view. With a view to classify the latest arabica selections according to their bean size and shape, 50 flat beans were taken at random from 31 cultures and precise measurements were taken of their length and breadth. The 31 single plant cultures fall into three grades, viz. longish, roundish oblong and roundish, and that the individual plant selections made from the same plant family do not always fall within the same classification.

Manurial experiments — A new manurial experiment was started during the year under natural shade with a view to study the effect of 40, 60, 80 and 100 lb. of nitrogen per acre on yield of coffee. The yield of ripe cherry as well as clean coffee was significantly enhanced by the doubling of nitrogen manure.

In another set of manurial experiments using nitrogen, phosphorus and potassium fertilizers, soil analyses were carried out periodically, once before the application of manures in May and again after the monsoon before the second application of nitrogenous manures, to assess the proportion of plant foods used by coffee and that lost by leaching. The amount of nitrogen in the 9-18 in. layer was found to be higher than in the 0-9 in. layer in all the treatments, thus indicating percolation of nitrogen into that layer. On the other hand, the potash content was slightly more in the 0-9 in. layer than in the 9-18 in. layer.

The experiment laid out in 1950-51 to study the release of nitrogen from the root nodules of *Erythrina lithosperma* plants consequent to lopping of branches was continued. In the first season the quantity of nitrogen contained in the nodules, before the treatments were applied, was quite high. A general reduction in the nitrogen content followed after lopping. From observations made on the percentage of average nitrogen content in soil samples around the plants, it appears that the nitrogen in the root nodules is not released to the soil on lopping but is utilized by the plant for vegetative growth.

Ten green manure plants were analysed with reference to their leaf/stem ratio, nitrogen and C/N ratio, P_2O_5 and K_2O content. *Crotalaria striata* and *Tephrosia vogelii* appeared to be the best of the plants investigated.

Abnormal fall of apparently healthy leaf, occurring usually after a wet spell, was traced to chlorosis due to carbohydrate deficiency.

Agronomy — Experiments were started to find out the viability of germination of arabica seed: (1) with parchment cover intact, (2) cover partially split, and (3) cover completely removed. Seeds sown after completely removing parchment cover at sowing were found to germinate 15 to 20 days earlier, those with split parchment cover a week to 10 days in advance compared to the seeds sown with parchment cover intact. Investigations on the growth of seedlings raised from seeds with and without seed cover at sowing for a period of one year failed to show any significant difference. It is concluded that any damage to the parchment cover at the time of sowing does not impair the germination capacity nor the growth of seedlings raised from them.

An investigation was carried out to find out the optimum concentrations of different factors promoting growth in order to produce high percentage of rooting in sucker cuttings. Auxin treatment for 12 hr. at a concentration of 100 parts per million was found optimum for the development of root. With dichloro-phenoxy acetic acid, however, the optimum concentration was found to be 5 parts per million. In the case of indole butyric acid though the roots were thinner compared to other treatments, the number of roots was more with profuse secondaries and tertiaries. In all cases first and second internodes started rooting earlier— within a month after planting. It is, therefore, not desirable to allow the suckers to grow beyond the fourth internode for quicker root formation in the cuttings.

INDIAN CENTRAL TOBACCO COMMITTEE, ANNUAL REPORT, 1952-53

AN INCREASE OF OVER 32 MILLION LB. IN THE production of tobacco was registered during the year ended March 1953, over the previous year. The area under cultivation also increased by 86,000 acres over 1951-52. The exports of manufactured and unmanufactured tobacco, however, declined from Rs. 22 crores in 1951-52 to Rs. 15·57 crores during the current year due primarily to increased consumption within the country and a fall in demand for certain grades of Indian tobacco from Hong-Kong, China, Russia and Pakistan. The data for the last three years are given in Table 1.

TABLE 1

YEAR	ACREAGE	PRODUCTION (million lb.)	EXPORTS	
			Quantity (million lb.)	Value (million Rs.)
1950-51	902000	589	113·70	182·8
1951-52	712000	459	123·69	220·2
1952-53	798000	490	80·89	155·7

Flue-cured tobacco — Nursery experiments indicated that 80 lb. nitrogen as ammonium sulphate and 3·33 lb. seed rate per acre of nursery was the best combination. Farmyard manure increased the total number of seedlings as well as number of transplants significantly. Rabbing of seeds proved beneficial and the number of transplants in rabbed beds was nearly thrice that in unrabbed ones.

Topping at inflorescence stage resulted in higher yields but there was a reduction in the percentage of brighter grades which was, however, higher in fertilizer treatments than in non-fertilizer treatments. At Rajahmundry in a study of the curing quality of leaves according to their morphological position on the plant the best percentage of bright grades was obtained from about the eleventh node.

It has been confirmed that incidence of Orobanche attacks due to wind-borne seeds from other fields is negligible compared to the incidence due to the seeds left in the fields from previous years. The method of control of Orobanche by hand-picking before it matures has proved successful, and is now recommended by the Tobacco Research Institute for adoption by the farmers.

Preliminary observations on the incidence of leaf-curl on 22 varieties of tobacco and two species of *Nicotiana* showed that all varieties took severe natural infection except *N. rustica*. Two insecticides, Pyrocolloid and Derryphytan, at 0·5 per cent concentration, were found to be effective against white-flies, the vector of leaf-curl virus. A new disease causing rot of the basal portions of stems had been observed on *Nicotiana rependa* plants during the season and the causal organism was identified as *Sclerotium* sp. *Nicotiana tabacum* (*var.* H.S.), *N. alata*, *N. trignophylla*, *N. glauca*, *N. plumbaginifolia* and *Capsicum annum* were found to be suscepts on artificial inoculation.

Cheroot tobacco — Studies on topping and manuring in relation to planting dates showed that application of 100 lb. nitrogen increased the yield by 31 per cent over no nitrogen and topping at 16 leaves by 6 per cent over 14 leaves. The incidence of Orobanche on tobacco was not reduced by the previous crop of chillies.

Wrapper tobacco — During the year a new station for wrapper tobacco was opened at Dinhata, Cooch Behar.

Bidi tobacco — Increase in the level of nitrogen generally increased the nicotine content of leaf, whatever be the source of nitrogen. Farmyard manure showed better residual effect than oil cakes.

Hookah tobacco: *N. tabacum* — In a new experiment to find out whether sodium nitrate can be used in place of ammonium sulphate, both the fertilizers were tried at 2 levels, 100 lb., 200 lb. nitrogen per acre, along with no manure and with and without farmyard manure at 300 lb. nitrogen per acre. The basal dressing suppressed the yield in this experiment and sodium nitrate at both levels yielded higher than ammonium sulphate at 200 lb. nitrogen.

The effect of yield on rotations was studied. Among the four rotations tried, tobacco-tobacco, tobacco-potato, tobacco-maize and tobacco-chari fodder, the yields of tobacco were in the order of rotations mentioned, all the differences being significant. In addition to yield, in tobacco-tobacco, the appearance of leaf was also good.

N. rustica — In an experiment to find out the best source of nitrogen, ammonium sulphate, ammonium phosphate, potassium nitrate and farmyard manure all at 100 lb. nitrogen per acre were tried with and without 50 lb. K_2O and with a basal dressing of 100 lb. nitrogen as farmyard manure. The fertilizers did not differ significantly but all were better than farmyard manure.

Of the 11 dates of planting from 1 February to 11 April, at weekly intervals, it was found that planting about the middle of February was optimum.

Nicotine estimations conducted for all the treatments in the different agronomical experiments showed that generally nicotine content increased with nitrogenous manuring.

Studies on the intake of nitrogen showed that *N. tabacum* and *N. rustica* absorbed 17·5 lb. and 22·0 lb. nitrogen per acre respectively when unmanured and the intake increased to 40-50 lb. when manured with 100 lb. nitrogen per acre. The intake was higher in the case of split doses of nitrogen than single dose at planting time. The ratio of nicotine to non-nicotine nitrogen was 16-17 per cent in *N. rustica* and 5-7 per cent in *N. tabacum*. Manuring with nitrogen had no effect on this ratio in *N. rustica* but an increase was recorded in *N. tabacum*.

Development — The improved method of curing developed by the Committee has been tried on the farms over a three-year period. Savings to the extent of 20 per cent in fuel and 7 per cent in the time of curing have been effected by this method as compared to the farmer's method of curing. The improved method also yields a better product which fetched an extra premium of Rs. 56/14 per candy of 500 lb. over that of the local method.

Marketing and trade — During the year over 97 million lb. of tobacco valued at approximately Rs. 12·04 crores were graded and marked for export at 33 different centres.

The question of regulation of export of tobacco on consignment basis and the maintenance of uniform percentage of moisture in re-dried tobacco exported to foreign countries received active consideration of the Committee during the year and the following measures have been adopted: (1) Every factory should maintain a proper record of analysis of moisture in tobacco samples in forms approved by the Agricultural Marketing Adviser to the Government of India; (2) the factories should undertake to test at least 10 per cent of the packages re-dried by them and furnish a copy of the analytical report on each parcel of tobacco re-dried and packed; (3) every authorized packer applying for a certificate of Agmark grading should enclose with his application a copy of the moisture analysis report; and (4) a standard moisture testing outfit should be maintained in the office of the Chief Inspector, Tobacco Grading.

WOOL RESEARCH IN BRITAIN

The annual report of the Wool Industries Research Association, U.K., records considerable progress in the various phases of its activities. In addition to its share of the statutory levy for research, the Association received funds for the purchase of equipment from Marshal Aid and £5,000 as Conditional Aid from the U.S.A. for investigating the relative merits of automatic and non-automatic looms in the woollen and worsted industries.

Some new machines were fabricated during the year, the more important of these being a wear tester and a resilience tester for carpets, a pilot plant for scouring wool having bowls of width one quarter that of the normal plants, a unit for measuring tension in weft, and a laboratory loom for studying the effect of loom timing and setting on fabric appearance.

Technology — Impregnation of wool fibres with radioactive phosphorus (as phosphoric acid) was used to investigate the drafting process. The results have shown that whether or not a fibre is accelerated from the speed of the back to the front rollers depends on chance contacts of the fibre in question with the fast-moving fibres which are gripped by the front roller nip. The theory of drafting should, therefore, be built up on the basis of chance contacts between fibres. This work has been useful in throwing light on the relative efficiency of different drafting systems.

Studies on weaving have revealed that the tension in the weft yarn drops very quickly when the shuttle stops, and may be only a small fraction of the picking tension by the time the warp shed crosses. This suggests that the effect of tension of yarn coming from a shuttle on the formation of weft bars is an indirect one depending on the decay of extension of the yarn, which is usually much less rapid than the decay of tension. Weft breakage has been shown to be unaffected by 30-60 per cent relative humidity.

Experiments on scouring of worsteds for flannel finish revealed the possibility of effecting considerable economy in the consumption of soda ash and soap, especially in the case of white shades, without detriment to the efficiency of the scour.

The practicability of dyeing wool at high temperatures without undue fibre damage has been confirmed provided the pH of the dye liquor is kept within certain limits and certain duration of treatment is not exceeded.

Testing — A rapid and simple method of comparing the strengths of two yarns without the help of a strength machine has been devised. Short lengths of the two yarns to be compared are joined together and broken by pulling, a note being made of the frequencies of breaks in the two yarns. The statistical method of sequential analysis is then used to determine which of the two yarns is stronger.

Biological research — Studies on the development of fleece and follicle population in different breeds of sheep have emphasized the importance of secondary to primary follicle ratio in the development of fine wool. Other factors which influence the secondary to primary ratio are nutrition of the sheep before and after birth of the lamb and breeding.

Chemistry — A study of partial hydrolysates of wool has shown aspartic acid to be preferentially liberated during high temperature hydrolysis of wool with hydrochloric acid. With boiling hydrochloric acid, valine is liberated more slowly than leucine or isoleucine. The carboxy terminal end groups of wool were found to be serine, glycine, threonine and alanine.

Diffusion experiments with the acid dye Orange II containing radioactive sulphur confirmed the result that the dye anion has a very low diffusion coefficient in horn membranes, and is strongly adsorbed by keratin so that it tends to eliminate smaller anions from wool fibres. Examination of the setting of snarly yarns by steaming has shown that the setting is temporary, and takes place to a large extent during the drying period after steaming. At constant strain, the stress relaxation is reversible so that an apparent increase in stress occurs on rewetting or resteaming after drying. Investigations with single fibres show that setting is a fibre property, and that the fibre becomes stiffer both with regard to binding and twist when steamed becoming more pliable on drying.

Surveys — Surveys undertaken by the Association include those on commercial scouring and carding processes. The data obtained from these surveys have provided valuable information on the efficiency of commercial scouring and on the fibre breakage that occurs in carding and later processes. A survey on neps showed that neps are related to the total fibre length in a top, i.e. to the total length obtained by placing every fibre end to end.

INDIAN PATENTS

[A few of the Patent Applications notified as accepted in the *Gazette of India*, Part III, Section 2, for May 1954, are listed below.]

Chemicals, plastics, rubber, paints and allied products

48344. Methods of preparing isonicotinic acid by oxidizing mixtures of pyridine homologues: *A mixture of pyridine homologues is oxidized with nitric acid or a mixture of nitric acid and a nitrate at a temperature not less than* 150°C. *and under super-atmospheric pressure* — Aktiebolaget Bofors

50112. Derivatives of phenthiazine: *N'-substituted* 10-*aminoalkyl phenthiazines, the alkyl group representing an aliphatic chain containing* 2 *or* 3 *carbon atoms, are prepared from the corresponding phenthiazine, aminoalkylphenthiazine, halogenophenthiazine or phenthiazine aldehyde used as starting materials* — Societe Des Usines Chimiques Rhone-Poulenc

50113. Phenthiazine derivatives: 10-*Alkylene-carbonamido alkyl phenthiazine derivatives are prepared by treating the corresponding alkyl ester, acid chloride or anhydride with primary or secondary amine or by reacting a phenthiazine with an N-alkyl-substituted haloalkylene carbonamide* — Societe Des Usines Chimiques Rhone-Poulenc

50576. New N-hydroxymethyl ureas and process for producing them: *Reacting urea of the formula* $H_2N\text{-}CO\text{-}N=CH\text{-}(CH\text{-}OH)\times CH_2OH$ *with formaldehyde at a* pH *above* 8 *at* 20°-50°C. — Cilag Ltd.

50612. Stabilization of cracked distillate fuel oils: *Oil is treated with an acid and then reacted with an alkali* — California Research Corporation

50613. Production of new di-substituted nicotinic acid amides: *Reacting nicotinic acid-*(1, 2-*di-phenylethyl*)-*amide or a N-metal derivative with a reactive ester of an amino alcohol of the formula* $HO\text{-}Alk\text{-}N(R_1, R_2)$ — Cilag Ltd.

47960. Process for the manufacture of new tri-substituted indene and indane compounds: *Reacting indane or indene compounds with reactive esters of alcohols* — Ciba Ltd.

50386. Manufacture of alkyd resins: *Characterized in adding methyl or ethyl methacrylate after rapid polymerization has ceased* — I.C.I. Ltd.

50400. Stabilization of peracids: *Peroxymonosulphuric acid is stabilized by incorporating dipicolinic acid therein* — Buffalo Electro-Chemical Co. Inc.

51208. Preparation of diethylamino-aceto-2-*m*-xylidide: *Reacting diethylamino-ethylacetate with* 2-*m-xylidide in presence of metallic sodium* — Sudhir Lal Mukherjee & Albert David Ltd.

48623. Manufacture of natural and synthetic rubbers and rubber articles: *Incorporating in natural and synthetic rubbers an antioxidant comprising bis-*(2-*hydroxy-*3-α-*alkyl-cycloalkyl-*5-*methyl*)-*methane* — I.C.I. Ltd.

49302. Process and composition for producing protective and decorative coatings on corrodible metals: *Solution containing hexavalent chromium fluoride ions and ions containing zirconium, titanium or tin or mixtures thereof but not containing phosphate ions* — American Chemical Paint Co.

50765. An improved process for the manufacture of soaps: *Reacting an oil or fat with a weak base like oxide or hydroxide of alkali or alkaline earth metal in presence of catalytic agent like glycerine and/or anhydrous soap* — Narayana & Leley

48217. Improvements relating to cooling arrangements using eutectic solutions: *Comprising tank containing eutectic solution, means for cooling said solution and means for promoting circulation of the solution* — J. Stone & Co. (Deptford) Ltd.

48449. Synthetic rubber compositions and methods for making the same: *Mixing oxy-carbon black with a low unsaturated solid olefin-multiolefin synthetic rubbery copolymer and heating the mixture* — Standard Oil Development Co.

48660. Process for separating one or more solid hydrocarbons or complex hydrocarbon compounds from a mixture thereof with a highly polar liquid: *The solid substance contaminated with a highly polar liquid is contacted with a non-polar or less polar carrier liquid such that the contact angle* θ_t *is less than* 90°, *whereby the solid merges into the carrier liquid* — N. V. De Bataafsche Petroleum Maatschappij

48704. Process for the production of dialdehydes or derivatives thereof: *Reacting diolefin with carbon monoxide and hydrogen in presence of a diluent or solvent, a polymerization inhibitor, a stabilizer and a cobalt compound for yielding cobalt hydrocarbonyl during the process* — Ruhrchemie Aktiengesellschaft

49026. Apparatus for electrolysis of metals: *Comprising a main chamber, a supplemental chamber abutting the main chamber, and electrodes disposed in the main chamber transversely relative to the wall between the chambers and molten metal collecting means extending over the cathodes* — Aluminium Laboratories Ltd.

49276. Derivatives of carboxylic acid hydrazides and method of making them: *Reacting a carboxylic hydrazide with formaldehyde and sulphurous acid or acid salts thereof* — Carlo Erba S.p.A.

50185. Polystyrene moulding powders: *Comprising a mixture of homopolymer of styrene and a copolymer of butadiene and styrene* — Monsanto Chemical Co.

50246. Production of 10-aminoalkyl phenthiazines: *Comprises reducing N-carbonamidephenthiazines* *with lithium-aluminium hydride* — Societe Des Usines Chimiques Rhone-Poulenc

51063. Stable aqueous emulsion of the oil-in-water type containing binding agents and process for making them: *Emulsion containing rubber and alcohol modified aminoplast in the inner phase and acid casein dissolved in the outer aqueous phase* — Ciba Ltd.

51175. A process for the manufacture of 3: 5-dioxopyrazolidine derivative: *Reacting 1 mol of n-butyl bromo malonyl chloride* $[(Br)\ (n\text{-}butyl){=}C{=}(COCl)_2]$ *with 0·75-1 mol of hydrazobenzene in presence of ether and a tertiary organic base* — Mukherjee & Albert David Ltd.

51263. Manufacture of basic copper chloride and of copper-containing fungicides: *Mixing cuprous oxide with a chlorine yielding compound in presence of water and exposing the mixture to reaction in atmospheric air* — Hindle

51511. Expanded thermoplastic materials: *Frothing a plastisol of the resin in the presence of a thickening agent, and heating the stabilized froth to gel the resin* — Dunlop Rubber Co. Ltd.

Chemical processes, engineering and equipment

49654. Improved device for providing inner lining on metal pipes with cement or the like material: *Pulleys are fitted to shafts and are driven by prime movers and other spaced pulleys are idle and rotate when metal pipes are mounted between pair of rollers* — Talati

49123. A process and furnace for the treatment of substances subjected to chemical reactions, with solid and gaseous reagents, particularly adapted for the disaggregation of chromite: *The solid reactants are kept on a bed and hot gaseous reagents are allowed to creep through it* — Cattaneo

49882. Process and apparatus for treating particles distributed in a liquid with mechanical vibrations, more particularly for artificial crystallization: *Liquid is subjected to sonic or supersonic vibrations* — International Physical Establishment

51170. Improvements relating to evaporating and distilling plants: *Ferrous or ferric ions are supplied to raw water* — G. & J. Weir Ltd.

48637. Mixing machines: *The gap between the mixing worm and the mixing trough, within the zone filled with the mix, is given the shape of a crescent, the tip of which at the entrance side of the worm being above the operational level of the mix* — August & Porta

Physics — general

49057. Improvements in electric amplifiers: *Comprising an elongated body of semiconductor, an emitter electrode near one end and a collector electrode near the other end of the body, means for causing charged carriers to flow along the body away from said one end and means between the electrodes for amplifying the number of charged carriers flowing along the body* — The General Electric Co. Ltd.

50354. Semiconductor devices: *Characterized by an arrangement which predetermines the sequence of application of operating voltages to the respective electrodes as the transistor is inserted in the socket* — Radio Corporation of America

Food and kindred products

49994. Improvements in foodstuffs: *Oleaginous foodstuffs are prepared by incorporating therein a small quantity of a lactone of an aliphatic hydroxy carboxylic acid having a lactone ring of 4-6 carbon atoms* — Anglo-Scottish Creameries Ltd.

Drugs and pharmaceuticals

48295. Purification of penicillin: *By treating penicillin with oxycaine and decomposing the resulting oxycaine penicillin under acid conditions to liberate penicillin* — The Distillers Co. Ltd.

48503. Antibiotic material and its production: *Amphomycin is produced by cultivating a strain of Streptomyces BL-456786 in an aqueous, nutrient containing, carbohydrate solution under submerged aerobic conditions until substantial antibacterial activity is imparted to the solution, and recovering the antibiotic from the broth* — Bristol Laboratories Inc.

50393. A method for the production of 21-esters of adrenal cortical hormones and other 21-hydroxy-steroid compounds with aminocarboxylic acids, and salts of these esters: *21-Hydroxy steroid compound is reacted with a salt of an acid-halogenide of halogeno-carboxylic acid, and then the halogenated ester is treated with ammonia or an amine* — K. Abildgaard-Elling

51168. Production of penicillin salts: *By reacting free penicillin G with a salt formed from procaine and an aliphatic or substituted aliphatic acid having not more than 8 carbon atoms in the straight chain* — Glaxo Laboratories Ltd.

51547. Pharmaceutical preparations containing a pure sedative-hypnotic and hypotensive substance: *Comprising reserpine and a substance suitable for parenteral or oral administration* — Ciba Ltd.

51258. Improvements in or relating to the preparation of composition having therapeutic value: *Trying green leaves of Akanda with common salt and powdering the product* — Borua

Fuels and lubricants

48385. New method of preparation of active carbons from coals and lignites: *Introducing steam during carbonization followed by air activation* — Council of Scientific & Industrial Research

Metals and metal products

48237. Method and apparatus for gaging and classifying sheets or the like: *Includes two or more conveyers in tendem over which the sheets pass, a deflector between adjacent conveyers and deflector operator responsive to gage* — United States Steel Corporation

48380. Sheet pin-hole detector: *Of the type having a source of light, a first photosensitive device for detecting pin-holes, a deflecting element operated by said photosensitive device and a second photosensitive device adjacent to said first photosensitive device* — United States Steel Corporation

48923. Production of single-twisted or twin-twisted steel bars: *Bars twisted without axial forces,* *bars shorten during twin twisting, and bars extend during single twisting* — COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

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51407. Improvements in zinc smelting: *Oxygen or oxygen-enriched air is introduced through a pipe into the blast furnace gases accumulating in the space above the level of the charge* — THE NATIONAL SMELTING CO. LTD.

48467. Apparatus for inspecting and classifying flat steel products: *Comprising steps of testing the product in strip form for pin-holes, applying a mark adjacent to the pin-hole, shearing the strip into sheets and classifying the sheets into prime and rejects* — UNITED STATES STEEL CORPORATION

49040. Method for concentrating and extracting germanium compounds from coals: *Washing coal gases with water, acidic or basic aqueous solution, concentrating and extracting germanium compounds in conventional ways* — ZAIDAN HOJIN SEKITAN SOGO KENKYUJO

49711. Cooling molten metal and separating molten metals by cooling: *Cooling molten metals by passing through a trough having cooling sections located therein* — THE NATIONAL SMELTING CO. LTD.

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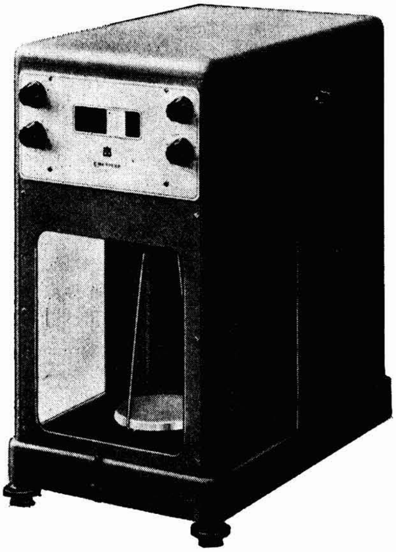
48293. Reinforced concrete poles from pre-cast component pieces: *At the jointing end of each short length component piece, a steel plate is provided having holes corresponding to the positions of the projecting reinforcement rods which are bolted down on the jointing faces by nuts* — KARANTHA

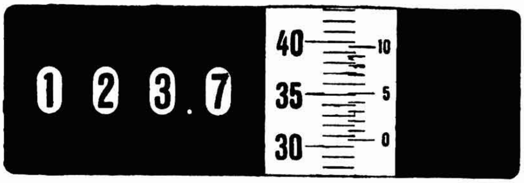
Miscellaneous

48496. A plant or installation for obtaining and storing energy from the wind: *Wind-driven direct current generators adopted to face the wind always and supplying current to batteries of voltameter or electrolytic cells for decomposing water* — WASDELL

47860. A new or improved process for the separation of the fibres from the bark, wood and other tissues of fibrous plants: *Treating the stems containing fibres with enzyme-containing decomposition effecting plant juices at a temperature of 30°-60°C.* — TURNBULL

49054. A process for the treatment of bamboo to further its utilization in the manufacture of pulp, paper, board or the like: *Bamboo chips are mechanically disintegrated to cause cleavage between fibres and parenchyma cells* — COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH & PRESIDENT, FOREST RESEARCH INSTITUTE & COLLEGES, DEHRA DUN

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Journal of
Scientific & Industrial Research

Vol. 13B, No. 7, JULY 1954

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PUBLISHED BY THE COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH, INDIA
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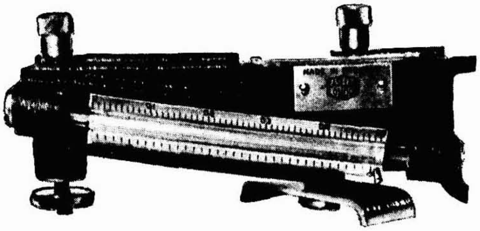

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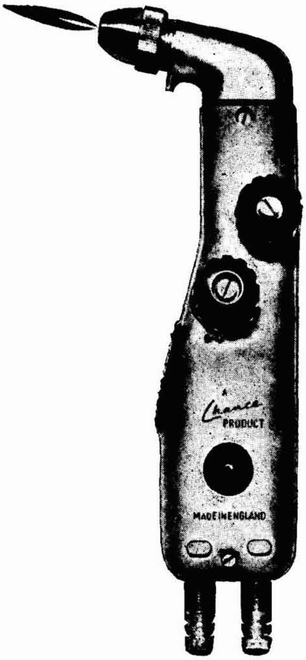

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The Application of Membrane Analogy for the Determination of Torsional Rigidity of Non-circular Solid Shafts

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National Physical Laboratory of India, New Delhi

The soap film analogy for the determination of torsion constant K of solid non-circular shafts is described. The analogy between the bubble surface and the torsion function ϕ is clearly illustrated. The experimental technique adopted in determining the constant K consists in the measurement of the rate of increase of height h against volume, instead of direct volume measurement, by making use of the method of " least squares ". This procedure has compensated for the experimental errors and intermediate hanging of the film, and has thus led to greater accuracy.

THE most common shapes of structural members desighed for torsion are circular, elliptical or rectangular for which direct mathematical analysis is available. In the case of right cylinder, where plane sections remain plane after twisting and radii remain straight, the internal resistance to the twist of the shaft is given by the relation

$$T=JG\theta \quad \ldots\ldots\ldots\ldots (1)$$

and at a distance r from the centre line of the shaft the shearing stress is

$$\tau=Gr\theta \quad \ldots\ldots\ldots\ldots (2)$$

Unlike the beam formula $\sigma = \frac{My}{I}$ which is general, the torsion formula is true only for circular rods and tubes. For other sections these formulae are not valid. The reason for this is that in non-circular shafts a transverse section warps during twisting with the result that at some points the shearing stress increases and at other points it decreases. This is the case in a rectangular section where the maximum shearing stress occurs at the centre of the long side and approaches zero at the corners, whereas if plane sections had remained plane and from equation (2) the stress should have a maximum value at the corner and minimum at the centre of the long arm. Further, the polar moment of inertia J in non-circular sections has no direct relation to the torsional stiffness and strength of the bar as in the case of the circular sections. For sections of equal areas and different shapes and with no re-entrant corners the torsional stiffness increases with decrease of J. In certain cases it is possible to find mathematically the new torsion constant K which is a measure of the torsional rigidity, modifying equation (1) into the common form $T=KG\theta$ where K is the equivalent polar moment of inertia J as used in circular section. Quite a large number of regular shaped cross-sections have been tackled mathematically, but the experimental determination of this constant K is by far the easiest.

Theory of torsion

It was shown by Saint Venant[1] that in prismatical bars subjected to pure torsion, i.e. where all cross-sections are free to warp, the general stress system is reduced to two shear components, which lie in planes parallel to those of the applied twisting couples. If the Z-axis coincides with the axis of the shaft, then the stress components are

$$\sigma_x=\sigma_y=\sigma_z=\tau_{xy}=0$$

$$\tau_{xz}=\frac{\partial\phi}{\partial y} \text{ and } \tau_{yz}=-\frac{\partial\phi}{\partial x}$$

where ϕ is the torsion stress function.

The equations of compatibility require

$$\frac{\partial^2\phi}{\partial x^2}+\frac{\partial^2\phi}{\partial y^2}=-2G\theta \quad \ldots\ldots\ldots (3)$$

where G is the shear modulus of the material and θ is the angle of twist/unit length.

Since the stresses at the boundary are tangent to the boundary curve, the relation between the components τ_{yz} and τ_{xz} is completely determined from the shape of the cross-section and it follows $\frac{d\phi}{ds}=0$ or ϕ is constant along the boundary (FIG. 1). In the case of singly connected bodies this constant ϕ is arbitrarily chosen and generally taken equal to zero.

Also by equating the resisting moment to twisting moment T, we have

$$T=2\iint\phi\,dxdy$$

which is the volume below the pillow surface representing the stress function.

Analogy

The differential equation $\nabla^2\phi=-2G\theta$ under the condition $\frac{d\phi}{ds}=0$ on the boundary can be solved in a number of ways. For simpler sections such as circular, elliptical or rectangular, the mathematical determination of the stress function ϕ is possible, but becomes involved for other complex shapes of practical interest.

It is known that the general equation of the flow of current in a thin homogeneous plate of constant thickness[2] h is

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}=0$$

where Ψ is the potential function. Similarly the deflections of a constant tension membrane stretched over an opening of the same shape as the cross-section of a bar and distended into a bubble-shaped surface is given by the equation $\nabla^2 z=-q/S$. There are many such examples where the governing differential equation is either Laplacian or of Poisson type. Since the differential equation governing torsion function ϕ is similar to one of the two given above, it is, therefore, necessary only to study one of these to gain insight into the other.

Of the various analogic experimental methods used for solving the torsional differential equation, the following four are quite commonly used[3]: (i) Prandtl pressure membrane analogy; (ii) electrical analogy, converting the Poisson's equation $\nabla^2\phi=-2G\theta$ into Laplacian form $\nabla^2\Psi=0$ where $\phi=\Psi+C$; (iii) hydrodynamical analogy; and (iv) photoelasticity.

Pressure membrane analogy method is the most commonly used as it requires minimum apparatus and yet gives a high degree of accuracy. Griffith and Taylor did much to improve this technique of stress and rigidity measurement though others have advanced the electrical analogies.

Membrane analogy

The importance of soap film membrane in determining the shear stresses and the torsional rigidity of a twisted rod consists in the analogy between the torsion function ϕ and the deflection function z of a thin membrane under the action of a uniform load. If such a soap film membrane is inflated over a hole of the same shape as the cross-section of the twisted bar (FIG. 2), then the surface of this membrane satisfies the following equation[4]:

$$\frac{\partial^2 z}{\partial x^2}+\frac{\partial^2 z}{\partial y^2}=-\frac{q}{S} \quad \ldots\ldots (4)$$

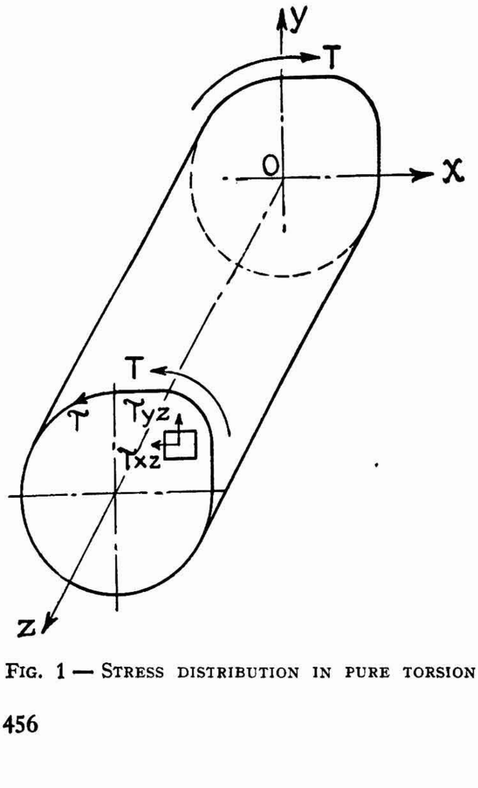

FIG. 1 — STRESS DISTRIBUTION IN PURE TORSION

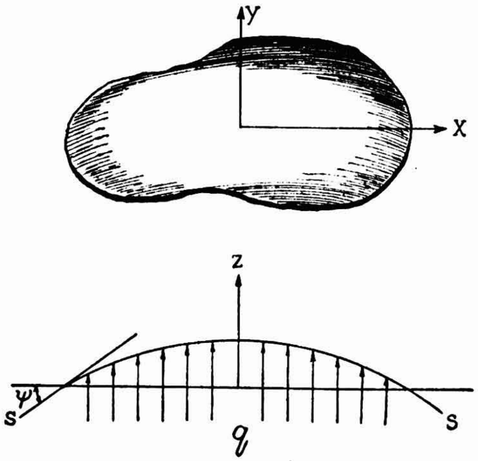

FIG. 2 — PRESSURE MEMBRANE

where z is the height of the membrane and x, y its rectangular co-ordinates, q the unit pressure under the film and S the unit tensile force in the film.

In order that the analogy may be valid the assumptions made are: (i) that the uniform pressure q under the thin film acts in a direction parallel to the axis rather than normal to the surface of the film; and (ii) the inclination Ψ of the membranes is small so as to satisfy $\Psi = \sin\Psi = \tan\Psi = \tau$.

If this bubble-shaped surface, governed by $\nabla^2 z = -q/S$, for a non-circular section ABCDE, be as shown in Fig. 3, then for any line tangent to this surface at O whose projection is x-axis, the shearing stress τ_{zy} at O′ the projection of O in the y-direction is proportional to the slope of the angle that the tangent at O makes with x-axis.

Since the slope at O in the x and y direction measures to a certain ratio the shear stresses τ_{zy} and τ_{zx} respectively at the corresponding point O′, the maximum shear stress at O′ is, therefore, proportional to the maximum slope of the film at the corresponding point O, i.e. $-\frac{d\phi}{dn}$.

Further, the volume under the bubble surface is proportional to the torsional rigidity of the section. Since volume under the soap film is $\iint z\,dx\,dy$ and volume under the stress surface is $\iint \phi\,dx\,dy = T/2$ where T is the twisting moment in the bar, it is clear that double the volume under the soap film represents the twisting moment.

Having established the analogy between the torsion function ϕ and bubble surface z we can put the analogic quantities in tabular form thus:

	Twisted bar	*Membrane*
1.	$\nabla^2\phi = -2G\theta$	$\nabla^2 z = -q/S$
	which implies that $\phi = z$ provided the pressure tension ratio	$q/S = 2G\theta$
2.	$\phi = 0$ along the boundary	$z = 0$ along the edge
3.	$T = 2\iint \phi\,dx\,dy$	$V_t = \iint z\,dx\,dy$
4.	$\tau_{zy} = -\frac{\partial\phi}{\partial x}$	Slope in x-direction $= \frac{\partial z}{\partial x}$
	$\tau_{zy} = \frac{\partial\phi}{\partial y}$	Slope in y-direction $= \frac{\partial z}{\partial y}$

From the two equations (3) and (4) we find that the constant of the analogy is q/S. Though q and S are not known quantities, the ratio q/S can be easily determined from the relation

$$\oint \tau\,ds = \frac{q}{S}\cdot A$$

where $\tau = \frac{dz}{dn}$ indicates the maximum slope (gradient) along the interior normal of the boundary; the integration is along this boundary and A is the enclosed area.

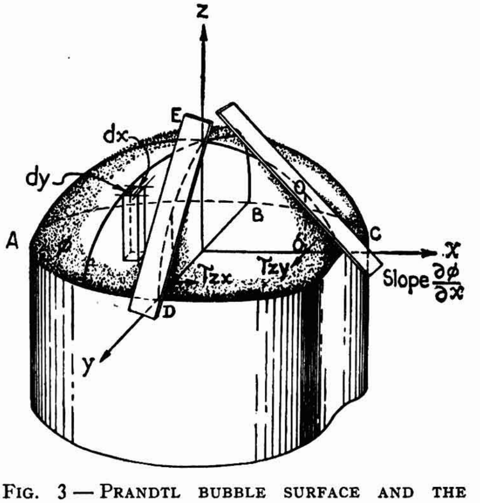

FIG. 3 — PRANDTL BUBBLE SURFACE AND THE SHEAR STRESSES

Instead of direct determination it is preferable to compare the shear stresses and torsional rigidity of the test section with those of a circular section under the same physical conditions and using the same soap solution. For the determination of shear stress at any point in a non-circular shaft it is, therefore, necessary to compare it with a circular section. Since stresses at corresponding point, i.e. points equally displaced from the plane of the plate, bear the same ratio as slopes at these two points, and since the slope at the desired point for a spherical section can be determined from its elevation, the shear stresses at the desired point in the non-circular section can be easily determined from the ratio of slopes at these two points.

Similarly the torsional rigidity of any non-circular section can be found if the ratio of volumes of the two bubble surfaces is determined experimentally and knowing the torsional rigidity of the circular section the exact value for the irregular section can be determined.

Apparatus

The pressure soap film apparatus[5,6] was designed after that used by Griffith and Taylor[7]. In this apparatus an aluminium plate with an experimental hole and a comparison circular hole cut in it was clamped between the two halves of a cast iron box. The box, which was a square, was supported on levelling screws. The lower half was in the form of a very shallow tray $\frac{1}{16}$ in. deep and a square frame formed the side of the box. The two parts were clamped together and the box was made airtight by means of thick wax. Over the frame was placed a piece of plate glass $\frac{1}{4}$ in. thick and sufficiently large, through the centre of which a hole was drilled for a micrometer height-gauge, reading to 0·001 in., and carried on its lower end a sharp steel needle point. This was adjusted exactly above the centre of the circular hole for determination of the volume V_c for the spherical film. By adjusting the micrometer for different displacements h, the volume of the two distended membranes were recorded. In carrying out the experimental work, the blowing up was done through a burette, connected through a displacement bottle to the lower end of the box. The readings of the burette were taken to 0·01 cc. by using a low power microscope.

For greater accuracy the boundary of the cross-section of both the test and comparison holes were bevelled at an angle of 45°. It was observed that in spite of this the film did not rest at the upper side of the bevelled edge but at an intermediate point. It has been found that at boundary points where the boundary line is highly concave even a small overlapping of the order of 0·004-0·005 in. above the surface of the plate is visible.

The following are a few other important precautions which were observed in this experiment: (i) to prevent evaporation of the soap film thereby to maintain the consistency and the tensile force in the film; (ii) to minimize the edge effect, the surplus solution was carefully drained off. Solution near the boundary was also removed to minimize overlapping at the boundary; and (iii) to measure the height of the film, the micrometer was set at an elevation giving the film a slight upward curvature. After each set of readings the micrometer height was readjusted to a new elevation and water was displaced from the burette till the film just ran up on the needle. Such a method gave readings correct to 0·0005 in.

Torsion constant K

The torsional constant K is proportional to the volume under the membrane. The volume V_t of the test section was determined directly by measuring the total displacement of soap-water in the burette and then subtracting from it the volume V_c of the circular bubble.

In terms of height h and diameter D the volume of the spherical film is

$$V_c=\tfrac{1}{8}\pi hD^2\left\{1+\frac{4}{3}\frac{h^2}{D^2}\right\} \quad \ldots\ldots \quad (5)$$

and if height h is small we have

$$V_c=\tfrac{1}{8}\pi hD^2 \quad \ldots\ldots\ldots \quad (6)$$

Knowing the total displacement $V=V_c+V_t$ from the burette and V_c from equation (6) the volume of the test bubble can be easily determined. The total volume of water introduced is, however, not exactly equal to the total volume of the two bubbles because of slight increase in pressure in the chamber but this is negligible.

For different values of vertical displacement h of the spherical bubble as measured with the help of micrometer, the value of the volume V displaced from the burette was recorded for drawing a plot relating h and V. For large value of displacements h the modified value of $h\left\{1+\frac{4}{3}\frac{h^2}{D^2}\right\}$ was used.

The equation of the best straight line nearly fitting all these points so recorded can be best put in the form

$$h = mV + c \quad \ldots\ldots\ldots\ldots (7)$$

where m is the slope and c is a constant. By using the method of least squares the value of the constants m and c is determined from the two simultaneous equations for n sets of paired observations as below:

$$m\Sigma V^2 + c\Sigma V - \Sigma Vh = 0$$
$$m\Sigma V + cn - \Sigma h = 0$$

The constant c here accounts for the intermediate hanging below the upper surface of the plate and the other errors in experimental observations. Inflating the film slightly upwards before taking the incremental data between h and V reduces errors in the final value of slope measurements. The slope measurement enables us to obtain the true total displacement V for a particular value of displacement h of the circular bubble, and knowing $V_c = \frac{1}{8}\pi h D^2$ we can find the volume V_t of the test hole by difference.

The ratio V_t/V_c gives us the rigidity ratio and this multiplied by J, the polar moment of inertia of the reference circular section, gives us the torsional rigidity of the non-circular test section.

A sample solution for a square section is shown in Table 1.

Using the method of least squares the equation of the straight line (Fig. 4) is

$$h = 0{\cdot}00988V + 0{\cdot}00238$$

From this we infer that for a total displacement of 20·0 cc. the displacement of the circular bubble is 0·1976 in. above the surface of the plate.

For calculating the torsional rigidity the procedure adopted is given below:

Side of the square 2a, 2·54 in.; diameter of the test hole D, 2·54 in.; V, total volume drawn from the burette, 20 cc.; V_c, calculated spherical volume, 8·2355 cc.; actual volume of the test section, 11·7645 cc.; torsional rigidity ratio, 1·4285; theoretical value $0{\cdot}1406.G\theta.(2a)^4/JG\theta = 1{\cdot}4316$; percentage error, 0·216 per cent.

The value of K was similarly calculated experimentally for (i) a sector of a circle with boundaries r = 0, r = 3·024 in. and angle $\alpha = \pi/2$; and (ii) a circular shaft of diameter 3 in. with a semicircular longitudinal groove of diameter 1 in. The results for both these experiments are given in Tables 2 and 3.

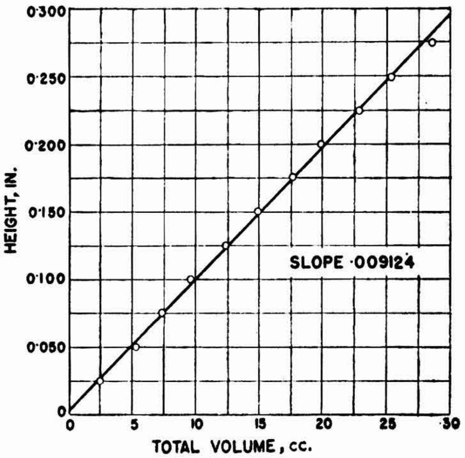

Fig. 4 — Relation between the total volume and height of the spherical bubble

TABLE 1

Height in.	Volume cc.
0·025	1·50
0·050	4·13
0·075	6·77
0·100	9·40
0·125	12·05
0·150	14·70
0·175	17·30
0·200	19·95
0·225	22·60
0·250	25·25
0·275	27·80
0·300	30·00

TABLE 2 — CORRELATION OF VOLUME WITH HEIGHT OF MEMBRANE FOR A SECTOR

(Side of the sector, 3·024 in. included angle $\alpha = \pi/2$; diameter of the comparison circle, 2·6325 in.)

Height in.	Volume cc.
0·1750	21·45
0·2000	23·92
0·2250	26·75
0·2500	28·74
0·2750	31·12
0·3000	33·88
0·3250	36·48
0·3500	39·12
0·3750	41·41
0·4000	44·45
0·4250	46·95
0·4500	50·10
Equation of the straight line	$h = 0{\cdot}00912\,V + 0{\cdot}01085$
Torsional rigidity factor	1·45673
Theoretical value $\frac{0{\cdot}0805a^4G\theta}{\pi/32.(2{\cdot}6325)^4}$	1·46246
% error	0·39300

TABLE 3 — CORRELATION OF VOLUME WITH HEIGHT OF MEMBRANE FOR A CIRCULAR SHAFT WITH A SEMICIRCULAR LONGITUDINAL GROOVE

(*Circular shaft of diameter 2a=3 in. with a semicircular longitudinal groove of diameter 2b=1 in.*)

Theoretical value of torsional rigidity

$$=\left\{\left(a^4-2a^2b^2-\frac{b^4}{2}\right)\Psi+\frac{ab}{4}\sin\Psi\,(7b^2+2a^2)\right\}=6\cdot50654\text{ in.}^4$$

where $\Psi=\cos^{-1}\frac{b}{2a}$

Diameter of comparison circle	2·6848 in.
J for circle	5·1026 in.^{4}
Theoretical torsional rigidity factor	1·2749

HEIGHT in.	VOLUME cc.
0·025	1·86
0·050	4·12
0·075	6·80
0·100	9·40
0·125	12·16
0·150	14·78
0·175	17·66
0·200	20·30
0·225	23·24
0·250	26·21
0·275	29·05
0·300	32·13
0·325	34·98

Slope of the best straight line	0·00955
The torsional rigidity factor calculated from this graph	1·2565
% error	1·44

In the above three examples representative of typical sections, such as a square or a sector of a circle where the boundary is discontinuous, and a circular shaft with a longitudinal circular groove which is a typical case of a section with re-entrant corner, the results obtained are in close agreement with the theoretical values.

Conclusion

The most important application of this analogy is in determining the torsion constant K which is proportional to the volume under the membrane. Instead of directly measuring the volume of the bubble, the rate of increase in height against volume has been plotted using the method of least squares which has eliminated the errors due to overlapping and intermediate hanging of the film.

This procedure has not only simplified the work but also resulted in higher degree of accuracy approaching theoretical values and has thus proved its applicability to other complicated sections for which mathematical analysis is highly involved.

APPENDIX 1

Radius of circular hole[8]

For a soap membrane stretched over a circular opening and slightly distended, and from Green's surface integral we have

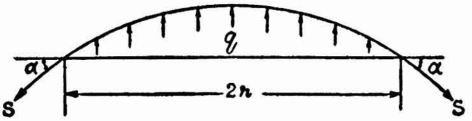

FIG. 5 — COMPARISON OF A BUBBLE SURFACE STRETCHED OVER A CIRCULAR HOLE WITH PRESSURE MEMBRANE

$$\pi r^2 q=2\pi r S\sin\alpha$$

$$\text{or } r=\frac{2S}{q}\sin\alpha$$

If a second film is stretched over a test hole by the side of this standard circular hole, then the value of q/S will be the same for both the holes (FIG. 5). If A is the area of cross-section of this test hole, then the force acting upwards is qA and the downward force is PS sin β where β is the mean angle around the boundary and P the perimeter, then

$$qA = PS\sin\beta$$

Since S/q is same for both, we have

$$r=\frac{2A}{P}\,\frac{\sin\alpha}{\sin\beta}$$

Since the average sine of the inclination of the test film is to be equal to the sine of the angle of inclination over the boundary of the circular section, i.e. sin α = sin β, we must, therefore, have a comparison circle of radius equal to $\frac{2A}{P}$.

If in some cases the size 2A/P is small, errors in the measurement of height h and volume V_c of the spherical film will increase considerably. In such cases it is better to fix the minimum diameter at 1·5 in. as the advantages gained in the measurement of h and V_c outweigh the advantages gained in making equal the analogy approximation. At the same time the volume V_c should not be increased much as the errors introduced in the measurement by difference of small volume V_t of the test hole will be more if V_c is several times more than V_t.

References

1. TIMOSHENKO, S. & GOODIER, J. N., *Theory of Elasticity* (McGraw-Hill Book Co., New York), 1951, 211-315.
2. HETENYI, M., *Handbook of Experimental Stress Analysis* (Wiley, New York), 1950, 736-38.
3. HIGGINS, T. G., *Analogic Experimental Methods in Stress Analysis as Exemplified by Saint-Venant's Torsion Problem, Soc. expt. Stress Anal.* (Wesley Press, Cambridge, Mass.), Vol. II, No. 2, 1944, 17-27.

4. TIMOSHENKO, S., *Strength of Materials* (Van Nostrand Co., New York), 1951, 266-74.
5. QUEST, H., *Eine Experimentelle Losung des Torsionsproblems* (Ingenieur-Archiv, Berlin), Vol. 4, 1933, 510-20.
6. ZACHRISSION, L. E., *On the Membrane Analogy of Torsion and Its Use in a Simple Apparatus* (Trans. roy. Inst. Technol., Stockholm), **44** (1951), 39.
7. TRAYER, G. W. & MARCH, H. W., *The Torsion of Members Having Sections Common in Aircraft Construction* (National Advisory Committee for Aeronautics, Washington, Report No. 334), 1929, 675-719.
8. CUSHMAN, P. A., *Shearing Stresses in Torsion anp Bending by Membrane Analogy* (Amer. Soc. Mech. Engrs. Advance Paper), June 1932.

A Voltage Regulator System for Stabilization of Field Current of a Solenoidal Beta-ray Spectrometer

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An experimental procedure for stabilizing magnetizing current in a beta-ray spectrometer using an electronically regulated d.c. generator is described.

CONSTANCY of magnetic field is an important requisite for attaining proper definition and sharpness of beta-spectra which lead to accuracy and precision of energy measurements by magnetic spectrometers. A constant magnetic field is obtained by keeping the magnetizing current constant, which may be effected by either an electronic current stabilizer[1,2] or a regulated d.c. generator[3-5]. The latter is preferred when the instrument involves the use of high magnetizing currents.

Magnetizing current supply from a d.c. generator fluctuates due to changes in the generator voltage and thermal variations of the resistance of the windings of the solenoid. Elaborate circuits have been developed to operate the d.c. generator compensating for both these effects[6].

In the course of work with the solenoidal beta-ray spectrometers under development in this laboratory[7,8], it has been found that magnetizing current fluctuation due to changes in resistance of the winding can be reduced to 1 part in 1,500 parts for a run of 30 min. by the following procedure which does not make use of a special current stabilizer. The stability of 0·06 per cent is quite adequate, in as much as the expected resolving power of the spectrometers under development is only of the order of 1·5 per cent.

Reduction of current fluctuation due to thermal changes in the resistance of the winding

The water-cooled solenoid of the spectrometer for low energy measurements[8] has a cold resistance of 130 ohms and its operating current ranges from 0 to 3 amp. The solenoid was preheated by passing a current of 4·5 amp. from a 10 kW. d.c. generator for 45 min., and then the current was switched off for 15 min. With this operation, the solenoid attained a steady resistance of 145 ohms in the first hour, and subsequently when a current of 1·5 amp. was supplied from the generator controlled by an electronic voltage regulator, the change in current due to resistance variations was found to be only of the order of 1 part in 1,500 for a run of half an hour.

This result suggests that suitable choice of preheating time and current can give a stability of the order of 0·1 per cent or better against thermal changes in resistance. A condition necessary for the success of this method is to control the field current by altering the voltage applied across the solenoid directly from the generator, instead of using series rheostats having uncontrollable variations in resistance due to thermal effects. The generator voltage, however, must be well stabilized against changes in the driving motor speed and other factors over the entire range.

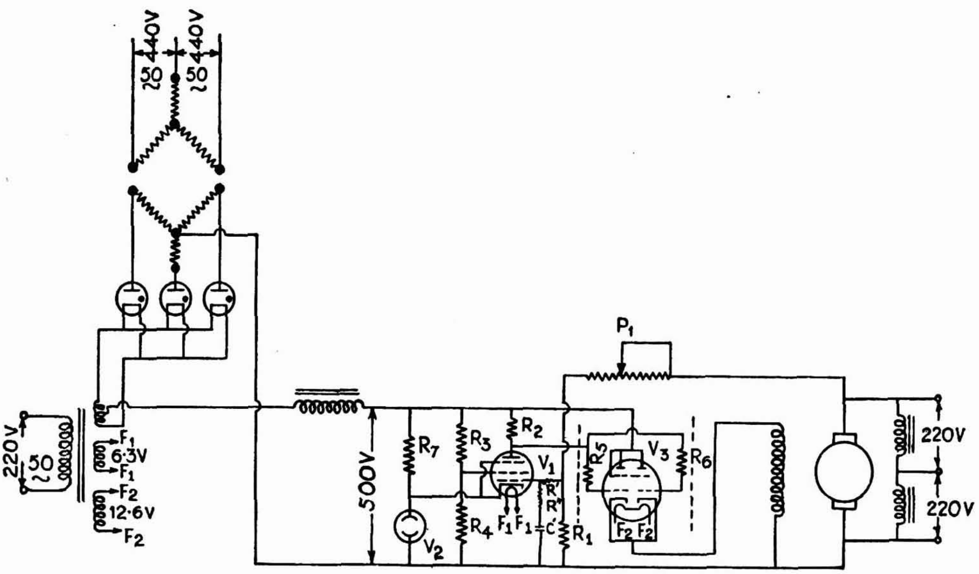

FIG. 1 — CIRCUIT DIAGRAM OF THE VOLTAGE REGULATOR [$P_1 = 100,000$ ohms; $R_1 = 30,000$ ohms; $R_2 = 1,000,000$ ohms; $R_3 = R_4 = 50,000$ ohms; $R_5 = R_6 = 10,000$ ohms; $R_7 = 20,000$ ohms; $V_1 = 6SJ7$; $V_2 = VR150$; $V_3 = 815$ (10 tubes in parallel)]

The voltage regulator

The generator voltage regulator illustrated in Fig. 1 is an improved form of similar units in use in many laboratories[9-11]. It stabilizes the generator voltage to 1 part in 2,000 at any output from 340 to 460 V. against the expected fluctuations in the driving motor speed which is of the order of 10 per cent. The generator is fitted with a three-wire distribution panel taken from a static balancer rated at a maximum out of balance current of 5 amp. connected across the lines, which helps in obtaining a range of 170-230 V. between line and neutral, and 340-460 V. between lines. This arrangement has rendered the use of series rheostats unnecessary in the useful current ranges for reasons mentioned earlier.

The field of the d.c. generator is supplied by a three-phase rectifier system through the voltage regulator. In this voltage regulator, V_1 amplifies the difference in the voltage obtained through the voltage divider consisting of R_1 and P_1, and a reference voltage obtained from a glow-tube stabilizer V_2. The output of V_1 is fed to the grids of ten beam-power amplifier tubes (type 815) operating in parallel. The grid of each tube has a separate limiting resistor. When the generator voltage rises, the bias in V_1 falls resulting in increased plate current flow. The consequent lowering in plate potential of V_1 increases the bias in the bank of power amplifiers, resulting in reduction of current through the field coil of the generator, fed by the power amplifiers. A reduction in generator voltage produces the opposite reaction. The generator voltage is controlled by the potentiometer P_1. R′R″C′ constitute the anti-hunt network, the individual values of the components of which were determined empirically.

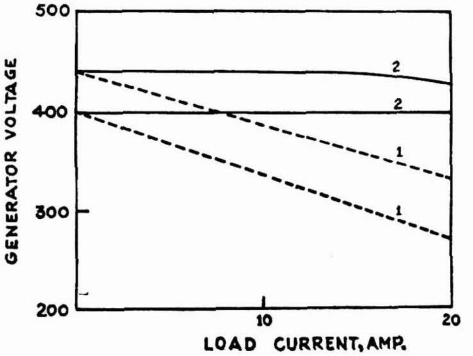

FIG. 2 — LOAD CHARACTERISTICS OF THE GENERATOR [(1) Without voltage regulator; (2) with voltage regulator]

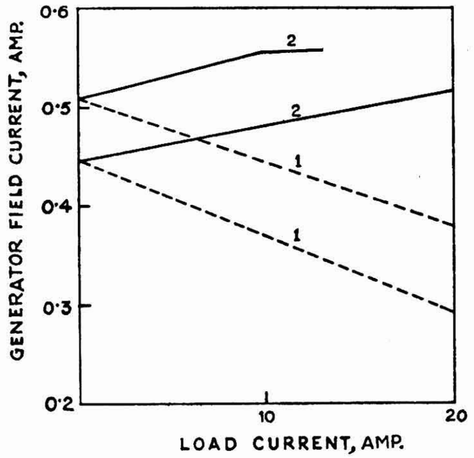

FIG. 3 — VARIATION OF GENERATOR FIELD CURRENT WITH LOAD [(1) Without voltage regulator; (2) with voltage regulator]

Fig. 2 shows the load characteristics of the generator when operated by the electronic regulator. Fig. 3 shows the generator field current variation with load. Above 460 V. the load regulation characteristics of the generator become unsatisfactory because of the saturation of the generator field magnet.

Acknowledgement

The authors express their thanks to Dr. Swami Jnanananda for supervising the work, and Miss Sarojini Pandit and Mr. C. Balakrishnan for going through the manuscript. They wish to record the valuable assistance given by Mr. Budh Singh in setting up the equipment. They are also grateful to Dr. K. S. Krishnan, Director, National Physical Laboratory, for permission to publish the paper.

References

1. HIPPLE, J. A., GROVE, D. J. & HICKAM, W. M., *Rev. sci. Instrum.*, **16** (1945), 69.
2. VAN DER WALT, N. T., *Rev. sci. Instrum.*, **24** (1953), 413.
3. SOMMERS, H. S., WEISS, P. R. & HALPERN, W., *Rev. sci. Instrum.*, **20** (1949), 244.
4. WOLFF, J. R. & FREEDMAN, M. S., *Rev. sci. Instrum.*, **22** (1951), 736.
5. CHANG, W. Y., *Phys. Rev.*, **69** (1946), 60.
6. CARO, D. E. & PARRY, J. K., *J. sci. Instrum.*, **26** (1949), 374.
7. JNANANANDA, S., *J. sci. industr. Res.*, **11B** (1952), 401.
8. MAHANTY, J., PANDIT, (Miss) S. & BALAKRISHNAN, C., *J. sci. industr. Res.*, **12B** (1953), 571.
9. VERMAN, L. C. & REICH, H. J., *Proc. Inst. Radio Engrs.*, **17** (1929), 2075.
10. KILPATRICK, F. E. & BERNHARDT, C. P., *Electronics*, **7** (1934), 352.
11. REICH, H. J., *Principles of Electron Tubes* (McGraw-Hill), 1941, 156.

Determination of Osmotic Coefficients: Part II—Aqueous Solutions

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Osmotic coefficients of aqueous solutions of potassium laurate, Aerosol M.A. and potassium salts of some dibasic acids have been determined at 30°C. by means of the thermistor technique. The results are in agreement with those evaluated from cryoscopic and other data. The high values of osmotic coefficients of potassium sebacate in dilute solutions are attributed to the cumulative effect of hydration and inter-ionic attraction.

THE construction and calibration of the thermistor bridge for the measurement of small vapour pressure differences have been described by McGee and Iyengar[1]. This method consists in measuring the equilibrium resistance differential (Δr) set up between a pair of matched thermistors to which adhere a drop of solution and a drop of solvent or reference solution in an atmosphere saturated with solvent vapour. Values for osmotic coefficients are easily derived from Δr, which is proportional to the vapour pressure difference between the drops.

The present paper elucidates the application of the thermistor technique for evaluating osmotic coefficients of aqueous solutions of potassium laurate, potassium salts of some dibasic acids and the synthetic detergent Aerosol M.A. The only other available data on studies by this technique are those of Huff, McBain and Brady[2,3] who investigated the vapour pressure of aqueous solutions of some detergents.

Experimental procedure

Resistance differentials were observed by means of the thermistor bridge described previously[1]. The air thermostat was maintained at 30°C. in all the experiments.

In the case of soap solutions, the required amount of alkali (about 4 equivalent per cent potassium hydroxide based on the weight of soap) was added to suppress hydrolysis. The necessary correction for the resistance differential due to this added alkali was applied in all such cases. Potassium laurate used in these experiments was prepared from trilaurin extracted from Pisa seeds.

The α, ω, -C_{18}-dibasic acid was prepared from *kamala* seeds by the procedure of Aggarwal *et al.*[4]. The oil extracted from the seeds was hydrolysed, acidified, hydrogenated and finally oxidized to give the α, ω, C_{18}-dibasic acid, which upon repeated recrystallization from acetone, had a melting point of 125°C. The mean value of the equivalent weight, as determined both by the silver salt and alkali titration methods, was 157·8 as compared to the calculated value of 157·2. The pure, crystalline dibasic acid was dissolved in acetone and the equivalent amount of alcoholic potash added. The ensuing precipitate of the potassium soap was recrystallized from alcohol.

Potassium sebacate was similarly prepared from pure sebacic acid.

The potassium salt of succinic acid was prepared by dissolving the pure acid in water and adding the requisite quantity of aqueous potassium hydroxide.

An *Analar* sample of potassium oxalate was used without further purification. A sample of Aerosol M.A. [di-hexyl (methyl amyl) ester of mono-sodium sulpho succinate, $(C_6H_{13}OCO)_2\ C_2H_3SO_3Na$ (100 per cent pure)] from American Cyanamide & Chemical Corporation was used as such after drying over P_2O_5 in a vacuum desiccator.

In all the experiments equilibrium was attained within 2-5 min.

Results and discussion

Osmotic coefficients (g) were calculated from the observed equilibrium resistance differential by the following expression:

$$g = \frac{\Delta r}{KVm}$$

where Δr = equilibrium resistance differential (ohms) between the drops of solvent and solution;

K = calibration constant for solvent (water) = 8·50 ohms/mol. for the Stantel thermistors used;

V = number of possible ions; and

m = molality (mols solute per 1,000 g. water).

The results are recorded in Table 1.

The osmotic coefficients of potassium laurate and Aerosol M.A. have been plotted against square root of molality (FIG. 1). For potassium laurate the results agree well with the available data of McBain and coworkers[5,6] obtained by the freezing point depression and the thermoelectric (thermocouples) methods. The present results are also in conformity with those obtained by Brady, Huff and McBain[2] by the thermistor technique. Their values, being very close to the present values, have not been shown

TABLE 1 — OSMOTIC COEFFICIENTS

m	Δr	g	m	Δr	g
Potassium laurate					
0·0219	0·35	0·95	0·2359	1·04	0·26
0·0481	0·46	0·56	0·4750	1·49	0·18
0·1192	0·65	0·32	1·0170	3·26	0·19
Aerosol M.A.					
0·0271	0·38	0·83	0·1754	1·08	0·36
0·0384	0·48	0·74	0·2974	1·32	0·26
0·0771	0·77	0·59	0·4982	1·75	0·21
0·1287	0·91	0·42	0·7979	3·12	0·23
Potassium oxalate					
0·0502	1·01	0·79	0·3098	6·12	0·78
0·1012	2·02	0·78	0·4764	9·24	0·76
0·1903	3·84	0·79	0·9343	17·95	0·75
Potassium succinate					
0·0532	1·09	0·80	0·3824	8·39	0·86
0·1009	2·08	0·81	0·6413	14·72	0·90
0·2039	4·21	0·81	—	—	—
Potassium sebacate					
0·0598	1·38	0·91	0·5259	13·20	0·96
0·1079	2·43	0·88	0·6642	16·64	0·98
0·1436	3·27	0·89	0·8299	21·48	1·02
0·2633	5·93	0·88	—	—	—
Potassium salt of α, ω, C-18 dibasic acid					
0·0216	0·39	0·71	0·0405	0·69	0·67
0·0309	0·56	0·70	0·0522	0·93	0·70

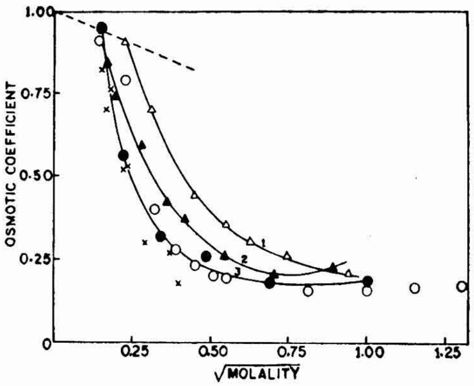

FIG. 1 — OSMOTIC COEFFICIENT VS. SQUARE ROOT OF MOLALITY [(1) Aerosol M.A. (cryoscopic); (2) Aerosol M.A. (thermistor); (3) potassium laurate (thermistor); o—o, potassium laurate (cryoscopic); ×—×, potassium laurate (thermocouple); - - - -, Debye-Huckel limiting slope for uni-univalent electrolytes ($g = 1-0{\cdot}4\sqrt{m}$)]

in Fig. 1. In the case of Aerosol M.A. the freezing point values reported by McBain and Bolduan[5] are consistently higher than the present results but follow essentially the same trend when plotted against concentration as the present results.

Brady and Huff[7], Fineman and McBain[6], and Huff *et al.*[3] have also reported a similar decrease in osmotic coefficients of potassium laurate, caprate and a number of other synthetic detergents with rise in temperature (0°, 30° and 50°C.). These lower values of "g" have been attributed to the decrease in the critical micelle concentration (c.m.c.) with increasing temperature. In this case (Aerosol M.A.) the c.m.c. appears to have fallen from 0·044 m. to 0·022 m. for an increase of temperature from 0° to 30°.

While the osmotic properties of the sodium and potassium salts of long chain monobasic acids have been extensively investigated, little work has been done on the corresponding salts of dibasic acids. Potassium sebacate, the first dibasic acid soap chosen for our investigations, shows first a slight fall of osmotic coefficient with concentration followed by an appreciable rise at higher concentration (FIG. 2). The minimum occurs at about 0·25 m. The value of the apparent osmotic coefficient at the highest concentration investigated (0·83 molal) is greater than unity (1·02). This behaviour of "g" with concentration is in direct contrast to that of the corresponding monobasic soap potassium caprate, investigated by McBain and Bolduan[5] by the freezing point method. Their values show that the osmotic coefficients decrease from 0·95 to 0·23 over a concentration range of 0·04 m. to 0·93 m., indicating micellar association. The behaviour of potassium sebacate is, on the other hand, very much analogous to that of potassium formate or potassium acetate whose osmotic coefficients reported by Scatchard and Prentiss[8] start increasing at higher concentrations (0·1-0·3 m.) after the initial fall in the dilute regions. McBain and Bolduan[5] have reported a similar behaviour in the case of potassium butyrate, whose apparent osmotic coefficients (cryoscopic) exceed unity beyond the concentrations of 0·4 m. This rise has been attributed by these authors to hydration. Association of solute molecules results in low values of apparent osmotic coefficients since the effective molality of the solution is reduced. Hydration, on the other hand, causes the effective molality of the solute to increase and consequently the true osmotic coefficients (g) will be lower than the apparent coefficients (g_o) evaluated without assumption of any hydration. Table 2 illustrates the manner in which the degree of hydration affects the osmotic coefficient.

It is also possible to qualitatively account for the observed high values of "g" on the basis of inter-ionic attraction. In the Debye-Huckel limiting law $g = 1-A\sqrt{m}$; A is inversely proportional to the dielectric

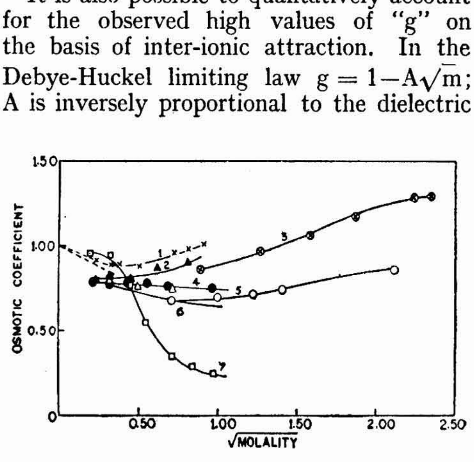

FIG. 2 — OSMOTIC COEFFICIENT VS. SQUARE ROOT OF MOLALITY [(1) Potassium sebacate (thermistor); (2) potassium succinate (thermistor); (3) potassium succinate (vapour pressure data, 100°C.); (4) potassium oxalate (thermistor); (5) potassium oxalate (vapour pressure data, 100°C.); (6) potassium sulphate (isopiestic, 25°C.); (7) potassium caprate (cryoscopic); Δ—Δ, potassium oxalate (cryoscopic); - - - -, Debye-Huckel limiting slope for 1:2 electrolytes ($g = 1-0{\cdot}46\sqrt{m}$)]

TABLE 2 — EFFECT OF HYDRATION ON THE OSMOTIC COEFFICIENT

(0·83 *molal potassium sebacate in water*)

DEGREE OF HYDRATION (n) (mols. H_2O/mol. solute)	0	1	2	5	10
$g=g_0\,(1-mn/55{\cdot}56)$	1·02 ($=g_0$)	1·00	0·99	0·94	0·87

constant of the medium (D_1). In the original derivation it was assumed that in dilute solutions D_1 is equal to the dielectric constant of the solvent D_0. Hydration as well as the polarity of the solute molecule would probably cause the " microscopic " dielectric constant to be different from the " macroscopic " value. Thus, an enhanced dielectric constant of the medium will increase the value of "g". It is interesting to note in this connection that in the case of amino acids (dipolar ions) Cohn *et al.*[9] have pointed out that the activity coefficient of the solute is related to the ratio of dielectric constant of the solvent to that of the solution. In view of this, it may be interesting to undertake the experimental measurements of dielectric polarization of the solutions of potassium sebacate and other esters of dibasic acids, which exhibit osmotic anomalies.

With a view to compare this behaviour of "g" with concentration, the potassium salts of the simple dibasic acids, oxalic and succinic, were investigated. For potassium oxalate, the osmotic coefficients calculated by us from the freezing point lowering data[10] agree well with the present values by thermistor technique, whereas those calculated from vapour pressure data at 100°C.[11] are systematically lower. The plot of osmotic coefficient of the electrolyte K_2SO_4 is included for comparison[12]. The thermistor data covering a concentration range 0·05-0·9 m. indicate that the osmotic coefficient does not vary to any appreciable extent in this region (g 0·75-0·8). The vapour pressure data at higher concentrations (0·5-2·0 m.) show a slight increase with concentration (g 0·68-0·75).

The osmotic coefficients of potassium succinate (thermistor) start increasing with concentration above 0·2 m. As in the case of potassium oxalate, the vapour pressure data at 100°C. are lower in the region where they can be compared with thermistor data, the highest value calculated from vapour pressure data being 1·30 at 5·5 m.

From the above results it is obvious that the osmotic behaviour of potassium sebacate which has eight CH_2 groups separating the two alkyl carboxyl groups is qualitatively similar to that of succinate having two CH_2 groups. This is in sharp contrast to the behaviour of the monobasic acid salts, where a transition in the osmotic properties starts at the butyrate with three CH_2 groups.

In order to study the changes that might be brought about by further increasing the number of CH_2 groups between the alkyl carboxyl groups, the investigation of the osmotic coefficients of the potassium salt of C_{18} dibasic acid prepared in this laboratory was undertaken. Owing to its limited solubility, it was not possible to study concentrations above 0·06 m. In the rather narrow range of molar concentration (0·02-0·05) investigated, the osmotic coefficient is 0·7. While this value is not low enough to indicate any appreciable micelle formation, it certainly indicates some form of association. It is interesting to note that this dibasic acid soap solubilizes dye (Orange OT) but not hydrocarbon (benzene). Inability to cover an appreciable range of concentration in the osmotic measurements prevents our arriving at a definite conclusion regarding the nature and extent of association.

The application of the thermistor technique to solutes which are soluble only in organic solvents and its usefulness in obtaining important thermodynamic data will be elaborated in a subsequent publication.

Acknowledgement

Thanks of the authors are due to (late) Prof. J. W. McBain and Dr. S. S. Marsden for their keen interest in this work and to Dr. Hira Lal for kindly supplying a sample of potassium laurate.

References

1. McGee, C. G. & Iyengar, B. R. Y., *Indian J. Phys.*, **35** (1952), 61.
2. Brady, A. P., Huff, H. & McBain, J. W., *J. phys. Chem.*, **55** (1951), 304.
3. Huff, H., McBain, J. W. & Brady, A. P., *J. phys. Chem.*, **55** (1951), 311.
4. Gupta, S. C., Sharma, V. N. & Aggarwal, J. S., *J. sci. industr. Res.*, **11B** (1952), 463.
5. McBain, J. W. & Bolduan, O. E. A., *J. phys. Chem.*, **47** (1943), 94.
6. Fineman, M. N. & McBain, J. W., *J. phys. Chem.*, **52** (1948), 881.
7. Brady, A. P. & Huff, H., *J. Colloid Sci.*, **3** (1948), 571.

8. SCATCHARD, G. & PRENTISS, S. S., *J. Amer. chem. Soc.*, **56** (1934), 807.
9. COHN, E. J., MCMEEKIN, T. L., FERRY, J. T. & BLANCHARD, M. H., *J. phys. Chem.*, **43** (1939), 169.
10. *International Critical Tables*, **4** (1928), 259.
11. *International Critical Tables*, **3** (1928), 209.
12. ROBINSON, R. A. & STOKES, R. H., *Trans. Faraday Soc.*, **45** (1949), 612.

Temperature Dependence of the Joshi Effect

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The photo-active electrode layer responsible for the Joshi effect $\pm\Delta i$ under silent electric discharge consists of electrons, ions and excited neutral particles. A rise in temperature t at constant applied potential V results in (1) decrease in the work function for electron emission, (2) desorption, (3) attenuation of the space charge and (4) increase in the potential V_g across the gas. (1) leads to an increase in $\pm\Delta i$, and (2) to an opposite change. A diminution in $-\Delta i$ follows (3). The influence of (4) is governed by the nature of dependence of $\pm\Delta i$ on V_g. For a medium rise in t, effects due to (1), (2) and (3) are small. The observed marked variations in the relative *effect* $-\%\Delta i$ with t, viz. progressive diminution at low and medium gas pressures p, and the initial enhancement and subsequent diminution at comparatively large p, are due, in the main, to increase in V_g.

WHILE much is not known as regards the influence of temperature t on the *positive* Joshi effect $+\Delta i$, dependence of the negative *effect* $-\Delta i$ on this factor has been more fully investigated[1-7]. Some of the observations, viz. of Deo[5] in chlorine in a Siemens' tube with a side bulb attached to it and maintained at a temperature different from that of the discharge space, and those of Atchuta Ramaiah[6] and Ramanamurti[7] in vapours of water and iodine respectively, the vapours being in contact with the parent substances, are influenced by simultaneous changes in the number of particles in the discharge space. For a constant mass of gas (vapour) excited in all-glass Siemens' and wire-in-cylinder type discharge tubes, at a given applied potential V ($>V_m$ the minimum "threshold potential" for dielectric breakdown of the gas), the relative *effect* $-\%\Delta i$ ($= -\Delta i \times 100/i_D$) decreases progressively, at low and medium gas pressures p, with t. The effect of t is to initially enhance $-\%\Delta i$ at comparatively large p, and then diminish it. Thus, e.g. the author[1] has observed that in oxygen at the medium pO_2 of 331 mm. Hg, and 2·93 kV. (r.m.s., 50$\sim$), increase of t from 33° to 125°C. changes $-\Delta i$ from 23·2 to 3·6 per cent. Mallikarjunappa[2] found that in high pressure (540 mm.) chlorine, $-\%\Delta i$ at (say) 1·87 kV. (500$\sim$) increases from 14·9 at 25°C. to 41·6 at 80°C. The author, Mohanty and Nanda[3] observed that in 641 mm. oxygen, $-\%\Delta i$ increases over 27° to 103°C., and diminishes with further rise in t.

The activated electrode layer postulated by Joshi[8-10] as the seat of $\pm\Delta i$ consists of electrons, ions and excited neutral particles, and is characterized by a low work function. Electrons are released from this layer on irradiation. These by themselves cause $+\Delta i$. Their attachment, on the other hand, to the electronegative elements in the discharge space forms slow-moving negative ions which bring about $-\Delta i$ as a space charge effect.

A rise in t results in: (1) Increase in the thermal energy of the electrons (and other particles) in the layer. This would entail a diminution in the work function, and a consequent enhancement in the emission. Shifts in the photoelectric thresholds of pure metals to the red with rise in t have been observed, in recent years, by a number of workers, e.g. Ives[11], Ives and Johnsrud[12], DuBridge[13], and Cardwell[14], and, as has been shown by Fowler[15], are in complete qualitative agreement with the Sommerfeld electron theory. (2) Desorption: Increase in the thermal energy of the adsorbed particles beyond a certain critical value, would lead to their escape from the layer. This also follows from the Le Chatelier and Braun principle of mobile equilibrium, since the reverse process, viz. adsorption, is attended by heat evolution. A diminution in emission would therefore result. Thus, Ives[16] found that emission from an alkali metal film of a certain critical thickness decreases with *t* rise. Further, positive ions ejected from the layer would neutralize the accumulated negative ions and diminish the space charge density. (3) Attenuation of the space charge due also to increased heat movement of the negative ions constituting the space charge, and the consequent loss through diffusion. (4) Increase in the effective potential across the gas V_g due to enhanced conductivity of the glass.

The effect of (1) is an increase in $\pm\Delta i$, and of (2) an opposite change. A diminution in $-\Delta i$ follows (3). The influence of (4) is governed by the nature of the variation of $\pm\Delta i$ with V_g (*vide infra*). Further, it is known that, depending upon the conditions, $+\Delta i$ and $-\Delta i$ co-occur; the current indicator shows the balance[17-19]. Consequently, an increase or decrease in the observed $-\Delta i$ would also result from an opposite change in the accompanying $+\Delta i$. For a rise in *t* of the order of a few tens of °C., effects due to (1), (2) and (3) are small. The observed marked variations in $-\%\Delta i$, over such ranges of *t*, can therefore be ascribed, in the main, to (4).

The variation of $-\%\Delta i$ with the applied V, at different *p*, is represented diagrammatically in Fig. 1. The curves (FIG. 1) refer to low (*c*. 50 mm.), medium (*c*. 300 mm.) and high (*c*. 600 mm.) *p*. Similar curves represent the dependence of $-\%\Delta i$ on V_g which is approximately a constant fraction of the applied V. It will be seen that at low *p*, $-\Delta i$ is unobservable immediately below V_m; $-\%\Delta i$ is maximum at this potential and decreases rapidly with $V(>V_m)$. As *p* is increased, both the initial rise and the subsequent diminution in $-\%\Delta i$ are distributed over wider ranges of V. Thus, e.g. $-\%\Delta i$ in chlorine[2] at 540 mm. (25°C.) increases from 9·4 at 1·60 kV. (500~) to 19·9 at 2·67 kV., and decreases thereafter.

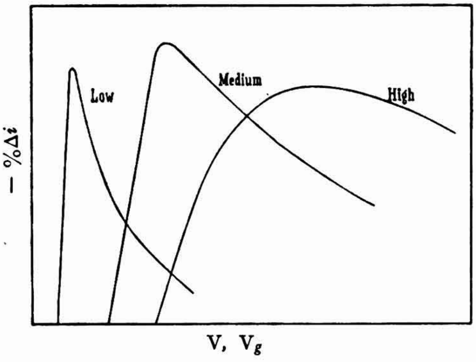

FIG. 1 — POTENTIAL DEPENDENCE OF THE JOSHI EFFECT AT DIFFERENT GAS PRESSURES

The initial rise in $-\%\Delta i$ is more marked the larger the electrode separation *d* (MOHANTY, S. R., unpublished data). Thus, for oxygen ($pO_2 = 207$ mm., 21°C.) under semi-ozonizer excitation and $d = 2$ mm., the *effect* is not observed below 1·87 kV. (50~), is maximum at this V, and diminishes progressively thereafter. At $d = 5$ mm., and under otherwise identical conditions, on the other hand, $-\%\Delta i$ increases over 1·87 to 5·07 kV.

The Siemens' tube[10,20,21] (FIG. 2) is equivalent to a compound condenser, consisting of three serial capacitances: C_1 and C_2 are associated with the inner and outer electrode walls respectively; the annular space filled with the gas represents the third C_g. The combined capacitance due to the inner and outer annular walls may be denoted by C_w, defined by

$$\frac{1}{C_w} = \frac{1}{C_1} + \frac{1}{C_2}.$$

R_g is the inverse of the conductivity produced in the gas above V_m due to ionization by collision. Further, glass possesses a final steady state conductivity[22,23]; the corresponding C_w behaves therefore as a condenser shunted across with a leak resistance R_w. The final conductivity I of glass increases with *t*, approximately according to the equation[24]

$$I_t = I_0 e^{\alpha t}$$

where α is a constant. In consequence of this increased leak (i.e. decrease in R_w), V remaining constant, V_g across the interelectrode space increases with *t*, and also the corresponding field E which (along with *p*) determines the probability of electron attachment[25] and the magnitude of $-\Delta i$.

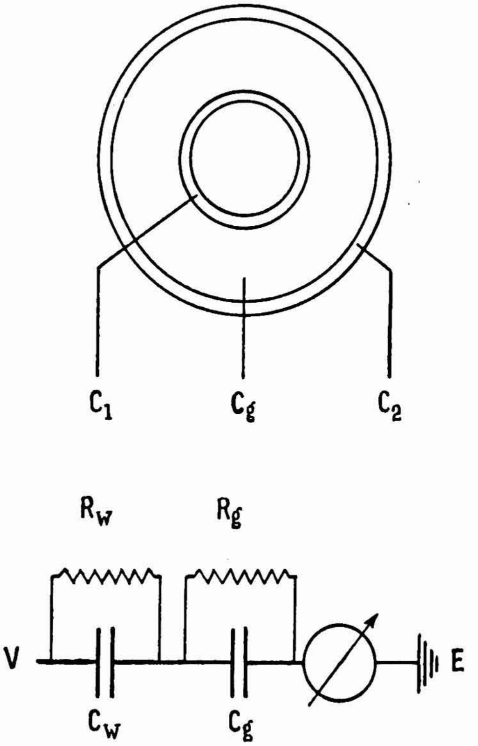

FIG. 2 — CIRCUIT DIAGRAM OF THE SIEMENS' OZONIZER

At a constant applied V corresponding to the descending portion of a curve (FIG. 1), an increase in V_g with t would diminish $-\%\Delta i$. Along the ascending portion, on the other hand, a similar variation in V_g would lead to an increase in $-\%\Delta i$. This last, in 540 mm. chlorine[2], increases progressively with V over the range 1·60-2·67 kV. (*vide supra*). The enhancement in $-\%\Delta i$ with t, over this V range, is therefore the consequence, in the main, of the similar variation in V_g. For a system near the peak on the ascending portion of a curve, an appreciable rise in t and a similar change in V_g would take the system over the peak to the descending portion of the curve; an initial rise and a subsequent diminution in $-\%\Delta i$ would therefore result. Such a change is evident from the results of the author, Mohanty and Nanda[3].

The potential dependence of the net *effect* $-\Delta i$ is similar to that of $-\%\Delta i$ (FIG. 1) with the modification that the initial rise is spread over an appreciable range of V at any p[26,27]. With rise in t, at constant p and V, $-\Delta i$ first increases and then decreases[1]. Due to increase in V_g, the maximum in the $-\Delta i$-V curve shifts towards low V.

The relative *effect* $-\%\Delta i$ is given by $-\Delta i \times 100/i_D$ (*vide supra*). Since the discharge current in dark i_D at constant V increases markedly with t[1], a small or no variation in $-\Delta i$ appears as a large diminution in $-\%\Delta i$.

The sparking potential, obtained with metal electrodes immersed in a gas, is independent of t, as long as the density is constant. Due to increase in V_g with t, V_m, on the other hand, diminishes[1].

Acknowledgement

Grateful thanks of the author are due to Prof. S. S. Joshi for valuable advice and kind interest.

References

1. MOHANTY, S. R., *J. Indian chem. Soc.*, **25** (1948), 557.
2. MALLIKARJUNAPPA, P., *J. Indian chem. Soc.*, **25** (1948), 197.
3. MOHANTY, S. R., MOHANTY, S. C. & NANDA, CH. B. N., *Proc. Indian Sci. Cong.*, 1952, *Part III, Phys. Sec.*, *Abst.* 23.
4. VISVANATHAN, K. S. & KUPPUSWAMY, K., *Indian J. Phys.*, **24** (1950), 13.
5. DEO, P. G., *Production of a Light Effect under Electrical Discharge in Chlorine, D.Sc. Thesis, Banaras Hindu Univ.*, 1946.
6. ATCHUTA RAMAIAH, N., *J. sci. Res., Banaras Hindu Univ.*, **1** (1950-51), 91.
7. RAMANAMURTI, M. V., *J. sci. Res., Banaras Hindu Univ.*, **2** (1951-52), 46.
8. JOSHI, S. S., *Proc. Indian Sci. Cong.*, 1946, *Part III, Phys. Sec.*, *Abst.* 26.
9. JOSHI, S. S., *Proc. Indian Sci. Cong., Part III, Phys. Sec.*, *Abst.* 25.
10. JOSHI, S. S., *Curr. Sci.*, **16** (1947), 19.
11. IVES, H. E., *J. opt. Soc. Amer.*, **8** (1924), 551.
12. IVES, H. E. & JOHNSRUD, A. L., *J. opt. Soc. Amer.*, **11** (1925), 565.
13. DUBRIDGE, L. A., *Phys. Rev.*, **29** (1927), 451.
14. CARDWELL, A. B., *Proc. nat. Acad. Sci.*, **14** (1928), 439.
15. FOWLER, R. H., *Phys. Rev.*, **38** (1931), 45.
16. IVES, H. E., *Astrophys. J.*, **64** (1926), 128.
17. SHUKLA, B. M., *J. phys. Chem.*, **53** (1949), 1239.
18. JATAR, D. P., *J. sci. industr. Res.*, **9B** (1950), 283.
19. MOHANTY, S. R., *J. Indian chem. Soc.*, **30** (1953), 9.
20. WARBURG, E., *Verhandl. deut. phys. Ges.*, **5** (1903), 382; *Ann. der Phys.*, **28** (1909), 1.
21. LUNT, R. W., *Phil. Mag.*, **49** (1925), 1238.
22. MOREY, G. W., *The Properties of Glass* (Reinhold Publ. Corpn., New York), 1938.
23. LITTLETON, J. T. & MOREY, G. W., *The Electrical Properties of Glass* (Wiley, New York), 1933.

24. WHITEHEAD, S., *Lectures on Dielectric Theory and Insulation* (McGraw-Hill, London), 1927.
25. LOEB, L. B., *Fundamental Processes of Electrical Discharge in Gases* (Wiley, New York), 1939.
26. MOHANTY, S. R. & KAMATH, G. S., *J. Indian chem. Soc.*, **25** (1948), 405.
27. MOHANTY, S. R., *J. Indian chem. Soc.*, **26** (1949), 552.

Kinetics of Hydration of Vinyl Acetate-Maleic Anhydride Copolymer

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The kinetics of hydration of vinyl acetate-maleic anhydride copolymer in aqueous acetone have been determined by conductivity measurements. The k_1 values for the copolymer are, under the same conditions, slightly less than those of succinic anhydride which is structurally akin to the reacting unit in the copolymer. Measurements with different samples of the copolymer show that the rate remains practically unaffected by a change of molecular weight. Addition of salt reduces the speed of the reaction and bases catalyse the reaction and also have a salt effect, the net result being the outcome of the two opposing effects.

It has been shown that the two reactions, viz. hydration of succinic anhydride and hydration of the polymeric anhydride, have nearly equal energies of activation and an approximately equal frequency factor, from which it is concluded that the hydration of a polymeric anhydride is essentially similar to that of a monomeric anhydride.

THE kinetics of hydration of acid anhydrides have been measured by various workers[1-6]. However, the rate of hydration of an anhydride which forms part of a high polymer chain has not been studied so far. This is of wider interest with regard to the general question of accessibility to attack of any chemical group located on a polymer molecule. With this end in view, we have measured the rate of hydration of vinyl acetate-maleic anhydride 1 : 1 copolymer (VAMA). The copolymer of styrene and maleic anhydride which has already been extensively studied from various aspects was found unsuitable for such a study as it is insoluble in water and the VAMA copolymer has been found to be the most suitable, being highly soluble in water.

Experimental procedure

Method of following the reaction — Menschutkin and Vasilieff[7] investigated the reaction of acetic anhydride with water in an acetic acid medium and showed that the reaction is by no means very rapid. An attempt was made by Benrath[6] to measure the rate by means of change of density. Lumiere and Barbier[8] adopted an analytical method in which the mixture after a lapse of a certain time is acted upon by aniline when the anhydride was precipitated as acetanilide with the liberation of an equivalent of acid. The total acid present was then titrated with alkali. They deduced no velocity constant for their experiments done at 0° and 15°C., but if their results are calculated on the unimolecular formula, an approximate constant is obtained. Barr and Plyer[5,9] have measured this rate of reaction with the help of infrared absorption spectra of mixtures of water and different acid anhydrides. They measured the kinetic constants and showed that the reaction is unimolecular.

We have endeavoured to determine the rate constant with greater accuracy and in a much simpler way by measuring the change in conductivity with the progress of reaction. The same method was successfully followed by Rivette and Sidgwick[1,2] and Wilsdon and Sidgwick[3,4] to determine the rate constant for a number of acid anhydrides.

The procedure adopted in our study was to measure at appropriate intervals the electrical conductivity of a solution of the anhydride in aqueous acetone and to determine the concentration of the anhydride from a calibration curve. The anhydride was first dissolved in a suitable quantity of anhydrous acetone in the cell itself, a measured quantity of water was then added so that the desired ratio of acetone and water is obtained in the mixture. The concentration of the anhydride taken was about 1 per cent in the case of the polymer and about half the amount in the case of succinic anhydride. Conductivity measurements were taken from 3 to 4 min. up to 15-20 min. in which period the reaction was more than half complete and the end point could be safely read after 2 or 3 hr. A calibration curve was prepared for the concentrations of the polymeric acid corresponding to the conductivity readings of the anhydride by measuring the conductivity at various dilutions of the acid finally obtained. The concentrations corresponding to different bridge readings during hydration were found out from this calibration curve. Time versus logarithm of anhydride concentration graph so obtained was a straight line which showed that the reaction of the polymeric anhydride with water is unimolecular. The velocity constant was determined from the slope of the straight line. In every experiment we determined the values at least twice and the results agreed very well. No attempt was made to buffer the solution as the change of *p*H during a reaction was very small (often less than 0·1 unit). The *p*H generally lies between 2 and 3 as measured by glass electrode with a Cambridge *p*H meter. It might be contended that the ester group might also hydrolyse and complicate matters. The rate of hydrolysis of an ester is, however, too small at this *p*H to be of any significance and this was further confirmed by the fact that methyl acetate, under conditions of *p*H and temperature employed by us, did not produce any perceptible change in conductivity.

Employing the usual precautions adopted in such experiments, the accuracy of the conductivity measurements obtained was sufficient for our purpose except perhaps at the very dilute end of the series. Since the viscosity of the solution is known to change considerably on conversion of the polyanhydride to the acid, we were doubtful of the applicability of the conductivity method in this case. Our results dispelled any such doubts and we found that the log c versus t curves were straight lines in spite of this possible uncertainty.

Samples — Three different samples of the copolymer, viz. VAMA-1, VAMA-2 and VAMA-3, of approximately 1:1 composition were used in these experiments. These differed in their molecular weights. The polymer VAMA-1 was prepared by reacting maleic anhydride with vinyl acetate in equimolecular proportion in benzene at 60°C. with constant stirring in a nitrogen atmosphere. The concentration of the catalyst (benzoyl peroxide) was 0·5 per cent on the weight of the monomer. The other two polymers were obtained by bulk polymerization at 60°C. with equimolecular proportions of maleic anhydride and vinyl acetate using 0·04827 and 0·02986 per cent of benzoyl peroxide respectively on the weight of the monomers. The yield was not allowed to exceed 20 per cent in any case. VAMA-1 precipitated out from benzene as it was formed. The other two samples were precipitated out by adding benzene. All the polymers were kept in benzene for 24 hr., dissolved in acetone, precipitated with petroleum ether and dried to constant weight at 40°-50°C. The samples differed in their molecular weight, VAMA-3 having the highest molecular weight and VAMA-1 the lowest. Succinic anhydride was prepared according to the procedure employed by Vogel[10].

All the measurements were done with a Doran direct reading conductivity bridge using a Kohlrausch type of cell (the cell was a stoppered flask of volume *c*. 45 cc. with sealed-in electrodes). The cell constant, 0·2375, was obtained from measurements with deci- and centi-normal potassium chloride solutions. The specific conductivity of the water used was 1-2 $\times 10^{-6}$ mhos.

Results and discussion

Fig. 1 represents a typical duplicate set of log c vs. time graphs for hydration of the polymeric anhydride, VAMA-1, at 35°C. in 1:4 acetone-water mixture. The two graphs are straight lines and are nearly parallel, and in fact practically super-impose on each other, and indicate the fairly high degree of accuracy attained in our experiments. They are, therefore, drawn on different scales for the ordinate. It can be seen from the results given in Table 1 that the reaction rate falls considerably on increasing the proportion of acetone in the solvent medium. This is evidently due to the low dielectric constant of acetone. It would have been of great interest to work with very small concentrations of water and find out the kinetic order with respect to

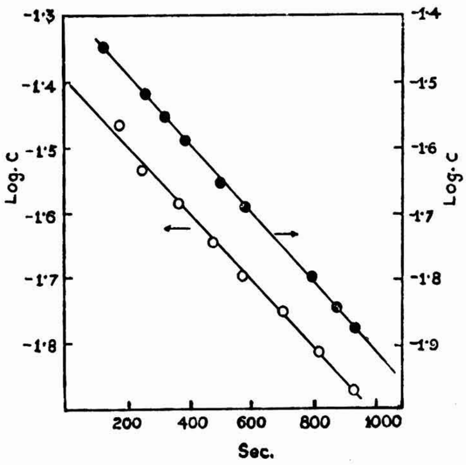

FIG. 1 — VELOCITY CONSTANT OF THE HYDRATION OF SUCCINIC ANHYDRIDE AND VINYL ACETATE-MALEIC ANHYDRIDE COPOLYMER

TABLE 1 — RATE OF HYDRATION OF ANHYDRIDE AT 35°C.

[$k_1 \times 10^4$ sec.$^{-1}$]

ANHYDRIDE	SOLVENT — WATER : ACETONE, BY VOLUME				
	9 : 1		4 : 1		1 : 1
Copolymer anhydride (VAMA-1)	8·15 7·44	Mean 7·80	5·00 5·29	Mean 5·14	1·13
Succinic anhydride	8·96 9·68	Mean 8·82	6·87 7·00	Mean 6·94	1·48

water but our present experimental method precludes such a measurement.

Effect of size of the polymer molecule — The question which first arises is whether the activity of a chemically reactive centre changes profoundly if it happens to be on a polymer molecule rather than on a smaller molecule. From Table 1 it can be seen that the anhydride group in a VAMA copolymer hydrates at a slightly lower rate than that in succinic anhydride. The latter is a small molecule with which the anhydride unit in the VAMA is structurally very similar. We can, therefore, conclude from the reaction kinetic standpoint that high polymeric structure decreases only slightly, if at all, the reactivity of a chemical group.

To probe into the question further we prepared two samples of the copolymer using varying concentrations of catalyst under otherwise identical conditions. These samples are designated VAMA-2 and VAMA-3, the last having the highest molecular weight as can be seen from their intrinsic viscosity values (TABLE 2).

It can be seen from the results in Table 2 that the reaction velocities in the same solvent for polymers of varying molecular weight are more or less constant within the limits of experimental error. The slight difference in the values is probably due to some difference in the polymer samples themselves as it is difficult to obtain different polymer samples of strictly identical nature due to chance variation occurring among them. This seems to point out that the shielding of a chemically reactive group by the folding or coiling of a polymer chain is materially the same for polymers of all sizes due probably either to free-draining nature of the coil or to an equal average folding per unit length of the chain under otherwise identical conditions.

Effect of salt and alkali — Alkalies catalyse the hydration of acid anhydrides very strongly, even a trace of alkali making the reaction too fast for kinetic measurements[11,12]. This is, however, not wholly true as our qualitative experiments with acidic anhydride have shown that with caustic alkali, up to 0·1 equivalent of the anhydride, the reaction takes place in a measurable time, and with bases in the Bronsted sense, e.g. acetate ion, the acceleration is rather small. This indicates that the matter requires careful re-investigation.

We have measured the effect of a small quantity of alkali, viz. one mole per cent of the monomeric unit and found a definite decrease in reaction rate. The same amount of sodium chloride is far more effective in decreasing the reaction rate. This is shown in Table 3. That alkali catalyses the reaction is no doubt the evident explanation but there is also a salt effect, which is in part due to polyelectrolytes chain in presence of salts, and the net result is the outcome of these

TABLE 2 — VARIATION OF k_1 WITH MOLECULAR WEIGHT AT 35°C.

[$k_1 \times 10^4$ (sec.$^{-1}$)]

POLYMER	SOLVENT — WATER : ACETONE, BY VOLUME		$[\eta]$*	APPROX. MOLECULAR WEIGHT†
	4 : 1	1 : 1		
VAMA-1	5·14	1·13	0·70	$5·856 \times 10^5$
VAMA-2	5·38	1·53	3·60	$68·290 \times 10^5$
VAMA-3	4·42	1·48	5·05	$113·400 \times 10^5$

*Measured in water in presence of 0·7218N hydrochloric acid to suppress the ionization of the polyelectrolyte.

†Calculated from the approximate general equation $\eta = 10^{-4} M^{\frac{2}{3}}$.

TABLE 3 — EFFECT OF SALT AND ALKALI ON THE RATE OF HYDRATION OF POLYANHYDRIDE (VA)

SOLVENT Water: acetone	SALT OR ALKALI*	$k_1 \times 10^4$ VAMA-1	(sec.$^{-1}$) SUCCINIC ANHYDRIDE
4:1	None	5·14	6·94
4:1	NaOH	$\left\{\begin{matrix}3{\cdot}79\\4{\cdot}26\end{matrix}\right\}$ 4·02	6·55
4:1	NaCl	$\left\{\begin{matrix}3{\cdot}27\\3{\cdot}27\end{matrix}\right\}$ 3·27	5·68
4:1	Na Acetate	$\left.\begin{matrix}4{\cdot}83\\4{\cdot}42\end{matrix}\right\}$ 4·62	6·66

*The amount of salt or alkali present was just equal to one molecule of the additive to 100 monomeric units in the copolymer or succinic anhydride.

TABLE 4 — CHANGE OF VELOCITY CONSTANT WITH TEMPERATURE

TEMP. °C.	$1/T \times 10^3$	Log k_1 VAMA-1	SUCCINIC ANHYDRIDE	ENERGY OF ACTIVATION cal.
35	3·247	−3·288	−3·159	15400 (VAMA-1)
40	3·195	−3·115	−3·069	—
45	3·145	−2·943	−2·841	—
50	3·096	−2·778	−2·732	15600 (succinic anhydride)

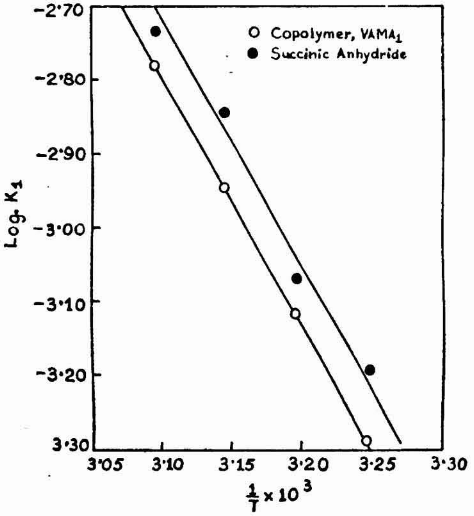

FIG. 2 — ENERGY OF ACTIVATION OF THE HYDRATION OF SUCCINIC ANHYDRIDE AND VINYL ACETATE-MALEIC ANHYDRIDE COPOLYMER

two opposing effects. It is rather difficult to understand why sodium acetate is less powerful in diminishing the speed of reaction than caustic soda, unless it be due to some specific effect. However, our conclusions are only of a tentative nature and more detailed studies are necessary to find out the actual role of salt and alkali in the hydration of these anhydrides.

Energy of activation — Table 4 represents the change of the velocity constant of the polymeric anhydride and succinic anhydride with change of temperature, and the corresponding graph of 1/T vs. log k_1 is shown in Fig. 2.

It is seen from the graphs in Fig. 2 that the points fall on straight lines and the two straight lines are almost parallel to one another. This shows that the two reactions are essentially similar and have nearly equal energies of activation and approximately equal frequency factor. It is, therefore, concluded that the kinetics of hydration of a polymeric anhydride exhibit very few special features which are different from those of a comparable monomeric anhydride.

Acknowledgement

One of the authors (A.K.S.) is thankful to the Council of Scientific & Industrial Research (India) for financial assistance.

References

1. RIVETTE & SIDGWICK, *J. chem. Soc.*, **98** (1910), 732.
2. RIVETTE & SIDGWICK, *J. chem. Soc.*, **98** (1910), 1677.
3. WILSDON & SIDGWICK, *J. chem. Soc.*, **103** (1913), 1959.
4. WILSDON & SIDGWICK, *J. chem. Soc.*, **107** (1915), 679.
5. BARR & PLYER, *J. chem. Phys.*, **4** (1936), 90.
6. BENRATH, *Z. phys. Chem.*, **67** (1909), 501.
7. MENSCHUTKIN & VASILIEFF, *J. Russ. phys. Chem. Soc.*, **21** (1889), 192.
8. LUMIERE & BARBIER, *Bull. Soc. Chim.*, **35** (iii) (1906), 625.
9. BARR & PLYER, *J. chem. Phys.*, **3** (1935), 679.
10. VOGEL, A. I., *Practical Organic Chemistry* (Longmans, Green & Co., London), 1948, 371.
11. RICE, *The Mechanism of Homogeneous Organic Reactions* (*American Chemical Society Monograph Series, No.* 39) (Chemical Catalog Co., New York), 1928, 105.
12. ORTON & JONES, *J. chem. Soc.*, **101** (1912), 1708.

Synthetic Experiments in the Benzopyrone Series: Part XLVIII—A Synthesis of Muningin Diethyl Ether

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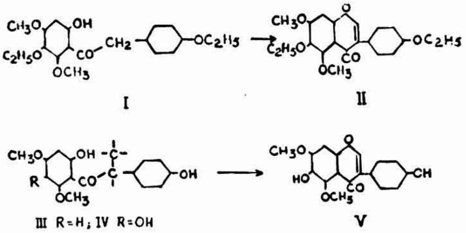
Following the procedure adopted earlier for the synthesis of tectorigenin trimethyl and triethyl ethers, the synthesis of muningin diethyl ether has now been carried out using 3 : 5-dimethoxy-4-ethoxy phenol and para ethoxy phenyl acetyl chloride as intermediates.

IN an earlier paper[1] a convenient method for the synthesis of 5 : 6 : 7-hydroxy isoflavones starting from antiarol was described. Using 3 : 5-diethoxy-4-methoxy phenol tectorigenin triethyl ether, useful for confirming the constitution of tectorigenin, was also obtained. Following the same general procedure the synthesis of muningin diethyl ether has now been accomplished. For this purpose 3 : 5-dimethoxy-4-ethoxy phenol is subjected to the Friedel and Crafts reaction with *p*-ethoxy phenyl acetyl chloride. The resulting ketone on isoflavone ring closure yields 5 : 7-dimethoxy-6 : 4′-diethoxy isoflavone. Its properties agree with those reported for muningin diethyl ether and thus this synthesis confirms the constitution of muningin (V) proposed by King *et al.*[2].

As a partial methyl ether, muningin is extraordinary in that the resistant hydroxyl in the 5-position is methylated. In a few flavones such as nobiletin and tangeretin also the resistant 5-hydroxyl gets methylated but in them there is complete methylation and no other hydroxyl is left unaffected. On the other hand, in muningin reactive hydroxyl groups in 6- and 4′-positions are left free. Though such partial methylation in the 5-position has not been known before, glycoside formation in this position has been recorded in sakuranin, salipurposide, galuteolin and in apigenin 5-glucoside. An explanation offered earlier for the evolution of these glycosides[3,4] would appear to be applicable also for the partial methylation as found in muningin. It could be suggested that methylation of the concerned hydroxyl groups took place before isoflavone ring closure (formula III). Actually even the introduction of the fresh hydroxyl group by nuclear oxidation should have taken place at that stage (formula IV) and this is in accordance with the suggestion made originally in connection with nuclear oxidation in the flavone series[5]. The details can be roughly pictured as given in the following formulae. The survival of the 4′-hydroxyl in the course of the methylation reaction could be attributed to its being engaged in glucoside formation or in a similar combination.



Experimental procedure

p-Ethoxy phenyl acetic acid — This was earlier obtained by ethylation of *p*-hydroxy phenyl acetic acid[6] and recently from *p*-ethoxy phenyl pyruvic acid[1]. The following procedure adopting the method used by King and Neill[7] for the preparation of 2: 4-dimethoxy phenyl acetic acid has been found to be more convenient. A mixture of *p*-ethoxy acetophenone (27 g.), morpholine (24 cc.) and sulphur (9 g.) was refluxed in an oil bath for 8 hr. The product was dissolved in chloroform and the chloroform solution was washed repeatedly with dilute hydrochloric acid to remove the excess of morpholine. The crude morpholide was refluxed for 8 hr. with a solution of sodium hydroxide (80 g.) in water (600 cc.). The solid obtained by acidifying the alkaline solution was crystallized from a large amount of water when *p*-ethoxy phenyl acetic acid separated in the form of leaflets melting at 88°-89°[6]; yield 9·5 g.

2-Hydroxy-4 : 6-dimethoxy-5-ethoxy phenyl p-ethoxy-benzyl ketone (I) — 4-Ethoxy-3: 5-

dimethoxy phenol required for this experiment was prepared according to the method of King, King and Warwick[2].

A solution of anhydrous aluminium chloride (6 g.) and 3: 5-dimethoxy-4-ethoxy phenol (5 g.) in dry ether (100 cc.) was cooled to 0° and treated with *p*-ethoxy phenyl acetyl chloride (5 cc.). The reaction mixture was shaken for *c.* 2 hr. and then left at room temperature overnight. Ether was removed on a warm water bath and the remaining organo-aluminium complex first treated with ice and hydrochloric acid and subsequently heated on the water bath to complete the hydrolysis. The mixture was then extracted with ethyl acetate, the extract washed successively with aqueous sodium bicarbonate solution (5 per cent) and water and then dried over anhydrous sodium sulphate. On evaporation it left a viscous mass which solidified on keeping. It was then crystallized from ethyl acetate when it came out in the form of colourless small plates melting at 104°; yield 0·8 g. It gave a brown colour with ferric chloride (found: C, 66·5; H, 6·4; $C_{20}H_{24}O_6$ requires: C, 66·7; H, 6·7 per cent).

5 : 7-*Dimethoxy*-6 : 4′-*diethoxy isoflavone* (II) — The above ketone (1 g.) dissolved in freshly distilled ethyl formate (30 cc.) was added in portions of 3 cc. at a time to pulverized sodium (0·6 g.) well cooled in ice. After shaking the mixture for about 2 hr. it was left in the refrigerator for 48 hr. It was then added to crushed ice to decompose the excess of sodium. The alkaline solution was acidified with hydrochloric acid and then extracted with ether. The ether extract was washed with aqueous sodium hydroxide solution (10 per cent) and then with water. Evaporation of the dried ether solution left a solid which when crystallized from methyl alcohol yielded the isoflavone as colourless rhombohedral plates melting at 158°; yield 0·25 g. (found: C, 67·8; H, 6·2; $C_{21}H_{22}O_6$ requires: C, 68·1; H, 6·0 per cent).

Acknowledgement

Our thanks are due to Dr. S. K. Mukerjee for microanalysis.

References

1. Krishnamurti & Seshadri, *J. sci. industr. Res.*, **12B** (1953), 120; *Proc. Indian Acad. Sci.*, **39A** (1954), 144.
2. King, King & Warwick, *J. chem. Soc.*, (1952), 96.
3. Seshadri, *Ann. Rev. Biochem.*, **20** (1951), 508.
4. Seshadri, *Proc. Indian Acad. Sci.*, **32A** (1950), 372.
5. Seshadri, *Proc. Indian Acad. Sci.*, **28A** (1948), 6.
6. Salkowski, *Ber. dtsch. chem. Ges.*, **12** (1879), 1438.
7. King & Neill, *J. chem. Scc.*, (1952), 4754.

Survey of Anthoxanthins: Part V — Colouring Matter of Liquorice Roots

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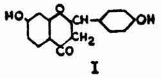
The yellow colour of liquorice root is due to the presence of iso-liquiritin whose constitution is established as the 4′-glucoside of iso-liquiritigenin (2 : 4 : 4′-trihydroxy chalkone) by complete methylation and hydrolysis. The structure of the hydrolytic product is confirmed by synthesis of the isomeric chalkone dimethyl ethers. Isoliquiritin is the only anthoxanthin component of the fresh roots and it undergoes partial conversion into liquiritin during drying and storage. Liquiritin is shown independently to be a 4′-glucoside and to yield on hydrolysis both liquiritigenin and iso-liquiritigenin.

LIQUORICE is a well-known drug widely used as a demulcent and sweetening agent. The root powder is markedly yellow and no explanation seems to have been given so far for this colour. Earlier, Shinoda and Ueeda[1] obtained from the alcoholic extract a colourless glucoside called liquiritin, which was reported to yield on hydrolysis glucose and a colourless aglucone, liquiritigenin, whose constitution was established as 7: 4′-dihydroxy flavanone (I). Since the above glucoside as well as the aglucone are colourless, the phenomenon of colour in liquorice has remained unexplained. Hence, the roots have now been re-examined. It is possible to remove all the colour from commercial liquorice roots by repeated extraction with cold alcohol. Examination of this coloured extract by chromatography revealed the marked presence of a chalkone glucoside besides a flavanone glucoside. On concentration colourless liquiritin could be obtained as the first fraction and from subsequent fractions was obtained a deep yellow substance whose reactions indicated that it was a chalkone glucoside. It did not give any colour with magnesium and hydrochloric acid but gave a permanent brown colour with alcoholic ferric chloride. Analytical results indicated that it was isomeric with liquiritin and hence it has been named iso-liquiritin. On hydrolysis it yielded besides one mole of glucose a mixture of chalkone and flavanone; circular chromatography of the aglucone mixture yielded two rings, one yellow before and the other after spraying. The two components could be separated by fractional crystallization; the colourless flavanone agrees in every respect with liquiritigenin (I). The chalkone is identical with a synthetic sample of 2: 4: 4′-trihydroxy chalkone[2] (II) and since this is an isomer of liquiritigenin it is now named iso-liquiritigenin. It may be mentioned here that Shinoda and Ueeda[1] reported that they obtained only liquiritigenin, a flavanone by the hydrolysis of liquiritin. From the results of recent experiments on the hydrolysis of butrin[3,4] it appeared that this was not fully correct. Hence the hydrolysis of liquiritin has now been repeated and it is found that a mixture of both liquiritigenin and iso-liquiritigenin is obtained. The above results are due to the easy interconversion[5] in hot acid solution of chalkones and flavanones which do not have the phloroglucinol unit and they lead to the conclusion that iso-liquiritin is a glucoside of 2: 4: 4′-trihydroxy chalkone (iso-liquiritigenin) and liquiritin is the glucoside of the corresponding flavanone.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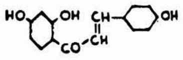
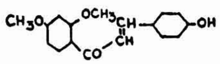
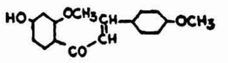
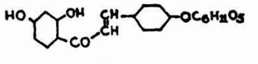

II

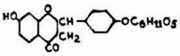
The location of the glucose unit in iso-liquiritin has been established using the method of complete methylation of the glucoside and subsequent hydrolysis. The product is found to be a dimethyl ether of iso-liquiritigenin, m.p. 143°-44°C. It gives no colour with ferric chloride and is soluble in sodium carbonate. 2-Hydroxy-4 : 4′-dimethoxy chalkone[6] was earlier reported by Kostanecki and Osius to melt at 113°-14°C. and give positive ferric reaction. Consequently the free hydroxyl group in the product of hydrolysis should be in the 4 or 4′-position of the chalkone. In order to settle this point two reference compounds have been prepared: (1) 2: 4-dimethoxy-4′-hydroxy chalkone (III) (m.p. 143°-44°C.) by the condensation of resacetophenone dimethyl ether with *p*-hydroxy benzaldehyde and (2) 2: 4′-dimethoxy-4-hydroxy chalkone (IV) (m.p. 183°-85°C.) by the condensation of iso-peonol with anisic aldehyde. The chalkone dimethyl ether obtained from iso-liquiritin is identical with the 4′-hydroxy compound and is different from the other isomers. Therefore, it follows that iso-liquiritin is a 4′-glycoside (V) of the trihydroxy chalkone. The chalkone itself has been very recently reported to be present in a variety of yellow dahlia[7].


III


IV


V

Earlier Shinoda and Ueeda[1] did some experiments to establish the position of the glucose unit in liquiritin itself. They methylated it with methyl iodide and potassium carbonate in acetone suspension, but they were not able to obtain any crystalline methyl ether either of the glucoside or of the aglucone. By direct fission of the methylation product with alkali they were able to characterize peonol and *p*-hydroxybenzoic acid as products. Hence they inferred that the sugar unit should occupy the 4′-position of the flavanone. Obviously there was only partial methylation even though the oxide ring might have opened. In view of the indefiniteness of these experiments the study of liquiritin has been again made now. Following the same lines as adopted for iso-liquiritin the fully methylated glucoside (coloured chalkone) was hydrolysed. The product was a chalkone identical with 2: 4-dimethoxy-4′-hydroxy chalkone obtained in the case of iso-liquiritin. Based on the analogy of butrin and other flavanone glycosides[8,9] it should be concluded that during complete methylation the flavanone ring has opened out producing a chalkone derivative. However, the position of the glucose unit is definite as 4′ (VI). It is, therefore, clear that liquiritin and iso-liquiritin are isomeric flavanone and chalkone glucosides, corresponding to similar pairs, butrin and iso-butrin, and salipurposide and iso-salipurposide. Related aglucone pairs occurring together are butin and butein, pedicin and iso-pedicin, 6: 7: 3′: 4′-tetrahydroxy flavanone and the corresponding chalkone.



VI

It should be interesting to note that in liquiritin and iso-liquiritin the sugar unit is present in the side phenyl nucleus. Such cases were not originally common. A number of them have been discovered in recent years. Butrin, iso-butrin and cannabiscitrin[10] carry glucose units in the 3′-position, the iso-rhamnetin glycoside[11] of croccus pollen and genistein glycosides[12,13] of *Sophora japonica* in the 4′-position. Very recently a variety of *Dahlia variabilis* is reported to contain apigenin 4′-glucoside[14].

We have been able to obtain a sample of fresh liquorice roots from the Indian Agricultural Research Institute, Delhi, by the courtesy of the Director and the Head of the Division of Agronomy. On examination the alcoholic extract is found to contain only iso-liquiritin, the chalkone glucoside and no liquiritin could be detected. It is only on boiling the alcoholic solution or on exposing the roots to sun drying and storage that some isomerization into liquiritin takes place. A pure sample of iso-liquiritin is easily obtained from the fresh roots. It is, therefore, established that the yellow colouring matter of the liquorice root is this chalkone glucoside. The preponderance of the chalkone is due to the comparative instability of the flavanone which does not have a hydroxyl in the 5-position[5]. An estimation has been made of the total anthoxanthin glucosides present in commercial dry roots and it is found to be approximately 2·2 per cent. In view of the physiological properties[15] which anthoxanthin glycosides are known to possess, when accounting for the beneficial effect of the drug the part played by iso-liquiritin and liquiritin should not be ignored. Actually they are bitter with a sweet after-taste and stimulate the salivary glands encouraging secretion.

Experimental procedure

Extraction of liquorice roots: (a) *Fresh liquorice* — Fresh roots were crushed and extracted in the cold with rectified spirits. Three extractions, each taking 24 hr., were found to be enough. When this extract was directly tested using circular paper chromatography, it gave only one marked yellow ring, R_f 0·70 (temperature 34°-36°C. and solvent water saturated with phenol), and there was no change on spraying with ammonia. Later the extract was concentrated to a small volume, poured into excess of water and then extracted with ether. The ether extract contained no pigment. The aqueous solution gave two rings in paper chromatography: (1) strong, with R_f value 0·71 before spraying and (2) weak, with R_f value 0·86 after spraying with ammonia. The second ring was identical with the one obtained from an authentic sample of liquiritin. The prominent first ring is attributed to iso-liquiritin.

The aqueous solution contained besides the pigments, sugar and other soluble components. Hence, it was treated with neutral lead acetate. A small dirty yellow precipitate was obtained. On examination it was found to contain only a small part of the same colouring matter mentioned hereafter. The main portion was precipitated as a bright yellow solid on adding basic lead acetate. This was filtered off, suspended as a thin paste in aqueous alcohol (rectified spirits 2 parts and water 1 part) and decomposed by saturating with hydrogen sulphide. The mixture was filtered off and the residue again subjected to the same treatment. The consolidated filtrate was allowed to concentrate in the presence of potash at the ordinary temperature. The first crop of crystals (a small quantity) was pale yellow in colour, and on recrystallization from hot water came out in the form of colourless needles, melting at 211°-12°C. An alcoholic solution of the substance gave a violet pink colour with magnesium powder and hydrochloric acid and no colour with ferric chloride. These properties agreed with the description of liquiritin, R_f value of the ring visible after spraying with ammonia, 0·87.

When the mother liquor was further concentrated it gave a deep yellow solid (main part). It crystallized from dilute alcohol in the form of deep yellow prismatic needles melting at 185°-86°C. (decomp.). In chromatography iso-liquiritin produced only one yellow ring requiring no spraying, R_f value 0·70. Its alcoholic solution gave a deep brown colour with ferric chloride, and no colour with magnesium powder and hydrochloric acid (found: C, 53·7; H, 5·8; $C_{21}H_{22}O_9$, $3H_2O$ requires: C, 53·4; H, 5·9 per cent).

(b) *Dried liquorice* — The fresh alcoholic extract gave two rings: (1) deep yellow before spraying, R_f value 0·71 corresponding to iso-liquiritin, (2) appeared yellow only after spraying, circular R_f value 0·86, corresponding to liquiritin.

The isolation of the pigments was made just as before. The yields of liquiritin and iso-liquiritin were almost equal.

Hydrolysis: (a) *Iso-liquiritin* — Iso-liquiritin (1 g.) was boiled with 7 per cent aqueous sulphuric acid (50 cc.) for 2 hr. The aglucone mixture separated out as a yellow solid. It was filtered and the solution extracted with ether to effect complete recovery. The aqueous solution was neutralized with barium carbonate, concentrated and tested for sugar. It gave glucosazone test and circular R_f value 0·59 using phenol-water (9: 1) corresponding to glucose.

The aglucones gave two rings in chromatography: (1) yellow before spraying, R_f value 0·50, (2) visible (yellow) only after spraying, R_f value 0·78. The mixture was dissolved in aqueous alcohol and allowed to concentrate at ordinary temperature. The first crop of crystals was pale yellow in colour. Recrystallization from aqueous alcohol gave almost colourless solid melting at 207°-8°C. Its alcoholic solution gave no colour with ferric chloride and a violet red colour with magnesium powder and hydrochloric acid; circular R_f value 0·78 after spraying with ammonia. This corresponded to liquiritigenin (7: 4′-dihydroxy flavanone).

The subsequent crop of crystals from the alcoholic solution was deep yellow. Recrystallization yielded small deep yellow prisms melting at 202°-4°C.; circular R_f value without spraying 0·50. An alcoholic solution gave a deep brown colour with ferric chloride and no colour with magnesium powder and hydrochloric acid. This corresponded to iso-liquiritigenin. Mixture with liquiritigenin gave a lower melting point whereas with 2: 4: 4′-trihydroxy chalkone the melting point was undepressed. A quantitative study of the hydrolysis using the dried glucoside yielded the following results — found: glucose, 42·1; aglucones, 59·9; $C_{21}H_{22}O_9$ requires: glucose (1 unit), 43·1; and aglucones dried at 100°C. ($C_{15}H_{12}O_4$), 61·2 per cent.

(b) *Liquiritin* — The experimental procedure was just the same as given above and the results were also the same. The aglucone was a mixture of chalkone and flavanone.

Methylation and hydrolysis: (a) *Iso-liquiritin* — Powdered iso-liquiritin (1 g.) was suspended in dry acetone (20 cc.), dimethyl sulphate (1 cc.) and anhydrous potassium carbonate (3 g.) added and the mixture refluxed on a water bath for 48 hr. It was then filtered and the residue washed with hot acetone. The acetone was distilled off from the filtrate and the red solid obtained was boiled with 25 cc. of 7 per cent aqueous sulphuric acid for 2 hr. The solution was cooled and extracted with ether. On removing the ether a yellow solid separated out which crystallized from rectified spirits as tiny pale yellow broad rectangular plates melting at 143°-44°C. The compound was soluble in sodium carbonate giving a red solution and its alcoholic solution gave no colour with ferric chloride. Mixed melting point with a synthetic sample of 2: 4-dimethoxy-4′-hydroxy chalkone was undepressed.

(b) *Liquiritin* — Adopting the same method a sample of liquiritin was separately methylated and hydrolysed. It gave the same product melting at 143°-44°C. whose mixed melting point with a synthetic sample of 2: 4-dimethoxy-4′-hydroxy chalkone was undepressed.

Conversion of liquiritin into iso-liquiritin — Liquiritin (1 g.) was dissolved in aqueous sodium hydroxide solution (5 per cent) and kept aside for 15 min. It was acidified with citric acid solution (5 per cent) while kept cool in ice. The solution was then evaporated at room temperature in the presence of caustic potash sticks. After one week a yellow crystalline powder separated which after recrystallization from dilute alcohol appeared in the form of yellow prismatic needles melting at 185°-86°C. In paper chromatography it gave a yellow ring without spraying, R_f value 0·70, same as that of iso-liquiritin. It gave the same colour reactions as iso-liquiritin and the mixed melting point with the sample of iso-liquiritin obtained directly from the roots was undepressed. The later crop of crystals was paler in colour and on crystallization from aqueous alcohol yielded colourless crystals of liquiritin melting at 212°C., R_f value 0·86.

Synthesis of iso-liquiritigenin (*2: 4: 4'-trihydroxy chalkone*) (II) — The condensation of resacetophenone and *p*-hydroxy benzaldehyde was effected in the same way as given by Nadkarni and Wheeler[2]. Preliminary cooling to 0° and keeping out air were not found necessary. The product was worked up by an improved method. The crude deep yellow solid was dissolved in ether and extracted with cold aqueous sodium bicarbonate. The bicarbonate extract was acidified and re-extracted with ether. Evaporation of the solvent yielded almost pure chalkone, m.p. 202°-4°C., R_f value 0·50. Recrystallization from aqueous alcohol yielded deep yellow small prisms. Colour reactions were identical with those of natural iso-liquiritigenin.

2: 4-'*Dimethoxy-4-hydroxy chalkone* (III) — Resacetophenone was fully methylated by boiling with excess of dimethyl sulphate in the presence of anhydrous potassium carbonate in acetone medium for 24 hr. After distilling off acetone, water was added and the product extracted with ether. The ether solution was washed with a dilute solution of sodium hydroxide, and then with water and evaporated. The crude dimethyl ether was obtained as an oil; it did not give any ferric reaction and was directly used for chalkone condensation.

A mixture of dimethoxy acetophenone (3 g.) and *p*-hydroxy benzaldehyde (1 g.) was dissolved in alcohol (20 cc.) and treated with caustic potash (30 cc.) (50 g. of potash in 35 cc. of water). It was then kept out of contact with air at room temperature for 3 days. The product was then diluted with water and acidified with hydrochloric acid while cooling under the tap. The amorphous solid which separated was extracted with ether and then the ether solution extracted with aqueous sodium carbonate solution (5 per cent). The carbonate extract was acidified and then re-extracted with ether. On evaporation of the solvent a deep yellow residue was obtained. It crystallized from rectified spirits as pale yellow broad rectangular plates melting at 143°-44°C. (found: C, 71·3; H, 5·5; $C_{17}H_{16}O_4$ requires: C, 71·8; H, 5·6 per cent).

2: 4'-*Dimethoxy-4-hydroxy chalkone* (IV) — Benzoate of iso-peonol[16] (2 g.) and anisic aldehyde (4g.) was condensed in the presence of alcoholic potash and the product purified as given in the above experiments. The crude chalkone obtained from the carbonate extracts was conveniently purified by taking it up in ether and adding petroleum ether until all the resinous impurities were precipitated. The substance obtained from the clear solution crystallized finally from alcohol in the form of narrow rectangular plates and needles melting at 183°-85°C. (found: C, 64·1; H, 5·8; loss on drying at 110°, 10·6; $C_{17}H_{16}O_4$, $2H_2O$ requires: C, 63·8; H, 6·3; H_2O loss, 11·3 per cent).

2: 4: 4'-*Trimethoxy chalkone* — (a) Iso-liquiritigenin was fully methylated by using excess of dimethyl sulphate and refluxing for 24 hr. The crude product was washed with aqueous sodium hydroxide and recrystallized from rectified spirits when it appeared in the form of broad colourless rectangular plates and tablets melting at 91°-93°C. It gave no colour with ferric chloride.

(b) It was synthesized by the condensation of 2: 4-dimethoxy acetophenone (2 g.) with anisic aldehyde (4 g.) in the presence of alcoholic potash. The product was crystallized twice from alcohol when it appeared as broad colourless rectangular plates and tablets melting at 91°-93°C. Mixed melting point with the trimethyl ether of iso-liquiritigenin was undepressed (found: C, 72·0; H, 5·5; $C_{18}H_{18}O_4$ requires: C, 72·5; H, 6·0 per cent).

Estimation of glucosides — Air-dried commercial liquorice roots (100 g.) were twice extracted with boiling alcohol, each extraction being carried out for 3 hr. The alcoholic concentrate was diluted with an equal volume of water and enough sulphuric acid added to make its concentration 7 per cent and the mixture boiled for *c.* 2 hr. Excess of water was added and the aglucones exhaustively extracted with ether. The ether extract was shaken up repeatedly with sodium bicarbonate, acidified and again extracted with ether. The ether solution was evaporated and the yellow crystalline residue dried at 110°C. to constant weight. The yield was 1·2 per cent of anhydrous aglucones which would correspond to 2·2 per cent of iso-liquiritin.

Acknowledgement

Our thanks are due to Dr. S. K. Mukerjee for microanalysis.

References

1. SHINODA & UEEDA, *Ber. dtsch. chem. Ges.*, **67** (1934), 434.
2. NADKARNI & WHEELER, *J. chem. Soc.*, (1938), 1320.
3. MURTI & SESHADRI, *Proc. Indian Acad. Sci.*, **13A** (1941), 395.
4. (Miss) PURI & SESHADRI, *J. sci. industr. Res.*, **12B** (1953), 462.
5. NARASIMHACHARI & SESHADRI, *Proc. Indian Acad. Sci.*, **27A** (1948), 223.
6. KOSTANECKI & OSIUS, *Ber. dtsch. chem. Ges.*, **32** (1899), 322
7. BATESMITH & SWAIN, *J. chem. Soc.*, (1953), 2185.
8. RANGASWAMI, SESHADRI & VEERARAGHAVAIAH, *Proc. Indian Acad. Sci.*, **9A** (1939), 328.
9. KING & ROBERTSON, *J. chem. Soc.*, (1931), 1704.
10. SESHADRI & VENKATESWARLU, *Proc. Indian Acad. Sci.*, **23A** (1946), 209.
11. KUHN & LOW, *Ber. dtsch. chem. Ges.*, **77B** (1944), 196.
12. ZEMPLEN & BOGNAR, *Ber. dtsch. chem. Ges.*, **75B** (1942), 482; *Brit. chem. Abstr.*, **AII** (1942), 302.
13. BOGNAR, *Chem. Abstr.*, **46** (1952), 8104.
14. NORDSTROM & SWAIN, *J. chem. Soc.*, (1953), 2767.
15. SESHADRI, *Ann. Rev. Biochem.*, **20** (1951), 488.
16. (Miss) PURI & SESHADRI, *J. sci. industr. Res.*, **13B** (1954), 321.

The Effect of Estradiol Dipropionate on the Development of *Trypanosoma equiperdum* in Rats & Mice

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Estradiol dipropionate exerts an inhibitory action on the development of *Trypanosoma equiperdum* in rats and mice, thereby prolonging the survival time of the infected animals. It is suggested that the hormone influences the development of the parasites through its action on some important constituents of the blood such as lipids, proteins and calcium.

CONSIDERABLE work has been done in recent years to elucidate the influence of hormones, particularly cortisone and adrenocorticotropic hormone (ACTH), on the course of infection in bacterial and virus diseases[1]. However, very little work has been done on hemosporozoan infections. Bennison and Coatney[2] were unable to neutralize the sex difference in the susceptibility of young chickens to *Plasmodium gallinaceum* infections by treatment with sex hormones. Robles Gill and Perrin[3] failed to detect any effect of ACTH on the tissue form of *Trypanosoma cruzi*, although the hormone was found to exert a beneficial influence on the clinical picture of infected dogs. Similarly von Brand *et al.*[4] found that ACTH and cortisone exerted no effect on parasitemia due to *T. equiperdum* infection in rats. Wolf *et al.*[5], however, observed that a latent *T. vickersae* infection in Rhesus monkeys was activated by cortisone. Findlay and Howard[6] noted that this hormone increased the virulence of *Plasmodium berghii* and *Toxoplasma* infections in the mouse. On the other hand, Galliard *et al.*[7] reported that cortisone did not accelerate the development of *T. brucei*, *P. berghii* and *Toxoplasma* infections in the rat.

It is evident from the above that while some data are available on the influence of cortisone and ACTH on hemosporozoan infections, there is a paucity of information regarding the effect of sex hormones on these parasites. An attempt was, therefore, made to study the influence of estradiol dipropionate on the development of *Trypanosoma equiperdum* in rats and mice.

Experimental procedure

Rats — Eighteen male rats (average weight 80 g.) were used in this study. Of these, 9 were injected intramuscularly with estradiol dipropionate at the rate of 2·5 mg. (in 0·5 cc. sterile sesame oil) twice a week.

The injections were spaced at intervals of 3 days. The control animals were injected with 0·5 cc. of sterile sesame oil alone in a similar manner.

Three days after the final injection, 0·2 cc. of blood from a rat carrying heavy infection of *T. equiperdum* was injected intraperitoneally into all the experimental rats. A drop of blood was removed from the caudal vein of both the control and estrogen-treated animals and examined daily. The parasites were counted by the method of Kolmer[8]. The percentage mortality and survival time were also noted.

Mice — Male mice of a pure strain imported from Switzerland (average weight 31 g.) were used. The animals were divided into two groups of 9 animals each. One group was injected intramuscularly with 1·5 mg. estradiol dipropionate (dissolved in 0·2 cc. sterile sesame oil) twice a week. The injections were given at an interval of 3 days. The control mice were injected with the same volume of sesame oil. The rest of the procedure followed was the same as in the case of rats.

Results

Rats — The parasite counts in control and estrogen treated rats are given in Table 1. In 72 hr. one rat (N3) out of 9 controls showed no infection and two (N7 and N9) succumbed to high parasitemia. In the estrogen treated animals, on the other hand, the course of parasitemia, in general, did not reach a sufficiently high level to cause any mortality although the figures for parasite count appear somewhat elusive when reckoned against those of the controls. A more or less similar picture is presented in 96 hr. In 120 hr., however, parasitemia attains the peak in the control animals and 100 per cent mortality is recorded. In contrast to this, mortality is only 55 per cent in the estrogen treated animals (TABLE 2). No change in mortality rate is observed in the latter group during the next 24 hr. but in 168 hr. all of them died. On an average the control animals survive for 107 hr. after inoculation, whereas the estrogen-treated animals survive 37 hr. longer (TABLE 2).

Mice — The parasites appear in significantly larger numbers in the peripheral circulation of control mice in 72 hr. than in the control animals (TABLE 1). In the estrogen-treated mice, however, the parasitemia is much lower than in the control animals. During the next 24 hr. the parasitemia rises in the control group and 77 per cent mortality is recorded as against 44 per cent in the controls. In 120 hr., mortality is 100 per cent in both the groups. The control mice survive on an average for 94 hr. after inoculation, whereas the estrogen-treated animals survive for 111 hr. (TABLE 2).

Discussion

The results in Tables 1 and 2 indicate that pre-treatment with estradiol dipropionate

TABLE 1 — THE PROTOCOL OF ACTUAL PARASITE COUNTS IN CONTROL AND ESTROGEN TREATED ANIMALS AT DIFFERENT INTERVALS

PERIOD AFTER INOCULATION hr.	RATS, NO. OF PARASITES (1000/cu. mm.)		MICE, NO. OF PARASITES (1000/cu. mm.)	
	Controls	Treated	Controls	Treated
72	(N1)* 75	(T1) 10	(C1) 634	(M1) 28
	(N2) 61	(T2) 18	(C2) 615	(M2) 83
	(N3) No inf.	(T3) 11	(C3) 196	(M3) 36
	(N4) 23	(T4) 22	(C4) 208	(M4) 34
	(N5) 122	(T5) 111	(C5) 166	(M5) 38
	(N6) 103	(T6) 137	(C6) 128	(M6) 56
	(N7)†	(T7) 89	(C7) 150	(M7) 25
	(N8) 71	(T8) 87	(C8) 92	(M8) 80
	(N9)†	(T9) 147	(C9) 23	(M9) No inf.
96‡	(N1) 544	(T1) 13	(C1)†	(M1)†
	(N2) 401	(T2) 70	(C2)†	(M2)†
	(N3) 97	(T3) 120	(C3)†	(M3)†
	(N4) 196	(T4) 51	(C4)†	(M4)†
	(N5) 409	(T5) 586	(C5)†	(M5) 400
	(N6) 873	(T6) 590	(C6)†	(M6) 300
	(N7)†	(T7) 569	(C7)†	(M7) 412
	(N8) 461	(T8) 479	(C8) 624	(M8) 486
	(N9)†	(T9) 484	(C9) 214	(M9) 81

*Figure in parenthesis indicates the number of the animal.
†Died.
‡After 96 hr. only the survival time was recorded (*see* TABLE 2).

TABLE 2 — THE MORTALITY RATE AND SURVIVAL TIME IN CONTROL AND ESTROGEN-TREATED ANIMALS

PERIOD AFTER INOCULATION hr.	RATS				MICE			
	Mortality %		Mean survival time hr.		Mortality %		Mean survival time hr.	
	Controls	Treated	Controls	Treated	Controls	Treated	Controls	Treated
96	22	0	107	144	77	44	94	111
120	100	55	—	—	100	100	—	—
144	100	55	—	—	—	—	—	—
168	100	100	—	—	—	—	—	—

inhibits the development of *T. equiperdum* in rats and mice, thereby prolonging their survival time.

The appearance of the parasites in the peripheral circulation after inoculation is significant. In mice the parasites are detectable in the blood in much larger numbers than in the rats. This difference is ascribable to the fact that rats are more resistant to *T. equiperdum* infection than mice. The rapid development of the parasites and the shorter survival period in both the control and the estrogen-treated mice provide logical grounds for such an interpretation.

A question may now be raised as to the mechanism responsible for the lowered parasitemia in the hormone-treated animals. Presumably, the drug acts on one or more of the chemical constituents of the blood which are utilized by the parasite for its development. Unfortunately, any attempt to postulate a mechanism based on the known action of estrogen on blood constituents is difficult, as the chemical factors necessary for the development of trypanosomes are still imperfectly understood[9]. However, it has been demonstrated that estrogen causes a rise in blood lipids and calcium[10] and a depletion of proteins[11-13]. Possibly, similar alterations in the level of these blood constituents due to estrogen pre-treatment proved detrimental to the development of *T. equiperdum* in the species under report.

Acknowledgement

Grateful acknowledgement is made to Dr. O. Wenger of Messrs Ciba Pharma Ltd., Bombay, for the supply of estradiol dipropionate (Ovocyclin P) used in this investigation.

References

1. Eggleston, C. & Gold, H., *Amer. J. med. Sci.*, **233** (1952), 553.
2. Bennison, B. E. & Coatney, G. R., *Science*, **107** (1948), 147.
3. Robles Gill, J. & Perrin, M., *Arch. Inst. Cardiol. Mex.*, **20** (1950), 314.
4. von Brand, T., Tobie, E. J. & Mehlman, B., *Amer. J. Hyg.*, **54** (1951), 76.
5. Wolf, A., Kabat, E. A., Bezer, A. E. & Fonesca, J., *Fed. Proc.*, **10** (1951), 375.
6. Findlay, G. M. & Howard, E. M., *Nature*, **169** (1952), 547.
7. Gallaird, M. H., Lapierre, J., Lariviere, M. & Berdonneau, R., *C.R. Acad. Sci. Paris*, **236** (1953), 1308.
8. Kolmer, J. A., *J. infect. Dis.*, **17** (1915), 79.
9. von Brand, T., *Chemical Physiology of Endoparasitic Animals* (Academic Press, New York), 1952, 201.
10. Burrows, H., *Biological Actions of Sex Hormones* (University Press, Cambridge), 1949, 460.
11. Cioffari, A., *Folia Endocrinol.*, **3** (1950), 479.
12. Tyslowitz, R. & Dingemanse, E., *Endocrinology*, **29** (1941), 817.
13. MacBryde, C. M., Castrodale, D., Helwig, E. B. & Bierbaum, O., *J. Amer. med. Ass.*, **118** (1942), 1003.

Enzyme Inhibition Studies in Relation to Drug Action: Part VI—Action of Certain Antibacterial Agents on the Succinic Oxidase System

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THE succinic oxidase system, encountered practically in all tissues, is associated with certain vital functions in the respiratory processes of the living cell and has, therefore, been the subject of intensive investigation[1]. The action of quinine[2] on succinic oxidase was the first to be investigated. Subsequently, the effect of mepacrine[3] and several antimalarial naphthaquinones[4] has been studied. In view of their specific action on essential sulphydryl groups, the action of organic mercurials[5] and arsenicals[6] has been investigated in some detail. Many sulphanilamide derivatives[7]

Action of penicillin G, dihydrostreptomycin, chloramphenicol, oxytetracyclin (terramycin), chlorotetracyclin (aureomycin), neomycin, isonicotinic acid hydrazide, promin, promacetin, diamidin and para-aminosalicylic acid has been studied on the succinic oxidase of heart pulp. Oxytetracyclin has been shown to irreversibly inhibit all the three catalytic components of the system. Factors influencing this action have been investigated.

have been shown to strongly inhibit the enzyme both *in vitro* and *in vivo*. Crude penicillin[8] and suramin[9] inactivated the succinic dehydrogenase activity of tissues. Recently chlorotetracyclin and oxytetracyclin[10] have been reported to inhibit the uptake of oxygen by *E. coli* in presence of succinate.

The aerobic oxidation of succinate is mediated through the cytochrome system, and it is conceivable, therefore, that an inhibitor to be effective must in some manner interfere with the linked chain reactions. In the observations reported so far on the inhibition of the succinic oxidase system, no attempt appears to have been made to locate the site of action of the inhibitor. For this investigation, it would be necessary to study the action of the inhibitors individually on the three main constituents of the system, viz. the succinic oxidase, cytochrome oxidase and succinic dehydrogenase. This communication describes such a study with six commonly used antibiotics, two anti-tubercular and three anti-leprosy drugs.

Experimental procedure

Enzyme — The heart pulp of pig, sheep or ox and the breast muscle of pigeons served as the source of enzyme. The tissues, obtained fresh from the slaughter house, were processed according to Keilin and Hartree[11] and preserved in the frozen state. Fresh homogenates were prepared from weighed quantities of the tissue by homogenization in a Waring blender in the cold with phosphate buffer and straining the viscous fluid through muslin. Centrifugation even in the cold was found to bring down the activity of the extract. Purification of the enzyme according to Slater[12] gave products of low activity which could not be restored to their original level by incubation with thiol compounds or albumin. In the present study both fresh homogenates and purified preparations were employed.

TABLE 1 — YIELD OF CYTOCHROME FROM SHEEP AND BUFFALO HEARTS

	No. of hearts	Wt. of tissue mince g.	Final volume of preparation cc.	Concentration moles/cc.
Sheep	15	670	30	$1{\cdot}8 \times 10^{-7}$
Buffalo	2	1250	62	$1{\cdot}4 \times 10^{-7}$

Cytochrome was prepared from freshly obtained bovine hearts according to the method of Keilin and Hartree[13]. The final preparation was standardized in a Unicam spectrophotometer according to Potter[14]. The iron content of the preparation was 0·348 per cent. The blood-red coloured solution obtained in the final stages of preparation was freeze dried.* In Table 1 are given the results of two typical experiments.

Antibiotics and drugs — All the drugs used were crystalline substances of the highest purity obtained from their respective manufacturers.

Assay of enzyme activity — The manometric methods used for the assay of the enzyme system were according to Slater[12]. Ascorbate was used as the reductant in the cytochrome oxidase assay with all drugs excepting oxytetracyclin which catalyses the auto-oxidation of ascorbic acid. Hydroquinone[14] was, therefore, used as the reducing agent in this case.

Results

The action of the drugs on the succinic oxidase system of pigeon breast homogenate was studied under identical conditions.

Succinic oxidase — Each flask (Warburg) contained 1 cc. of 0·18M phosphate buffer (*p*H 7·2), 1 cc. water or 1 mg. of drug dispersed in water and 0·5 cc. of 20 per cent homogenate of pigeon breast pulp in 0·02M phosphate buffer (*p*H 7·2). The centre cup contained 0·2 cc. of 10 per cent KOH and filter paper. 0·2 cc. of 0·4M succinate and 0·2 cc. of cytochrome ($1{\cdot}8 \times 10^{-7}$ moles/cc.) were kept in the side arm. After equilibration and incubation at 39°C. for 30 min., the succinate-cytochrome mixture was tipped in and readings taken every 10 min. for 1 hr.

Cytochrome oxidase — The contents of the main chamber were the same as in succinic

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*Freeze drying was carried out with the kind cooperation of Dr. Govind Rau, Biological Products Officer to the Government of Uttar Pradesh.

oxidase assay. The side arm contained 0·8 cc. cytochrome ($1 \cdot 8 \times 10^{-7}$ moles/cc.) and 0·3 cc. ascorbate (50 mg./cc. prepared fresh and neutralized prior to use) which were added to the reactants after 30 min. of pre-incubation. Oxygen uptake values in presence of ascorbate, the enzyme and the drugs read from control experiments were subtracted from the respective experimental values and represent cytochrome oxidase activity. For the assay of cytochrome oxidase in presence of oxytetracyclin, 0·3 cc. of freshly prepared hydroquinone (50 mg./ cc.) replaced the ascorbate.

Succinic dehydrogenase — In addition to the reagents listed in succinic oxidase assay, the main chamber contained neutral cyanide (0·1M, 0·3 cc.). Methylene blue (0·3 cc. of 0·01M) and succinate (0·2 cc. of 0·4M) were added from side bulb after 30 min. of incubation. The homogenate used was a 50 per cent extract of breast muscle pulp.

A set of typical results is presented in Table 2. It would be seen that neomycin, oxytetracyclin and isonicotinic acid hydrazide exhibited an inhibitory action, whereas promin, promeacetin and diamidin showed an accelerating action on the oxidase. Dihydrostreptomycin, neomycin and oxytetracyclin had, however, an inhibitory action on cytochrome oxidase. Only dihydrostreptomycin and oxytetracyclin had any significant depressing action on dehydrogenase.

Figs. 1 and 2 represent the time activity curves of pigeon breast enzyme and a purified pig heart preparation for the activity of oxidase under the influence of oxytetracyclin and isonicotinic acid hydrazide. It would be seen that the drugs inhibit the enzyme activity progressively and that the degree of inhibition with oxytetracyclin is more pronounced with the purified enzyme preparation. The time activity curves for cytochrome oxidase in presence of the drug are given in Fig. 3. Figs. 4 and 5 illustrate the corresponding curves for the activity of the succinic dehydrogenase as affected by dihydrostreptomycin and oxytetracyclin. Here again the purified preparation was more sensitive to the action of the drug.

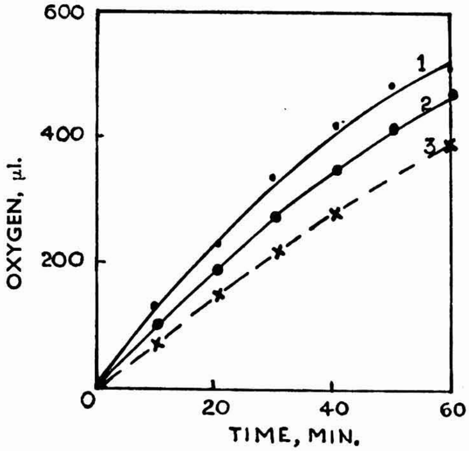

FIG. 1 — EFFECT OF ISONICOTINIC ACID HYDRAZIDE AND OXYTETRACYCLIN ON SUCCINIC OXIDASE [(Pigeon breast homogenate) (1) control; (2) isonicotinic acid hydrazide; and (3) oxytetracyclin]

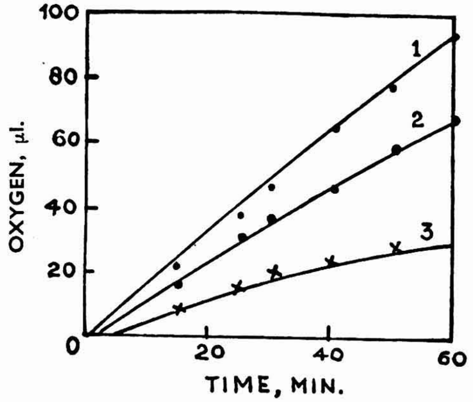

FIG. 2 — EFFECT OF ISONICOTINIC ACID HYDRAZIDE AND OXYTETRACYCLIN ON SUCCINIC OXIDASE [(Pig heart-purified preparation) (1) control; (2) isonicotinic acid hydrazide; and (3) oxytetracyclin]

TABLE 2 — ACTION OF ANTIBIOTICS, ANTI-TUBERCULAR AND ANTI-LEPROSY COMPOUNDS ON THE SUCCINIC OXIDASE SYSTEM

[*Values (average of 6 readings) expressed in µl. of oxygen taken up in 10 min.*]

	SUCCINIC OXIDASE	CYTOCHROME OXIDASE		SUCCINIC DEHYDROGENASE
		Ascorbate	Hydroquinone	
Water	94·0	70·3	72·0	10·3
Chlorotetracyclin	93·0	72·0	—	9·7
Chloramphenicol	94·0	68·3	—	9·2
Dihydrostreptomycin	95·0	61·3	—	7·2
Neomycin	77·0	59·7	—	9·0
Penicillin G	103·0	75·7	—	9·7
Oxytetracyclin	70·0	—	57·4	5·0
Isonicotinic acid hydrazide	82·0	75·0	—	9·0
Para-aminosalicylic acid	104·0	71·2	—	10·5
Diamidin	121·0	71·0	—	10·0
Promin	114·0	70·8	—	10·2
Promacetin	113·0	71·2	—	10·2

Factors influencing the rate of inactivation of oxidase by oxytetracyclin — The effect of different concentrations of the drug (0·2-1·0 mg.) was studied on a pig heart preparation. The main chamber of the flask contained phosphate buffer (1 cc., 0·18M), purified enzyme (pig heart, 0·2 cc.) and water (1 cc.) containing different amounts of the drug. The side arm contained succinate (0·2 cc., 0·4M) and cytochrome (0·2 cc.; 1·8 × 10^{-7} moles/cc.). Potassium hydroxide solution (10 per cent, 0·2 cc.) was placed in the centre cup with the filter paper. The substrate cytochrome mixture was tipped in after 30 min. of pre-incubation with enzyme and the drug.

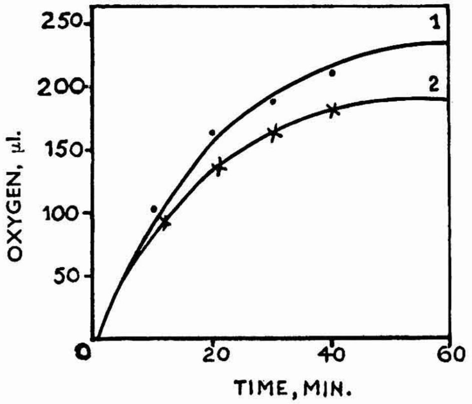

FIG. 3 — EFFECT OF OXYTETRACYCLIN ON CYTOCHROME OXIDASE OF PIGEON BREAST MUSCLE HOMOGENATE [(1) Control; and (2) oxytetracyclin]

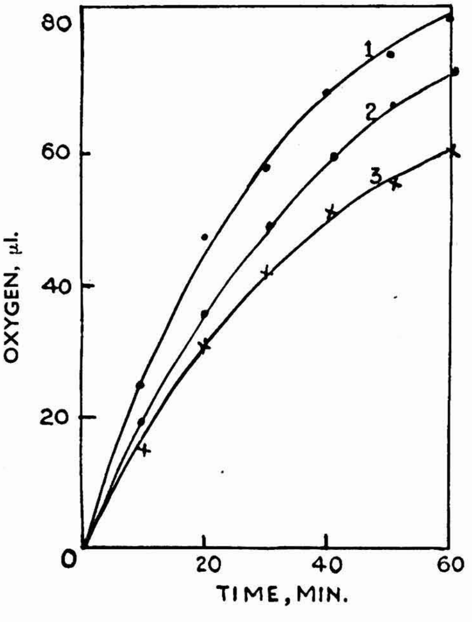

FIG. 4 — EFFECT OF DIHYDROSTREPTOMYCIN AND OXYTETRACYCLIN ON SUCCINIC DEHYDROGENASE OF PIGEON HOMOGENATE [(1) Control; (2) DHS; and (3) oxytetracyclin]

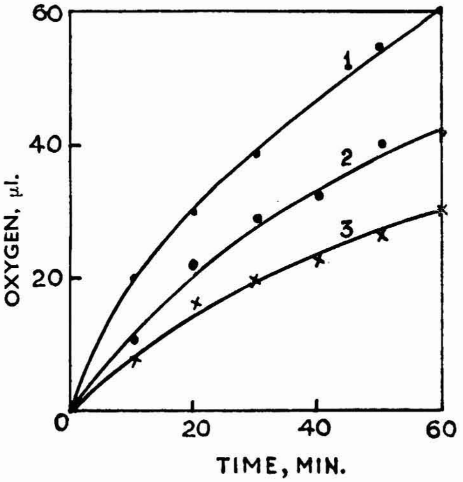

FIG. 5 — EFFECT OF DHS AND OXYTETRACYCLIN ON SUCCINIC DEHYDROGENASE OF PIG HEART (PURIFIED ENZYME) [(1) Control; (2) DHS; and (3) oxytetracyclin]

It is evident from the results given in Table 3 that there is a continuous rise in the degree of inhibition with concentration of the drug.

The influence of time of contact of the drug with a pig heart oxidase preparation was also studied. The constituents of the flasks were as in experiments on the effect of concentration of oxytetracyclin on succinic oxidase (TABLE 3). The oxytetracyclin (1 mg.) and purified enzyme (pig heart, 0·2 cc.) were used. After incubation, a mixture of 0·2 cc. cytochrome and 0·2 cc. 0·4M succinate was tipped in from the side arm.

TABLE 3 — EFFECT OF CONCENTRATION OF OXYTETRACYCLIN ON SUCCINIC OXIDASE

(*Values expressed in µl. of oxygen taken up*)

TIME min.	WATER	OXYTETRACYCLIN mg.				
		0·2	0·4	0·6	0·9	1·0
20	52·0	46·8	39·6	40·6	38·0	27·0
40	99·0	95·0	79·2	74·2	72·0	55·0
60	151·2	138·8	118·8	116·2	112·0	86·2

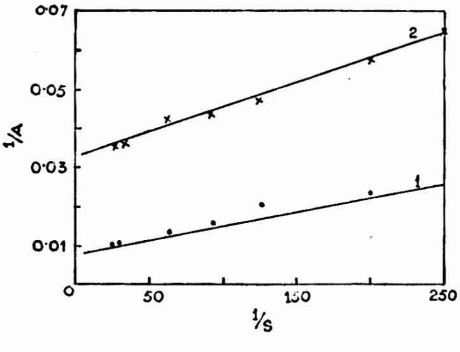

FIG. 6 — EFFECT OF SUBSTRATE CONCENTRATION ON INHIBITION OF SUCCINIC OXIDASE BY OXYTETRACYCLIN [(1) Control; (2) oxytetracyclin; S, substrate; and A, activity]

TABLE 4 — EFFECT OF TIME OF CONTACT OF OXYTETRACYCLIN ON SUCCINIC OXIDASE INHIBITION

(*Values expressed in μl. oxygen taken up in 60 min.*)

	TIME OF CONTACT BETWEEN ENZYME AND INHIBITOR min.			
	0	30	60	120
Water	150·0	148·0	140·0	121·0
Oxytetracyclin	127·0	83·0	68·0	48·0

The results given in Table 4 indicate that the degree of inhibition progresses with the time of contact of the drug with the enzyme. The action of the drug on the enzyme preparation was studied with different concentrations of succinate (FIG. 6) and the type of inhibition is non-competitive with respect to the substrate.

Effect of increasing concentration of cytochrome on the inactivation of succinic oxidase by oxytetracyclin — In view of the fact that the inhibitory effect of several reagents on succinic oxidase is known to be counteracted by excess of cytochrome, the inhibition of the enzyme by oxytetracyclin was studied in presence of increasing concentrations of cytochrome. Each flask contained phosphate buffer (1 cc., 0·18M; *p*H 7·2), water or oxytetracyclin (1 cc.) and purified enzyme preparation (0·2 cc.). The side bulb contained succinate (0·2 cc. 0·4M) and different amounts of cytochrome made up to a volume of 1 cc. Potassium hydroxide solution (10 per cent, 0·2 cc.) was placed in the centre cup with filter paper.

It would be evident from the results given in Table 5 that the latter, even in a concentration of 1·8 × 10^{-7} moles, does not abolish or diminish the degree of inhibition by the antibiotic.

Reversal of succinate inhibition by cysteine and glutathione — Thiol compounds are known to protect the succinic dehydrogenase from inactivation by several reagents[16,17]. Attempts were, therefore, made to reverse the inhibition of succinic oxidase system with the aid of cysteine and glutathione. The contents of the Warburg's flasks were as in experiments on the action of the drugs on succinic oxidase system (TABLE 2), except that instead of 1 cc. of water or inhibitor solution 0·5 cc. water and 0·5 cc. of inhibitor and activator solution were added as desired, so that there was no change in the effective volume of the reactants. The inhibitor or activator solutions used had a concentration of 2 mg./cc. Oxygen uptake was measured over a period of 60 min. at 10 min. intervals.

From the results reported in Table 6 it would be seen that whereas glutathione provides a certain degree of protection to the enzyme from the inactivating influence of neomycin, isonicotinic acid hydrazide and dihydrostreptomycin, it is ineffective in arresting the inhibitory action of oxytetracyclin. The behaviour of cysteine is similar

TABLE 5 — EFFECT OF DIFFERENT AMOUNTS OF CYTOCHROME ON OXIDATION OF SUCCINATE

(*Values expressed in μl. of oxygen taken up in 60 min.*)

	CYTOCHROME cc.					
	0·0	0·1	0·2	0·3	0·6	1·0
Water	46·0	92·0	143·0	153·0	160·0	160·0
Oxytetracyclin	26·0	42·0	69·0	76·0	79·0	78·0

TABLE 6 — REVERSAL OF INHIBITION OF SUCCINIC OXIDASE SYSTEM BY ANTIBIOTICS

(*Values expressed in μl. of oxygen taken up in 10 min.*)

	WITHOUT ACTIVATOR	WITH CYSTEINE	WITH GLUTATHIONE
Succinic oxidase			
Water	75·1	62·2	80·3
Oxytetracyclin	18·0	21·0	28·3
Isonicotinic acid hydrazide	66·0	65·0	72·8
Neomycin	61·5	60·0	71·4
Cytochrome oxidase			
Water	83·4	85·0	84·0
Oxytetracyclin	67·0	63·8	64·9
Dihydrostreptomycin	70·5	79·3	82·6
Neomycin	69·0	80·0	83·0
Succinic dehydrogenase			
Water	12·0	12·0	12·2
Oxytetracyclin	6·7	6·4	7·1
Dihydrostreptomycin	9·6	12·7	13·4

except in the case of succinic oxidase which is inhibited to an extent by this reagent.

Discussion

Out of the eleven drugs studied only oxytetracyclin and neomycin have shown any significant depressing action on the succinic oxidase system of the heart muscle. Of these oxytetracyclin is the more potent. The inhibitory effect of this drug is manifest alike on all the three enzyme systems, although cytochrome oxidase is the least susceptible. In view of the further observations that excess of cytochrome has no neutralizing action and that the thiol compounds fail to afford protection to the enzyme system, it would appear that oxytetracyclin blocks essential groups other than sulphydryl.

Chlorotetracyclin, which is structurally very similar to oxytetracyclin[17], has no action whatsoever on the enzyme. Presumably the absence of the chlorine atom and the additional presence of a hydroxyl group in the twelfth position jointly confer upon oxytetracyclin the specific inhibitory action on the succinic oxidase system. Both these drugs have, however, been recently shown to inhibit the respiration of *E. coli*[10] considerably in the presence of succinate. A somewhat similar kind of difference in the behaviour of the two drugs has already been shown in their action on alkaline phosphatase[18] which is stimulated by chlorotetracyclin and inhibited by the oxy-compound. Similarly, while oxytetracyclin has a high catalytic action on the auto-oxidation of ascorbic acid[15], chlorotetracyclin does not possess any such property.

Summary

1. The action of six antibiotics, two antitubercular and three anti-leprosy compounds has been studied *in vitro* on the succinic oxidase system of pig heart and pigeon breast homogenates.

2. Oxytetracyclin, neomycin and isonicotinic acid hydrazide have inhibitory action on succinic oxidase, cytochrome oxidase and succinic dehydrogenase activities. Diamidin, promin and promacetin have stimulatory action on the oxidase only. Isonicotinic acid hydrazide has inhibitory action only on the oxidase. Dihydrostreptomycin inhibits both succinic dehydrogenase and cytochrome oxidase and has no action on succinic oxidase.

3. The inhibitory effects of isonicotinic acid hydrazide, neomycin and dihydrostreptomycin are counteracted by cysteine or glutathione which have no protective action on the inhibition brought about by oxytetracyclin.

4. The degree of inhibition of the oxidase system by oxytetracyclin is dependent upon the concentration of the drug and its time of contact with the enzyme. The inhibition is non-competitive with respect to substrate. Excess cytochrome has no action on the degree of inhibition by the antibiotic.

Acknowledgement

The authors' grateful thanks are due to Messrs Parke, Davis & Co., Lederle Laboratories, New York, Charles Pfizer & Co., UpJohn & Co., Squibbs Ltd., Indian Penicillin Committee and Glaxo Laboratories for the supply of the drugs used in this study.

References

1. SUMNER, J. B. & MYRBACK, K., *The Enzymes: Part I* (Academic Press, New York), **1** (1952), 157.
2. JOHNSON, F. H. & LEWIN, I., *J. cell. comp. Physiol.*, **28** (1946), 1-22.
3. ALLEGRETTI, N., *Archiv. Kem.*, **20** (1948), 105-13.
4. BALL, E. G., ANFINSEN, C. B. & COOPER, O., *J. biol. Chem.*, **168** (1947), 257-70.
5. KREKE, C., KROGER, M. H. & COOK, E. S., *J. biol. Chem.*, **180** (1949), 565.
6. GORDON, J. J. & QUASTEL, J. H., *Nature*, **159** (1947), 97-98.
7. PRAZAK, V., *Biol. Abstr.*, **21** (1947), 38.
8. HOSOYA, S. & MITSUHASHI, S., *J. Penicillin* (*Japan*), **1** (1947), 296-97.
9. TOWN, B. W., WILLS, E. D. & WORMALL, A., *Nature*, **164** (1949), 233.
10. DONALD, T. O., WONG, S. B. & SAMUEL, J. AJL., *Antibiotics and Chemotherapy*, **3** (1953), 607.
11. KEILIN, D. & HARTREE, E. F., *Biochem. J.*, **41** (1947), 500.
12. SLATER, E. C., *Biochem. J.*, **45** (1949), 1.
13. KEILIN, D. & HARTREE, E. F., *Proc. roy. Soc.*, **122** (1937), 298.
14. POTTER, V. R., *Manometric Techniques in Tissue Metabolism* (Burgers Pub. Co., Minneapolis), 1949.
15. DUDANI, A. T. & KRISHNA MURTI, C. R., *Biochem. Biophys. Acta*, **13** (1954), 505.
16. HOPKINS, F. G. & MORGAN, E. J., *Biochem. J.*, **32** (1938), 611.
17. HOPKINS, F. G., MORGAN, E. J. & LUTWAK-MANN, C., *Biochem. J.*, **32** (1938), 1829.
18. GHATAK, S. & KRISHNA MURTI, C. R., *J. sci. industr. Res.*, **12B** (1953), 160.
19. DUGGAR, B. M. & SINGLETON, V. L., *Ann. Rev. Biochem.*, **22** (1953), 462.

Studies on Biotin: Part VI—Influence of Biotin on the Inositol-γ-hexachlorocyclohexane Relation in *Aspergillus oryzae*[*]

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Evidence is presented to indicate that the gamma isomer of hexachlorocyclohexane exerts a non-specific inhibitory action on amylase and riboflavin synthesis in *Aspergillus oryzae*, and the inhibitory effects are not overcome by inositol. Biotin alone is able to overcome the inhibitory effect to an appreciable extent and other vitamins of the B group (except folic acid) do not significantly affect the metabolism of the fungus in the presence of the inhibitor. Folic acid augments the toxicity of the insecticide, and in the presence of folic acid the insecticide inhibits the synthesis of amylase and riboflavin to a greater extent than in its absence. In the presence of folic acid, however, biotin is not able to overcome the inhibitory effect of the insecticide.

It is suggested that inositol is mainly responsible for the production both of amylase and riboflavin, and the non-specific inhibitory action of the insecticide is more due to an incapacity on the part of the fungus to utilize exogenous inositol.

ALTHOUGH considerable amount of work has been carried out on the metabolite-anti-metabolite relationship between inositol and the insecticide, γ-hexachlorocyclohexane, no conclusive proof has been obtained to prove the existence or otherwise of such a relationship. Kirkwood and Phillips[1] and Buston, Jacobs and Goldstein[2] have shown that inositol is able to overcome the growth inhibition by the insecticide in yeast and *Nematospora gossypii* respectively. Chargaff *et al.*[3] showed that the insecticide inhibits the metaphase and induces tumour formation in *Allium cepa*, and this inhibition is overcome specifically by meso-inositol, while *d*-sorbitol and *d*-inositol are inactive. However, D'Amato[4] suggested that this effect of inositol in overcoming the inhibitory effect of the insecticide in the onion root meristem may be due more to an alteration in permeability, in view of the fact that other sugars also exerted a similar effect, rather than a specific antagonism between inositol and γ-hexachlorocyclohexane. Sarma[5] established a relation between these two compounds, and showed for the first time that in the rice-moth larva (*Corcyra cephalonica* St.) the insecticide inhibits the growth of the larva and that there is a considerable accumulation of cholesterol in the tissues. These manifestations were apparently overcome when inositol was included in the diet of the larva.

While the above investigations served to establish a relation between inositol and the insecticide as metabolite and antagonist, there have been reports doubting the existence of such a relation. Fromageot and Confino[6], Chaix[7] and Chaix, Lacroix and Fromageot[8] have not been able to establish any relation between these two compounds in a variety of inositol-dependent and inositol-independent bacteria. Results of X-ray studies have also not been convincing, and it has been indicated that inositol and γ-hexachlorocyclohexane do not possess isomorphous crystalline structures[9,10]. Recently Fuller *et al.*[11], using a wild strain and an " inositolless " mutant of *Neurospora crassa*, indicated that γ-hexachlorocyclohexane produces two types of inhibitions, one affecting inositol metabolism, and another, which they were not able to account for. The first type of inhibition, affecting the metabolism of inositol, was shown to be reversed by inositol specifically in the mutant strain, while there was no such demonstrable relationship in the wild type. Recently we have shown[12] that γ-hexachlorocyclohexane specifically affects inositol metabolism in the same

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[*] The work reported here forms part of the thesis submitted to the University of Madras for the degree of Master of Science by one of us (M.O.T.).

organisms, and that it may not produce two types of inhibitions as postulated by Fuller *et al.* It was also shown for the first time that biotin influences the relation between the two compounds to an appreciable extent in *Neurospora crassa*, and that it is in some manner involved in the biosynthesis and utilization of inositol in the mold.

It was shown by Ramachandran and Sarma[13] that γ-hexachlorocyclohexane inhibits the synthesis of α-amylase by pigeon pancreas *in vitro*. Based on these observations, experiments have been carried out with a strain of *Aspergillus oryzae* to study in greater detail the different aspects of inhibition caused by γ-hexachlorocyclohexane and the results are reported in this paper.

Experimental procedure

The organism *Aspergillus oryzae* (*N.C.T.C.* 536) obtained from the National Collection of Type Cultures, National Chemical Laboratory, Poona, was carried by monthly subcultures on malt-agar. The organism was grown on a modified Czapek-Dox medium containing *d*-glucose, 20 g.; potassium monohydrogen phosphate, 1 g.; sodium nitrate, 3 g.; potassium chloride, 1 g.; magnesium sulphate, 0·5 g.; trace elements (molybdenum), 0·04 mg.; iron, 0·4 mg.; copper, 0·2 mg.; manganese, 0·04 mg.; boron, 0·02 mg.; and zinc, 4·0 mg. per litre. The *p*H of the media was adjusted to 5·0, dispensed in 50 cc. lots in 250 cc. Erlenmeyer flasks, and sterilized at 15 lb. for 17 min. They were then inoculated with a drop of a spore suspension obtained by suspending in 10 cc. washed spores from a 7 day old slant of the medium. The flasks were incubated for 10 days at room temperature. A 99 per cent pure γ-hexachlorocyclohexane was made up in ethanol and added before sterilization. The mycelia were washed over sintered glass funnel (the washings added to the culture filtrate for riboflavin estimations), pressed between folds of filter paper and dried to constant weight.

All experiments involving the determination of riboflavin were carried out in subdued light. Total riboflavin, both in the culture medium and the mycelium, was determined fluorimetrically according to the procedure of Scott, Hill, Norris and Heuser[14]. The procedure involved hydrolysis under pressure with 0·1N hydrochloric acid, the proteins precipitated with sodium phosphate, treated with permanganate in acid *p*H followed by hydrogen peroxide, and made up to a convenient volume. Aliquots from this were taken to estimate riboflavin fluorimetrically and the difference in fluorescence with and without added hydrosulphite was taken as being due to riboflavin.

For the determination of amylase activity of the mycelium the following procedure was adopted. The mycelia at the close of the incubation period were separately ground in a Waring blendor using glass distilled water cooled to below 5°C. An aliquot of this was taken for determination of total solids and the remaining used for enzyme assay. Amylase activity was determined as indicated by Somogyi[15] by incubating starch solution with the enzyme preparation and measuring the reducing sugar formed at the end of a specified period. The *p*H of the reaction mixture was 5·6, and 0·2M phosphate buffer was used. The amylase activities are represented in terms of " amylase units ", i.e. the number in milligrams of reducing sugar (glucose equivalent) formed by 1 g. of the mycelium from starch solution at 37°C. in 60 min. at *p*H 5·6.

Results and discussion

Table 1 indicates the inhibitory effect of the γ-hexachlorocyclohexane on the amylase and riboflavin synthesis by *A. oryzae*. Table 2 shows the influence of the B complex vitamins individually on the inhibition produced by the insecticide. The effect of combinations of inositol, biotin and folic acid on the inhibition produced by the insecticide is indicated in Table 3.

Although the metabolic functions of inositol are not yet clearly known, the amount of the vitamin occurring in pancreatic amylase, as determined by Williams, Schlenk and Eppright[16], is such as to suggest that it may function as an integral part of the enzyme. The findings of Lane and

TABLE 1 — INFLUENCE OF γ-HEXACHLOROCYCLOHEXANE ON GROWTH, AMYLASE AND RIBOFLAVIN SYNTHESIS BY *A. ORYZAE*

γ-HEXACHLOROCYCLOHEXANE μg./cc.	WT. OF MAT mg.	AMYLASE UNITS	RIBOFLAVIN μg./g.
0	235·0	2300	24·6
20	243·0	1730	16·6
40	217·6	1740	14·3
60	200·0	1500	14·6
80	194·2	1090	15·0
100	203·0	1105	15·2

TABLE 2 — INFLUENCE OF B-COMPLEX VITAMINS ON γ-HEXACHLOROCYCLOHEXANE INHIBITION IN *A. ORYZAE*

VITAMIN SUPPLEMENT μg./50 cc. (values in parenthesis)	WT. OF MAT mg.	AMYLASE UNITS	RIBOFLAVIN μg./g.
Basal medium (BM)	222·4	2120	22·5
BM + γ-hexachlorocyclohexane (G) (2000)	201·6	1580	16·9
BM + G + inositol (1000)	214·0	1590	16·8
BM + G + biotin (2)	198·0	2040	20·5
BM + G + choline (100)	199·6	1560	17·2
BM + G + pABA (100)	205·8	1575	17·0
BM + G + folic acid (10)	212·0	1180	14·5
BM + G + thiamin (100)	207·6	1600	17·0
BM + G + niacin (100)	210·0	1585	16·9
BM + G + Ca pantothenate (100)	200·4	1560	17·1

TABLE 3 — EFFECT OF SUPPLEMENTING INDIVIDUALLY AND IN COMBINATION INOSITOL, BIOTIN AND FOLIC ACID ON γ-HEXACHLOROCYCLOHEXANE INHIBITION IN *A. ORYZAE*

EXPT. No.	BIOTIN 2 γ	INOSITOL 1 mg.	FOLIC ACID 10 γ	MAT WT.	AMYLASE UNITS	RIBOFLAVIN μg./g.
1*	−	−	−	226·4	2460	23·5
2	−	−	−	214·2	1720	18·9
3	+	−	−	212·8	2150	20·8
4	−	+	−	208·6	1700	18·5
5	−	−	+	200·0	1460	16·7
6	+	+	−	207·8	2080	20·2
7	+	−	+	202·0	1480	16·2
8	−	+	+	205·2	1455	16·5
9	+	+	+	208·0	1500	17·0

*Control, without added inhibitor; the rest had 40 μg./cc. of γ-hexachlorocyclohexane.

Williams[17] that the inhibition by lindane of pancreatic α-amylase was competitively overcome by inositol lend support to this view. On the other hand, Fisher and Bernfield[18] showed that crystalline pancreatic α-amylase and crystalline malt α-amylase are neither inhibited by γ-hexachlorocyclohexane nor activated by inositol. It has been shown further that *A. oryzae* synthesizes only the α-type amylase which converts starch to glucose and iso-maltose[19]. We have been able to find that the insecticide inhibits the production of amylase in this organism (TABLE 1), and that exogenous inositol is not able to overcome this inhibition. But, as may be observed from the results in Table 2, biotin is able to reverse this inhibition. In an earlier communication[12] we have shown that in *Neurospora crassa* also this insecticide affects only inositol metabolism, and that biotin is concerned in the synthesis and utilization of inositol.

The insecticide also inhibits the synthesis of riboflavin in the organism. As in the case of amylase, the inhibition of riboflavin synthesis by the insecticide is overcome by biotin and not by inositol. It has been shown[20] that in *Eremothecium ashbyii*, riboflavin production is largely influenced by inositol alone, and that the addition of biotin or thiamine to the basal medium containing inositol did not in any way increase the riboflavin level over that obtained by inositol alone in the medium. Since the insecticide inhibits riboflavin production, it is very likely that it affects only the metabolism of inositol in *A. oryzae.*

Relationship between folic acid and biotin — In a previous communication from this laboratory[21], it was indicated that while biotin is able to overcome the inhibitory effects of the insecticide in *A. oryzae*, folic acid augments its toxicity. It has now been found that biotin is unable to overcome the inhibition in the presence of folic acid (TABLE 3). The relationship between folic acid and biotin is rather peculiar. Hitherto there have not been many instances of biological antagonism between metabolites, although that of lysine and arginine in *Neurospora* may serve as a classical example[22]. There is yet another instance of biological antagonism between folic acid and biotin. Sreenivasan[23] reported that while folic acid and vitamin B_{12} augmented the synthesis of nucleic acids in *Lactobacilli*, biotin exerted a depressing effect. Further study is needed to reveal the exact relationship between folic acid and biotin.

In conclusion it may be mentioned that *A. oryzae* behaves in essentially the same way as the wild strain of *Neurospora crassa* in that γ-hexachlorocyclohexane exerts only a non-specific inhibitory action and inositol is not able to overcome the inhibition even to a slight extent. On the other hand, biotin is the only vitamin that is able to overcome the inhibition in both the organisms. It is this non-specific inhibition that has given rise to much confusion regarding the existence of a metabolite-anti-metabolite relationship between inositol and γ-hexachlorocyclohexane. This in turn is largely dependent upon the genetic make-up or capacity of the cell to utilize externally added inositol. Non-specific inhibition by the insecticide occurs only where the organism is unable to make use of externally added metabolite, and it should doubtless be possible to establish a relationship between inositol and γ-hexachlorocyclohexane in all those organisms which have a natural capacity to utilize exogenous inositol or which have been rendered inositolless by mutation.

Summary

1. Evidence is presented to indicate that γ-hexachlorocyclohexane inhibits the production of both amylase and riboflavin in *Aspergillus oryzae.*

2. The inhibition is non-specific as it is not overcome by inositol.

3. Biotin alone, among the B group of vitamins, is able to overcome the inhibitory effects of γ-hexachlorocyclohexane to an appreciable extent.

4. Other vitamins of the B group, excepting folic acid, do not significantly affect the metabolism of the fungus in the presence of the inhibitor.

5. Folic acid augments the toxicity of the inhibitor and its presence results in greater inhibition of amylase and riboflavin synthesis.

6. Biotin is not able to overcome the inhibitory effects in the presence of folic acid, and a combination of inositol, folic acid and biotin has little effect on the inhibition caused by γ-hexachlorocyclohexane.

7. It is suggested that it would be possible to demonstrate a relationship between inositol and the gamma isomer of the inhibitor only in those organisms which have a natural capacity to utilize exogenous inositol or which have been rendered " inositolless " by mutation.

Acknowledgement

The authors wish to express their gratitude to Dr. W. H. Tisdale of E.I. du Pont de Nemours & Co., Delaware, and the Hooker Electrochemical Co., New York, for the generous gift of 99 per cent pure γ-hexachlorocyclohexane, and Messrs Hoffmann La-Roche & Co. Inc., Basle, Switzerland, for the synthetic *d*-(+) biotin used in this investigation.

References

1. KIRKWOOD, S. & PHILLIPS, P. H., *J. biol. Chem.*, **163** (1946), 251.
2. BUSTON, H. W., JACOBS, S. E. & GOLDSTEIN, A., *Nature*, **158** (1946), 22.
3. CHARGAFF, E., STEWART, R. N. & MAGASANIK, B., *Science*, **108** (1948), 556.
4. D'AMATO, F., *Carylogia*, **1** (1949), 223.
5. SARMA, P. S., *Curr. Sci.*, **19** (1950), 315.
6. FROMAGEOT, C. & CONFINO, M., *Biochem. Biophys. Acta*, **2** (1948), 142.
7. CHAIX, P., *Bull. Soc. Chim. biol. Paris*, **30** (1948), 835.
8. CHAIX, P., LACROIX, L. & FROMAGEOT, C., *Biochem. Biophys. Acta*, **2** (1948), 57.
9. BIJVOET, J. M., *Rec. Trav. chim.*, **67** (1948), 777.
10. VAN VLOTEN, G. W., KRUISSINK, C. A., STRIJK, B. & BIJVOET, J. M., *Nature*, **162** (1948), 771.
11. FULLER, R. C., BARRATT, R. W. & TATUM, E. L., *J. biol. Chem.*, **186** (1950), 823.
12. TIRUNARAYANAN, M. O. & SARMA, P. S., *J. sci. industr. Res.*, **12B** (1953), 251.
13. RAMACHANDRAN, S. & SARMA, P. S., *Indian J. med. Res.*, in press.
14. SCOTT, M. L., HILL, F. W., NORRIS, L. C. & HEUSER, G. F., *J. biol. Chem.*, **165** (1946), 65.
15. SOMOGYI, M., *J. biol. Chem.*, **195** (1952), 19.
16. WILLIAMS, R. J., SCHLENK, F. & EPPRIGHT, M. A., *J. Amer. chem. Soc.*, **66** (1944), 896.
17. LANE, R. L. & WILLIAMS, R. J., *Arch. Biochem.*, **19** (1948), 329.
18. FISCHER, ED. H. & BERNFIELD, P., *Helv. chim. Acta*, **32** (1949), 1146.
19. AHLBORG, K. & MYRBACK, K., *Biochem. Z.*, **308** (1941), 187.
20. DULANEY, E. L. & GRUTTER, F. H., *Mycologia*, **42** (1950), 717.
21. TIRUNARAYANAN, M. O. & SARMA, P. S., *Curr. Sci.*, **23** (1954), 55.
22. DOERMANN, A. H , *Arch. Biochem.*, **5** (1944), 373.
23. SREENIVASAN, A., *Technical Report, Scientific Advisory Board, Indian Council of Medical Research*, 1952, 79.

Enzymes of Ragi (*Eleusine coracana*) & Ragi Malt: Part III — Pyro & Glycerophosphatases

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The nature and properties of glycero and pyrophosphatases of ragi (*Eleusine coracana*) and its malt have been investigated. The resting grain possesses only slight phosphatase activity. Germination of the grain leads to a pronounced increase in the activity of both pyro and glycerophosphatases. Magnesium and zinc ions do not affect the activity of the two enzymes but fluoride ion strongly inhibits their activity.

THE nature and properties of phosphatases present in resting and germinating seeds have been investigated by a number of workers[1-4]. Leurs and Malsch[3] observed an increase in phosphatase activity of barley during germination. Ignatieff and Wasteneys[2] studied the distribution of phosphomonoesterases in wheat prior to and during germination. Booth[1] has made a detailed study of phosphatases of wheat. Sarma and Giri[4] have reported that the glycerophosphatases of rice, ragi and soyabean exist in two forms, i.e. bound and free. They noted an increase in the enzyme activity during germination. The present study was undertaken to investigate the activity and properties of pyro and glycerophosphatases of ragi and its malt. A preliminary account of this work has been published earlier[5,6].

Experimental procedure

Ragi malt was prepared according to the procedure described in an earlier publication[5]. The malt was dried at 40°-45°C. and used for the determinations.

Enzyme extract — Several extraction media were tried for the extraction of the enzymes from the malt. M/5 acetate buffer (*p*H 5) was found to be the best. The enzyme extracts were prepared as follows:

Pyrophosphatase — Five grams of the powdered malt or ragi were suspended in 100 cc. acetate buffer and shaken for 2 hr. This was centrifuged and the supernatant was used as the enzyme extract. Ten cc. of the extract contained the enzymes from 0·5 g. of the material.

Glycerophosphatase — Twenty grams of the powdered malt or ragi were extracted with 100 cc. of acetate buffer, and further treatment was the same as in the case of pyrophosphatase extraction. Ten cc. of the extract contained the enzyme from 2 g. of the material.

Substrate for pyrophosphatase — Sodium pyrophosphate (0·25 g.; A.R.) was dissolved in 80 cc. of M/5 acetate buffer of *p*H 5·0. The solution was adjusted to *p*H 5·0 by adding N/5 acetic acid and finally made up to 100 cc. by adding M/5 acetate buffer (*p*H 5·0).

Substrate for glycerophosphatase — Sodium glycerophosphate (0·25 g.; A.R.) was dissolved in 80 cc. of M/5 acetate buffer of *p*H 5·6. The mixture was adjusted to *p*H 5·6 by adding N/5 acetic acid and finally made up to 100 cc. by adding M/5 acetate buffer (*p*H 5·6).

The above solutions were used in all the experiments except in those dealing with the effect of *p*H on enzyme activity for which 0·25 per cent substrate solutions of different *p*H values were prepared in buffer solutions.

Determination of pyro and glycerophosphatase activity — Sixteen cc. of the appropriate buffer substrate solution were brought to 37°C. (unless otherwise stated). Two cc. of the enzyme extract were then added and the mixture incubated for 2 hr. at 37°C. (unless otherwise stated). At the end of 2 hr., 6 cc. of 20 per cent trichloracetic acid solution were added. The solution was filtered and an aliquot (suitably diluted with 5 per cent trichloracetic acid solution, if necessary) was used for the determination of orthophosphate by the colorimetric method of Fiske and Subba Rao[7] using a Klett-Summerson photoelectric colorimeter. The following blanks were run: (1) Determination of phosphorus present in the digestion mixture at the beginning of incubation; (2) incubating the substrate with boiled enzyme extract under conditions of experiment; (3) incubation of the enzyme extract with buffer; and (4) incubation of the buffered substrate. The sum of the blank values of (3) and (4), being nearly the same as (2), was adopted in all experiments.

Results

Choice of extraction medium — Sarma and Giri[4] found that about 60 per cent of the glycerophosphatase in resting ragi was in a bound form and could not be extracted with water at 0°C. while all the enzyme was released when the grain was germinated for 72 hr. Booth[1] extracted the phosphatases of wheat with water at 20°C. for 16-20 hr. and reported that only a part of the total enzyme was extracted by water. In the present study the enzymes were extracted from the powdered material with different extractants for 2 hr. at room temperature (28°-30°C.). The activity of the extracts was compared with that of the whole powder. The results are given in Table 1.

It will be seen from the results given in Table 1 that (1) M/5 acetate buffer and 1 per cent sodium chloride solution are more efficient than water in extracting the enzymes; (2) almost all the enzymes present in ragi malt are extracted by both M/5 acetate buffer (*p*H 5·0) and by 1 per cent sodium chloride solution and only 60-80 per cent by water, (3) about 80-90 per cent of the enzyme present in resting ragi is extracted by M/5 acetate buffer and 90-95 per cent by 1 per cent sodium chloride solution and only 40-50 per cent by water.

TABLE 1 — EXTRACTION OF PYRO AND GLYCEROPHOSPHATASES OF RAGI AND RAGI MALT

(*Enzyme activity expressed in mg. of P released/g. of powdered grain or malt; reaction time, 2 hr.; temp., 37°C.*)

EXTRACTANT	PYROPHOSPHATASE ACTIVITY mg. P released/g.		GLYCEROPHOSPHATASE ACTIVITY mg. P released/g.	
	Resting grain	Ragi malt	Resting grain	Ragi malt
Water	1·49	16·1	0·30	1·54
1% NaCl solution	3·47	20·8	0·52	1·97
M/5 acetate buffer (*p*H 5·0)	2·98	19·1	0·36	1·88
Control (whole powder added to substrate)	3·57	21·7	0·61	2·51

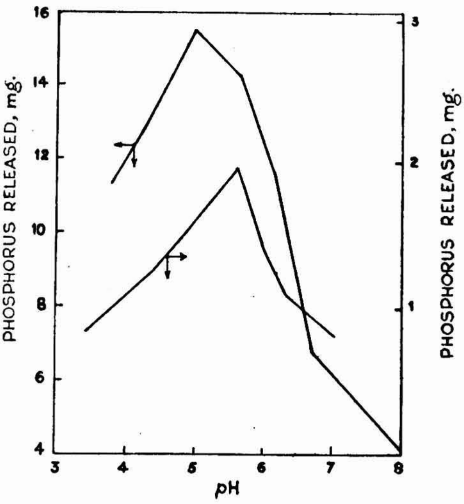

FIG. 1 — *p*H VS. ACTIVITY OF PYRO AND GLYCEROPHOSPHATASES OF RAGI

TABLE 2 — EFFECT OF TEMPERATURE ON THE ACTIVITY OF PYRO AND GLYCEROPHOSPHATASES OF RAGI MALT

(*Enzyme activity exprressed in mg. of P released/g. of powdered grain or malt; p*H, 5·0; *reaction time,* 2 *hr.*)

ENZYME	MG. P RELEASED/G. MALT			
	30°C.	37°C.	45°C.	55°C.
Pyrophosphatase	13·74	16·88	18·74	16·30
Glycerophosphatase	1·50	1·80	2·32	2·28

Optimum pH for pyro and glycerophosphatases — The optimum *p*H for the enzymes was determined using M/5 acetate buffer for the *p*H range 3·8-5·6 and Michaelis veronal-acetate buffer for the range 6·5-8·5. The results are shown in Fig. 1. It is evident from Fig. 1 that the optimum *p*H is 5·0 for pyrophosphatase and 5·6 for glycerophosphatase.

Effect of temperature on enzyme activity — The activities of pyro and glycerophosphatases at different temperatures ranging from 27° to 55°C. were determined. The results are given in Table 2. The results indicate that the optimum temperature for the activity of both the enzymes is *c.* 45°C.

Critical inactivation temperature — The critical inactivation temperature was determined for the two enzymes by maintaining the extracts at various temperatures for 1 hr.

TABLE 3 — EFFECT OF VARYING ENZME CONCENTRATION

(Enzyme activity expressed in mg. of P released/g. of powdered grain or malt; reaction time, 2 hr.; temp., 37°C.)

ENZYME EXTRACT cc.	PYROPHOSPHATASE ACTIVITY	GLYCEROPHOSPHATASE ACTIVITY
2	8·58	1·37
4	13·44	2·16
8	15·86	3·24
16	22·10	5·20
20	23·30	6·18

After treatment, the extracts were rapidly cooled to 37°C. and the enzyme activity determined. The results are shown in Fig. 2. The critical inactivation temperature for both pyro and glycerophosphatases is *c.* 57°C.

Effect of varying enzyme concentration — The results given in Table 3 show that the orthophosphate released by the increased concentrations of the enzyme inhibits the activity of the enzyme.

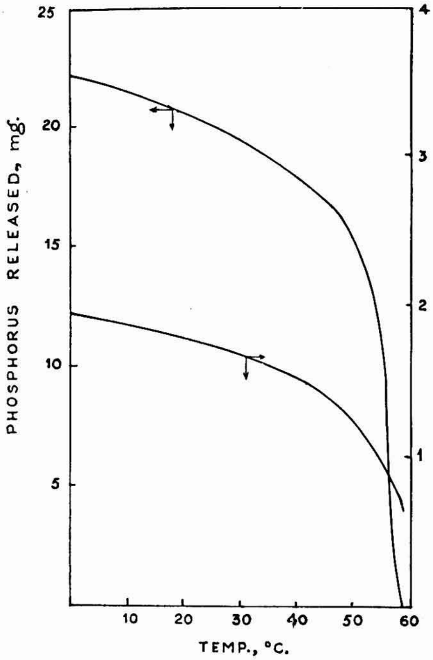

FIG. 2 — INACTIVATION OF PYRO AND GLYCEROPHOSPHATASES BY HEAT

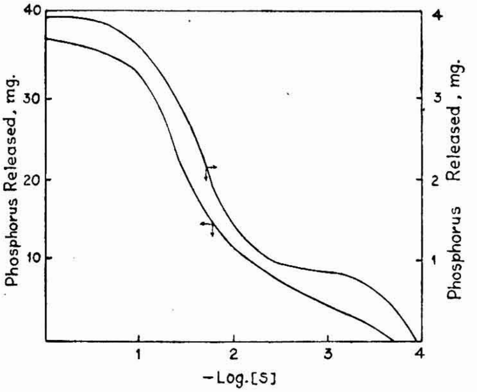

FIG. 3 — EFFECT OF VARYING SUBSTRATE CONCENTRATE ON PYRO AND GLYCEROPHOSPHATASE ACTIVITY

TABLE 4 — EFFECT OF Mg^{++}, Zn^{++} and F^- NO THE ACTIVITIES OF PYRO AND GLYCEROPHOSPHATASES OF RAGI MALT

(Enzyme activity expressed in mg. of P released/g. of powdered grain or malt)

SALTS USED	MOL. CONCENTRATION OF ION IN REACTION MIXTURE	PYROPHOSPHATASE ACTIVITY	GLYCEROPHOSPHATASE ACTIVITY
Nil	nil	16·08	1·54
Zinc sulphate	5×10^{-4}	18·88	1·34
Magnesium sulphate	1×10^{-4}	15·60	1·54
Sodium fluoride	1×10^{-3}	5·20	0·32

Effect of varying substrate concentration — In Fig. 3 are presented the results obtained by varying substrate concentration. From the data the Michaelis-Menton constant Km has been calculated, using the following equation:

$$Km = \frac{([E]-[ES])\ [S]}{[ES]}$$

where [E] and [ES] are the concentrations of the enzyme and enzyme-substrate complex respectively.

When the velocity of reaction is half the maximum

$$[ES] = \frac{[E]}{2} \text{ and } Km = [S]$$

The value of Km has been found to be $16{\cdot}6\times10^{-3}$M for glycerophosphatase and $26{\cdot}92\times10^{-3}$M for pyrophosphatase.

Activation and inhibition of the enzyme activity — Booth[1] reported that the activity of phosphatases of wheat was not affected by Mg ions and was slightly inhibited by F ions. The effect of Zn^{++}, Mg^{++} and F^- ions on the activity of glycero and pyrophosphatases of ragi malt was, therefore, studied. The enzyme extract was dialysed in a

TABLE 5 — INHIBITION OF PYRO AND GLYCEROPHOSPHATASE ACTIVITY BY FLUORIDE ION

(*Enzyme activity expressed in mg. of P released/g. of powdered grain or malt*)

CONCENTRATION OF F^- ADDED (M)	PYROPHOSPHATASE			GLYCEROPHOSPHATASE		
	Enzyme	Activity as % of original	K_F*/K_o	Enzyme	Activity as % of original	K_F*/K_o
0 (control)	3·53	—	$K_o = 4{\cdot}201 \times 10^{-4}$	3·87	—	$K_o = 8{\cdot}405 \times 10^{-4}$
$1{\cdot}0 \times 10^{-4}$	2·72	77	0·786	1·99	51	0·52
$2{\cdot}5 \times 10^{-4}$	2·40	70	0·676	1·25	26	0·34
$7{\cdot}5 \times 10^{-4}$	1·81	51	0·498	0·88	23	0·24

*K_F is velocity coefficient for the fluoride inhibited reaction.

Webcell dialyser for 8 hr. against tap water and for 2 hr. against distilled water and the dialysed extract was used for this study. The results are given in Table 4.

It is evident from the results given in Table 4 that Zn^{++} and Mg^{++} do not affect the activity of the two enzymes to any appreciable extent; on the other hand F^- inhibited the activity of the two enzymes considerably. The effect of different concentrations of fluoride ions on the activity of the enzymes was further studied. The concentrations of the enzymes used in the experiment were so adjusted that the amount of orthophosphate released by pyro and glycerophosphatases was nearly the same. From the data obtained, the velocity of the reaction, K, was calculated (assuming the reaction to be of the first order) by the formula

$$K = \frac{2{\cdot}303}{t} \log \frac{a}{a-x}$$

where a is the initial concentration and a—x the concentration at the end of the time interval t.

The results are given in Table 5.

The results given in Table 5 show that fluoride ion inhibits glycerophosphatase to a greater extent than pyrophosphatase and the enzyme activity is progressively inhibited by increasing the concentration of fluoride ion.

Effect of period of germination on the glycero and pyrophosphatase activities — The effect of germinating ragi for different periods on the pyro and glycerophosphatase activity was investigated. The results are given in Fig. 4. The activities of pyro and glycerophosphatases were found to increase in the grain with the progress of germination.

It is evident from the results obtained in the present investigation that the phosphatases of ragi and its malt have properties similar to those of the phosphatases found in wheat[1,2]. The optimum temperature and *p*H, and critical inactivation temperature for the two enzymes are similar. The two enzymes are not affected by Zn and Mg ions but F ion inhibits considerably the activity of both the enzymes; the glycerophosphatase activity is inhibited to a greater extent.

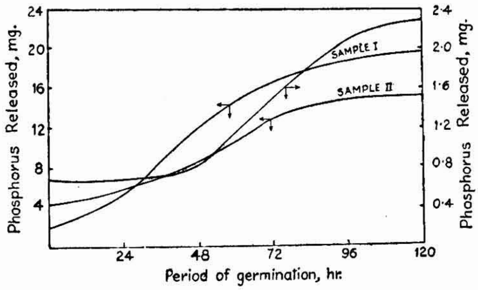

FIG. 4 — EFFECT OF GERMINATION ON PYRO AND GLYCEROPHOSPHATASE ACTIVITY

Summary

1. The glycero and pyrophosphatase activities of ragi (*Eleusine coracana*) have been determined both before and after germination of the grain. The resting grain possessed slight phosphatase activity. Germination of the grain led to a pronounced increase in the activity of both pyro and glycerophosphatases.

2. The two enzymes can be extracted from the powdered grain or malt by M/5 acetate buffer (*p*H 5) or 1 per cent sodium chloride solution. The optimum *p*H was 5·6 for glycerophosphatase and 5·0 for pyrophosphatase.

3. The optimum temperature for the activity of both the enzymes was *c.* 45°C. The critical inactivation temperature for both the enzymes was *c.* 57°C.

4. Magnesium and zinc ions do not affect the activity of the enzymes but fluoride ion strongly inhibits their activity.

Acknowledgement

Our grateful thanks are due to Dr. V. Subrahmanyan, Director, Central Food Technological Research Institute, Mysore, for his keen interest and helpful suggestions during the course of these investigations.

References

1. BOOTH, R. G., *Biochem. J.*, **38** (1944), 355.
2. IGNATIEFF, V. & WASTENEYS, H., *Biochem. J.*, **30** (1936), 1171.
3. LUERS, H. & MALSCH, L., *Wschr. Brau*, **46** (1929), 143.
4. SARMA, M. L. & GIRI, K. V., *Ann. Biochem. exp. Med.*, **2** (1942), 17.
5. CHANDRASEKHARA, M. R. & SWAMINATHAN, M., *J. sci. industr. Res.*, **12B** (1953), 610.
6. CHANDRASEKHARA, M. R. & SWAMINATHAN, M., *Bull. cent. Food technol. Res. Inst.*, **2** (1953), 212.
7. FISKE, C. H. & SUBBA RAO, Y., *J. biol. Chem.*, **66** (1925), 375.

Stability of Added Vitamin A Acetate in Groundnut Oils

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The stability of vitamin A acetate in crude and refined groundnut oils and in blended and straight-hardened hydrogenated groundnut oils has been studied. Straight-hardened groundnut oil retains the maximum amount of vitamin A both at 37·5° and 60°C., refined oil retaining the least. Ethyl gallate affords a small but significant degree of protection to vitamin A acetate in all the samples. Vitamin A acetate promotes instability of the oils which, however, is counteracted to some extent by ethyl gallate. Rancidity (smell) is, however, not appreciably promoted by vitamin A acetate.

Both crude and hydrogenated sesame oil stabilize vitamin A added to hydrogenated groundnut oil. With refined sesame oil the stability of vitamin A is less. The addition of ethyl gallate is beneficial in all the cases.

Vitamin A acetate in hydrogenated groundnut oil, subjected to ordinary heating and cooking, is protected to some extent by ethyl gallate.

FORTIFICATION of various foods and food products with vitamin A is now accepted as an important step in enhancing their nutritive value. Some work has been done on vitamin A enrichment of margarine[1-4] and edible oils[5-8]. In all these investigations, the source of vitamin A was marine fish oil concentrates. The fishy odour of these concentrates is often a drawback in their large-scale use in edible oils and fats. Synthetic vitamin A, which promises to be available in bulk quantities in the near future, is free from this objectionable odour, and its use for fortifying edible oils and fats in place of fish oil concentrates deserves attention. The stability of vitamin A acetate in crude and refined groundnut oils and in blended and straight-hardened hydrogenated groundnut oils under different conditions has been investigated and the results of these investigations are reported in this paper.

Materials and methods

Crude, refined and hydrogenated (m.p. 37°C.) groundnut oils and blended (1 part hydrogenated, m.p. 55°C., and 5 parts refined oil were mixed to give a m.p. of 37°C. to the product) hydrogenated groundnut oil were employed in these studies. The characteristics of the oils are recorded in Table 1. Samples (100 g. each) of the oil

TABLE 1 — CHARACTERISTICS OF THE OILS

GROUNDNUT OIL	PEROXIDE VAL. CC. N/500 THIOSULPHATE/G.	ACID VAL.	SAP. VAL.	IOD. VAL.
Crude	2·4	2·02	193·0	91·35
Refined	4·0	0·82	195·5	91·94
Straight-hardened	0·1	0·21	185·4	61·46
Blended	2·9	0·30	189·6	76·25

were stored in loosely covered 1 lb. new tin cans after adding vitamin A acetate at two different levels (30 and 100 I.U./g.). One I.U. of vitamin A was taken to be equivalent to 0·34 γ of crystalline vitamin A acetate (Hoffman-La Roche). The cans were stored at 37·5° and 60°C.; the latter temperature was employed to accelerate the deterioration of vitamin A. Samples containing 0·005 per cent ethyl gallate as antioxidant were similarly stored. Liquid paraffin (Merck) was chosen as the inert vehicle for vitamin A. The peroxide value (cc. of N/500 thiosulphate/g. oil) was determined at different intervals. The acid, saponification and iodine values of the samples were determined according to the method recommended by the American Oil Chemists' Society[9]. The vitamin A content of the samples was measured by the ultraviolet absorption method[10]. A Lumetron photoelectric colorimeter with a filter combination, supplied by the Photovolt Corporation, New York, and which isolates the specific absorption band of vitamin A, was employed. This procedure gives reliable values which are comparable to the values obtained with the Beckmann spectrophotometer (TABLE 2).

Results and discussion

The results of stability tests are recorded in Table 3. The results show that straight-hardened hydrogenated groundnut oil retains the maximum amount of vitamin A acetate both at 37·5° and 60°C. while the refined oil retains the least amount. The retention of vitamin A acetate is slightly better in crude oil than in blended hydrogenated oil. Ethyl gallate affords significant protection to vitamin A acetate in all the samples, though the degree of protection is small.

Vitamin A acetate promotes the instability of the oils which, however, is

TABLE 2 — ESTIMATION OF VITAMIN A WITH LUMETRON PHOTOELECTRIC COLORIMETER AND BECKMANN SPECTROPHOTOMETER

SOLN.	μG. VITAMIN A ACETATE/CC.	
	Lumetron photoelectric colorimeter	Beckmann spectrophotometer
1	0·40	0·38
2	0·47	0·45
3	0·60	0·55
4	1·40	1·36
5	2·40	2·33

TABLE 3 — STABILITY OF VITAMIN A ACETATE IN DIFFERENT MEDIA WITH AND WITHOUT ETHYL GALLATE

SAMPLE	VITAMIN A ACETATE (I.U./G.) AFTER							PEROXIDE VAL. AFTER							RANCIDITY* AFTER					
	Initial val.	60°C.			37·5°C.			Initial val.	60°C.			37·5°C.			60°C.			37·5°C.		
		7 days	14 days	21 days	14 days	29 days	59 days		7 days	14 days	21 days	14 days	29 days	59 days	7 days	14 days	21 days	14 days	29 days	59 days
Crude oil	100	69·5	17·7	0·0	66·6	37·3	5·1	2·4	7·1	13·0	32·9	4·7	6·7	30·9	S	S	R	F	S	R
Crude oil + E.G.	100	75·9	34·4	14·4	70·1	39·0	8·6	2·4	3·2	15·4	28·4	2·5	2·8	12·9	F	S	R	F	F	R
Crude oil	30	16·0	3·5	0·0	19·0	13·1	0·0	2·4	10·9	20·0	37·8	5·1	9·1	27·7	F	S	R	F	F	R
Crude oil + E.G.	30	21·1	16·2	9·2	20·5	15·0	3·5	2·4	4·6	15·7	32·2	3·9	8·4	8·8	F	S	S	F	F	V.S.
Refined oil	100	57·0	0·0	0·0	63·6	31·6	1·7	4·0	14·7	27·7	30·8	8·0	11·6	49·0	S	R	R	S	S	R
Refined oil + E.G.	100	62·1	26·8	5·1	66·9	37·2	7·0	4·0	5·7	12·9	15·4	4·9	5·3	6·6	F	S	R	F	S	R
Refined oil	30	17·3	0·0	0·0	20·3	12·5	0·0	4·0	21·7	41·3	118·3	6·1	6·7	48·6	S	S	R	S	S	R
Refined oil + E.G.	30	20·1	10·2	0·0	24·0	17·3	3·5	4·0	8·1	12·6	57·1	4·2	4·6	26·2	F	S	S	S	S	R
St.-hardened oil	100	61·2	10·4	10·4	77·0	50·3	17·8	0·1	1·2	3·5	6·9	0·8	1·4	2·8	F	V.S.	V.S.	F	F	V.S.
St.-hardened oil + E.G.	100	80·4	68·3	12·1	80·1	53·1	17·8	0·1	0·2	0·2	4·2	0·3	1·0	1·5	F	F	F	F	F	F
St.-hardened oil	30	20·0	19·2	8·6	22·1	17·0	10·2	0·1	0·2	0·4	3·5	0·6	1·5	3·2	F	V.S.	V.S.	F	F	V.S.
St.-hardened oil + E.G.	30	26·1	7·9	3·5	24·1	19·0	13·5	0·1	0·1	0·1	0·1	0·3	1·0	1·4	F	F	V.S.	F	F	F
Blended oil	100	60·0	3·5	0·0	68·9	32·7	1·7	2·9	10·6	19·3	58·8	7·7	15·1	33·6	F	V.S.	S	F	V.S.	V.S.
Blended oil + E.G.	100	77·1	30·4	10·5	70·0	35·1	8·6	2·9	5·5	8·1	8·9	4·8	7·7	9·8	F	V.S.	V.S.	F	V.S.	V.S.
Blended oil	30	11·9	6·0	0·0	18·7	8·2	0·0	2·9	24·0	35·2	153·3	7·2	12·6	25·9	F	V.S.	S	F	V.S.	S
Blended oil + E.G.	30	18·3	12·1	6·3	18·9	10·7	7·0	2·9	5·1	8·1	13·7	10·1	6·5	8·7	F	V.S.	V.S.	F	V.S.	V.S.
Liquid paraffin	100	73·0	49·3	20·3	79·1	58·8	33·0	0·0	0·0	0·1	0·0	0·1	0·0	0·0	—	—	—	—	—	—
Liquid paraffin + E.G.	100	77·1	49·9	21·1	79·5	60·2	37·2	0·0	0·1	0·0	0·1	0·0	0·0	0·0	—	—	—	—	—	—
Liquid paraffin	30	21·2	15·3	8·7	22·2	17·0	12·2	0·0	0·0	0·1	0·0	0·0	0·1	0·0	—	—	—	—	—	—
Liquid paraffin + E.G.	30	23·2	17·0	9·0	24·0	17·5	14·1	0·0	0·0	0·1	0·0	0·0	0·1	0·1	—	—	—	—	—	—

E.G., ethyl gallate; F, oil had the aroma of fresh oil; V.S., very slight rancidity; S, slight rancidity; R, appreciable rancidity.
*The oils at the start of experiment had the aroma of fresh oil.

counteracted to an appreciable extent by ethyl gallate. Rancidity (as detected by smell) is, however, not promoted appreciably by vitamin A acetate. Vitamin A being an easily oxidizable compound might have been expected to prevent the oxidation of fat thus acting as an antioxidant, but divergent opinions are held by different workers. Herisset[11] is of the opinion that vitamin A is anti-oxygenic, but Chevallier[12] observed that it is slightly pro-oxygenic. Monaghan and Schmitt[13] reported that vitamin A in small concentrations completely inhibited the oxygen uptake by linoleic acid and this inhibition wore off when vitamin A was destroyed by oxidation. In the present case, vitamin A appears to act in a pro-oxygenic manner thereby promoting the instability of oil and vanaspati.

Effect of adding sesame oil to hydrogenated groundnut oil on the stability of added vitamin A acetate — It is compulsory to add sesame oil to vanaspati before it is marketed. It was, therefore, of interest to examine the effect of adding sesame oil (crude, refined and hydrogenated) on the stability of added vitamin A in vanaspati.

To all the samples of oils, vitamin A at a level of 30 I.U./g. was added and the samples stored as before. Similarly samples containing ethyl gallate (0·01 per cent) were also prepared and stored. The characteristics of the oil samples before storage are given in Table 4. The stored samples were analysed at intervals and the results of analysis are given in Table 5.

TABLE 4 — CHARACTERISTICS OF THE SESAME OIL SAMPLES

OIL SAMPLE	IOD. VAL.	PEROXIDE VAL.	ACID VAL.	SAP. VAL.
Crude sesame oil	111·8	1·7	2·70	190·5
Refined sesame oil	104·3	3·7	0·27	188·1
Hydrogenated sesame oil, m.p. 37°C.	84·7	0·0	0·23	187·0
Hydrogenated groundnut oil, m.p. 37°C.	66·6	0·0	0·27	192·0

TABLE 6 — EFFECT OF HEATING ENRICHED VANASPATI WITH AND WITHOUT ETHYL GALLATE

(*Vitamin A*, 30 *I.U./g.*)

HEATING TIME min.	TEMP. °C.	VITAMIN A AFTER HEATING (I.U./g.)		LOSS %	
		Without ethyl gallate	With ethyl gallate	Without ethyl gallate	With ethyl gallate
2	110	28	30	6·7	0·0
5	110	20	28	33·3	6·7
2	150	20	27	33·3	10·0
5	150	15	21	50·0	30·0
2	200	17	24	42·3	20·0
5	200	10	14	66·7	52·3
2	250	9	15	70·0	50·0
5	250	0	9	100·0	70·0

It is clear from the results in Table 5 that addition of crude and hydrogenated sesame oil to vanaspati stabilizes vitamin A present to the same extent. Refined oil retains a lesser amount of vitamin than crude or hydrogenated oil. It appears that the natural antioxidants in crude oil and saturation of some of the double bonds in hydrogenated oil are responsible for greater stability of vitamin A in their presence. As observed earlier, vitamin A tends to increase the peroxide value of the oils which is counteracted to some extent by ethyl gallate.

Stability of vitamin A acetate in vanaspati during heating and cooking — Hydrogenated groundnut oil (m.p. 37°C., 100 g.) containing 30 I.U. of vitamin A acetate and with and without ethyl gallate (0·01 per cent) was heated (without stirring but with gentle shaking) in an open pyrex beaker in an oil bath at different temperatures and for different periods. Samples were withdrawn at intervals, cooled rapidly and analysed for

TABLE 5 — STABILITY OF VITAMIN A IN VANASPATI SAMPLES CONTAINING SESAME OIL WITH AND WITHOUT ETHYL GALLATE

(*Storage temp.*, 37°C.)

ADDITIVE	PEROXIDE VAL. AFTER weeks							VITAMIN A IN VANASPATI AFTER weeks							RANCIDITY IN VANASPATI AFTER 14 WEEKS
	0	2	4	6	10	12	14	0	2	4	6	10	12	14	
Crude oil	0·1	0·1	0·3	1·0	1·7	2·5	3·1	30	26	20	17	15	13	12	nil
Crude oil + ethyl gallate	0·1	0·1	0·2	0·3	1·0	1·7	2·5	30	26	22	18	17	16	16	Slight
Refined oil	0·2	0·4	0·7	1·0	2·4	2·8	4·2	30	22	15	11	8	8	7	do
Refined oil + ethyl gallate	0·2	0·3	0·3	0·7	1·4	1·7	2·8	30	25	22	18	13	11	11	do
Hardened oil, m.p. 37°	nil	nil	0·3	1·0	1·4	1·5	2·5	30	27	21	17	14	12	11	nil
Hardened oil + ethyl gallate	nil	nil	nil	0·3	1·0	1·4	2·0	30	28	23	19	17	16	16	Slight

TABLE 7 — VITAMIN A LOSS IN VANASPATI DURING COOKING

(30 *I.U./g. vitamin A*)

ITEMS	INITIAL TEMP. °C.	VITAMIN A INITIALLY PRESENT IN VANASPATI		VITAMIN A IN FOOD PREPARED		VITAMIN A LEFT IN THE OIL		LOSS %	
		Without ethyl gallate	With ethyl gallate	Without ethyl gallate	With ethyl gallate	Without ethyl gallate	With ethyl gallate	Without ethyl gallate	With ethyl gallate
*Luchi**	200	9000	9000	1360	1570	6910	7550	19·0	10·5
Haluwa†	200	900	900	640	780	—	—	29·0	13·3
Potato chips‡	200	900	900	320	375	400	440	20·0	9·5

*Flour + water + oil (5: 2: 1) made into dough, 25 g. of which made into a sheet of 4 in. diam.
†*Suji* 30 g. + sugar 25 g. + oil 30 g. + water.
‡Slices of area *c.* 1 sq. in. and thickness *c.* 1/16 in.; 30 g.

vitamin A. Cooking experiments were carried out in a small iron pan.

It will be seen from Table 6 that longer the duration of heating and higher the temperature of heating, greater is the destruction of vitamin A in enriched vanaspati. Ethyl gallate affords protection to vitamin A both during ordinary heating and cooking (TABLE 7).

Summary

1. Among crude, refined, straight-hardened and blended hydrogenated groundnut oils tested, straight-hardened oil retains the maximum amount of vitamin A both at 37·5° and 60°C. and refined oil the least.

2. Ethyl gallate affords a small but significant degree of protection to vitamin A acetate in all samples.

3. Vitamin A acetate promotes instability of the oils, which, however, is counteracted to some extent by ethyl gallate.

4. Rancidity of the samples is not appreciably promoted by vitamin A acetate.

5. Vitamin A added to vanaspati is stabilized to the same extent by crude and hydrogenated sesame oil. The stability of vitamin A is lessened when refined sesame oil is used. Addition of ethyl gallate is beneficial in all cases.

6. The longer the duration and higher the temperature of heating, the greater the destruction of vitamin A. Ethyl gallate affords protection to vitamin A both during ordinary heating and cooking.

Acknowledgement

Grateful thanks are due to Prof. B. C. Guha for his kind interest in the work, to the Hindusthan Vanaspati Manufacturing Co. Ltd., Bombay, for the generous supply of samples of groundnut and sesame oils, to Volkart Brothers, Bombay, for a gift of crystalline vitamin A acetate (Hoffmann La-Roche) used in this investigation and to the Council of Scientific & Industrial Research for a grant.

References

1. HAWK, *Amer. Food J.*, **19** (1924), 379.
2. VAHLTEICH, H. W., *Food Ind.*, **13**(6) (1941), 39; *J. Amer. chem. Soc. (News Ed.)*, **21** (1943), 1238.
3. BASU, U. P. & ROY, N., *Sci. & Cult.*, **13** (1947), 73.
4. FEIGENBAUM, J., *Nature*, **157** (1946), 770.
5. ORGANON, N. W., *Dutch Pat.* 45193 (1939).
6. BASU, U. P., *Ann. Biochem. exp. Med.*, **1** (1941), 165.
7. BASU, U. P. & SEN GUPTA, J. C., *Curr. Sci.*, **10** (1941), 288.
8. HOLMES, A. D. & MANDELEINE, G. P., *J. Amer. phar. Ass.*, **31** (1942), 521.
9. *Official and Tentative Methods* (American Oil Chemists' Society), 1946, ca, 5-40; cd, 3-25; cd, 1-25.
10. Association of Vitamin Chemists, *Methods of Vitamin Assay* (Interscience Publishers, New York), 1951, 34.
11. HERISSET, A., *Bull. Soc. chim. Biol.*, **30** (1948), 187; *C.R. Acad. Sci., Paris*, **223** (1946), 47.
12. CHEVALLIER, A., BURG, C. & MANUEL, S., *C.R. Acad. Sci. Paris*, **226** (1948), 2098.
13. MONAGHAN, B. R. & SCHMITT, F. O., *J. biol. Chem.*, **96** (1923), 387.

Trypsin Inhibitors in Indian Foodstuffs: Part I—Inhibitors in Vegetables

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Of the 65 vegetables tested, trypsin inhibitors were found to be present in 11. The properties of the inhibitors obtained from different sources, viz. precipitability with alcohol, acetone and ammonium sulphate, solubility in trichloracetic acid, heat stability and dialysability, show that they are different from one another.

THE presence of a trypsin inhibitor in soyabeans was first reported by Ham and Sandstedt[1]. Borchers and Ackerson[2] found that the trypsin inhibitor was entirely absent in non-leguminous seeds, while it was present in some of the leguminous seeds. The trypsin inhibitors from soyabeans, navy beans and lima beans have been crystallized and their physical and chemical properties have been studied in detail[3-10]. Jaffé[11] has studied the protein digestibility and trypsin inhibitor activity of leguminous seeds.

While studying the digestibilities of certain Indian pulses, Gaitonde and Sohonie[12,13] found that the proteins of field bean (*Dolichos lablab*) were resistant to digestion with trypsin. Further studies on this subject revealed the presence of a trypsin inhibitor in field bean. The presence of trypsin inhibitor in three more pulses was also reported by them.

Kendall and Touchberry[14] found a trypsin inhibitor in soyabean forage only at the onset of seed formation. They also observed that trypsin activity upon casein was retarded by the vegetative portion of green soyabean plants, from which seeds had been removed. Trypsin activity was inhibited more by seed extracts than by leaf or stem extracts. The concentration of the inhibitory factor increased as the plant matured. Kendall[15] also observed the presence of a trypsin inhibitor in alfa-alfa and ladino clover. Besides these, there is no reference in literature to the presence of trypsin inhibitor in other green plants. The present investigation was, therefore, undertaken with a view to test various vegetables for the presence of trypsin inhibitor and study their behaviour.

Experimental procedure

Sixty-five vegetables were examined for the presence of the trypsin inhibitor. These included 16 root vegetables, 5 stem vegetables, 13 leaf vegetables, 2 flower vegetables and 29 fruit vegetables. Three samples of each vegetable purchased from 3 different local markets were used in each case.

The edible part of each vegetable (100 g.), was washed to remove adhering dirt particles, cut into small pieces and blended with 100 cc. of 0·05N hydrochloric acid for 2 min. to give a uniform suspension. The suspension was transferred to a 250 cc. beaker and kept at room temperature for 1 hr., with occasional stirring, for the extraction of the inhibitor. At the end of 1 hr., the suspension was squeezed through muslin cloth. Five cc. of the suspension were taken and after adjusting the *p*H to 7·7 was diluted to 15 cc.; 3 cc. of the diluted suspension were used for the experiment.

The formal titration method was followed for the detection of the inhibitor. The reaction mixture consisting of 4 cc. of 5 per cent gelatin solution + 3 cc. of the diluted vegetable extract + 1 cc. of 2 per cent trypsin solution after adjusting the *p*H to 7·7 was incubated at 37°C. for 1 hr. Controls without the test extract and those to which neutral formaldehyde was added before the addition of the enzyme were run, side by side. At the end of 1 hr., the reaction was stopped by the addition of 1 cc. of neutral formaldehyde. These reaction mixtures were titrated against 0·05N sodium hydroxide using phenolphthalein as indicator. The presence of the inhibitor in the extract is indicated when the reaction mixtures with the vegetable extracts gave a titre value lower than that obtained without the test extracts.

Of the 16 root vegetables investigated, kone, sweet potato, taro roots and turnips contained the inhibitor. Among the 5 stem vegetables investigated, potato contained the inhibitor. Of the 29 fruit vegetables examined, the inhibitor was found in Bengal gram, cowpea, double bean, field bean, Goa bean and red gram. It was absent in leafy and other vegetables.

In the case of turnips, the inhibitor was found to be present in the crop grown during October, November and December months, and was absent in crops grown in other months of the year.

The tender legumes of field beans, Goa bean and cowpea did not show the presence of the inhibitor. However, when the legumes mature and the seeds are formed, the inhibitor makes its appearance. The inhibitor was found to be present only in the seeds and was absent in the outer coverings of the legumes.

Concentration of the inhibitor — The hydrochloric acid extracts of the vegetables obtained after squeezing through muslin cloth were centrifuged for 15 min. at 2,000 r.p.m. The supernatant was treated as follows: Ethyl alcohol or acetone was added to the hydrochloric acid extract in the ratio 5 : 1 by volume. The precipitate obtained was centrifuged for 5 min. at 2,000 r.p.m. The precipitate was taken up with distilled water, the volume taken being equal to the original hydrochloric acid extract. The suspension was filtered and the filtrate tested for inhibitor activity.

Solubility of the alcohol precipitated inhibitor in trichloracetic acid — The precipitate obtained after treating an aliquot of the extract with alcohol or acetone was treated with 2·5 per cent trichloracetic acid, the volume of the acid taken being equal to that of the original hydrochloric acid extract. The precipitate was mixed with trichloracetic acid and the flask containing the mixture kept in boiling water bath for 5 min., filtered and the filtrate tested for inhibitor activity.

Dialysis — The hydrochloric acid extract was dialysed overnight in a cellophane bag under running tap water. The supernatant liquid and the precipitate were separately tested for the inhibitor.

The purification of the inhibitors achieved by these methods is shown in Tables 1 and 2.

Estimation of inhibitor activity—The activity of the inhibitor is expressed in terms of the trypsin inhibitor units described by Borchers *et al.*[9].

The activity of the inhibitor was estimated as follows: The reaction mixture consisting of 5 cc. of 5 per cent skimmed milk + 1 cc. of the test extract + 1 cc. of water + 1 cc. of 2 per cent trypsin solution was adjusted to *p*H 7·7 and incubated at 37°C. for 10 min. Immediately after the addition of the enzyme 1 cc. of the reaction mixture was pipetted out and added to 10 cc. of the 2·5 per cent trichloracetic acid solution, the rest of the reaction mixture being incubated. After 10 min. incubation, the undigested protein was precipitated with 10 cc. of 2·5 per cent trichloracetic acid. Controls were run side by side. The reaction mixtures were allowed to stand for 30 min. and then filtered. To an aliquot (0·4 cc.) of the filtrate 10 cc. of 0·5N sodium hydroxide solution was first added and then 3 cc. of phenol reagent of Folin and Ciocalteu[16] (diluted 3 times) was added to give a blue colour with the liberated tyrosine. The test-tubes in which the colour was developed were allowed to stand for 10 min. and the intensity of the

TABLE 1 — CONCENTRATION OF INHIBITORS BY PRECIPITATION WITH ALCOHOL OR ACETONE

(*Activity expressed in inhibitor units* × 10^{-6}*/mg. of dry weight of the material*)

VEGETABLE	HCl EXTRACT	ALCOHOL PPT.	ALCOHOL PPT. + CCl_3COOH	ACETONE PPT.	ACETONE PPT. + CCl_3COOH
Bengal gram	45·4	490·1	640·4	146·1	221·9
Cowpea	72·7	1458·0	nil	388·7	207·7
Double bean	77·1	192·8	2121·0	209·2	2832·0
Field bean	80·2	535·6	737·9	226·9	266·2
Goa bean (*Psophocarpus tetragonobolus* DC.)	126·6	590·7	381·7	2643·0	375·1
Kone	451·6	2640·0	1426·0	883·3	560·8
Potato	337·6	nil	nil	3886·0	nil
Red gram (*Cajanus cajan* Linn. Mill sp.)	99·5	1074·0	469·9	667·9	296·8
Sweet potato	212·3	nil	nil	5967·0	nil
Taro roots	159·1	12680·0	763·7	2075·0	768·3
Turnip	71·6	510·2	131·7	4883·0	706·0

TABLE 2 — CONCENTRATION OF INHIBITORS BY DIALYSIS

(*Activity expressed in inhibitor units* $\times 10^{-6}$*/mg. of dry weight of the material*)

VEGETABLE	HCl EXTRACT	DIALYSED EXTRACT	
		Supernatant	Ppt.
Bengal gram	144·3	2372·0	nil
Cowpea	31·2	1400·0	*
Double bean	170·6	433·4	nil
Field bean	75·0	1465·0	nil
Goa bean (*Psophocarpus tetragonobolus* DC.)	279·7	1484·0	nil
Kone	270·2	552·9	nil
Potato	602·2	2523·0	†
Red gram (*Cajanus cajan* Linn. Mill sp.)	249·7	7731·0	nil
Sweet potato	138·8	1017·0	nil
Taro roots	97·7	505·4	nil
Turnip	159·4	774·1	nil

*About 12% activation of trypsin.
†About 21% activation of trypsin.

TABLE 3 — EFFECT OF HEATING AND AUTOCLAVING ON THE ACTIVITY OF THE INHIBITOR

(*Values expressed in percentages of the original activity*)

VEGETABLES	% DESTRUCTION AFTER HEATING FOR min.				
	15	30	45	60	Auto-claved
Bengal gram	21·4	50·0	64·3	85·7	90·4
Cowpea	47·1	52·9	58·8	64·7	83·3
Double bean	nil	nil	nil	nil	nil
Field bean	3·3	3·3	3·3	3·3	31·4
Goa bean	1·0	1·0	1·0	2·1	61·0
Kone	nil	nil	nil	nil	66·7
Potato	97·8	97·8	97·8	97·8	100·0
Red gram	nil	nil	nil	nil	83·3
Sweet potato	72·7	100·0	100·0	100·0	100·0
Taro roots	83·3	83·3	86·7	90·0	100·0
Turnip	nil	nil	nil	3·2	100·0

colour compared in a Klett-Summerson photoelectric colorimeter using a green filter.

Separation of the inhibitor by saturation with ammonium sulphate was carried out with a view to find out the saturation of ammonium sulphate at which the inhibitor is precipitated. Three saturations, namely half, three-fourth and full saturation, were tried.

The inhibitors from Bengal gram, double bean, Goa bean, kone, potato, sweet potato, taro roots and turnips are precipitated at half saturation, that from field bean at three-fourth saturation and those from cowpea and red gram at full saturation of ammonium sulphate.

Stability of the inhibitor towards heat — The different extracts were heated in a boiling water bath for different intervals and the percentage trypsin inhibiting activity of the heat-treated extracts was measured.

In another set of experiments the original hydrochloric acid extract was autoclaved at 15 lb. pressure for 30 min. and the autoclaved extract tested.

The percentage destruction of the inhibitor by heating in the water bath and on autoclaving is given in Table 3.

Discussion

It is clear from the results given in Tables 1-3 that the inhibitors from different vegetables differ in their properties. Inhibitors from all the vegetables with the exception of those from potato and sweet potato are precipitated by alcohol. The activity of the precipitated inhibitor from different vegetables was 5-80 times the original activity of the extract. On treating the alcohol precipitated inhibitor with trichloracetic acid, the activity of inhibitors from different vegetables, with the exception of those from Bengal gram, double bean and field bean, shows a decrease. This might be due either to partial destruction of the inhibitor or its low solubility in trichloracetic acid. Acetone appears to be a better precipitating agent than alcohol for the inhibitor present in double bean, Goa bean, potato, sweet potato and turnip. The activity of the precipitated inhibitor from these vegetables was enhanced 20, 12, 28 and 68 times respectively of the original activity of the extract. In all these cases, however, a decrease in the activity of the inhibitor is observed, except in the case of double bean, on treating the acetone precipitated inhibitor with trichloracetic acid. In the case of potato and sweet potato complete absence of the inhibitor is observed.

The inhibitors from Bengal gram, cowpea, potato, sweet potato and taro roots are destroyed, partially in the case of cowpea and Bengal gram and completely in the case of others, on heating in a boiling water bath for 1 hr. The inhibitors from double bean, field bean, Goa bean, kone, red gram and turnip are not affected. On autoclaving, the inhibitors from field bean, Goa bean, kone, red gram and turnip are destroyed to the extent of 31·4, 61·0, 66·7, 88·3 and 100 per cent respectively. The inhibitor from double bean is extremely stable.

The inhibitors from all the vegetables examined are found to be non-dialysable, since on dialysis the activity of the inhibitor is retained in the supernatant. Bowman[5] showed that the trypsin inhibitor of navy bean is quite distinct from the crystalline soyabean inhibitor of Kunitz[7]. Tauber *et al.*[10] isolated a trypsin inhibitor from lima beans which was shown to be a globulin and resembled somewhat the soyabean inhibitor but differed from it in its complete thermostability. The double bean inhibitor studied by us appears to resemble closely the lima bean inhibitor. Lineweaver and Murray[17] and Fredericq and Deutsch[18] crystallized a trypsin inhibitor from egg white and showed it to be different from soyabean inhibitor. The presence of two inhibitors in soyabean, one which can be extracted with 60 per cent alcohol and precipitated with acetone and the other which can be extracted with water and precipitated with 60 per cent alcohol, has been demonstrated by Bowman[4]. Laskowski (Jr.) and Laskowski[19] crystallized the trypsin inhibitor from colostrum and Laskowski (Jr.), Mars and Laskowski[20] differentiated it from the inhibitors from soyabean and egg white. Green and Work[21] isolated two inhibitors from pancreas, which can be differentiated from each other, one being dialysable and the other non-dialysable. From the results presented in Tables 1-3 it appears that the inhibitors from potato and sweet potato are similar. The inhibitor from double bean forms a group by itself by its extreme thermostability. The inhibitors from field bean, Goa bean, kone, red gram and turnip resemble each other in respect of their complete thermostability at water bath temperature and partial thermostability on autoclaving.

Summary

1. Trypsin inhibitors are found to be present in the following 11 vegetables: Bengal gram, cowpea, double bean, field bean, Goa bean, kone, potato, red gram, sweet potato, taro roots and turnip.

2. In leguminous vegetables, the inhibitor is located only in the seeds. The inhibitor is absent in legumes in which the seeds are not developed.

3. The inhibitor in turnips shows seasonal variation; it is present only in some months during the year.

4. The inhibitors are precipitated by alcohol except in the cases of potato and sweet potato.

5. Acetone is a better precipitant than alcohol.

6. All the inhibitors isolated are non-dialysable and the inhibitory activity is retained in the supernatant.

7. Inhibitors from Bengal gram, double bean, Goa bean, kone, potato, sweet potato, taro roots and turnip are precipitated at half saturation of ammonium sulphate, from field bean at three-fourth saturation and from cowpea and red gram at full saturation.

8. Inhibitors from Bengal gram, cowpea, potato, sweet potato and taro roots are destroyed by heating at 100°C. for 1 hr., whereas the inhibitors from double bean, field bean, Goa bean, kone, red gram and turnip are stable. Autoclaving destroys most of the inhibitors with the exception of double bean inhibitor.

Acknowledgement

We wish to express our thanks to the Council of Scientific & Industrial Research for financial assistance and for a personal grant to one of us (A.P.B.).

References

1. Ham, W. E. & Sandstedt, R. M., *J. biol. Chem.*, **154** (1944), 505.
2. Borchors, R. & Ackerson, C. W., *Arch. Biochem.*, **13** (1947), 291.
3. Bowman, D. E., *Proc. Soc. exp. Biol. Med.*, **57** (1944), 139.
4. Bowman, D. E., *Proc. Soc. exp. Biol. Med.*, **63** (1946), 547.
5. Bowman, D. E., *Arch. Biochem.*, **16** (1948), 109.
6. Kunitz, M., *J. gen. Physiol.*, **29** (1946), 149.
7. Kunitz, M., *J. gen. Physiol.*, **30** (1947), 291.
8. Almquist, H. J. & Merrit, J. B., *Arch. Biochem. Biophy.*, **31** (1951), 450.
9. Borchers, R., Ackerson, C. W. & Sandstedt, R. M., *Arch. Biochem.*, **12** (1947), 367.
10. Tauber, H., Kershaw, B. B. & Wright, R. D., *J. biol. Chem.*, **179** (1949), 1155.
11. Jaffé, W. G., *Proc. Soc. exp. Biol. Med.*, **75** (1950), 219.
12. Gaitonde, M. K. & Sohonie, K., *Curr. Sci.*, **20** (1951), 217.
13. Gaitonde, M. K. & Sohonie, K., *J. sci. industr. Res.*, **11** (1952), 339.
14. Kendall, K. A. & Touchberry, R. W., *J. Anim. Sci.*, **11**(2) (1952).
15. Kendall, K. A., *J. Dairy Sci.*, **34** (1951), 499.
16. Folin, O. & Ciocalteu, J., *J. biol. Chem.*, **73** (1927), 627.
17. Lineweaver, H. & Murray, C. W., *J. biol. Chem.*, **171** (1947), 565.
18. Fredericq, E. & Deutsch, H. F., *J. biol. Chem.*, **181** (1949), 499.
19. Laskowski, M. (Jr.) & Laskowski, M., *J. biol. Chem.*, **190** (1951), 563.
20. Laskowski, M. (Jr.), Mars, P. H. & Laskowski, M., *J. biol. Chem.*, **198** (1952), 745.
21. Green, N. M. & Work, E., *Biochem. J.*, **54** (1953), 257.

The Metabolic Products of *Penicillium fellutanum**

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Four acidic mould metabolic products, which are derivatives of tetronic acid, have been isolated from the metabolism solution of ***Penicillium fellutanum*****. The cultural methods for the production of these substances, the chemical methods used for their isolation and purification and their general properties have been described.**

THE mould *Penicillium fellutanum*, when grown on Czapek-Dox solution, makes the culture medium strongly acid, reduces potassium permanganate instantly in the cold and gives an intense orange-red colour with ferric chloride. In view of similar observations recorded for *Penicillium charlesii* G. Smith[1] from which five tetronic acid derivatives were isolated, it was of interest to investigate the metabolic products of *P. fellutanum*.

Experimental procedure

The organism used in this investigation was a strain of *Penicillium fellutanum* (TRL 1014), received from Timber Research Laboratories, South Africa, and identified in the Department of Biochemistry, London School of Hygiene and Tropical Medicine, by Mr. G. Smith. The mould was grown on Czapek-Dox medium.

Cultivation of P. fellutanum in the routine metabolism investigation — Fifty 1 litre conical flasks were inoculated with the spore suspension made from *P. fellutanum* cultures grown for 2-3 weeks on beer wort agar slopes.

The flasks were incubated at 24°C. for 28 days, when practically all the sugar had disappeared from the culture medium.

Isolation of metabolic products — At the end of 28 days of incubation the metabolic solution was filtered. The metabolic products were separated into a number of fractions which were later examined individually. The general scheme of this fractionation is shown in the flow sheet.

Results

After the removal of polysaccharides by precipitation with an excess alcohol, the concentrated metabolism solution was first extracted with ether and then with chloroform. From the ether extract of the metabolism solution three crystalline products were isolated. The identity of these products was established by their general chemical properties and by melting point and mixed melting points with the corresponding authentic samples as:

(A) Carolic acid (m.p. 132°-33°C.; reset m.p. 113°-14°C.) (I, $R = -CH$; $X = -CO.CH_2.CH_2.CH_2OH$)[1,2]

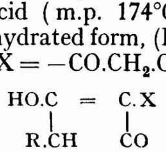
(B) Carlosic acid (m.p. 179°-80°C.; reset m.p. 179°-80°C.) (I, $R = -CH_2COOH$; $X = -CO.CH_2.CH_2.CH_3$)[1,3]

(C) 1-γ-Methyl tetronic acid (m.p. 114°-15°C.) (I, $R = -CH_3$; $X = H$)[4]

The chloroform extract of the ether extracted metabolism solution gave two crystalline products. These were also identified by their general chemical properties, melting point and mixed melting points as:

(A) Carolic acid (m.p. 132°-33°C.; reset m.p. 113°-14°C.)

(D) Carlic acid (m.p. 174°C.; reset to a gum) [hydrated form, (I) $R = -CH_2.COOH$; $X = -CO.CH_2.CH_2.CH_2OH$][1,3]



(I)

The yields obtained were: carolic acid, 23·0; carlic acid, 2·8; carlosic acid, 0·16; and 1-γ-methyl tetronic acid, 1·9 g.

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*The work reported forms a part of the Ph.D. thesis presented to the University of London, 1951.

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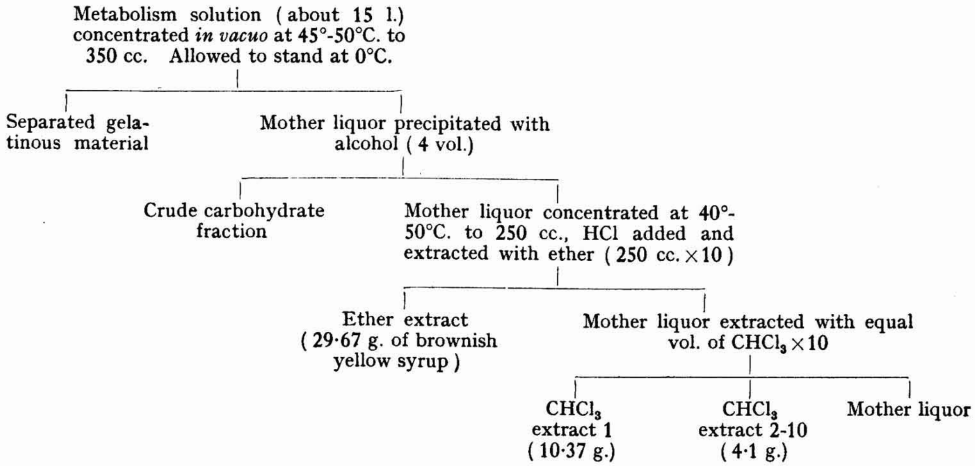

Discussion

From the biochemical point of view it is interesting to note the resemblance between *P. charlesii* G. Smith and *P. fellutanum* which belong to two different strains of *Penicillia monoverticillata*[5]. As compared with *P. charlesii* G. Smith, carolinic acid was found to be absent in the metabolic solution of *P. fellutanum*. A series of acidic mould metabolic products each of which is a derivative of tetronic acid (I, R = H; X = H) has been obtained previously from *P. charlesii* G. Smith[1], *P. terrestre* Jensen[6] and *P. cinerascens* Biourge[7].

The synthesis of tetronic acid by the present strain of *P. fellutanum* is not surprising in view of the fact that carolic acid and dehydrocarolic acid have been previously isolated from *P. cinerascens* Biourge. Although *P. cinerascens* is listed as a separate species by Biourge, Thom states that it approximates very much to *P. fellutanum* with distinct morphological differences which could be found in different strains of any particular mould. From this point of view it may prove even more interesting to investigate the various other strains listed by Biourge as separate species but which according to Thom are very similar to *P. fellutanum.*

Acknowledgement

The author wishes to thank Prof. H. Raistrick for providing laboratory facilities in his department and encouragement and guidance during the course of the investigation.

References

1. Clutterbuck, P. W., Haworth, W. N., Raistrick, H., Smith, G. & Stacey, M., *Biochem. J.*, **28** (1934), 94.
2. Clutterbuck, P. W., Raistrick, H. & Reuter, F., *Biochem. J.*, **29** (1935), 300.
3. Clutterbuck, P. W., Raistrick, H. & Reuter, F., *Biochem. J.*, **29** (1935), 871.
4. Clutterbuck, P. W., Raistrick, H. & Reuter, F., *Biochem. J.*, **29** (1935), 1300.
5. Raper, K. B. & Thom, C., *A Manual of Penicillia* (Williams & Wilkins Co., Baltimore), 1949.
6. Birkinshaw, J. H. & Raistrick, H., *Biochem. J.*, **30** (1936), 2194.
7. Bracken, A. & Raistrick, H., *Biochem. J.*, **41** (1947), 569.

A New Method for the Determination of the Bleach Index of Lac

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The bleaching characteristic of any sample of lac is generally expressed in terms of its bleach index or bleachability. In the different methods currently in use for determining the bleach index or bleachability of lac, the lac samples are treated with the required amount of bleach liquor so as to result in " complete " bleaching and the volume of bleach used up is noted. In the new method described, the same amount of bleach liquor is added to all samples of lac and the degree of bleaching effected in each case is determined from the colour of the bleached solution (filtered free from wax) in terms of N/1,000 iodine.

The advantages of the new method over the existing ones are: (1) no standard seedlac is required, (2) repeated additions of small quantities of bleach liquor (from time to time) and repeated filtrations and testings are avoided, and (3) the necessity of different procedural details for different grades of lac is eliminated. The comparison of the colour of the bleached lac solutions is simple, quick and accurate, and the results obtained are independent of moderate variations in laboratory temperature.

BLEACHED lac is one of the major forms in which lac resin is put into practical use. Large quantities of bleached lac, both regular and refined, are annually manufactured in foreign countries, especially in the United States, United Kingdom and Germany. America alone is estimated to be manufacturing over 7,000 tons of bleached lac annually. The chief raw materials used are shellac and seedlac. The latter is finding increasing favour as this material is invariably free from orpiment and rosin which are sometimes mixed in certain grades of shellac for better appearance and flow and which are very detrimental for bleaching purposes.

Crude lac, in its natural form, contains two colouring matters. One of them is a water-soluble dye known as laccaic acid[1] and the other a water-insoluble but spirit-soluble dye called erythrolaccin[2]. When crude lac is refined into seedlac by crushing and washing with water, with or without the addition of mild alkaline reagents such as sodium carbonate or triethanolamine, practically the whole of the water-soluble laccaic acid is removed. Seedlac and shellac are, therefore, practically free from this dye. The material that imparts to shellac and seedlac the familiar pale yellow to deep reddish brown colour is erythrolaccin. The methods used in the bleaching of lac aim at eliminating or destroying erythrolaccin. This dye can be removed by physical methods such as treatment with decolourizing agents or it can be transformed into colourless derivatives by reduction or oxidation. Reductive processes lighten the colour of shellac solution which, however, darkens on exposure to air due to reversion of the quinol to quinone system in the dye[3-4]. Oxidative bleaching of lac includes both chemical[5-16] and electrolytic[17-18] methods. The most widely used bleaching agent in commercial practice is sodium hypochlorite.

The bleaching characteristics of different specimens of seedlac and shellac differ widely depending upon a number of factors and are of considerable importance in grading lacs for purposes of bleaching. There is apparently no definite relation between the depth of colour of lac and its bleachability.

Bleaching characteristics of lac are expressed in terms of " bleach index " or the recently introduced term " bleachability ". " Bleach index " is usually determined by treatment of an alkaline solution of lac with sodium hypochlorite (3 per cent available chlorine) under definite conditions. The number of cubic centimeters of sodium hypochlorite required to bleach a solution of the lac to the desired end-colour is the bleach index. Bleachability is assessed by adding specific amounts of standard sodium hypochlorite to the alkaline lac solution and by comparing the end-colour with that of standard samples of seedlac bleached under the same experimental conditions. Bleachability is categorized into four groups requiring 80, 100, 115 and 140 cc. respectively of bleach liquor for 30 g. of the lac to produce a shade equal to, or lighter than, the shade produced by standard samples under identical experimental conditions[19].

The bleach index methods[20] used or advocated, although basically similar, differ in procedural details, particularly in regard to (1) particle size of the test sample, (2) method of dissolution of lac, and (3) determination of end-colour.

Particle size — The degree of fineness of seedlac samples influences the consumption of bleach liquor[21,22]. Finely ground samples enhance the solubility of nitrogenous matters present in seedlac and thereby increase the demand for bleach. Fineness of samples currently recommended for bleach index or bleachability determination is recorded in Tables 1 and 2.

The need for a uniform particle size of the samples is obvious from the data presented in Tables 1 and 2. As a result of a series of experiments carried out by us it was found that samples ground to pass through a 10-mesh sieve gave uniformly satisfactory and reproducible results. No advantage appears to be gained by grinding the sample finer. This particle size has the additional advantage of being more in line with the actual works practice as seedlacs are not generally powdered fine for use in the manufacture of bleached lac.

Extraction — All the existing methods specify approximately 10 per cent anhydrous sodium carbonate on the weight of seedlac taken. But in respect of other details, there is some divergence of opinion. These are brought out in Table 3.

Seedlac samples were extracted under all the conditions detailed in Table 3. It was found that when the extraction was carried out at 65° ± 2°C., the voluminous froth accumulating over the surface of the extract did not subside within 1 hr. Further, most of the wax was left over as residue during subsequent filtration. When the extraction was carried out at the temperature of boiling water and with mechanical stirring, the frothing in the initial stages was so uncontrollable that the solution often overflowed the sides of the beaker vitiating the experiment. Hand-stirring while extracting at the temperature of boiling water was found to be quite convenient and dissolution was complete within half an hour. Extraction for a longer period (say, 1 hr.) is, therefore, unnecessary and only leads to further darkening of the extract.

TABLE 1 — PARTICLE SIZE OF SEEDLAC FOR BLEACH INDEX DETERMINATION

METHOD	PARTICLE SIZE OF SAMPLE	
	Kusmi	*Baisakhi*
Angelo Bros., Calcutta	To be used as such if free; to be ground to pass through 10 mesh sieve, if blocked	To be used as such if free; to be ground to pass through 10 mesh sieve, if blocked
Indian Lac Research Institute (ILRI)	do	do
United States Shellac Importers' Association (USSIA)	40 mesh	40 mesh

TABLE 2 — PARTICLE SIZE OF SEEDLAC FOR BLEACHABILITY TESTS

METHOD	PARTICLE SIZE OF SAMPLE	
	Grade I A and B mesh	Grade II A and B mesh
USSIA	40	40
Indian Standards Institution (ISI)	40	10

TABLE 3 — DISSOLUTION OF SEEDLAC

METHOD	TEMP.	MODE OF STIRRING	DURATION hr.
Angelo Bros., Calcutta	65° ± 2°C.	Mechanical	1
ILRI	Boiling water	Manual	1
USSIA (bleach index)	do	do	1
USSIA (bleachability)	do	Mechanical	1
ISI	do	do	½

Preparation of bleach liquor — The usual methods recommended are: (1) treating a suspension of good quality bleaching powder with sodium carbonate solution and filtering off the precipitated calcium carbonate, and (2) direct chlorination of sodium hydroxide or carbonate. Since it is not always easy to obtain bleaching powder of the required quality, method (1) is not always convenient. Again, a stable bleach liquor of 3 per cent available chlorine is difficult to obtain starting from sodium carbonate. Preparation of bleach liquor by chlorination of sodium hydroxide is free from these limitations and a bleach liquor of approximately 5 per cent available chlorine can be conveniently prepared by passing chlorine gas through ice-cooled 1·5N solution of caustic soda. The associated sodium carbonate that is invariably present in caustic soda has no deleterious effect on the stability or efficiency of the bleach liquor.

Free alkalinity of bleach liquor — The stability of a hypochlorite solution is directly proportional to its free alkalinity while its bleaching efficiency is just the reverse. For the bleaching of lac what is required is a bleach liquor of reasonable stability and high bleaching efficiency. This means that the bleach liquor should contain only the minimum amount of free alkali. As a result of a series of experiments carried out by us it has been found that a sodium hypochlorite solution with a free alkalinity of 0·02-0·04N serves quite well for the purpose. A higher amount of free alkali increases the bleach consumption and reduces the bleaching rate while with lower amounts the liquor is rather unstable. A bleach liquor containing this range of free alkali may be conveniently made by controlling the degree of chlorination by the following simple test. Approximately 1 cc. of the solution is transferred periodically to a test-tube and treated with one drop of 0·5 per cent phenolphthalein solution. Chlorination is continued up to the point when a distinct pink colouration is noticed and which persists for not more than 5 sec. Several batches of sodium hypochlorite solution were prepared according to this procedure and all of them were found to have free alkalinities within the range of 0·02-0·04N. These were found to be quite satisfactory for bleaching and for use in the determination of bleach index of lac. The stability of a typical sample of bleach liquor so prepared and preserved in glass stoppered brown bottles, both in a refrigerator (3°-5°C.) as well as at room temperature, is indicated in Table 4.

Influence of free alkalinity of the bleach liquor on the results of the bleach test — It has been recognized that excessive alkalinity in the bleach liquor introduces errors in bleach tests. But no attempt appears to have been made to fix the permissible range of alkalinity. The present investigations have conclusively shown that bleach liquors of free alkalinities within the range of 0·02-0·04N are quite satisfactory. In order to determine the variation in the values of bleach index with the free alkalinity of the bleach liquor, the bleach index of the same sample of seedlac was determined using bleach liquors containing different amounts of free alkali. The results are given in Table 5.

By plotting the bleach index values against the free alkali content of the bleach liquor (TABLE 5), a curve (FIG. 1) is obtained from which it is clear that practically constant values for bleach index are obtained up to a maximum free alkalinity of about 0·04N, and above this figure, the value of bleach index rises rapidly with increase in free alkalinity.

End-point of bleaching — No uniform procedure is followed for fixing the end-point of bleaching nor is there any agreed standard for the end-colour of bleached lac solution. This is partly because a uniform reproducible shade cannot be ensured for every type of lac to be bleached, and consequently the value of bleach index or bleachability has often to be supplemented

TABLE 4 — STABILITY OF SODIUM HYPOCHLORITE SOLUTION OF FREE ALKALINTY 0·032N

TIME OF STORAGE months	AVAILABLE CHLORINE IN SAMPLE KEPT IN	
	Refrigerator (3°-5°C.) %	Room temp. (20°-30°C.) %
Freshly prepared	6·137	6·137
1	6·095	5·813
2	6·061	5·449
6	5·954	4·815

TABLE 5 — BLEACH INDEX OF THE SAMPLE OF SEEDLAC USING BLEACH LIQUORS CONTAINING DIFFERENT AMOUNTS OF FREE ALKALI

NORMALITY OF FREE ALKALI	COLOUR RATIO	BLEACH INDEX
0·0144	1·800	100
0·0296	1·960	97
0·0353	1·990	96
0·0642	1·725	101
0·1534	1·180	113
0·3602	0·340	145

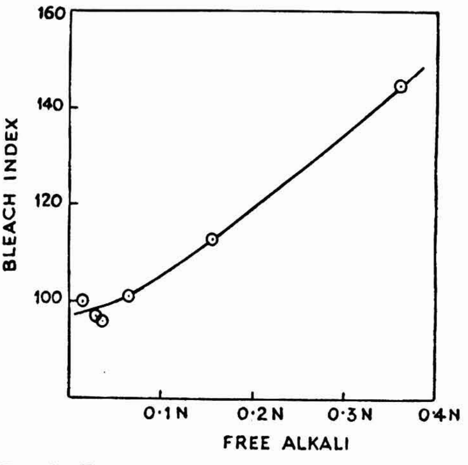

FIG. 1—FREE ALKALI CONTENT OF BLEACH LIQUOR VS. BLEACH INDEX

by remarks on the shade or colour of the bleached lac solution eventually obtained.

In the method used by Messrs Angelo Bros. Ltd., Calcutta, the *speed* of absorption of bleach liquor is made use of in ascertaining the end-point. A sample is considered to have been fully bleached when 5 cc. of standard bleach are not consumed within 90 min. under the given conditions. In Sen's modified method[20], bleaching is assumed to be complete when the colour of the wax-free solution matches that of N/2,000 iodine solution.

In the United States Shellac Importers' Association (USSIA) method for bleach index the comparison of end-colour is made with the suspended wax particles against that of a standard seedlac bleached simultaneously. For these tests, therefore, standard seedlacs are essential.

In the recently introduced bleachability test of the USSIA, the sample is treated with a definite volume of bleach, namely 80, 100, 115 or 140 cc., depending upon the grade of seedlac used, and the end-colour is compared with that of standard seedlacs which are simultaneously bleached under identical conditions.

The bleachability test is an improvement over the existing bleach index methods, but it still suffers from two shortcomings: (1) standard seedlac samples are needed, and (2) the results are relative and are expressed in terms of " equal to " or " lighter than " or " darker than " the standard.

The object of the present investigation was to modify the bleachability test in such a way that (1) the use of standard samples could be eliminated, and (2) the bleaching characteristics of all samples of seedlac, irrespective of grade, could be determined by a single uniform method and fairly accurately. This latter point is of importance to the industry. These objectives have been fulfilled by employing the modified method.

In the modified method, lac samples are extracted and treated with a definite volume of bleach (80 cc. of 3 per cent available chlorine for 30 g. of the lac) under standard conditions and the resulting solution is filtered. The transparent filtrate is then matched against N/1,000 iodine in a Dubosque (cup and plunger type) colorimeter. The ratio of the readings is noted and by reference to the curve (FIG. 2) the bleach index of the sample is found out.

Procedure — Seedlac is coarsely powdered so as to pass through a 10-mesh sieve and rolled on paper to ensure uniformity. Seedlac (37·5 ± 0·1 g.) and anhydrous sodium carbonate (3·7 ± 0·1 g.) are weighed into a 400 cc. tall beaker and mixed up with 110 cc. of hot water at 70° ± 2°C. The beaker with its contents is then quickly transferred to a boiling water bath. The contents of the beaker are kept stirred with a glass rod by hand, vigorously at first, till the initial frothing is over and thereafter only occasionally. After exactly half an hour the beaker is removed from the water bath and 25 cc. of hot water (70° ± 2°C.) are run down the sides of the beaker. The extract is then well mixed and immediately strained through a copper or brass 100 mesh wire-gauze filter into a 500 cc. graduated cylinder. The beaker and the residue are washed with hot water at 70° ± 2°C. taking care that the filtrate (including washings) does not exceed 250 cc. The extract is then cooled to room temperature in a stream of running water and made up to 280 cc. with distilled water. It is then drained into a 400 cc. tall beaker and mixed with 95 cc. of bleach liquor having an available chlorine content of 3 ± 0·05 per cent. The solution is occasionally stirred with a glass rod during the next half an hour and then allowed to stand overnight in a dark place, preferably at about 27° ± 2° C. Next morning the wax collecting on the surface is cautiously stirred into the solution by means of a glass rod without disturbing any sediment present. Exactly 300 cc. of the sediment-free supernatant solution are then measured and poured into a 400 cc. beaker and treated with an additional 4 cc. of the bleaching agent. The solution is mixed well and allowed to stand for half an hour. A small portion is then filtered, through a dry filter paper, the first 1 or 2 cc. of the filtrate being rejected, as this is likely to be cloudy. The colour of the subsequent clear filtrate is then determined by matching against N/1,000 iodine in potassium iodide solution in Dubosque colorimeter.*

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*It has been ascertained experimentally that no change of colour takes place during filtration of the wax and that the results of colour comparisons of bleached lac solutions are practically the same irrespective of whether the comparisons are carried out visually in the presence of the full complement of wax or colorimetrically after filtering off the wax.

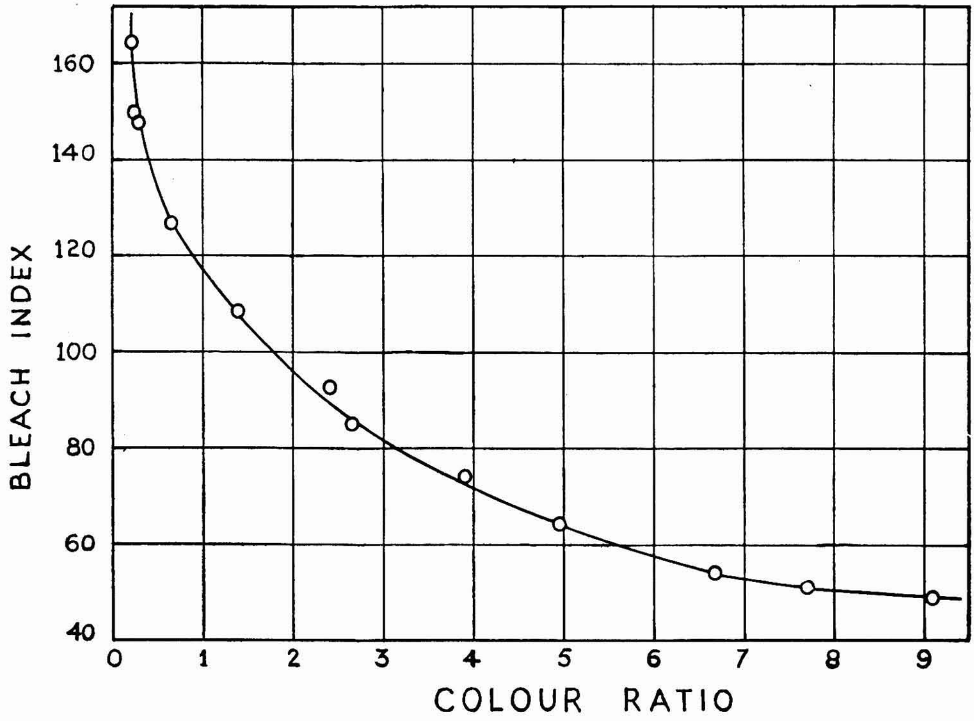

FIG. 2 — COLOUR RATIO VS. BLEACH INDEX

The ratio of the length of the column of the filtered bleached solution to that of the column of the iodine is indicative of the bleach index of the sample. For example, with seedlacs of a bleach index of 80 cc. this value is found to be between 3 and 3·6. Obviously for any sample, the bleach index of which is higher, this ratio will be smaller because the solution would have been only partially bleached in view of the insufficiency of bleach. Conversely, for a sample of a bleach index lower than 80 the ratio will be higher as the sample would have been overbleached.

From this simple relationship the bleach index of any sample is easily determined. A number of seedlac samples of known bleach indices were examined under the above conditions using a total of 80 cc. of bleach liquor for 30 g. of the sample. A curve (FIG. 2) was drawn by plotting the colour ratio against the bleach index of the respective samples. To determine the bleach index of any unknown sample, it is only necessary to determine the colour ratio under the conditions described above. The bleach index may then be directly read from the curve. The procedure is universal and applicable to all types of seedlac irrespective of grade. This method combines simplicity with economy of time and enables one to use the bleachability method with the same accuracy as bleach index method. It also avoids the use of any " standard " seedlac and makes use of only N/1,000 iodine solution as the standard.

The particular volume of 80 cc. bleach has been chosen because it corresponds to Grade 1A of USSIA bleachability test. Any other value near about 80 cc. might also serve the purpose but the standard colour ratio (and consequently the location of the curve) would be different. With standard Grade 1A seedlac the eventual colour ratio after treatment with 80 cc. bleach was found to be between 3 and 3·6. Therefore, this value has been taken to be the standard for an adequately bleached sample.

Verification of the accuracy of bleach index curve — It was realized that the reliability of this method depends entirely upon the accuracy of the bleach index curve. In order to verify the accuracy of the curve, a number of samples of seedlac were examined under the above conditions and their bleach indices read from the curve. The same seedlacs (37·5 g.) were then extracted with sodium carbonate solution (3·7 g.) as usual and the extracts made up to a volume equal to 375—x cc., where

$$x = \frac{\text{bleaching index} - 4}{4} \times 5.$$

Bleach (x cc.) was then added and, after allowing to stand overnight, 300 cc. of the solution were treated with a further 4 cc. of the bleach and allowed to stand for half an hour. The colour ratio of the bleached solutions after filtration was then determined in terms of N/1,000 iodine. If the curve is accurate, this ratio should be between 3 and 3·6. The results of a number of experiments are shown in Table 6.

The values in column 4 (TABLE 6) are not very wide off the expected range 3-3·6 and may be considered to be within the limits of experimental error.

Reproducibility of the results — Many seedlac samples were examined by the above method using the same as well as different batches of bleach liquor. Concordant results were obtained as shown in Table 7 for two typical samples.

Effect of temperature — Temperature has considerable influence on the speed of hypochlorite bleaching. It was, therefore, considered necessary to determine how far the results obtained by the improved method are affected by the temperature at which bleaching is carried out. With this end in view, the determinations were carried out on a number of seedlac samples, the solution in contact with the bleach liquor being allowed to stand overnight (1) at the laboratory temperature (30°-35°C.), (2) in a refrigerator at 3°-5°C., and (3) in a thermostat at 35°C. The colour ratios of some of the solutions before the addition of 4 cc. of bleach were also determined. The results obtained are given in Table 8.

TABLE 6 — VERIFICATION OF THE ACCURACY OF THE BLEACH INDEX CURVE

SAMPLE No.	COLOUR RATIO OBSERVED	BLEACH INDEX FROM CURVE cc.	COLOUR RATIO AFTER TREATMENT WITH VOLUME OF BLEACH SHOWN IN COL. 3
A	3·95	73	4·01
A	3·84	74	3·94
B	6·25	56	3·82
B	6·52	55	3·42
C	2·45	92	3·92
C	2·50	92	3·64
D	1·40	109	3·70
D	1·40	109	2·96
E	1·64	105	3·09
E	1·64	105	3·42
F	0·87	120	3·34
F	0·64	127	3·62

TABLE 7 — COLOUR RATIO AND BLEACH INDEX OF SEEDLAC SAMPLES USING DIFFERENT BATCHES OF BLEACH LIQUOR

COLOUR RATIO	BLEACH INDEX FROM CURVE
Sample 1	
0·26	150·0
0·28	148·0
0·25	150·0
0·25	150·0
0·29	148·0
0·28	148·0
0·30	148·0
0·29	148·0
Sample 2	
7·69	51·0
6·66	54·0
6·58	54·5
6·59	54·5
6·73	54·0

TABLE 8 — COLOUR RATIOS OF DIFFERENT SEEDLAC SOLUTIONS

SAMPLE	BEFORE ADDITION OF FINAL 4 CC. OF BLEACH		½ HR. AFTER ADDITION OF FINAL 4 CC. BLEACH		
	30°-35°C.	3°-5°C.	30°-35°C.	3°-5°C.	35°C.
P	4·30	4·56	5·64	5·32	—
Q	—	2·61	3·12	2·64	—
Q	0·81	2·91	2·77	2·94	—
R	1·24	3·48	4·27	4·27	—
S	0·51	1·05	1·39	1·41	—
S	0·45	1·22	1·25	1·44	—
S	0·56	1·40	1·47	2·19	—
T	2·24	6·24	8·84	8·90	—
T	1·98	7·44	8·98	8·94	—
A	—	—	3·40	3·49	3·40
B	—	—	3·35	3·49	3·37
C	—	—	2·74	3·06	2·75
D	—	—	0·95	0·88	0·80
E	—	—	3·00	3·48	3·52
F	—	—	3·17	3·24	3·00

It is evident from the figures in Table 8, columns 4, 5 and 6, that varying the temperature from 3° to 35°C. has no appreciable effect on the results obtained in the bleaching experiments. This observation may, at first sight, appear to be surprising, but the following considerations provide a satisfactory explanation.

In the bleaching process two factors play an important role: (1) the speed of bleaching

(as observed by rate of change of colour of the solution), and (2) duration of the bleaching operations. That the speed of bleaching is accelerated by higher temperature[23] has been noticed by us also. However, when practically the whole of the added bleach has been consumed, a reversion or darkening of colour of the solution takes place. When the determination is carried out at the higher temperature, the added bleach liquor is consumed (exhausted) in a shorter time. Consequently, during overnight keeping the reversion or darkening of colour goes on for a longer period and possibly at a quicker rate before the addition of the 4 cc. of bleach next day. Hence the darker colour of the solution which is maintained overnight at the higher temperature (TABLE 8, column 2) than at the lower temperature (TABLE 8, column 3). This would also explain why the colour of the sample in the latter case is closer to the end-colour (TABLE 8, columns 4 and 5).

The darkening or reversion of colour on standing of the fully or partially bleached lac solution is due to causes other than those due to the original colouring matter of lac[24]. The final 4 cc. of bleach added after overnight standing helps to discharge only the colour regained. The solution is thereby brought back to the same colour which it had when bleaching was complete and the darkening had not commenced; in other words, to the same colour the bleached solutions would have had if there had been no darkening. This should naturally depend only upon the *amount* of bleach used and not on the *temperature* of bleaching although the time required to reach this stage may be shorter at higher temperatures than at lower temperatures.

Determination of the bleach index of a number of samples by the method described above was made not only by one of the authors (Y.S.) but also by junior workers in this Institute and no difficulty whatsoever was experienced by them in obtaining consistent and satisfactory results.

Acknowledgement

We wish to take this opportunity to express our thanks and appreciation of the interest taken in this work by Mr. E. J. Breuleux of Messrs R. V. Briggs & Co. Ltd., Calcutta, and for the several samples of " standard " and commercial seedlacs so kindly supplied by him. We also wish to express our thanks to Sri P. C. Ghosh and Sri K. K. Sarkar of this Institute for carrying out some of the tests.

References

1. SCHMIDT, R. E., *Ber. dtsch. chem. Ges.*, **20** (1887), 1285.
2. TSCHIRCH, A. & FARNER, *Arch. int. Pharmacodyn.*, (1889), 35; FARNER, *Diss. Bern.*, (1899).
3. *Indian Lac Res. Inst., A.R.*, 1949-50, 25.
4. MURTHY, N. N., *Indian Lac Res. Inst. Bull. No.* 29 (1937), 9.
5. MURTHY, N. N., *Indian Lac Res. Inst. Bull. No.* 29 (1937); *Bull. No.* 32 (1939).
6. MURTHY, N. N., GROSS, B. & GARDNER, W. H., *Indian Lac Res. Inst. Bull. No.* 35 (1939).
7. NARASIMHA MURTHY, N., *Indian Lac Res. Inst. Tech. Note No.* 3 (1937).
8. STUHLMANN, P., *U.S. Pat.* 1809738 (1931).
9. VAN ALLAN, L. R., *U.S. Pat.* 2454796 (1948).
10. HAMPEL, C. A., *U.S. Pat.* 2429317 and 2433661 (1947).
11. VINCENT, G. P., *U.S. Pat.* 2397389 (1946).
12. VENUGOPALAN, M., *J. Indian Inst. Sci.*, **11A**(2) (1928), 17-22.
13. ANON, *La Revie des Produits Chimiques*, **31** (1939), 17.
14. GIBSON, A. J., *Oil Col. Tr. J.*, **86** (1934), 1416-20.
15. FAUCETT, P. H., *Drugs Oils Pts.*, **52**(9) (1937), 264-66; **52** (1939), 405-7.
16. GIDVANI, B. S. & KAMATH, N. R., *Ind. Chem.*, **22** (1946), 414-19.
17. MYLO, P., *Germ. Pat.* 517096 and 521292 (1931).
18. SEISAKUJO, K. K. H., *Jap. Pat.* 111607.
19. *Indian Standard Specification for Seedlac*, IS: 15 (1949), 5.
20. RANGASWAMI, M. & SEN, H. K., *A Handbook of Shellac Analysis* (Indian Lac Res. Inst.), 2nd ed., 1952, 95-106.
21. MURTHY, N. N., GROSS, B. & GARDNER, W. H., *Indian Lac Res. Inst. Bull. No.* 35 (1939), 5.
22. *Indian Lac Res. Inst., A.R.*, 1950-51, 29-31.
23. MURTHY, N. N., *Indian Lac Res. Inst. Bull. No.* 29 (1937), 5-7.
24. MURTHY, N. N., *Indian Lac Res. Inst. Bull. No.* 29 (1937), 7.

Stability of Bleaching Powders

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The stability of bleaching powders (Indian and imported) during storage has been evaluated. A quality rating for bleaching powders has been defined and an empirical equation developed relating stability to moisture and metallic oxides (R_2O_3) in the bleaching powders.

THE causes contributing to the instability of bleaching powders have been investigated by several workers[1-12]. Temperature, light, humidity, moisture and metallic oxides all contribute in some measure to the loss of available chlorine in bleaching powder. It is difficult to single out any one agent as the dominant factor.

Bleaching powders manufactured in India are often reported to be less stable than imported ones. Under the tropical conditions of temperature, light and humidity encountered in most parts of India, bleaching powder, during storage, is subjected to more severe conditions than in milder climates. The bulk of the imported and some of the indigenous bleaching powders are specially " stabilized " against tropical deterioration and are known as " tropical bleaches ". Stabilization consists in the addition of substances such as calcium oxide, gypsum, etc., to the bleaching powders.

Materials and methods

Five samples of bleaching powders (A-E) from well-known Indian manufacturers and two imported samples (IF and IG) were employed in these studies. Two Indian samples (C and E) and the foreign samples were of the stabilized variety.

The samples were stored in steel cans (*c*. 4 in. diam. × 6 in. high) with press lids which were kept closed during the tests. This, together with the fact that the cans were stored in the dark, eliminated the influence of light on the deterioration of bleaching powder.

The stability tests were conducted over a period of six months. During this period, the average daily temperature and humidity were as follows: temperature, max. 97°C. and min. 53°F.; relative humidity, max. 84 and min. 19 per cent.

The samples were analysed at the end of every month for available chlorine, chlorate and chloride. The results of analysis of the samples, at the commencement of the tests and thereafter, are given in Tables 1 and 2.

The total chlorine, chlorine as chlorate, and available chlorine were estimated by standard methods[13]. In the titrations for chlorate, Zimmermann and Reinhardt solution[14] was used. Chlorine as chloride was obtained from the total chlorine by difference.

Metallic oxides (R_2O_3) and insolubles, including silica, were estimated by standard methods using hydrogen peroxide for decomposing the hypochlorite.

Calcium and magnesium were determined using the oxalate-permanganate and 8-hydroxyquinoline methods respectively.

The estimation of water in the samples was carried out according to the technique of Goldenson and Danner[15] with the modification that tetrachloroethylene (b.p. 120·8°C.)

TABLE 1 — ANALYSES OF BLEACHING POWDERS

SAMPLE No.	AVAILABLE CHLORINE %	CHLORINE AS ClO_3 %	TOTAL CHLORINE %	CHLORINE AS CHLORIDE %	SiO_2 %	R_2O_3 %	CALCIUM %	MAGNESIUM %	MOISTURE %
A	25·30	0·28	32·10	6·52	0·30	1·55	37·00	0·11	4·00
B	27·00	0·08	31·70	4·62	0·32	1·48	36·20	0·16	3·75
C	24·25	0·20	29·98	5·54	1·11	1·84	46·45	0·11	0·75
D	19·00	0·74	21·60	1·86	1·70	2·46	40·50	0·19	1·38
E	24·80	0·65	36·80	11·35	3·24	1·74	34·60	0·16	3·38
IF	26·90	0·55	35·83	8·39	0·62	0·77	48·25	0·19	3·88
IG	31·85	0·54	37·60	5·23	0·37	0·79	48·25	0·19	1·00

TABLE 2 — LOSS OF AVAILABLE CHLORINE IN BLEACHING POWDERS

SAMPLE No.	AVAILABLE CHLORINE %						
	Days: 0	30	61	91	129	150	189
A	25·30	20·30	17·60	12·80	8·10	5·30	1·70
B	27·00	24·80	21·80	15·80	15·10	11·70	5·80
C	24·25	23·40	23·40	23·40	22·80	22·40	20·50
D	19·00	19·00	17·15	15·70	15·00	13·50	12·00
E	24·80	24·00	19·80	18·80	18·10	14·50	11·20
IF	26·90	24·30	22·50	20·70	19·50	16·10	12·10
IG	31·85	30·50	30·20	27·80	27·40	26·30	23·40

was used in place of *o*-dichlorobenzene (b.p. 180·3°C.). The use of tetrachlorethylene has the following advantages: (1) The time of estimation is considerably shortened; (2) bumping, invariably encountered when using *o*-dichlorobenzene, is eliminated; and (3) the results are reproducible and compare favourably with those obtained with *o*-dichlorobenzene (b.p. 175°-76°C.; B.D.H. technical grade).

Discussion

Rate of loss of available chlorine — The available chlorine in different samples has been plotted against time of storage in Figs. 1-3. It will be observed that although all the samples undergo a progressive deterioration, the stabilized samples lose their available chlorine at a markedly slower rate.

Sample D, although exhibiting fair stability, was of poor quality, containing only 19 per cent initial available chlorine. Its relatively stable nature and low percentage available chlorine may be due to the admixture of a large quantity of unslaked lime with it.

The loss of available chlorine (expressed in percentage loss per day) in the various samples was calculated by dividing the total loss of available chlorine by the duration of test. The results are given in Table 3.

Quality rating — Besides the rate of loss of available chlorine an equally important factor which determines the quality of the bleaching powder is its initial available chlorine content. The relative importance of the factors depends on whether the bleaching powder is to be stored or used fresh. Any evaluation of the quality of bleaching powder must, therefore, take both these factors into account. If L denotes the per cent loss of available chlorine per day, and C_0 the initial available chlorine content, the ratio C_0/L can be considered as a criterion

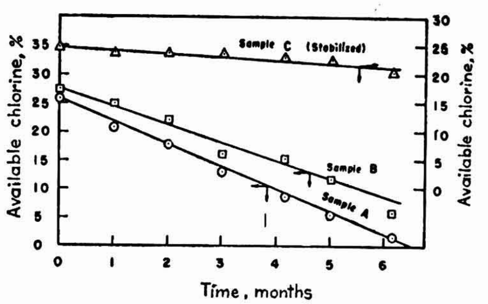

FIG. 1 — LOSS OF AVAILABLE CHLORINE IN COMMERCIAL BLEACHING POWDERS ON STORAGE

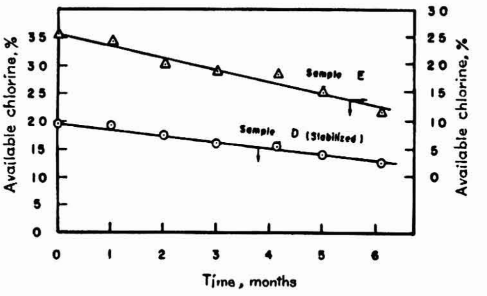

FIG. 2 — LOSS OF AVAILABLE CHLORINE IN COMMERCIAL BLEACHING POWDERS ON STORAGE

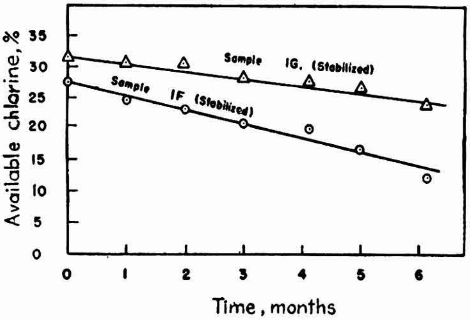

FIG. 3 — LOSS OF AVAILABLE CHLORINE IN COMMERCIAL BLEACHING POWDERS ON STORAGE

TABLE 3 — STABILITY AND QUALITY RATING OF BLEACHING POWDERS

SAMPLE	INITIAL AVAILABLE CHLORINE % (C_o)	LOSS OF AVAILABLE CHLORINE %/day (L)	RELATIVE QUALITY RATING
A	25·30	0·125	17
B	27·00	0·114	20
C*	24·25	0·020	100
D*	19·00	0·037	43
E	24·80	0·072	28
IF*	26·90	0·078	29
IG*	31·85	0·045	60

*Stabilized sample.

of the quality of bleach (quality rating). This ratio tends towards infinity with increasing stability.

The relative quality ratings of the test samples are presented in Table 3. These values are based on a value of 100 for the most stable sample (actual value of C_o/L for this sample is 1,210). The sample with the quality rating of 100 is a stabilized bleach of Indian manufacture. It is superior to the imported sample IG which comes next with a relative quality rating of 60. Sample D, third in quality rating with a value of 43, can be used to observe the relative importance of the factors C_o and L. The value of C_o for this product is 19·0, showing that it is a poor bleach. Its L value, however, is 0·037 indicating that it possesses comparatively good stability. The use of this product could, therefore, be considered in cases where the bleach has to be stored over a long period.

The quality ratings for the unstabilized products range between 17 and 28.

Stability in relation to composition of bleach — Ochi[6] has reported that free and combined water in the bleaching powder accelerate its deterioration. He has further reported that Fe_2O_3 and Mn_2O_3 also render bleaching powder unstable, while the effect of Al_2O_3 and SiO_2 is small. Gill[7] found that FeO and MnO_2 in bleaching powder catalyse the liberation of oxygen. Stepanov[4] observed that traces of iron, manganese, nickel and cobalt catalyse the decomposition of bleaching powder.

The loss of oxygen from bleaching powder may be represented thus:

$$CaOCl_2 = CaCl_2 + O$$

and it is this reaction that is most likely catalysed by the metallic oxides present as impurities.

When the metallic oxides are present together with water, it is further likely that the reaction represented by the equation

$$OCl_2 = O + Cl_2$$

is also catalysed by them.

It is thus reasonable to expect that the moisture and metallic oxides (R_2O_3 group) present in bleaching powder bear some relation to its stability. Table 4 gives the percentage loss of available chlorine per day (L), and moisture plus metallic oxides (x) in the test samples.

A semi-logarithmic plot of x versus L is shown in Fig. 4, where x represents moisture

TABLE 4 — RELATION BETWEEN MOISTURE AND R_2O_3 CONTENT OF BLEACHING POWDERS AND LOSS OF AVAILABLE CHLORINE

SAMPLE	MOISTURE %	R_2O_3 %	MOISTURE + R_2O_3 (x) %	L*
A	4·00	1·55	5·55	0·175
B	3·75	1·48	5·23	0·114
C	0·75	1·84	2·59	0·070
D	1·38	2·46	3·84	0·037
E	3·38	1·74	5·12	0·072
IF	3·88	0·77	4·65	0·078
IG	1·00	0·79	1·79	0·045

*L, percentage loss of available chlorine per day.

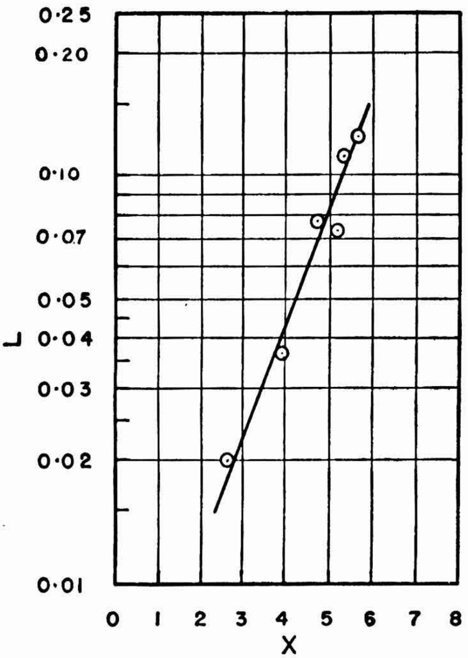

FIG. 4 — LOSS OF AVAILABLE CHLORINE IN RELATION TO MOISTURE AND IMPURITIES IN BLEACHING POWDERS

plus metallic oxides content. The graph obtained is a straight line indicating a relationship of the type

$$L = ae^{bx} \quad \ldots\ldots\ldots \quad (1)$$

where a and b are constants. From Fig. 4 the values of a and b are found to be 0·0035 and 0·6370 respectively. Equation (1) may, therefore, be written as

$$L = 0{\cdot}0035e^{0{\cdot}637x} \quad \ldots\ldots \quad (2)$$

Equation (2) represents the relationship between the stability of the test samples and their moisture plus R_2O_3 content. This relationship holds good for bleaching powders of widely different stabilities and qualities.

Magnesium present in all the samples has virtually no influence on stability. This can be inferred from the fact that if the per cent Mg. content of the samples is added to the value of x in equation (2), the relationship between L and the new value of x is almost identical with that of equation (2). Ochi[7] has also observed that magnesium oxide has no influence on the stability of bleach.

It must not, however, be assumed that moisture and R_2O_3 are the only factors that influence the loss of available chlorine, although they appear to be the main causes. When the value of x is zero, L is equal to 0·0035, indicating a slight deterioration even in the absence of moisture and R_2O_3.

The presence of carbon dioxide in bleach due to the poor quality of lime may also have some influence on stability[11] although this has not been taken into account in the present study.

A correlation of the type obtained in equation (2) enables the stability of a bleach to be calculated from its composition. Knowing the initial available chlorine content, the available chlorine present after any interval can be calculated.

For example, it is required to calculate the available chlorine content after 100 days of storage of a sample initially having 26 per cent available chlorine, 2 per cent moisture and 1·5 per cent R_2O_3.

From equation (2), $L = 0{\cdot}0326$ when $x = 3{\cdot}5$. The loss of available chlorine in 100 days is (0·0326) × (100) or 3·26 per cent. Therefore, after 100 days of storage, the available chlorine content of the sample will have decreased to 22·74 per cent.

It must, however, be emphasized that equation (2) is valid only under the experimental conditions employed in the testing procedure adopted by us. Similar correlations can be developed for other conditions.

The calcium chloride and calcium chlorate contents of the samples determined, initially and at monthly intervals, could not be correlated with the stability of the samples.

Summary

1. Storage tests on five Indian and two imported samples of bleaching powder showed that while all the samples steadily lost available chlorine, the stabilized samples had a lower rate of deterioration.
2. A quality rating has been specified for bleaching powders based on the initial available chlorine content, and the loss of available chlorine per day. The samples have been classified on the basis of this rating. A stabilized Indian bleach was found to have the highest quality rating.
3. The main causes of deterioration of bleaching powder are moisture and metallic oxides of the R_2O_3 group.
4. An empirical equation has been developed to express the relationship between stability and the moisture plus metallic oxides (R_2O_3) content of bleaching powders.

References

1. LUNGE, G. & SCHAPPI, H., *Dinglers J.*, **237** (1880), 63.
2. MELLOR, J. W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans, Green & Co., New York), Vol. II, 1937, 260.
3. OPL, C., *Dinglers J.*, **215** (1875), 232, 325.
4. STEPANOV, D. V., *Trans. Karpov. Inst. Chem.* (*Russia*), **4** (1928), 107.
5. OCHI, S., *Chem. Abstr.*, **18** (1924), 1390.
6. OCHI, S., *Chem. Abstr.*, **18** (1924), 884.
7. GILL, A. H., *Industr. Engng. Chem.*, **16** (1924), 577.
8. TAYLOR, R. L., *Chem. Abstr.*, **12** (1918), 979.
9. URANO, S., *Chem. Abstr.*, **22** (1928), 1443, 2442.
10. SANO, R. & SHOJI, T., *Chem. Abstr.*, **24** (1930), 922.
11. LOVE, S., *Chem. Abstr.*, **42** (1948), 2407.
12. GANDHI, K. A., *Indian med. Gaz.*, **57** (1922), 78.
13. SCOTT, W. W., *Standard Methods of Chemical Analyses* (D. Van Nostrand Co., New York), Vol. 2 (1939), 2160.
14. SCOTT, W. W., *Standard Methods of Chemical Analyses* (D. Van Nostrand Co., New York), Vol. 1 (1939), 476.
15. GOLDENSON, J. & DANNER, C. E., *Anal. Chem.*, **20** (1948), 359-60.

Photomicrographic Study of Leather

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Photomicrographic studies of pelts at different stages of processing, prior to tanning, have been carried out with a view to explain the effect of soaking, liming and bating on the structure of the pelt and on the properties of the finished leather. These studies have shown that proper control of the pre-tanning processes is of as much importance as the tanning process for imparting desirable properties to leather.

IN an earlier paper[1], the characteristics of fibrous tissues of hides and skins were discussed, and it was indicated that the structure and arrangement of the fibres in the skins may be altered by chemical or mechanical treatment. For example, the collagen fibre bundles can be swollen or shrunken, the elastin fibres can be digested, and the reticulin sheath can be ruptured. It is, therefore, obvious that the structure and quality of leather depend to a large extent on the different chemical and mechanical treatments which the hides and skins receive during the earlier stages of processing for tanning. The pre-tanning processes are, therefore, as important, with respect to the quality of leather obtained, as tanning itself.

The object of this paper is to explain with the help of photomicrographs the effects of pre-tanning processes on the fibre structure of the pelt and the resultant leather.

Soaking — Hides and skins received by tanners in dry and dry-salted condition have to be soaked to make them soft and supple. The hide fibre bundles in their natural state are more or less wavy, but in the process of drying, the fibre bundles, due to loss of water, become flattened and the component fibrils are glued together (FIG. 1) by intermolecular cross bonds. The interfibrillary proteins, which in the fresh skin are semi-fluid, get coagulated if the temperature of drying is high or simply dry up if the temperature is low. It is well known that unless and until these coagulated or dried proteins are removed, proper opening up of the fibre structure is difficult and the dry hides and skins do not get soaked. Substances which disperse coagulated interfibrillary proteins are, therefore, used in soaking dry hides and skins. If in the process of soaking the dehydrated fibre bundles do not get soaked efficiently, they retain this flattened weave pattern and the result is a disordered fibre structure with horizontal type of weaving (FIG. 2). Horizontal weaves with unsplit fibres are indicative of flat thin leather of a tinny nature. Over-soaking, on the other hand, brings about a large amount of opening up, which may lead to a soft and rather spongy leather (FIG. 3). Proper soaking is imperative for the production of good leather.

Liming — For the production of desired properties in the finished leather the liming operation requires careful control. The properties of a leather depend to some extent on its fibre structure, which in turn is dependent on the liming process. Though the primary object of liming is the removal of epidermal structures, it has other important functions. The hide fibre substance, because of its amphoteric nature, reacts with alkali and the fibres get swollen in alkaline solutions rupturing the reticulin network. The fibre bundles open out and are split

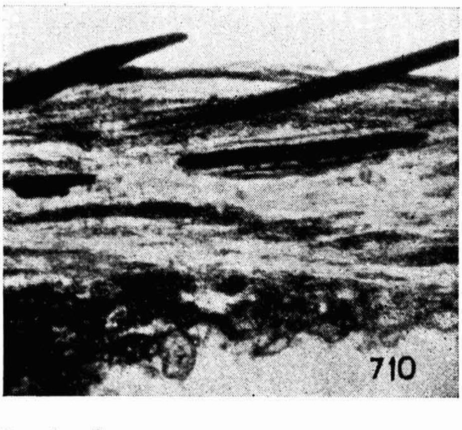

FIG. 1 — SECTION OF DRY GOAT SKIN SHOWING FLATTENED AND GLUED FIBRE BUNDLES × 37

FIG. 2 — SECTION OF GOAT SKIN UNDER-SOAKED × 37

FIG. 3 — SECTION OF GOAT SKIN EXCESSIVELY SOAKED × 37

up into their component fibres and fibrils, and the interfibrillary proteins are more or less dissolved, thereby increasing the permeability of the skin and offering a much larger surface for subsequent tanning (FIG. 4). At the same time the weave pattern is reoriented depending upon the composition of lime liquor[2] and the nature of treatment, and the structure of the skin which is apparent in the limed state is to a large extent reproduced in the finished leather[3]. The extent of the splitting of the fibre bundles into fibres and fibrils gives a measure of the suppleness of finished leather. Liming for an unduly long period makes the finished leather loose and spongy, and reduces its

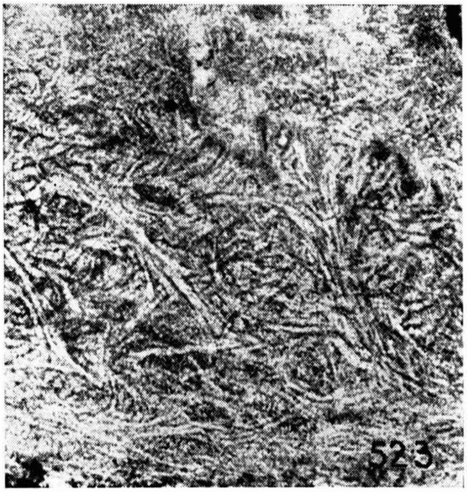

FIG. 4 — SECTION OF GOAT SKIN AFTER PROPER LIMING × 37

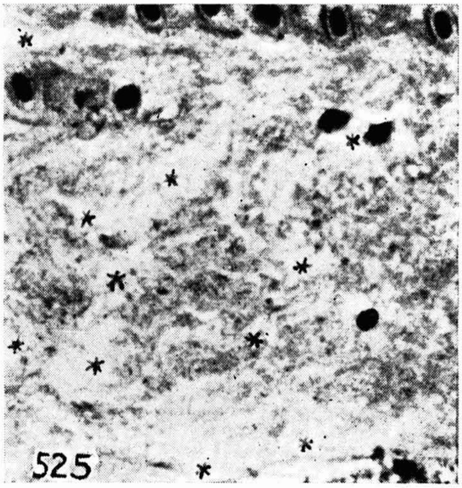

FIG. 5 — SECTION OF GOAT SKIN AFTER LIMING FOR A LONG PERIOD × 37 [*Places where damage to hide fibrils has occurred]

FIG. 6 — SECTION OF GOAT SKIN AFTER LIMING FOR A SHORT PERIOD SHOWING IMPROPER OPENING UP OF BUNDLES × 37

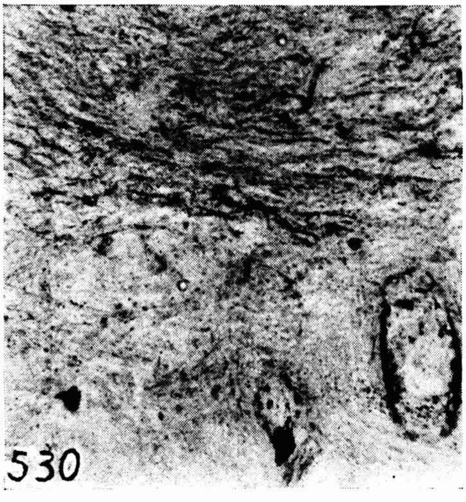

FIG. 7 — SECTION OF GOAT SKIN AFTER 24-HR. BATING, SHOWING PARTLY DIGESTED ELASTIN FIBRES × 105

tensile strength due to too much loss of hide fibrils causing separation between the fibres and fibrils (FIG. 5). Too short a liming period, on the other hand, causes inadequate splitting of the fibre bundles and the pelt cannot be thoroughly tanned. Such a fibre structure (FIG. 6) may produce a hard or boardy leather with an open weave.

Bating — The function of a bating agent is to dissolve out all or part of the lime from the limed pelt and to digest part of the skin fabric, viz. elastin, to impart to the skin pliability and smoothness[4]. The elastin fibres constitute a very small proportion of the skin, forming only 1 per cent of the whole skin substance[5]. Although partial disinte-

FIG. 8 — SECTION OF GOAT SKIN BEFORE BATING, SHOWING ELASTIN FIBRES IN THE GRAIN LAYER × 105

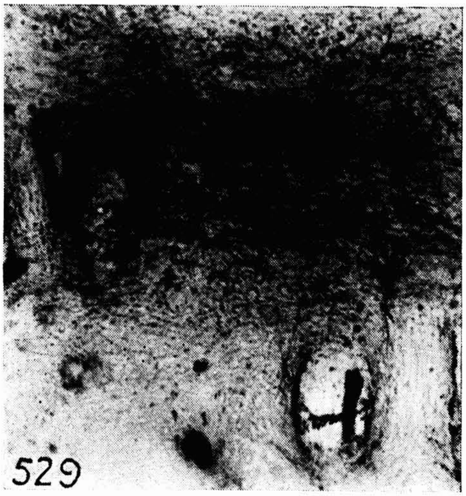

FIG. 9 — SECTION OF THE SAME SKIN AS IN FIG. 8, AFTER 8-HR. BATING SHOWING GRAIN ELASTIN × 105

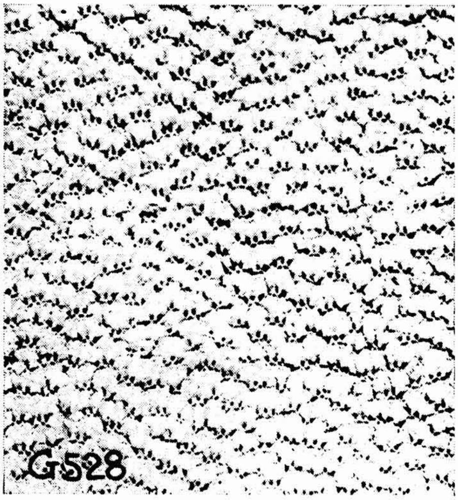

FIG. 10 — GRAIN SURFACE OF BATED GOAT SKIN

FIG. 11 — GRAIN SURFACE OF UNBATED GOAT SKIN SHOWING DARK PATCHES

gration and removal of the elastin fibres were observed under the microscope after prolonged bating (FIG. 7), it is difficult to say with accuracy whether their removal, even partial, is essential for the production of quality leather. It is evident from Figs. 8 and 9 that the bating process as normally carried out by tanners has little effect on elastin fibres. From the histological studies it appears that the effect of the bate on elastin fibres under normal conditions is not so much of digestion and removal as of loosening them from their moorings. The present-day concept of bating is that, besides removing some lime from pelt, bating removes the keratoses formed by the degradation of the epithelial tissue during liming and digest to some extent the cementing or interfibrillary substance. All these products are forced out of the bated pelt during scudding operation, thus cleansing the grain layer of the pelt. The bates, because of their ammonium salts content, also largely reduce alkaline plumping of the pelt.

While it is not known whether the effect of bate upon elastin fibres has got anything to do with the pipiness of the grain of the finished leather, it is the experience of the tanner that bating has a very important bearing on the appearance and the feel of the finished leather. Unless the grain surface and hair follicles are thoroughly cleansed by bating and subsequent scudding, the clear, uniform grain and high gloss characteristic of all types of quality leather cannot be obtained. This cleansing effect of bating on the grain surface of the pelt is shown in Figs. 10 and 11.

References

1. DAS & MITRA, *Tanner*, **1** (1951), 15.
2. DAS & MITRA, *J. int. Soc. Leath. Tr. Chem.*, **24** (1940), 371.
3. MARRIOT, *J. int. Soc. Leath. Tr. Chem.*, **19** (1935), 169.
4. WOOD, *Puering, Bating and Drenching of Skins* (E. & F. N. Spon, London), 1912, 124.
5. WILSON, *The Chemistry of Leather Manufacture* (Chemical Catalogue Co., New York), 1923, 330.

Effect of Shortening Consistency & Added Antioxidants on the Keeping Quality of Biscuits

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The " free oil " content in biscuits is one of the causes of spoilage in biscuits. The keeping quality of biscuits can be improved by keeping down the " free oil " content by incorporating a shortening of higher melting point (41°C.) in the bake.

The shelf life of biscuits can be further increased by incorporating in the bake a mixture of antioxidants consisting of butylated hydroxy anisole, propyl gallate, lecithin and citric acid.

THE keeping quality of biscuits is affected by several factors; the type of packaging and the nature of the shortening used are two of the more important ones. Spoilage in baked foods may be due to the changes undergone by one or more of the ingredients in it, and oxidative deterioration of the fat is one of the major causes. This can be retarded in several ways such as selection of high grade raw materials, minimizing exposure to air, light and heat, avoiding metallic contamination and incorporation of antioxidants.

In India, the shortenings commonly used for biscuits are made from groundnut oil which generally melt at *c*. 37°C. Our preliminary studies on several Indian biscuits indicated that the fat extracted from them melts within a range of 32°-39°C. which is lower than that of fat obtained from standard foreign biscuits which are known to have a longer shelf life.

The " free oil " content of a product (expressed as percentage of oil or fat in the product seeping through at a given temperature and interval) is another factor causing spoilage in biscuits as a result of development of rancidity. Rancidity appears to originate in the fat which seeps and spreads over on the packaging material thus providing a greater reactive surface (TABLE 1). The " free oil " content of a product depends, apart from other factors, on the melting point of the fat used.

In the present investigation, the effect of the melting point (consistency) on the keeping quality of biscuits and the " carry through " properties of butylated hydroxy anisole (BHA) alone and in combination with propyl gallate and citric acid have been studied.

Experimental procedure

The " free oil " content of the biscuits was determined by the modified method of Landrock and Proctor[1] and the keeping quality was determined on the basis of Schaal's accelerated oven test by peroxide and Kreis values and organoleptic evaluation of biscuits stored at 26°C. (79°F.) and 37°C. (98·6°F.) by a selected panel of judges were also carried out. A preliminary report on the results of the Schaal's accelerated test has already been reported by us earlier[2]. For determining the peroxide value[3] of fat, 5 g. of the powdered biscuits were shaken up with 50 cc. of chloroform for 30 min., filtered, washed and made up to 60 cc. An aliquot (20 cc.) was taken for the gravimetric determination of fat and another 20 cc. was treated with 30 cc. of glacial acetic acid and 0·5 cc. freshly prepared

TABLE 1 — PEROXIDE VALUE OF FAT FRACTIONS

(*Sample stored in half lb. pack, containing 20 biscuits in a row, at 26°-29°C. for 12 weeks*)

FAT EXTRACTED FROM	PEROXIDE VALUE OF FAT m. eq./kg.
Paper lining	10·5
Outer trimmings of biscuits*	6·5
Inner core of the pack	2·8

*Two biscuits from each end of the pack were taken as a whole, while others were trimmed all round (1 cm.).

saturated potassium iodide solution. The released iodine was titrated with 0·01N sodium thiosulphate, using starch as indicator. Under the particular conditions of extraction, chloroform extracted 75-80 per cent of fat from the biscuits (the amount of extracted fat was almost constant for a particular product). With each determination of peroxide value, the amount of the fat in a given volume of the extract was also determined.

Kreis value was determined by the modified colorimetric method of Walters *et al.*[4] in a petroleum ether extract of the biscuit powder and is expressed in Klett-Summerson units (with a 54 filter) per g. of fat.

Organoleptic tests — A panel of five judges (4 men and 1 woman) was selected on the basis of (1) triangular difference tests[5,6], and (2) grading test. The grading test was carried out to test the ability of the judges for ranking samples of known peroxide values ranging between 2 and 20 m. eq./kg.

A special score card was evolved for organoleptic tests. A judge was given 4 samples at a time, always between 10 a.m. and 12 noon. It was observed that after lunch hour the sensitivity of the judges was reduced. All the selected judges were nonsmokers and were between the ages of 25 and 35 years. The samples were assessed with respect to:

1. *Appearance* — (a) Surface, (b) shape, (c) colour, and (d) texture;
2. *Crispness* — (a) Feel, (b) bite, and (c) eating quality; and
3. *Taste and odour* — (a) Rancidity, (b) bitterness, and (c) any other undesirable feature.

The assessment of taste and odour of the samples were made according to the procedure outlined by Grant *et al.*[7]. Each factor, viz. appearance, crispness and taste and odour, was assigned a maximum rating of ten.

Keeping quality — Two shortenings prepared from hydrogenated groundnut oil were used: (I) a proprietary brand commonly used in India and (II) an experimental emulsified product containing lecithin and glyceryl monostearate. The characteristics of the two shortenings are given in Table 2.

Based on the comparative antioxygenic activities of several substances[8] in groundnut oil and its hydrogenated products, butylated hydroxy anisole (BHA) at a level of 0·015 per cent of fat and a combination of BHA, propyl gallate and citric acid (2: 1: 1) at 0·02 per cent level were used. The antioxidants were first dissolved in a small quantity of the shortening and then mixed in the batch.

Baking — Six experimental batches (50 lb. each) of " Nice " brand biscuit doughs were prepared from wheat flour (*maida*), sugar, shortening, honey, liquid glucose and coconut shreds. The ingredients used for

TABLE 2 — CHARACTERISTICS OF EXPERIMENTAL SHORTENINGS

	SHORTENING I	SHORTENING II
M.P., °C.	37·00	41·00
Iod. val.	63·20	48·50
Thiocyanogen val.	61·00	43·80
Smoke point, °C.	210·00	212·00
Free fatty acid (% oleic)	0·08	0·04
Fatty acids composition		
Saturated, %	27·20	38·45
Oleic, %	72·36	61·43
Linoleic, %	0·44	0·12

TABLE 3 — PEROXIDE AND KREIS VALUES OF FAT IN PRODUCTS STORED AT 26°-27°C.

STORAGE PERIOD weeks	BATCH No.											
	1		2		3		4		5		6	
	Peroxide val.	Kreis val.	Peroxide val.	Kreis val.	Peroxide val.	Kreis val.	Peroxide val.	Kreis val.	Peroxide val.	Kreis val.	Peroxide val.	Kreis val.
4	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
8	2·5	nil	1·0	nil	nil	nil	nil	nil	nil	nil	nil	nil
12	5·0	nil*	3·2	nil	nil	nil	nil	nil	nil	nil	nil	nil
14	8·5	nil	3·2	5	2·5	nil	nil	nil	nil	nil	nil	nil
16	15·0	5	7·9	10*	6·8	nil	1·0	nil	nil	nil	nil	nil
17	20·5	58	10·2	60	8·5	nil	3·0	nil	nil	nil	nil	nil
18	22·6	25	15·8	25	8·6	nil	3·5	nil	2·2	nil	nil	nil
20	22·6	31	16·5	39	8·9	5*	4·0	nil	2·2	nil	nil	nil
26	22·8	60	18·2	85	10·5	39	4·8	5*	3·5	10	1·8	5
30	33·5	62	20·5	15	11·2	60	6·2	10	3·5	10	1·8	7
36	42·6	68	22·5	105	15·2	52	10·1	85	8·6	21*	2·0	nil
40	50·8	100	22·9	100	15·4	50	9·5	79	8·2	83	2·0	10
44	56·2	120	32·6	120	18·2	60	10·2	58	9·9	67	3·0	6
48	56·2	210	34·8	100	10·5	68	12·3	29	12·5	62	3·6	22
52	—	—	—	—	—	—	—	—	—	—	8·6	25*

*Organoleptic detection of rancidity.

different batches were from the same lot. Biscuits were baked under factory conditions in a conveyer belt oven at 400°-450°F. and packed after cooling in small units of 8 biscuits each.

The details of the experimental batches were as follows: batch 1 contained shortening I; batch 2 contained shortening I with BHA; and batch 3 contained shortening I with BHA, propyl gallate and citric acid; and batches 4-6 were compositions prepared as above with shortening II.

The products were packed in grease-proof paper, butter paper and cellophane paper cut to a uniform size of 5·5 × 8·5 in. This sample paper packaging was done in preference to tin containers in order to obtain results quickly.

The results of organoleptic tests, peroxide and Kreis values are recorded in Tables 3-5.

Seepage studies — Three fats, namely refined groundnut oil and shortenings I and II, were used for studying the effect of melting point and quantity of the fat on the " free oil " content of the baked product.

Doughs were prepared from wheat flour (*maida*), sugar and shortening using a mixture of ammonia and sodium bicarbonates as the leavening agent (0·75 per cent of flour). The amounts of shortening used were calculated to give 8, 12, 15, 20 and 30 per cent of fat in the final product. The biscuits were baked in a laboratory oven at 450°F. for 8 min. The results are given in Tables 6 and 7.

TABLE 6 — INFLUENCE OF TOTAL FAT CONTENT ON THE FREE OIL CONTENT OF BISCUITS

[*Values expressed as percentages of fat in the product seeping through during* 48 *hr. at* 37°C. (90% *relative humidity*)]

	FAT IN BISCUITS, %				
	8	12	15	20	30
Refined groundnut oil	1·02	3·24	5·90	6·80	10·2
Shortening I	0·52	1·06	2·16	4·10	5·0
Shortening II	0·10	0·48	0·05	1·12	3·1

TABLE 7 — SEEPAGE OF FREE OIL IN BISCUITS WITH TIME

[*Expressed as percentage of fat in the product* (12%) *seeping through at* 45°C.]

SHORTENING	SEEPAGE TIME hr.					
	6	12	24	36	48	60
Shortening I	0·6	0·8	1·3	2·0	2·1	3·5
Shortening II	0·1	0·3	0·5	0·8	1·0	2·5

TABLE 4 — ORGANOLEPTIC ASSESSMENT OF BISCUITS STORED AT 26°-27°C.

BATCH No.	COMPOSITION OF SHORTENING	SHELF LIFE* weeks
1	S$_1$†	12
2	S$_1$ + BHA	16
3	S$_1$ + BHA + PG + CA	20
4	S$_2$	26
5	S$_2$ + BHA	36
6	S$_2$ + BHA + PG + CA	52

*Period when the product was adjudged rancid.
†S$_1$ and S$_2$ denote shortenings I and II.

Discussion

The results presented in Tables 2-7 indicate the beneficial effects of higher melting shortening on the keeping quality of biscuits. The products baked with shortening II were found acceptable even after 26 weeks as compared to 12 weeks in the case of shortening I (TABLE 4).

The use of BHA alone results in a slight improvement, the shelf life being about 1½ times that of the control. The protective effect of BHA is further enhanced when it is used in combination with propyl gallate and citric acid. The antioxygenic activity of the combination appears to be more pronounced with shortening II than with shortening I.

TABLE 5 — PEROXIDE AND KREIS VALUES OF FAT IN PRODUCTS STORED AT 37°C. (98·6°F.)

STORAGE PERIOD weeks	BATCH No.											
	1		2		3		4		5		6	
	Peroxide val.	Kreis val.	Peroxide val.	Kreis val.	Peroxide val.	Kreis val.	Peroxide val.	Kreis val.	Peroxide val.	Kreis val.	Peroxide val.	Kreis val.
4	2·6	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
8	10·1	10*	1·2	nil	2·0	nil	nil	nil	nil	nil	nil	nil
12	10·2	10	8·4	nil	4·6	6	1·9	nil	nil	nil	nil	nil
16	29·5	29	10·1	20	6·2	10*	1·6	nil	1·5	nil	nil	nil
18	35·2	45	15·3	48	6·5	9	4·5	nil	nil	nil	1·2	nil
20	36·1	150	25·6	120	8·6	20	6·6	8*	3·6	nil	1·6	nil
22	32·8	106	27·2	100	20·5	100	8·6	6	6·2*	nil	2·8	6
24	30·2	220	28·9	100	32·0	80	10·2	29	5·2	10	3·0	10*

*Organoleptic detection of rancidity; all biscuits had an objectional flavour after 24 weeks.

The shelf life of biscuits is increased from 26 to 52 weeks in the case of shortening II and 12 to 20 weeks in the case of shortening I.

A correlation between the rate of seepage of fat and the shelf life of the biscuits is observed; the amount of fat oozing out being directly proportional to the amount of fat incorporated (ranging from 8 to 30 per cent).

In a similar study on ration biscuits, Grant *et al.*[7] and Lips *et al.*[9] have shown that the type of the shortening used has a more pronounced effect on the keeping quality than fat concentration or plant practice. Stabilized hydrogenated vegetable shortenings (m.p. ranging between 37·3° and 41·9°C.) were more stable in biscuits stored at 43·4°C. than animal-vegetable shortening melting at 49°C.

In the light of observations made in the present investigations, it is evident that shortening of m.p. 41°C. is more stable in biscuits than shortening melting at 37°C. This finding is of special significance considering the tropical conditions obtaining in India.

References

1. LANDROCK, A. H. & PROCTOR, B. E., *Mod. Pack.*, **24** (1951), 107.
2. SAHASRABUDHE, M. R. & BHATIA, D. S., *J. sci. industr. Res.*, **12B** (1953), 35.
3. LEA, C. H., *Rancidity in Edible Fats*, Food Investigations Special Report No. 46 (H.M.S.O., London), 1938, 125.
4. WALTERS, W. P., MUERS, M. M. & ANDERSON, E. B., *J. Soc. chem. Ind. London*, **57** (1938), 53, 56.
5. HELM, E. & TROLLE, B., *Wallerstein Lab. Comm.*, **9** (1946), 181.
6. LOCKHART, E. E., *Food Technol.*, **5** (1951), 428.
7. GRANT, G. A., MARSHALL, J. B. & WHITE, W. H., *Canad. J. Res.*, **23F** (1945), 123.
8. SAHASRABUDHE, M. R., *J. sci. industr. Res.*, **12B** (1953), 63.
9. LIPS, H. J., CROWSON, N. C. & WHITE, W. H., *Canad. J. Res.*, **25F** (1947), 51.

Letters to the Editor

STEADY-STATE TEMPERATURE DIFFERENCES BASED ON THE THEORIES OF THE PSYCHROMETER & OF THE EVAPORATION OF DROPLETS

EXPRESSIONS BASED ON THE THEORIES OF the psychrometer and of the evaporation of droplets have been derived for evaluating the steady-state temperature difference, δ, between a drop of a solvent and that of a unit molal solution suspended in a chamber saturated with the vapour of the solvent. It was shown[1,2] that for the case of water at ordinary temperatures both theories lead to similar values of δ. This apparent identity is now shown to be due to a fortuitous numerical coincidence of certain factors which, in effect, renders the two expressions almost identical.

A comparison of the two expressions[1] for δ reveals that the condition for identity is given by

$$\frac{k'RT}{M^2p'DL} \times \frac{10^5}{3{\cdot}189} = \frac{hMaP_m}{kM^2p'L}$$

$$\text{or} \quad \frac{k'RT}{D} \times \frac{10^5}{3{\cdot}189} = \frac{hMaP_m}{k} \quad \ldots \ (1)$$

Since

$$\frac{RT \times 10^5}{3{\cdot}189} = \frac{MaP_m}{d}$$

where d is the density of air, equation (1) reduces to

$$\frac{k'}{Dd} = \frac{h}{k} \quad \ldots\ldots\ldots\ldots \ (2)$$

Now $\frac{h}{k}$, the ratio of the heat and mass transfer coefficients, is given, according to the Arnold's[3] psychrometric theory, by the expression

$$\frac{h}{k} = s \times \frac{\left\{1 - r + r\left(\frac{\eta}{Dd}\right)\right\}}{\left\{1 - r + r\left(\frac{s\eta}{k'}\right)\right\}} \quad \ldots \ (3)$$

where s, η, d and k′ are the specific heat, viscosity, density and thermal conductivity respectively of air, and D is the diffusion coefficient of the vapour concerned in air. The factor r has been defined by Arnold as the ratio of the fluid velocity at the outer boundary of an assumed film around the liquid surface to that in the main fluid stream.

For the case of water $\frac{\eta}{Dd}$ is nearly equal to $\frac{s\eta}{k'}$, with the result that $\frac{h}{k}$ approximates to s. It is in fact due to this approximation that the adiabatic cooling lines of the conventional humidity charts are used for the interpretation of wet and dry-bulb temperatures. Thus, for water

$$\frac{h}{k} = s = \frac{k'}{Dd}$$

which in fact is the condition [cf. equation (2)] of equality of the expressions based on the two theories under consideration.

For the case of other liquid-air systems for which $s \neq k'/Dd$, it is seen that the identity given by equation (2) is true only if $r \rightarrow 1$ [equation (3)], which means that there is negligible convection. In fact, one of the fundamental assumptions in the derivation of the expressions for the evaporation of droplets in air is that convectional effects do not exist[4]. This assumption is justifiable for sufficiently small enclosures, whereas for bigger enclosures Langstroth *et al.*[4] actually observed a higher rate of evaporation than that predicted by the simple theory neglecting convection effects. On the other hand, when $r \rightarrow O$ (convectional resistance being a controlling factor), $\frac{h}{k} \rightarrow s$. For the usual organic solvents the diffusion coefficient "D" is of such a magnitude that $s < k'/Dd$, whence δ, as given by the theory of evaporation, is less than that evaluated by the psychrometric theory.

The above equations pertain to the case of negligible heat loss by radiation. If, however, radiation effects are appreciable the heat loss per unit time due to radiation is given by

$$q_r = \sigma \epsilon A \; (T^4 - T_o^4) \; . \; . \; . \; . \; . \; (4)$$

where σ is the emissivity; ϵ, the Stefan-Boltzmann constant; A, the area of the drop; T_o and T, the ambient and drop temperatures respectively. For the small temperature difference $(T - T_o)$ involved in the present case, equation (4) reduces to

$$q_r = 4\sigma A \epsilon T_o^3 . \Delta T = h_r A . \Delta T$$

where h_r is the coefficient of radiant heat transfer.

Thus the total heat loss according to the theory of evaporation of drops becomes

$$q = 4\pi k' S . \Delta T + 4\pi . h_r . a'^2 . \Delta T \; . \; . \; . \; (5)$$

where a′ is the radius of the spherical drop and "S" is a shape factor. Proceeding similarly as in the previous derivation[1], "δ" is now given by

$$\delta = \frac{10^{-3}}{\{ k' RT \times 10^{-5} (1 + h_r a'/k') / M^2 L p' D \times 3{\cdot}189 \} + L/RT^2} \; . \; . \; (6)$$

The factor due to radiation is $h_r a'/k'$. According to the psychrometric theory the total heat loss is given by

$$q = h\bar{A} . \Delta T + h_r A . \Delta T = h . \bar{A} \Delta H L \; . \; . \; (7)$$

where A is the surface area of the drop; $\bar{A}$, the average area involved in heat and mass transfers; ΔH, the difference between the absolute humidity corresponding to saturation at the temperature of liquid surface and that of ambient air; and L, the latent heat of vaporization of the liquid in cal. g.

Starting from equation (7) and proceeding as before[1], "δ" is now given by

$$\delta = \frac{10^{-3}}{\{ h M a P_{in} (1 + h_r A / h\bar{A}) / k M^2 p' L \} + L/RT^2} \; . \; . \; . \; (8)$$

the radiation factor being $h_r A / h\bar{A}$. A comparison of equations (6) and (8) shows that despite the fact that $\frac{h}{k} = \frac{k'}{Dd}$ for water, the values of "δ" evaluated by the two theories do not agree with each other *unless* $h\bar{A}/A = k'/a'$, which happens only under conditions of negligible convection as shown below. According to Arnold the heat transfer coefficient is given by

$$h = \frac{\left(\frac{k'}{B}\right)\left(\frac{s\eta}{k'}\right)}{(s\eta/k' + \overline{1 - r}/r)} \; . \; . \; . \; . \; . \; (9)$$

where "B" is the film thickness. When convection is negligible $r \rightarrow 1$ and hence $h = \frac{k'}{B}$.

$$\text{Now } q = \frac{4\pi k' . \Delta T}{-\int_{a'} dx/x^2} = \frac{4\pi k' a a'}{(a - a')} = \frac{k'}{B} \cdot \bar{A}$$

where $B = (a - a')$ and $\bar{A} = 4\pi a a'$, a and a′

being radii of the enclosure and the drop respectively.

$$\text{Since } a' << a, \ \frac{h\bar{A}}{A} = \frac{k'}{a-a'} \times \frac{4\pi aa'}{4\pi a'^2} \cong \frac{k'}{a'}$$

making equations (6) and (8) identical. Thus, when radiation and convection are appreciable ($r << 1$), the two equations give different values of "δ" for water. The effect of radiation is indeed quite appreciable when the size of the drop is considerable and also when convection is small. For a drop of radius 2 mm., assuming negligible convection, it is found that

$$\text{since } h_r = 4\,\sigma\,\epsilon T^3 = 4\times 0{\cdot}9\times 1{\cdot}37\times 10^{-12} \times (303)^3$$

$$= 1{\cdot}37\times 10^{-4} \text{ cal./sq. cm./sec./°C.}$$

$$\text{and } k' = 5{\cdot}7\times 10^{-5} \text{ cal./sq. cm./sec./°C./cm.}$$

$$\therefore\ h_r a'/k' = 0{\cdot}48$$

which is appreciable as compared to unity in equation (6).

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1. IYENGAR, B. R. Y., *J. sci. industr. Res.*, **13B** (1954), 73.
2. BRADY, A. P., HUFF, H. & MCBAIN, J. W., *J. phys. Coll. Chem.*, **55** (1951), 304.
3. ARNOLD, J. H., *Physics*, **4** (1933), 255.
4. LANGSTROTH, G. O., DIEHL, C. H. H. & WINHOLD, E. J., *Canad. J. Res.*, **28** (1950), 580.

THE SHIFT IN THE " THRESHOLD POTENTIAL " DUE TO CHANGE IN THE NATURE OF THE ELECTRODE SURFACE AS A FUNCTION OF THE GAS PRESSURE

MOHANTY[1] HAS RECENTLY SHOWN THAT THE " threshold potential " V_m in silent electric discharge shifts by an amount ΔV_m due to change in the nature of the electrode surface, and, therefore, in the coefficient[2] γ. That ΔV_m is an inverse function of the gas pressure p is seen from Fig. 1. Thus, ΔV_m due to a film of sodium chloride on the glass walls of an oxygen-filled Siemens' tube was 0·15 kV. (rms, 50 ∼) at 50 mm. pO_2, and diminished progressively to 0·05 kV. at 450 mm. Neuman[3], and Ehrenkrantz[4] found that ΔV_s, the change in the sparking potential V_s with cathode material, was similarly less pronounced at higher values of $p\delta$, δ being the electrode separation. The above observations arise from the circumstance that for low values of X/p, where X is the field, α/p (α is the first Townsend coefficient) is sensibly an exponential function[5] of X/p. Hence, setting $\alpha/p = A \exp (BX/p)$, one obtains

$$V_m = \frac{p\delta}{B}\left[\log\left(\frac{1}{Ap\delta}\log\frac{1}{\gamma}\right)\right]$$

an equation identical in form to that for V_s, so that V_m, as in the case of V_s, is very little dependent on changes in γ.

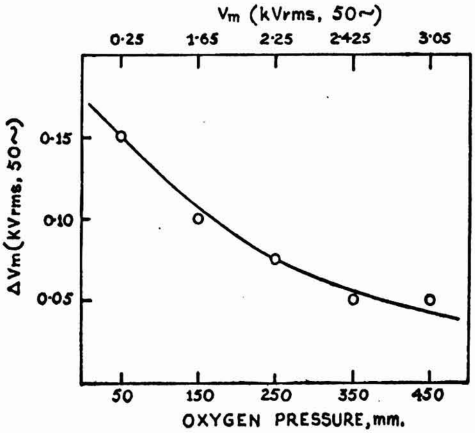

FIG. 1 — ΔV_m FOR SODIUM CHLORIDE CONTAMINATION OF GLASS ELECTRODES AS A $f(p)$

Grateful thanks of the authors are due to Prof. S. S. Joshi for his keen interest in the work.

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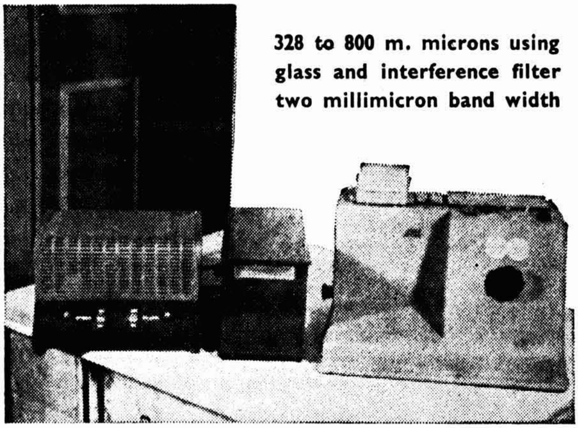
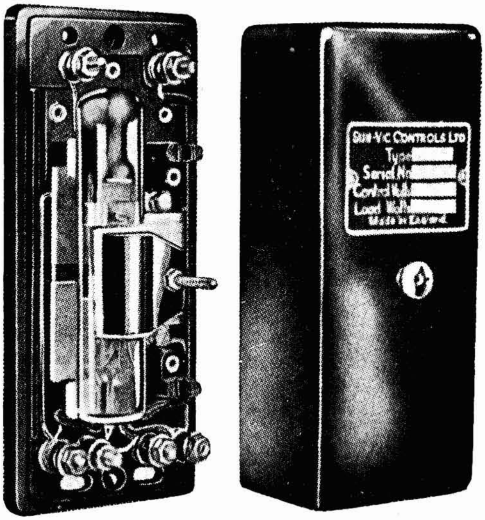
21 *April* 1954

1. MOHANTY, S. R., *J. sci. industr. Res.*, **13B** (1954), 145.
2. LOEB, L. B., *Fundamental Processes of Electrical Discharge in Gases* (John Wiley & Sons, New York), 1939, 383.
3. NEUMAN, L. J., *Proc. nat. Acad. Sci.*, **15** (1929), 259.
4. EHRENKRANTZ, F., *Phys. Rev.*, **55** (1939), 219.
5. LOEB, L. B., *Fundamental Processes of Electrical Discharge in Gases* (John Wiley & Sons, New York), 1939, 344.





Printed by H. Jacquemotte, S.J., at the Catholic Press, Ranchi, India
Published by the Council of Scientific & Industrial Research, India. Editor : B. N. Sastri, M.Sc.

Regd. No. P-842