Journal of Scientific & Industrial Research

Vol. 13, No. 8, AUGUST 1954

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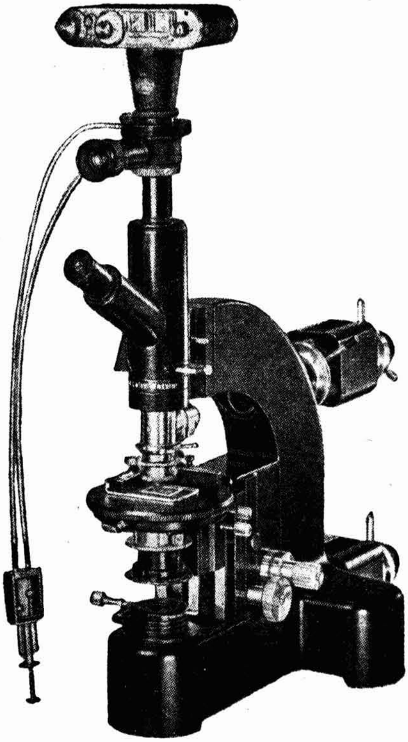

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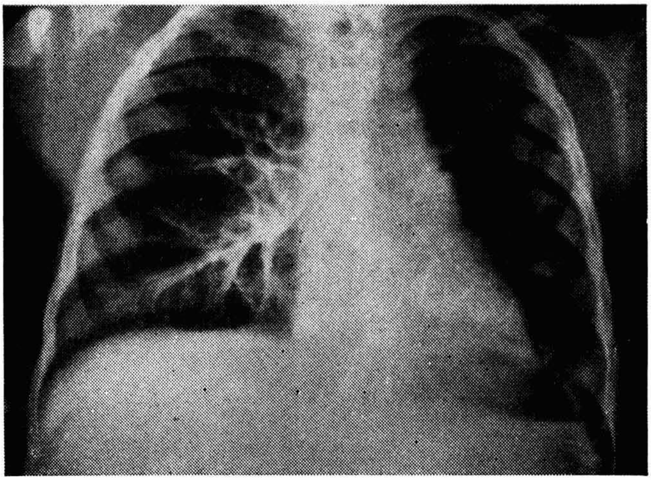

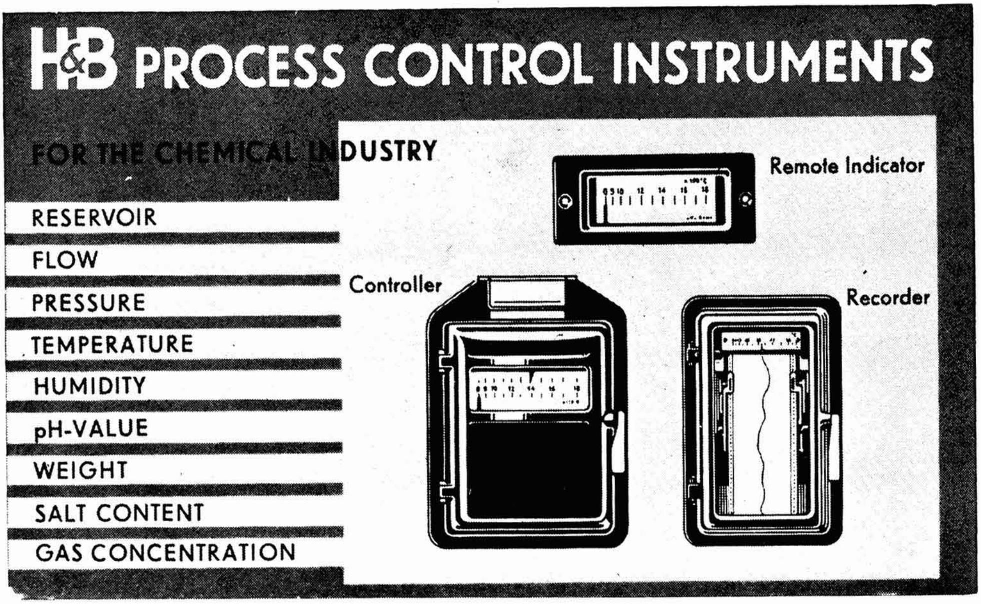

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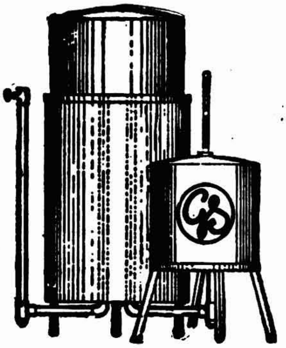

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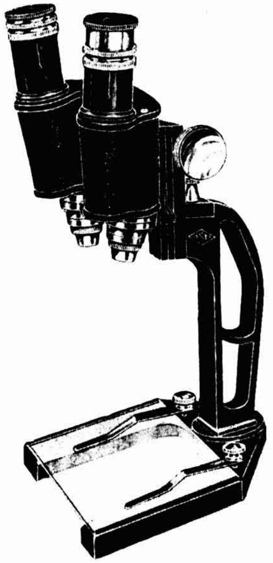

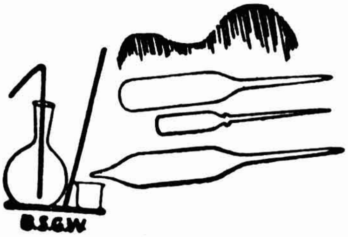
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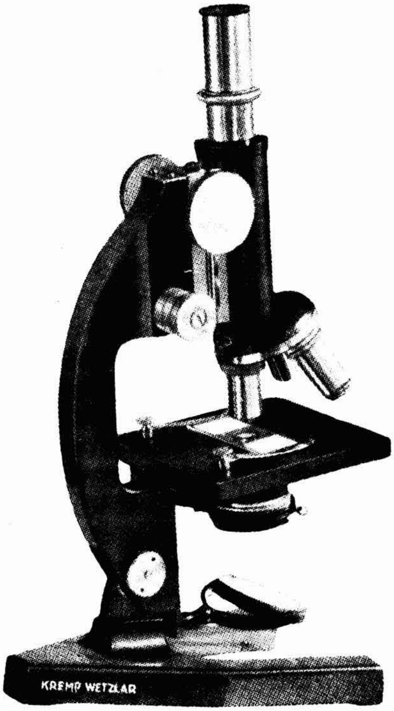
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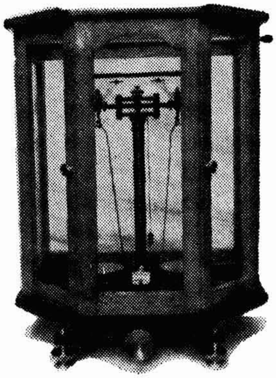

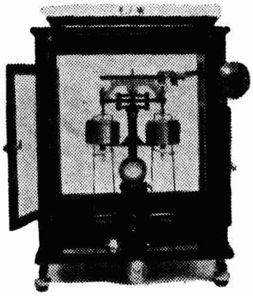

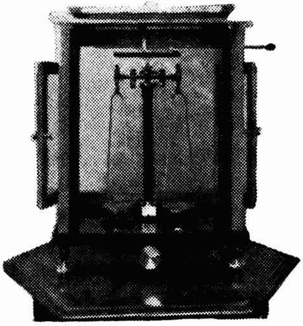

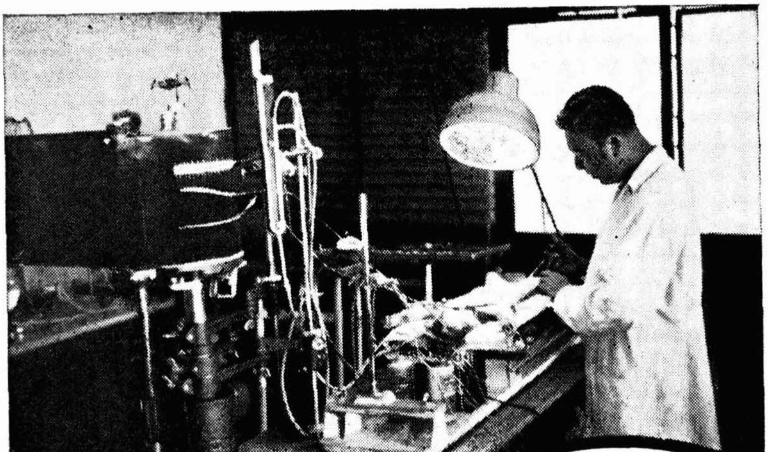
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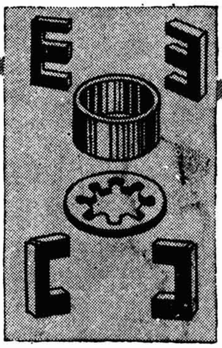

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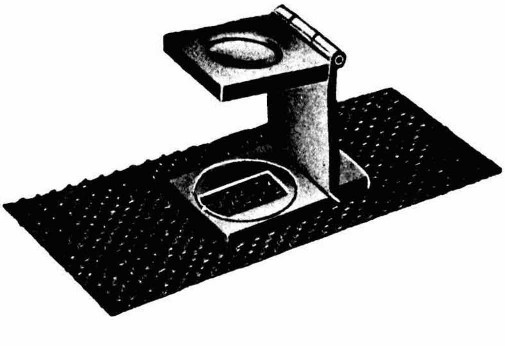

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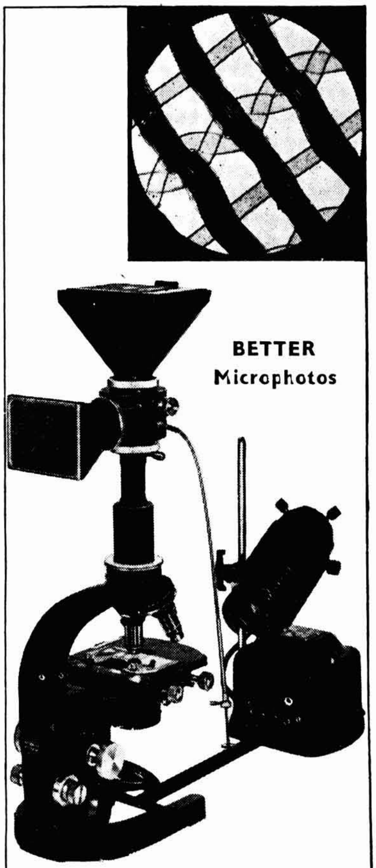
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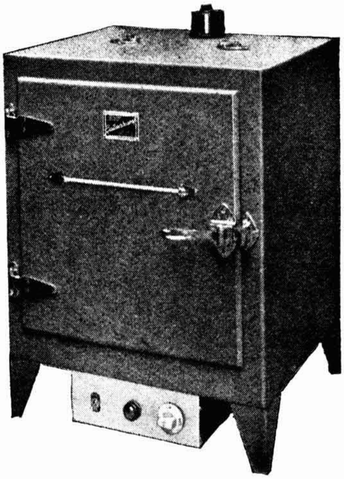

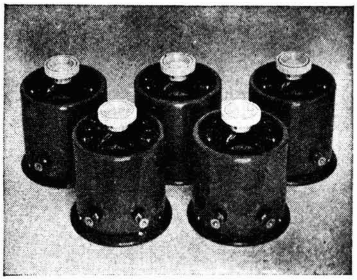

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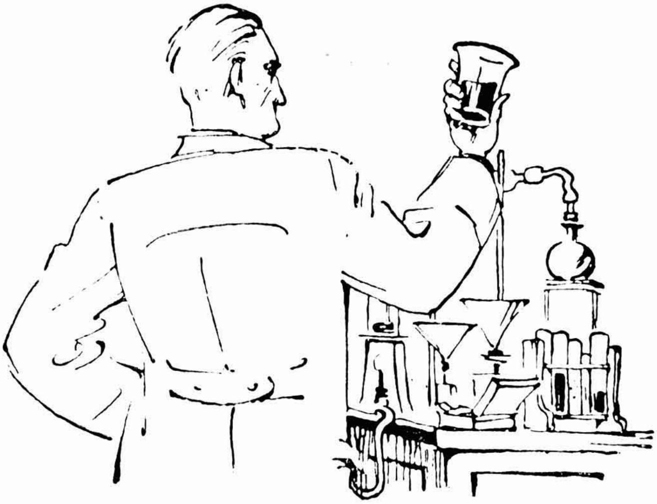

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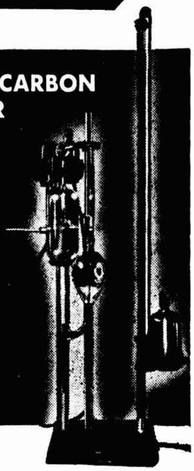

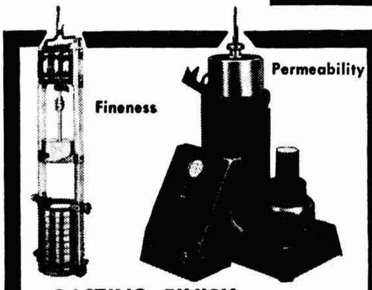
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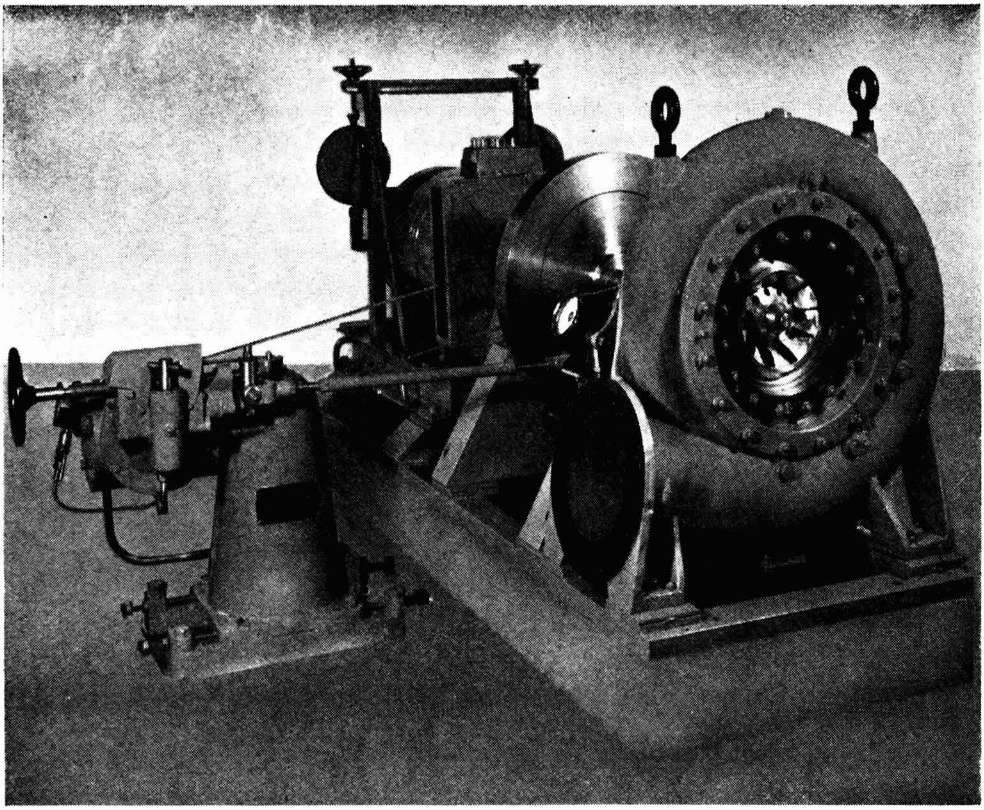

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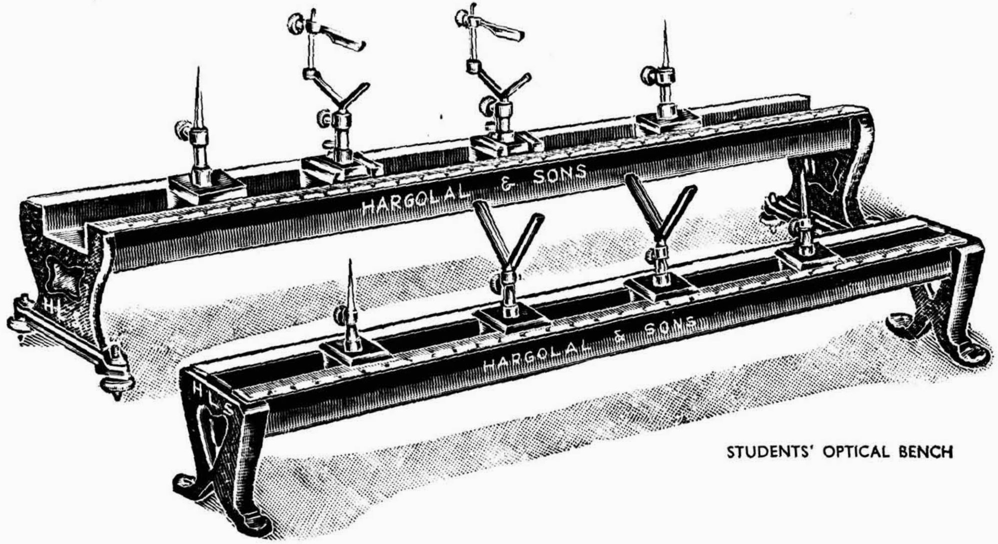

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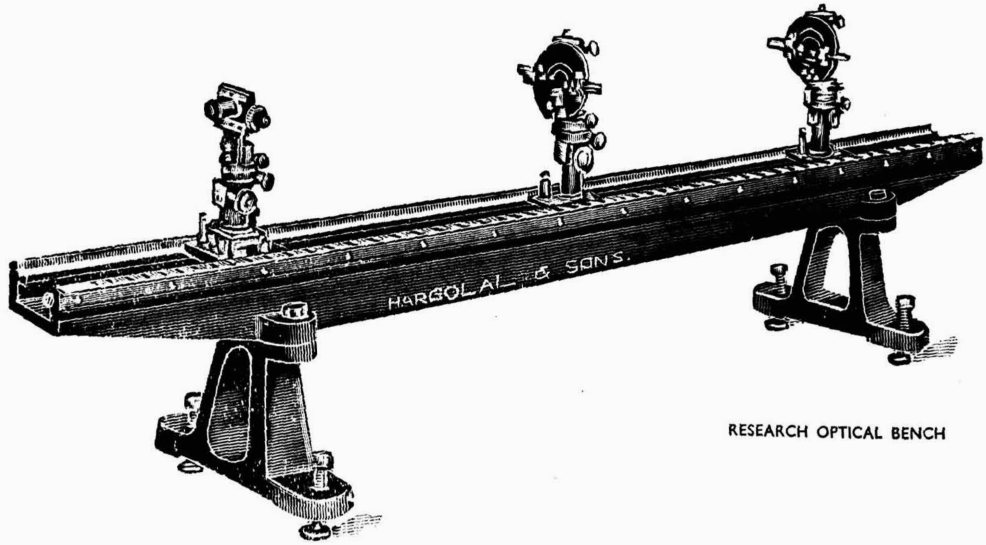

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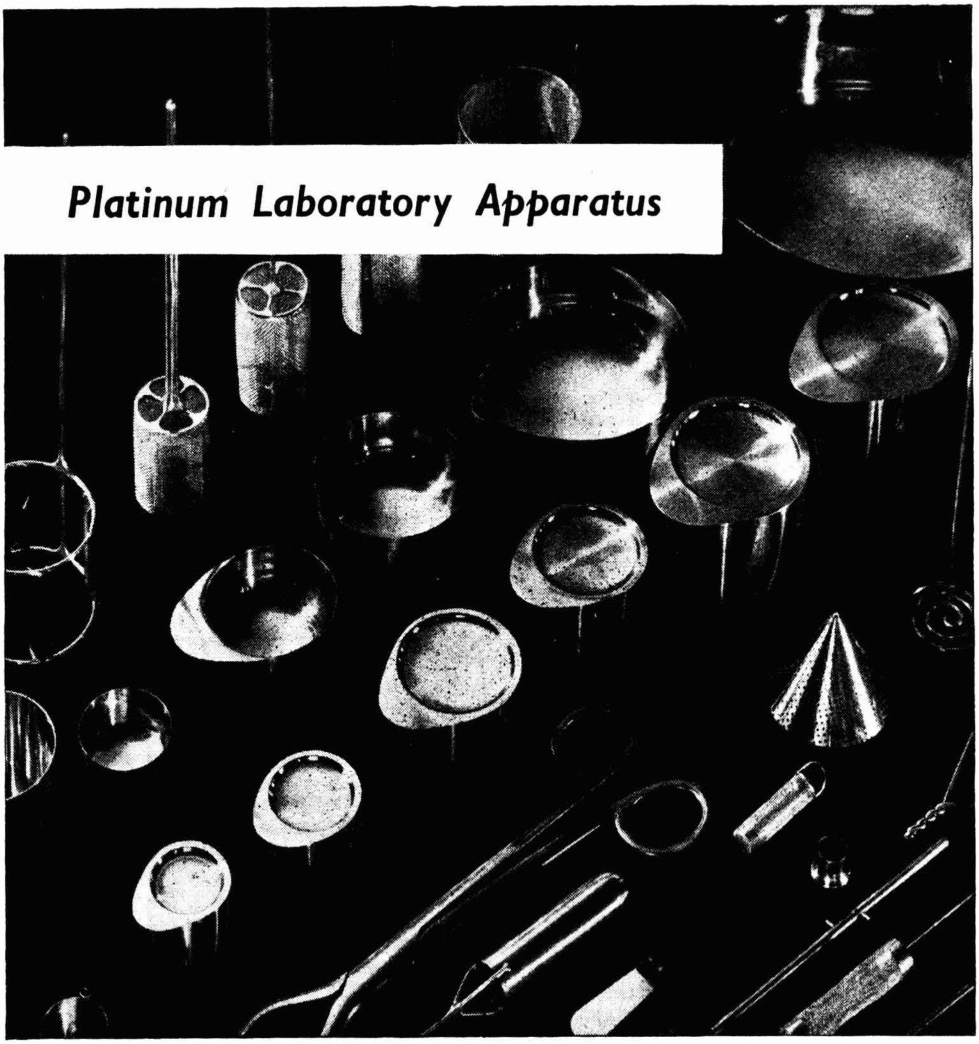

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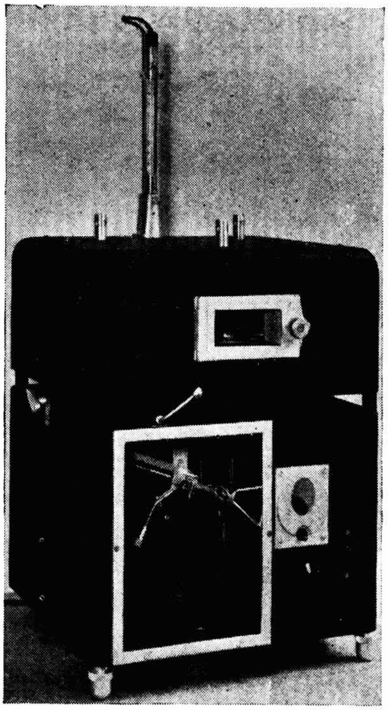

Low Temperature Physics

DR. DAVID SHOENBERG, F.R.S.*
Royal Society Mond Laboratory, Cambridge

WITH the installation of a helium liquefier in the National Physical Laboratory late in 1952, India entered the field of active research at very low temperatures and this year also happens to mark the twenty-first anniversary of the opening of my own laboratory in Cambridge. This then is an appropriate time to take stock of the position in low temperature physics, to review the significance of this branch of physics, its aims and achievements and its possibilities for the future.

In general the effects of cooling are just opposite to those of heating — for instance, cooling produces contraction while heating produces expansion — and since heating is easier to achieve than cooling, it might at first sight seem unnecessarily complicated to use cooling for studying the temperature variation of physical properties. This argument, however, overlooks the existence of the absolute zero of temperature: although the temperature of a body can be raised indefinitely it cannot be lowered below this absolute zero, which lies at −273°C. This in turn implies that studies at very low temperatures can be of interest in two ways: first, simplifications of the theory explaining the physical properties of matter often occur when the temperature is low enough — more precisely when kT becomes small enough compared to some characteristic energy involved in the particular phenomenon concerned. Secondly, a particular property is often determined by two competing processes, one of which becomes dominant only at very low or at very high temperatures; thus by going to low temperatures one of these processes, which is hidden at higher temperatures, makes itself apparent and can be studied in isolation. Examples of both these aspects will be given later.

Even if it were not for these two reasons for studying the properties of matter at very low temperatures, in order to confirm in greater detail theories which have already been worked out in broad principle, there is yet a third reason. This is based on the purely empirical approach of the experimental physicist who has a slight mistrust of all theories and feels it is unwise to accept any theoretical prediction until it has been tested over as wide a range of the variables — in this case the temperature — as possible. This last approach has in fact yielded handsome dividends and provides perhaps the major interest of low temperature physics today. Thus although the electron theory of metals provides a good qualitative picture of electrical resistance at high and fairly low temperatures, it completely failed to predict the occurrence of superconductivity, discovered by Kamerlingh Onnes in 1911 mainly as a result of the empirical approach just outlined. Again the properties of liquid helium proved to be quite strikingly different from those of ordinary liquids and have provided another exciting field of research in recent years.

Although in broad principle it is clear that these qualitatively new effects arise from interaction effects between elementary particles (the electrons in superconductivity and the helium atoms in liquid helium), which are not so important at higher temperatures, the difficult quantum theory of these inter-

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*Temporarily acting as Unesco Expert on Low Temperature Physics at the National Physical Laboratory of India, New Delhi.

actions has not yet been properly worked out, so that the phenomena still offer a powerful challenge to the theoretician. Since the theory is so incomplete, the experimental study of superconductivity and liquid helium, and for that matter the search for other new and unpredicted effects, offers a most attractive field for the experimental physicist; he can feel that he is not merely dotting the i's and crossing the t's of existing knowledge but may always be on the threshold of quite new discoveries. One last general point: since everything except helium solidifies at very low temperatures, it is evident that the contribution of low temperature techniques must lie mainly in the field of solid state physics, and this will be illustrated by the examples discussed later.

Before surveying the actual problems of low temperature physics it is as well first to explain how low temperatures are achieved and how they are used. The basic principle is to immerse the substance to be tested in a sufficiently cold liquid bath, and since the coldest liquid of all is liquid helium, the problem of attaining very low temperatures reduces essentially to the problem of liquefying helium. There are four broad principles used in cooling a gas to its liquefaction point: (a) the cascade principle, in which the gas is cooled by circulation in tubes immersed in some other liquefied gas (e.g. air or hydrogen), (b) allowing the gas to do mechanical work by approximately adiabatic expansion, (c) the use of the Joule-Kelvin effect, in which the flowing gas suffers a pressure drop and cools down, provided it is already below a certain so-called "inversion" temperature and (d) the heat exchange principle in which the already cooled gas is circulated in such a way as to cool the incoming gas.

Most helium liquefiers use (c) and (d) combined with either (a) and (b) or with (a) alone. Since the inversion temperature of helium is very low — about 15°K.— liquid hydrogen is essential if (a) is to be used without (b), and this principle is used in most of the older cryogenic laboratories, often in the ingenious miniature liquefiers developed by Simon and his school in the early 1930's in Germany and later in Oxford. Alternatively, if only liquid air is available, (b) is applied by using a special type of expansion engine. This last method, which was pioneered by Kapitza in Cambridge in 1934, has been considerably developed in recent years, particularly by Collins at M.I.T., and the Collins cryostat, as it is called, is now manufactured commercially in the United States and works (though less efficiently) even without liquid air. This development has led to a remarkable expansion of research in low temperature physics all over the world, and particularly in the United States, since it is no longer necessary for a laboratory to embark on the lengthy and complicated task of building its own liquefier, if it can afford to purchase the ready-made model. It is one of these Collins cryostats, purchased through the American Point Four Programme of technical assistance, which has been installed at the National Physical Laboratory of India, and forms the central feature of the new low temperature division set up with the help of the Unesco Technical Assistance Programme.

It is a long cry from the days of Kamerlingh Onnes, who after years of effort first successfully liquefied helium in 1908 by the cascade principle combined with the Joule-Kelvin effect. Describing his first liquefaction he concluded: " At 9.40 p.m. only a few ccs. of liquid helium were left. Then the work was stopped. Not only had the apparatus been strained to the uttermost during the experiment and its preparation, but the utmost had been demanded from my assistants." Nowadays helium liquefaction has become quite a routine operation lasting only a few hours in all, but if much of the excitement and romance of preparing liquid helium has gone, there is still plenty of excitement left in the problems that remain to be solved with its aid.

Once sufficient liquid helium has been prepared, it is siphoned into a Dewar flask containing the apparatus which is to be cooled down (though in the miniature liquefiers the liquefier itself is used as the experimental vessel) and to reduce flow of heat through the walls of the Dewar, it is usually surrounded by a second Dewar flask containing liquid air. In this way the specimen to be studied can be kept at 4·2°K., the temperature of liquid helium boiling at atmospheric pressure, for as long as liquid helium remains in the Dewar flask — several hours in typical conditions. To lower the temperature further, the pressure above the bath is reduced by a pump, and in this way temperatures as low as 1·0°K. (exceptionally 0·7°K.) can be reached; further reduction by this means is not, however, practicable, since the necessary pressure falls off exponentially and rapidly gets outside the range of practical possibilities.

Here the method of adiabatic demagnetization of a paramagnetic salt comes into its own and it is possible to cool the salt (and any body in thermal contact with it whose entropy is small compared with that of the salt) to as low as 0·005°K. Just as there is a natural limit for the temperature attainable by pumping liquid helium, here too a limit is set by the properties of the salt. More precisely it is not possible to go very much lower than the temperature T given by $kT = \epsilon$, where ϵ is the small separation of the energy levels of the paramagnetic ion, caused by interactions with the crystal lattice and the other ions; this temperature is at best about 0·1°K., so 0·005°K. already represents extreme conditions. This technique is more difficult to use in practice than that of pumping helium above 1°K. and even though much ingenuity has been exercised in applying it to special problems, many properties of matter which have been thoroughly studied above 1°K. have not yet been tackled in the adiabatic demagnetization range. At present the most hopeful method of reaching still lower temperatures is to exploit the small paramagnetism of atomic nuclei, and theoretically this nuclear demagnetization method might enable temperatures as low as 10^{-6} °K. to be reached; the practical difficulties are, however, much more formidable than in the ordinary demagnetization method and have not yet been overcome.

Let us now survey briefly some of the properties of matter at low temperatures, dealing first with those where the theory is already clear in broad outline, but where a study at low temperatures has been particularly helpful in bringing about a clearer understanding in the past, or is likely to be so in the future. The specific heat of a solid at ordinary temperatures is due mostly to the fact that the energy of the thermal vibrations of its crystal lattice increases with temperature. Quite a simple application of quantum theory and statistical mechanics shows that the specific heat is determined primarily by the frequency spectrum of these lattice vibrations, but it is a much more difficult problem to calculate the detailed form of this spectrum in terms of the basic properties of the solid — the forces between the atoms which hold them together in a particular crystal lattice. Fortunately this detailed form is not required in two limiting cases. At high temperatures only the total *number* of modes of vibration matters, and this is just three times the number of atoms; from this follows the explanation of Dulong and Petit's empirical law that all solids have approximately the same specific heat, 3R per gram atom, provided the temperature is high enough. Essentially this limiting case involves the assumption that kT is greater than the elementary quantum $h\nu$ corresponding to any of the possible modes of vibration. At low temperatures the theory again becomes simple, for now it is only the modes of low frequency which matter, and the vibration spectrum for sufficiently low frequencies is a simple one — the same as that for an ideal continuum with no atomic structure at all. This leads to Debye's famous law that the specific heat at sufficiently low temperatures — usually of the order of 10°K. or lower — varies as T^3, the constant of proportionality being precisely predictable in terms of the elastic constants of the solid. Here then is our first example of a problem where measurements at very low temperatures permit a particularly direct check of a theory — a more searching check in fact than is possible at high temperatures, where the result is independent of the special (quantum) form of the theory required to predict the low temperature behaviour.

There is also another contribution to the specific heat of the solid if it is a metal: this comes from the kinetic energy of the conduction electrons, which, although large, varies only slightly with temperature, essentially because of the Pauli exclusion principle which does not permit more than two electrons to occupy any one quantized state of motion. Consequently at ordinary temperatures this small electronic specific heat, which turns out to be proportional to T, is masked by the much larger lattice specific heat and it is only at low temperatures where the lattice specific heat falls off as T^3 that the electronic specific heat makes itself apparent. Thus the study of specific heats of metals at low temperatures is also of importance for the electronic theory of metals which, although satisfactory in broad outline, is still far from complete, so that compilation of data is still required to provide clues for its improvement. At the N.P.L., Dr. K. G. Ramanathan is developing a new type of calorimeter for studying both the lattice and electronic aspects of the specific heat problem.

Another problem being taken up at the N.P.L. (by Mr. S. L. Surange and Mr. P. N. Dheer) is the study of thermal expansion at low temperatures. Essentially thermal expansion comes about because of a slight anharmonicity of the lattice vibrations, for if the vibrations were exactly simple harmonic, the average separation of the atoms from each other would be independent of the amplitude of the vibrations (i.e. of temperature) and there would be no thermal expansion at all. The theory involves a knowledge of how the vibration spectrum depends on stress (e.g. pressure) and as in the case of specific heats it cannot be fully worked out without rather crude simplifying assumptions. In this case the assumptions are even cruder than those required for calculating the specific heat and the theory does not become simple even for high temperatures; at low temperatures, however, considerable simplifications become possible and the theory predicts that the thermal expansion should be proportional to the specific heat, with a constant of proportionality which depends on the pressure variation of the elastic constants. This prediction is also very roughly valid at higher temperatures and measurements down to moderately low temperatures have indeed confirmed that it does correctly indicate the general trend of the results, but so far it has not been verified experimentally in the region of very low temperatures, where it might be expected to hold more precisely. For metals there should also be a component of the thermal expansion proportional to the electronic specific heat and depending on the pressure variation of the parameters describing the electronic motions, and this component should become comparable to the lattice component in just about the same range of low temperatures as that in which the electronic specific heat becomes observable. Experimentally, this is a difficult problem to study, because the thermal expansion at liquid helium temperatures should be between 100 and 1,000 times smaller than at room temperature, so much so more sensitive methods must be developed before any useful observations can be made.

Electrical resistivity provides another example of two competing processes which may be sorted out by low temperature measurements. The electrons which carry electric current in a metal may be thought of as waves and it is the scattering of these waves which is responsible for the finite mean free path of the electrons and hence for the existence of a finite resistance. At ordinary temperatures, this scattering is caused mainly by the lattice vibrations of the metal and since these become stronger as the temperature rises, the resistance rises with temperature. There is, however, also some scattering caused by imperfections in the metal — slight irregularities in the perfect geometrical arrangement of the atoms caused by stresses or by impurities — and this scattering produces a small extra resistance which does not vary with temperature, but depends on the degree of imperfection. At sufficiently low temperatures, where the lattice vibrations have practically died out, the resistance component due to scattering by the vibrations — the " ideal " resistance as it is called — falls off as a high power of T (often T^5) and the small " residual " resistance due to the imperfections becomes dominant. This residual resistance could be a useful tool in studying the mechanical properties of metals and could throw light on the processes of plastic deformation and so on, but so far this application of low temperature techniques has not been much exploited. Although the theory of electrical resistance s understood in broad outline, it cannot be regarded as complete, since it does not at all account for the sudden disappearance of all resistance — superconductivity — which occurs for many (but not all) metals in the liquid helium range, or for a peculiar slight rise of resistance which is found for some non-superconducting metals when the temperature is still further lowered.

The thermal resistance of metals arises mainly from mechanisms precisely parallel to those causing electrical resistance. The electrons are slightly more energetic where the temperature is higher and so can transfer heat along a temperature gradient to an extent determined by the lack of scattering they encounter. Just as for electrical resistance there is an " ideal " and a " residual " thermal resistance each roughly proportional to R/T where R is the corresponding electric resistance. It follows that at sufficiently low temperatures, where R is constant, the thermal resistance increases as 1/T; when it becomes large enough, however, another mechanism of thermal conduction, which acts " in parallel ", begins to show itself and eventually becomes dominant. This is a direct transport of heat by the lattice itself, the heat being carried by the " phonons " of vibrational energy to an extent limited by their scattering by other " phonons ", and for a metal also by the conduction electrons. This process is similar to that of the feeble thermal conduction in insulators, where there are no conduction electrons to help carry the heat, and experiments on thermal conduction at low temperatures, both in metals and insulators, have in recent years been valuable in showing up the considerable limitations of the theory.

Magnetism at low temperatures is another field with many features of interest. In paramagnetic salts the magnetic susceptibility is predominantly due to the permanent magnetic moments of the individual positive ions which are lined up by a magnetic field to an extent limited by the tendency of the temperature agitation to keep them oriented at random. The theory of this effect explains Curie's empirical law that the susceptibility is inversely proportional to the temperature; thus at low temperatures the susceptibility becomes hundreds of times larger than at room temperature. When the temperature is sufficiently low, however, Curie's law begins to fail because of the interactions of the elementary magnets both with each other and with the strong electric fields arising from the positive and negative ions. It is just these interactions which set a limit to the usefulness of the adiabatic demagnetization method, and the development of this method has provided a stimulus for an intensive study of paramagnetism at low temperatures in recent years.

Another interesting effect which shows up at low temperatures is that of saturation. Ordinarily the disorienting effects of temperature agitation are so strong that the alignment of the elementary magnets is only slight and the magnetization produced is proportional to the field. At low temperatures, however, the alignment becomes much more appreciable and with fields of the order of 30,000 gauss at 1°K. it can be made almost complete, so that the magnetization no longer increases much with further increase of field, and saturation is approached. The study of saturation effects in single crystals of paramagnetic salts has so far been little studied, and it is hoped to get interesting information from experiments at liquid helium temperatures using the large electromagnet of the N.P.L. Dr. A. Bose of the Indian Association for the Cultivation of Science has recently come as a guest worker to the N.P.L. to initiate such studies.

Valuable auxiliary information about the interactions which limit the " freedom " of the paramagnetic ions to orient themselves can also be obtained by the method of paramagnetic resonance, which it is hoped to set up soon at the N.P.L. The various orientations of an ion really correspond to definite quantum states of slightly different energies and it turns out that these energy differences are just of the order of the magnitude of the energies of single quanta of microwave electromagnetic radiation. Thus if a paramagnetic salt in a magnetic field is exposed to microwave radiation, resonance can occur when the frequency of the microwaves has just the right value to allow a quantum to be absorbed in changing the orientation of an ion by lifting it from one quantum state to another. The effect of the interactions is to modify the quantum states slightly and from a study of the various resonance frequencies and how they vary with the magnetic field, a complete energy level picture can be built up, which is a valuable aid in the detailed interpretation of the paramagnetic behaviour. The energy level picture is not itself sensitive to temperature but the conditions which determine the sharpness of the resonance do vary with temperature, and it is often advantageous to study the resonance at low temperatures.

Another aspect of magnetism, which has special features of interest at low temperatures, is the feeble magnetic susceptibility (usually diamagnetic) of metals. This feeble susceptibility is made up partly of a diamagnetism due to the curvature of the paths of the conduction electrons by the magnetic field and partly of a paramagnetism due to the orientation by the field of the electron spins, which act as elementary magnets. Both effects are explained qualitatively by the electron theory of metals, though, as already indicated, this theory is far from satisfactory and cannot explain in detail some aspects of the results, such as the appreciable temperature variation of the susceptibility which, in the simplest form of the theory, should be absent.

At temperatures in the liquid helium range quite a new effect comes in, first discovered by de Haas and van Alphen and much studied in recent years. The susceptibility is no longer independent of field but shows oscillations as the field is varied, whose amplitude is the stronger, the lower the temperature. Theoretically such an effect is to be expected for a gas of free electrons, due to the peculiar quantization of the motion of electrons in a magnetic field, but although the theoretical formulae fit the facts well in a formal way, the parameters describing the electronic motions have to be given rather unplausible values to achieve the fit. Some aspects of the theory show up best at high magnetic fields, and during my stay in India I have, with Mr. J. S. Dhillon's assistance, used the large electromagnet of the N.P.L. to study the harmonic content of the de Haas-van Alphen oscillations in bismuth. According to the theory the successive harmonics should be alternately added and subtracted to give the resultant curve of field variation of susceptibility, but the experiments indicate that they must all be added. This new discrepancy may help in showing how the theory should be improved.

Turning finally to the low temperature phenomena which are quite new in character and where the theory is particularly incomplete, a very brief survey will be given of the properties of liquid helium and of superconductivity. It is already remarkable that helium should be a liquid at all and remain liquid right down to the lowest attainable temperatures (it solidifies only under a pressure of about 30 atmospheres). This finds a plausible interpretation as the manifestation of a characteristic feature of quantum theory — the existence of a " zero-point " energy independent of temperature, which is the greater the lighter are the atoms, and which, as it were, keeps the atoms sufficiently stirred up to prevent solidification. More remarkable and less understood, however, is the peculiar change which occurs in liquid helium at 2·19°K., the so-called λ-point. As the temperature is lowered through this point, the liquid suddenly appears to stop boiling and becomes completely quiet with a sharp surface undisturbed by bubbles. It turns out that nearly all the physical properties undergo sharp changes in passing through this λ-point. The name itself comes from the shape of the specific heat-temperature curve which is somewhat like the Greek letter λ, with a very high maximum at the λ-point itself and a rapid fall off on either side. The apparent cessation of boiling proves to be due to an enormous thermal conductivity below the λ-point; this irons out the small temperature fluctuations responsible for the production of bubbles in a boiling liquid, and evaporation can take place only directly from the surface. Yet another peculiarity is that the viscosity of the liquid practically disappears if measured by its flow through fine channels, but is not much changed if measured by the damping of an oscillating vane, and there are many more peculiar effects.

Many of these properties can be correlated in terms of a "two-fluid" model of the liquid; in fact below the λ-point the liquid behaves very much as if it were a kind of mixture of ordinary liquid helium and a " superfluid " variety which carries no entropy and encounters no resistance to flow. The proportion of superfluid is to be taken as temperature dependent, being just zero at the λ-point and 100 per cent at very low temperatures. If the liquid flows through a fine channel it is only the superfluid which passes and encounters no resistance, thus making it appear that the liquid has no viscosity; in the damping of an oscillating vane, however, the normal component rubs against the vane and is responsible for the observed viscosity. Along a temperature gradient there is also a gradient of the concentration of superfluid and since the superfluid can flow without resistance, it immediately flows in such a way as to equalize its concentration everywhere and thus equalize the temperature; this then can explain the enormous thermal conductivity.

Many other peculiar properties of liquid helium below the λ-point can also be interpreted in terms of this model, but the theoreticians have so far been only partly successful in explaining in more fundamental terms why this model should work. F. London has shown that a peculiar transition should occur in an " ideal " gas of helium atoms with the density of the liquid at just about the actual λ-point temperature, because of the Bose-Einstein statistics which helium atoms obey, but his demonstration ignores the interactions between the atoms and moreover does not really show that the superfluid properties should be characteristic of the liquid below the transition point. Landau, by considering the " excitations " characteristic of a quantum liquid (an approach a little similar to that used in analysing the vibration spectrum of a solid), has successfully explained the general features of the two-fluid model, but it is not evident why his theory should apply particularly to liquid helium. Recently the rare isotope of helium of mass 3 rather than 4 has been produced in atomic piles in sufficient quantities to enable its properties to be studied. The important point about He^3 is that its atoms obey Fermi-Dirac rather than Bose-Einstein statistics, and it has turned out that liquid He^3 has no λ-point at all, thus suggesting that the statistics which plays such an important role in London's theory is indeed significant. Probably the true theory will reconcile both the London and the Landau theories to some extent, and it is indeed possible that a recent new approach by Feynman may already have achieved this synthesis.

The remarkable disappearance of all electrical resistance in many metals at a characteristic transition temperature (usually below 10°K.) has already been mentioned. The magnetic properties of the metal in this superconducting state are even more remarkable than the electric ones, for it turns out that a superconductor is unable to carry any appreciable magnetic flux through itself and behaves like a " perfect " diamagnetic. The specific heat shows a discontinuity when the metal becomes superconducting, rather reminiscent of the λ-point of liquid helium, and this discontinuity can be explained thermodynamically in terms of the magnetic behaviour and the fact that there is a temperature dependent critical magnetic field which destroys superconductivity. In recent years a good deal of attention has been paid to the depth of penetration of a magnetic field into a superconductor. Although this penetration is small enough to be negligible for a specimen of ordinary size, it is nevertheless there, for clearly the currents which screen off the magnetic field from the interior require a small depth in which to flow, and within this depth the magnetic field falls off to zero from its external value. Experiments on specimens of microscopic dimensions and specially delicate experiments on larger specimens have shown that the penetration depth is of the order of 10^{-6} to 10^{-5} cm. and varies with temperature, falling rapidly as the temperature falls below the superconducting transition and then more slowly towards absolute zero.

The brothers F. and H. London developed a phenomenological electrodynamical theory which neatly correlates the electric and magnetic properties and in which the penetration depth finds a natural place and is inversely proportional to the square root of the number of electrons carrying the superconducting current. The temperature variation of the penetration depth thus suggests a temperature variation of the number of " superconducting " electrons and this fits tidily into a two-fluid model of superconductivity, rather analogous to the one used for liquid helium. As the temperature falls below the transition temperature, some sort of "condensation" takes place in the electron system as a whole, and an increasing proportion of the electrons becomes "superconducting ", the rest remaining " normal " or " uncondensed ". This picture fits well with the form of the specific heat curve and also explains qualitatively the variation of thermal resistance and the fact that at very high frequencies the resistance is no longer zero, though it falls as the temperature is lowered. More recent research, particularly on the high frequency behaviour, has, however, revealed many flaws in this phenomenological picture which combines the Londons' electrodynamics with the two-fluid model.

Indeed the theoretical situation is rather worse than with liquid helium, for not only has there been less success in a fundamental theory, but even the phenomenological picture which the fundamental theory must explain is none too sound. A year or two ago it looked as if Fröhlich's and Bardeen's attempts at a fundamental theory, in which a rather special kind of interaction between electrons was taken into account, would lead to a final answer, but now the situation looks less promising, for some of the difficulties appear to be more formidable than was thought at first. The solution of the problem of superconductivity is likely to have important repercussions in many other branches of the theory of metals, for the neglect of the interaction effects which are presumably responsible for superconductivity is probably also responsible for some of the discrepancies of detail between theory and experiment which have been pointed out earlier in the behaviour of non-superconducting metals. Thus if a method can be worked out for dealing with these interactions successfully, it may lead to improvements in the theory of metals in general.

Although this survey is necessarily sketchy and many aspects of the subject have not even found mention, perhaps enough has been said to show that the use of very low temperature techniques has made and can still make important contributions to physics, particularly to the physics of the solid state. With the setting up of a low temperature section at the National Physical Laboratory of India, it is to be hoped that India will now also be able to play a part in the future progress in this important field of science.

Ionospheric Data—May 1954

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 May 1954. The f°F_2 variation curve has been compared to that predicted three months before. The percentages of the total number of occasions during routine observations when the critical frequency for the sporadic E layer (fE_s) was greater than 3, 5 and 7 Mc./s. have been plotted for the different hours in Fig. 2. Table 1 gives the median values for the different ionospheric parameters for May 1954.

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

The intensity and frequency of occurrence of sporadic E were very high during May 1954. Correlation between incidence of thunderstorms and intense sporadic E ionization was observed as in the previous years. The behaviour of the F_2 region was normal.

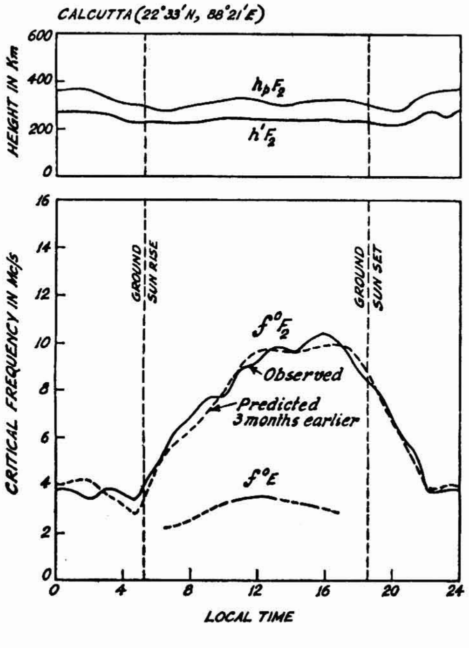

FIG. 1 — MONTHLY MEAN IONOSPHERIC CHARACTERISTICS FOR MAY 1954

TABLE 1 — MONTHLY MEDIAN HOURLY VALUES

(*May* 1954)

TIME*	f°F_2 Mc./s.	hpF_2 km.	h'F_2 km.	f°E Mc./s.	fE_S Mc./s.	(M3000)F_2
00	3·90	360	255			2·75
01	3·70	360	270			
02	3·45	360	270		3·25	
03	3·80	330	270		3·20	2·95
04	3·50	307	240			
05	3·75	300	225			
06	4·85	270	225			3·30
07	6·40	285	225	2·30	4·70	
08	6·90	300	225		3·70	
09	7·65	300	240		3·85	3·10
10	7·80	330	240		4·30	
11	8·95	300	240	3·30	4·00	
12	9·20	300	240	3·55		3·10
13	10·00	300	240	3·50		
14	10·00	300	240		4·00	
15	10·30	308	240	3·20	3·80	3·10
16	10·50	300	240		3·85	
17	9·85	315	240		4·15	
18	8·50	300	240		4·15	3·10
19	8·50	300	210		3·90	
20	7·08	270	210		3·55	
21	6·10	285	225			3·20
22	3·85	352	270			
23	3·65	352	240		3·85	

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

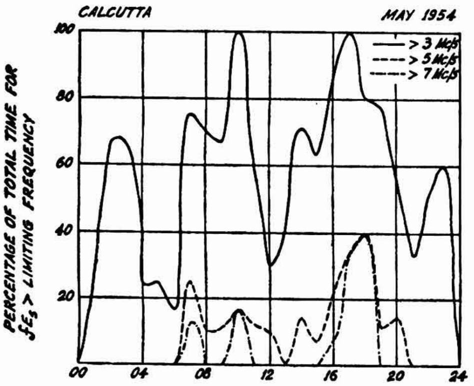

FIG. 2 — PERCENTAGES OF TOTAL NUMBER OF OCCASIONS WHEN fE_S WAS GREATER THAN 3, 5 AND 7 Mc./s. DURING MAY 1954

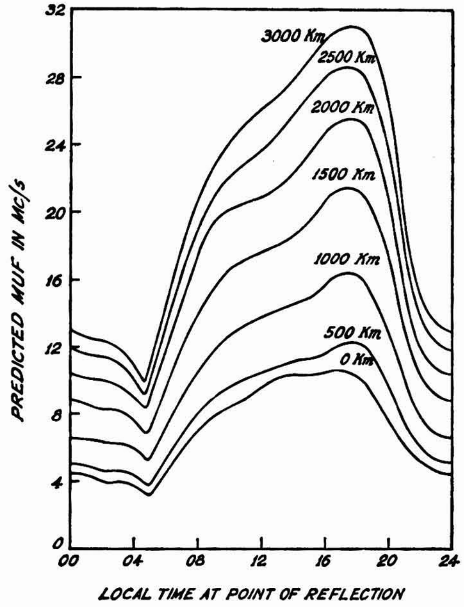

FIG. 3 — PREDICTED M.U.F. FOR TRANSMISSION VIA F_2 REGION OVER CALCUTTA DURING AUGUST 1954

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 occurrence 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 May 1954 were lower during day hours and higher during night hours than in the previous month. The median critical frequencies of F_1 round noon hours were also lower than in the previous month. The general level of critical frequencies of all the regions in this month has come down from that of the corresponding month of the last year.

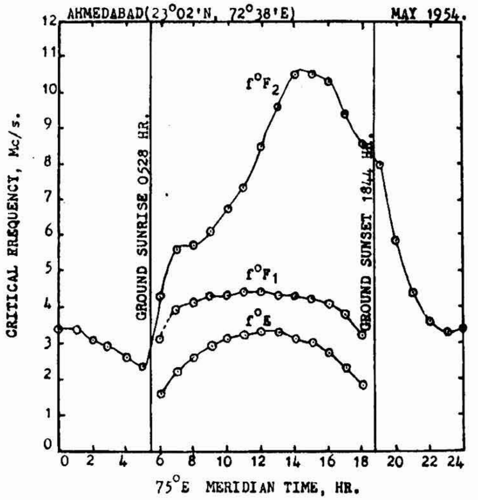

FIG. 1 — DIURNAL VARIATIONS OF CRITICAL FREQUENCIES OF ORDINARY WAVES REFLECTED FROM E, F_1 AND F_2 REGIONS

The intensities and frequencies of occurrence of the sporadic E layer were appreciably higher than those in the previous month and in May 1953. On many occasions, sporadic E blanketed the higher regions and obscured the normal E region critical frequencies.

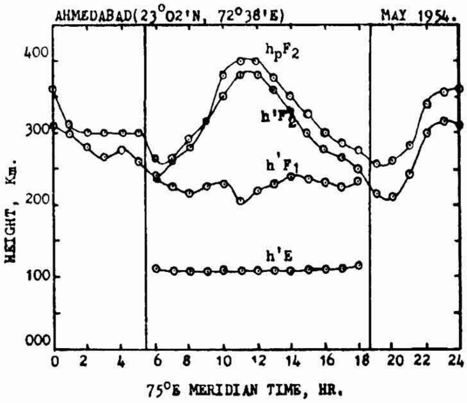

FIG. 2 — DIURNAL VARIATIONS OF VIRTUAL HEIGHTS OF E, F_1 AND F_2 REGIONS

TABLE 1 — IONOSPHERIC DATA — AHMEDABAD, MAY 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
	$f^\circ F_2$ Mc./s.	h_pF_2 km.	$h'F_2$ km.	$f^\circ F_1$ Mc./s.	$h'F_1$ km.	$f^\circ E$ Mc./s.	$h'E$ km.	fE_S Mc./s.	$fE_S >$ 3 Mc./s.	$fE_S >$ 5 Mc./s.	$fE_S >$ 7 Mc./s.	
00	3·4	360	310	—	—	—	—	3·8	21	4	2	24
01	3·4	310	300	—	—	—	—	3·9	18	7	2	22
02	3·1	300	280	—	—	—	—	4·0	16	7	2	22
03	2·9	300*	265	—	—	—	—	4·0	15	5	2	22
04	2·6	300*	275	—	—	—	—	3·8	15	6	2	22
05	2·3	300	260	—	—	—	—	3·8	17	4	1	22
06	4·3	265	240	3·1*	235*	1·6	110	4·1	19	5	2	22
07	5·6	265	260	3·9	225	2·2	107	4·3	18	7	4	22
08	5·7	290	280	4·1	215	2·6	107	5·2	16	10	3	21
09	6·1	315	315	4·3	225	2·9	107	4·3	18	7	1	24
10	6·7	380	350	4·3	230	3·1	107	5·3	16	8	4	23
11	7·3	400	380	4·4	205	3·2	107	6·6	13	7	5	25
12	8·5	400	380	4·4	220	3·3	107	5·4	14	7	2	24
13	9·6	375	360	4·3	230	3·3	107	5·2	11	5	3	25
14	10·5	350	330	4·3	240	3·1	107	4·7	10	5	4	25
15	10·5	325	300	4·2	235	3·0	107	5·0	12	6	—	25
16	10·3	300	275	4·1	230*	2·7	110	4·2	13	5	2	25
17	9·4	285	265	3·8	225	2·3	110	4·4	19	9	6	25
18	8·6	275	250	3·2	235*	1·8*	115*	5·3	21	13	6	26
19	8·0	255	215	—	—	—	—	4·5	26	11	4	26
20	5·9	260	210	—	—	—	—	4·7	20	10	5	26
21	4·4	280	240	—	—	—	—	4·1	20	9	5	26
22	3·6	340	300	—	—	—	—	4·3	20	7	3	25
23	3·3	355	315	—	—	—	—	3·8	22	6	2	25

*Median based on observations less than ten.

Differential Thermal Analysis Technique & Its Applications

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OF the various methods generally employed to study the structural changes occurring in solids during thermal treatment, the technique of differential thermal analysis has been found to be an important tool for such investigations for the last two decades. Though it has been mainly applied in the field of ceramics, this technique has recently attained considerable importance in other fields also.

The principle of differential thermal analysis (D.T.A.) consists in measuring the heat changes associated with physical or chemical changes occurring when a solid substance is gradually heated. These changes may be dehydration, transition from one crystalline variety to another, destruction of crystalline lattice, oxidation, decomposition, etc.

History of the method

The method was suggested by Le Chatelier[1,2] in 1887 and was applied in the study of clays[3-5]. Robert Austen[6] effected improvement by using differential couple in place of single couple. Following the work of Burgess[7], Wallach[8], Orcel and Caillére[9], the method has been extensively applied in the identification of clays[10-31].

All the clay minerals are characterized by an endothermic reaction between 500° and 700°C. due to the loss of (OH) water and an endothermal reaction at higher temperature due to the expulsion of adsorbed water and/or destruction of lattice and an exothermal change at still higher temperature due to the crystallization of a new phase.

The thermal behaviour of a typical clay mineral of kaolinite group, halloysite, $Al_4Si_4O_{10}(OH)_8$, is shown in Fig. 1.

The initial endothermal effect between 120° and 270°C. is due to the expulsion of the adsorbed water. The second endothermal effect with a peak at 580°C. is due to the dissociation of halloysite into water vapour and an intimate mixture of amorphous Al_2O_3 and SiO_2. The sharp intense exothermic peak at 950°C. is caused by the crystallization of γAl_2O_3 from amorphous Al_2O_3[32].

The predicting of the firing behaviour of structural clay minerals has been made by Everhart and Van der Beck from D.T.A.[33].

Description of the method

The sample to be studied is placed in one of the holes of the specimen holder made of platinum, silica, nickel, stainless steel or inconel[21,34-36]. In the second hole of the holder is placed a material, usually α-Al_2O_3, which does not undergo any transformation even up to 1,000°C. Two sets of thermocouples are placed and connected as in Fig. 2. Pt-Rh of each couple is connected together and the two platinum wires are left free. This constitutes the differential couple. Into the third hole of the block is imbedded a thermocouple which measures the temperature of the block. The thermocouples which are widely used are either Pt(Pt-Rh) or chromel-alumel[37]; the latter is preferred as it gives higher e.m.f. as compared with the former. Kracek[38] has used (Au-Pd)(Pt-Rh) thermocouple as it is more sensitive to higher temperatures. Johnstone and Mcquillan[39] have recently des-

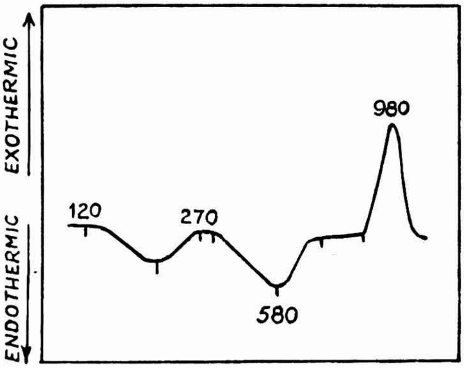

FIG. 1 — THERMAL CURVE FOR HALLOYSITE

cribed W-Mo thermocouples which can be used up to a temperature of about 2,000°C.

The block is placed in a furnace which is heated at a uniform rate. The temperature of the furnace can be raised uniformly by an autotransformer or by a motor-driven transformer[40-42]. Different types of automatic controllers have been described by the workers in this field[36,43-48].

The differential couple records zero e.m.f. so long the substance under investigation does not undergo any kind of change. Whenever a change occurs, there is either absorption of heat (endothermic reaction) or evolution of heat (exothermic reaction), as a result of which the temperature of the substance becomes lower or higher than that of the inert material. A differential e.m.f. is thus set up, the direction of which depends on whether the reaction is endothermic or exothermic. The differential e.m.f. can be measured either by a potentiometer or a galvanometer or automatically with an electronic device. In some laboratories, the photographic method is adopted in which a spot of light is reflected from the galvanometer on to a photographic paper attached to a drum rotating at a uniform speed[40].

In the thermograms, usually the differential temperature (ΔT) and the temperature of the furnace (T) are recorded or plotted such that the endothermal peaks are shown downwards and the exothermal peaks upwards with respect to the base line $\Delta T = 0$.

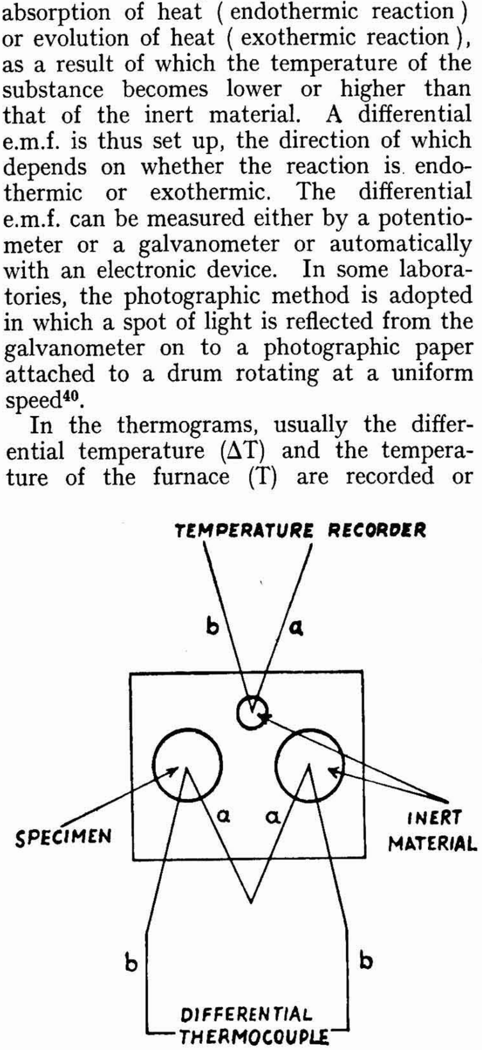

FIG. 2 — SPECIMEN HOLDER [a = Pt–Pt.Rh, b = Pt wire]

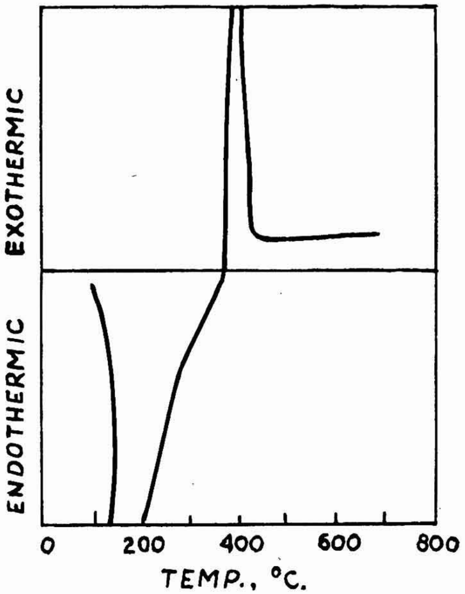

FIG. 3 — DIFFERENTIAL THERMAL CURVE FOR CHROMIC OXIDE GEL

A representative differential thermal curve for chromic oxide gel[49] obtained by the addition of ammonium hydroxide to a solution of chromic nitrate is shown in Fig. 3. The endothermic reaction with a peak temperature at 175°C. (range 100°-300°C.) is due to the loss of water from the gel. The sharp exothermic effect with a peak at 395°C. (range 375°-405°C.) is due to the amorphous Cr_2O_3 transforming to crystalline form.

Factors influencing the results

Particle size — In general the size of the thermal peak and the temperature of the peak decrease as the particle size decreases[50]. It is important to keep the particle size constant for a particular reaction.

Packing of the sample — Uniform packing is necessary as it does not allow the variation in thermal diffusivity. Gruver[43] uses loose packing but many others prefer solid packing[50].

Thermocouples — The intensity of the thermal peak depends on the kind of thermocouple used. Usually S.W.G. 22 or 24 is used and it should be well insulated from the specimen block.

Heating rate — The heating rate affects the peak temperature, though the area of the curve is independent of the rate of heating. Usually the rate of 10°-15°C./min. is preferred.

Furnace atmosphere — Reproducible results can be obtained only when the atmosphere of the furnace is kept constant for a particular experiment. Especially in the case of oxidation it is important that condition should be equally favourable for the oxidation of all samples.

Theoretical considerations

From theoretical consideration Speil[51] has shown that the area enclosed under a thermal curve peak is proportional to the heat of transformation. It can be very briefly summarized with the aid of Fig. 4.

The curve shows a reaction beginning at "a" and continuing towards "c".

$$\text{Area abc}\alpha\int_{a}^{c}\text{TdT} = \frac{\text{M}(\Delta\text{H})}{\text{gk}} \; . \; . \; . \; . \; (1)$$

where M = mass of the reaction specimen; ΔH = specific heat of the reaction; g = geometrical shape constant; and k = thermal conductivity of the reacting specimen.

Equation (1) neglects the temperature gradient as well as differential factors which are insignificant.

Transposing terms,

$$\text{area abc}\alpha\text{gk}\int_{a}^{c}\text{TdT} = \text{M}\Delta\text{H} = \text{Q} \; . \; . \; . \; (2)$$

and area abc$\propto$Q. Q = heat of reaction.

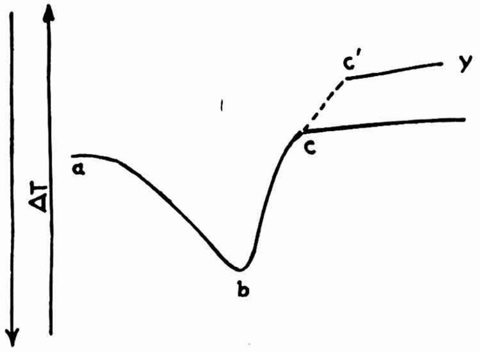

FIG. 4 — THERMAL PEAK FOR $CaCO_3$ DECOMPOSITION

The thermographic base line in Fig. 4 is not linear, as is found to be the case with calcium carbonate decomposition. This is due to the accompaniment of sharp change in thermal conductivity and specific heat capacity due to the decomposition

$$CaCO_3(S) \rightarrow CaO(S) + CO_2(g).$$

Hence there is a thermal gradient and a non-linear base line. In the Fig. 4, point C is displaced C′ and continues towards Y.

Wittels[52] has shown a precise relationship between the thermographic response and two functions, the heating rate and the mass of the sample. A series of straight lines are obtained when area is plotted against the heat of reaction.

Suppose, A = area; R = rate of heating; Q = calories; $\theta = \tan^{-1}\left(\frac{A}{Q}\right)$ – (1): A = area (in sq. in.) and Q = calories (in tenths).

Graphical representation of R and θ indicates the existence of an exponential relation between the two functions. In fact, a plot of R against θ gives an exponential curve. The function R may be replaced by θ in equation (1) thus

$$R = e^{\theta/K} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (2)$$

$$\text{and } K\ln R = \theta \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (3)$$

Substituting the above values of R and θ in equation (3) and solving for K, plot of R against K shows a general form Y = mx + C

$$\text{so} \quad R = mk + C$$

$$K = \frac{R-C}{m}$$

Substituting in equation (2) we have

$$R = e^{m\theta/R-C}$$

$$\ln R = \frac{m\theta}{R-C}$$

$$\text{and } \theta = \frac{\ln R(R-C)}{m}$$

A final substitution in equation (1) gives

$$Q = \frac{A}{\tan\left[\frac{\ln R(R-C)}{m}\right]} \; . \; . \; . \; . \; (4)$$

This equation is found to hold good for heating rates between 10° and 30°C./min.

Application

In addition to clay minerals, D.T.A. technique has satisfactorily been applied to the study of other minerals and compounds.

The method has been applied successfully in the study of various carbonate minerals[53-57]. Fig. 5 shows the differential curves for calcite, magnesite, dolomite, siderite, rhodochrosite and ankerite. From the thermograms it is easy to distinguish them from one another.

Fig. 6 gives the D.T.A. curves for pyrites and marcasite. The exothermic peaks are due to the oxidation of the sulphur present in the minerals.

The method has also been applied to the study of hydrous ferric oxides[58-60].

Thermograms of various oil shale specimens of America and Australia[61] have been obtained.

A new mineral, Belyankite (after the name of the Russian mineralogist) has been investigated by D.T.A.[62].

Organic compounds — The application of D.T.A. to the study of organic compounds has brought out very interesting results. Transitions in beryllium oxyacetate crystals have been studied recently by Jaffray[63].

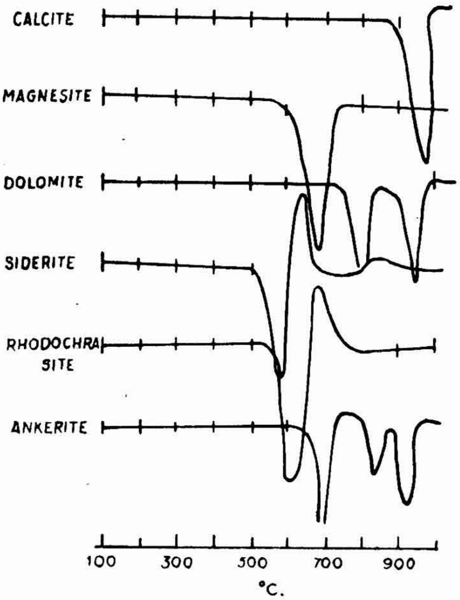

FIG. 5 — D.T.A. OF SOME CARBONATE MINERALS

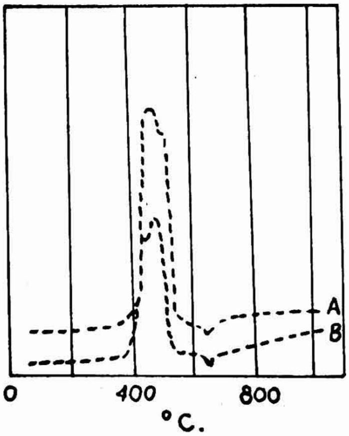

FIG. 6 — D.T.A. CURVES FOR (A) PYRITES AND (B) MARCASITE

Phase transitions in barium-dicalcium butyrate by Seiichikondo and Tsotomu Oda have yielded characteristic peaks for their identification[64]. The polymorphic transitions in calcium stearate have been studied by Vold *et al.*[45].

D.T.A. finds ready application in sugar chemistry also. D.T.A. of various sugars like sucrose, glucose, lactose, raffinose, xylose, etc., have been recently published by Costa *et al.*[65].

D.T.A. is useful in soap technology also. Phase changes in the systems sodium stearate-cetane, lithium stearate in cetane and in decalin and transitions in greases have been studied by Vold and co-workers[18,66,67].

Coal technology — Recently the study of lignites by D.T.A.[68,69] has revealed that lignite is related to lignin. The first exothermic peak obtained (FIG. 7) in presence of air in the furnace is absent in flowing nitrogen which shows clearly that this exothermic reaction is not due to (OH) decomposition as was assumed previously. Polyethylene behaves similarly in which there are few (OH) groups.

A systematic study of various coals heated up to 1,000°C. has been made by Hideharu Yagishita[70] who has reported that the thermal decomposition of coals differ with degree of coalification.

Catalysts — Very little work has been done in the study of solid catalysts by the technique of D.T.A. Attempts have been

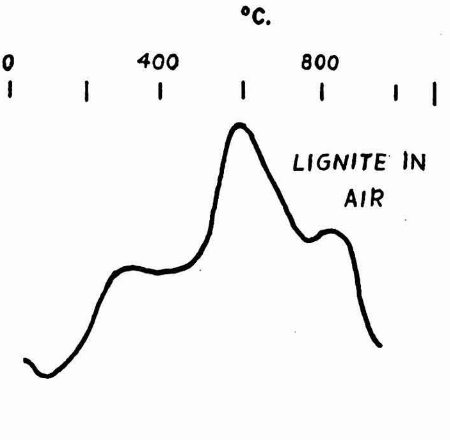

FIG. 7 — DIFFERENTIAL CURVES FOR LIGNITE AND POLYETHYLENE

made to study the Fischer-Tropsch catalysts and MgO-SiO_2 system by D.T.A.[71,72].

D.T.A. of several catalysts like Cr_2O_3[49], Fe_2O_3[73], ZnO[74], ZnO-Cr_2O_3[75], Fe_2O_3-Cr_2O_3[76], NiI_2-SiO_2[77] have been studied by the authors and interesting results have been obtained. The D.T.A. of chromic oxide gel exhibits an exothermic peak at 395°C. due to the amorphous form changing to crystalline form (FIG. 3). The catalytic activity of chromic oxide has been reported to be suddenly destroyed[78] when heated to temperature above 380°C. which may be due to the decrease in the surface area consequent on crystallization.

The differential thermal analyses of the coprecipitated as well as the mechanically mixed samples of ZnO-Cr_2O_3 show a high temperature exothermic peak due to the formation of the spinel $ZnCr_2O_4$ which is catalytically inactive. It has been observed that, in each case, the activation temperature of ZnO-Cr_2O_3 is found to be about 100°C. below the peak temperature (corresponding to the formation of $ZnCr_2O_4$). The results are in conformity with those of Frost *et al.*[79].

A mutual protective action against crystallization has been observed in the system $Fe_2O_3 : Cr_2O_3$. The D.T.A. shows $Cr_2O_3 : Fe_2O_3 = 40 : 60$ (mole per cent) and exhibits maximum protective action against crystallization. This composition should correspond to enhanced surface properties and catalytic activity.

ZnO precipitates, prepared by different methods, have been subjected to D.T.A. All the samples show an endothermic peak between 210° and 300°C., at which the dehydration is complete. The catalytic activity as well as the adsorptive capacity of ZnO are found to be maximum at 325°C. which corresponds to the temperature where the dehydration appears to be complete.

It has been shown by the thermograms of the hydrous ferric oxides that the catalyst loses its activity completely with the formation of αFe_2O_3.

Radioactive minerals

Very recently D.T.A. technique has been applied in the study of radioactive minerals of the type $A_mB_nO_{2mn}$[80-82] where A = U, Th, rare earths, etc.; B = Nb, Ta, Ti, etc. These minerals have been exposed to the α-rays for millions of years and the lattice is so much damaged that X-rays fail to show any indication of the structure. When the mineral is heated, the atoms are restored to the normal positions and there is an evolution of energy. Evidently D.T.A. technique can be applied to measure this energy. Fig. 8 shows the thermal curves for two radioactive minerals, polycrase (a titano-niobate) and radioactive quartz. The exothermal effect at 460°C. is similar in air, nitrogen or in a vacuum of 4 mm. showing that it is not due to oxidation. This peak corresponds to energy = 21 cal./g. The radioactive quartz shows an exothermic peak at 440°C. in air which is absent in nitrogen or vacuum of

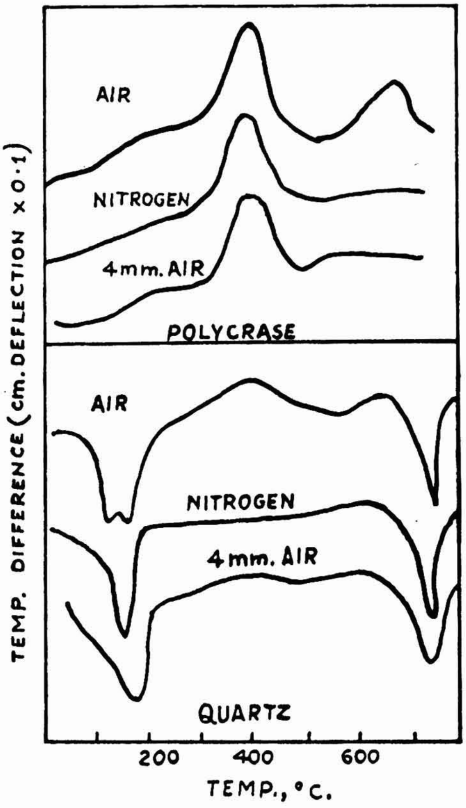

FIG. 8 — D.T.A. OF RADIOACTIVE MINERALS

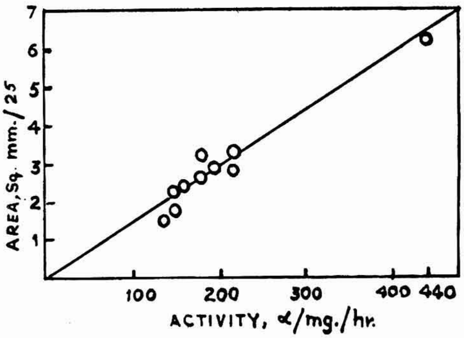

FIG. 9 — RELATION BETWEEN AREA AND α-ACTIVITY FOR SAMARSKITE

4 mm. The exothermic peak is probably due to oxidation of Fe or S.

Fig. 9 shows the relationship between the area under the thermal peak and α-activity of samarskite (radioactive) from the same district. The relationship is found to be linear. The lattice disruption increases with α-activity. If the activity and degree of lattice disruption can be measured, the age of the mineral can be estimated.

Other substances

Interesting results have been obtained in the study of alumina gels[83,84], natural graphites[85], carbides[86], phosphates[87,88], zinc silicate phosphors[89], chromium orthophosphate[90], transitions in ammonium chloride and bromide[91], aluminium silicates[92], aluminium trifluoride[93], calcium hydrosilicates[94], silver sulphate[95], manganese dioxide[96], etc.

A new transition of ammonium dichromate crystals at −120°C. has been reported recently[97].

Dual systems like Na_2O-SiO_2[98], alumina-silica gels, magnesia-silica gels[72], etc., have also been studied by D.T.A.

Heats of reaction

The D.T.A. provides data for the study of heats of reactions. Excellent agreement between determined and known heats of reaction of several substances has attested to the accuracy of D.T.A. as a powerful tool for the determination of heats of reaction[44,99-102].

A successful study of ΔH values of coals have been made by D.T.A.[103]. The ΔH values obtained for semi-bituminous coal from the peroxide bomb are directly related to the thermograms of the specimens.

The effect of injecting steam into the inert specimen as well as the specimen to be studied results in endothermal as well as exothermal effects. The area under the exothermic peak should be proportional to the energy of reaction and hence D.T.A. technique in conjunction with gravimetric method should make possible the determination of heats of adsorption[104].

In many cases the difficulty arises in identifying clay minerals in presence of a small amount of an impurity which obscures the other effects by getting itself oxidized. In such cases the petrographic, X-ray or chemical methods fail to give a clear picture. By controlling the furnace atmosphere such effects can be annulled by D.T.A. Valuable data have been reported consequent on the control of atmosphere of the furnace[105].

Thermographic analysis at high pressures (in nitrogen atmosphere) has yielded interesting results on the dissociation temperatures of several substances[106].

It is thus clear that the technique of D.T.A., which finds wide applications in the field of clay technology, also provides a valuable tool for the study of physical or chemical changes occurring during thermal treatment of various other solid substances.

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Combination Tannages: Part III — Studies in Semi-chrome Tanning

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SEMI-CHROME tanning—retanning vegetable tanned leather with basic chrome salts — has received considerable attention in England where the British leather dressers have developed this technique using East India tanned kips and skins as the raw materials. India exports every year large quantities of these lightly vegetable tanned kips (light cow and buffalo hides), goat and sheep skins worth about 15 to 18 million pounds sterling to England principally from Madras. There are about 600 tanneries in South India which manufacture tanned kips mainly to cater to the needs of the British leather dressers.

The British leather dressers usually semi-chrome the better selections of the tanned kips to produce shoe upper leathers for both civilian and military use. A certain quantity of tanned goat skins are also semi-chromed to produce imitation glace kid, suedes, gloving and clothing leather. These semi-chrome leathers are processed so well that it is hard to distinguish them from similar varieties of full-chrome leathers.

In India, the semi-chrome process has not yet come into vogue. Its adoption, however, is of vital importance to the economy of the industry. If, instead of exporting E.I. tanned kips and skins in the crust tanned condition, as is the practice now, at least the better selections of them are semi-chromed, finished and exported, they would fetch higher returns. The problems that confront semi-chrome leather manufacture in respect of its practical and theoretical aspects have been recently reviewed[1]. The technical know-how[2-4] appears to be the main hurdle in the way of the adoption of semi-chrome tanning process in India.

A systematic study of this important subject was considered necessary and work was, therefore, initiated at the Central Leather Research Institute, Madras, as a major project. In the first instance investigations have been confined to semi-chroming of E.I. tanned kips.

The process of semi-chroming E.I. tanned kips for the manufacture of shoe upper leathers similar to box and willow sides consists of the following operations: (1) soaking, (2) samming, (3) splitting, (4) shaving, (5) stripping, (6) chroming, (7) neutralizing, (8) dyeing, (9) fat liquoring and (10) finishing.

Among these, the first four operations are mechanical and do not require much investigation for satisfactory working. The last six operations involve chemical reactions and research is necessary to discover efficient ways of performing them to ensure best results. Our investigation has two objectives: firstly, to study the chemical mechanism of these operations and secondly, from the knowledge of the chemical mechanism of the operations, to work out the most efficient techniques.

Ever since the introduction of semi-chrome process in tanning practice, a great deal of stress has been laid on the stripping operation. It has been held that to impart to semi-chrome leather the characteristics of the full-chrome variety, the vegetable matter consisting of insoluble non-tans (bloom), soluble non-tans and as much tannin as possible should be removed from the vegetable tanned stock. The object of removing the vegetable tan matter is to give the chrome a chance to impart its characteristics to the finished leather, unhampered by the presence of a large amount of vegetable tannin. For maximum removal of the vegetable matter, the tanned kips, after shaving, are washed thoroughly in a drum either in running water or in several changes of water and then stripped of loose and some bound tans in the same drum with a weak solution of mild alkalies like borax, sodium bicarbonate, soda crystals, soda ash or soap. After this treatment, the kips are again washed in running water to remove the dissolved vegetable matter. The kips so stripped are then chromed.

The stripping of vegetable tanned leather with water has received a good deal of attention. Page[5], after successive extractions of the tanned leather with water, concluded that the water solubles stripped might be of two types, viz. free and bound. The balance left in the leather after the removal of the water solubles was termed by him as "fixed tannin". The values so obtained by him for fixed tannin were in fair agreement with those obtained by the method of Wilson and Kern[6] wherein the leather was continuously washed with water until practically nothing more could be extracted. Colin-Russ[7], though critical of Page's technique, did not dispute his system of classification of free and bound water solubles and fixed tannins. Mariott[8], following a different method of stripping, namely stripping with saturated borax and 0·05 N sodium carbonate solution, came to conclusions similar to those of Page.

In this paper, the effect of successive extractions of leather with water on the removal of the free and loosely bound tannins and their effect on the subsequent chrome tannage have been dealt with.

Experimental procedure

E.I. tanned kip leathers, classed as "prime tannage", were purchased locally and trimmed to remove the bellies, shanks and shoulder portions. The centre portions were cut into 2 mm. cubes. The cubes were well mixed up and the product analysed for its chemical constituents. The results of the analysis are given in Table 1.

Extraction of water solubles — The E.I. kip sample prepared as above was extracted successively with water to remove water solubles. Ten grams of leather were treated

TABLE 1 — ANALYSIS OF KIP LEATHER

Moisture, %	15·30
Fat, %	7·13
Insoluble ash, %	0·17
Hide substance, %	46·52
Free water solubles, % (Page's method)	3·63
*p*H of water solubles	4·90
Combined water solubles, %	13·27
Fixed tans, %	13·98

with a fixed volume of water (sufficient to bring the total volume including that of the leather to 100 cc.). The material was kept in contact with water for 24 hr. at the end of which the extract was carefully decanted, made up to a convenient volume and an aliquot evaporated to determine the solubles. When decantation was found difficult, the water solubles were filtered using suction. To the extracted material, a suitable volume of distilled water was added again to make up the total volume to 100 cc. and the whole left over for another 24 hr. In all, 46 extractions were carried out. The results are presented graphically in Fig. 1. It would be seen that the curve is made up of three distinct parts: viz. (1) a steep incline which shows a break at extraction 4, (2) a flat region which exhibits a break at extraction 34 and (3) a flat region. These three stages, according to Page, represent the free water solubles, combined water solubles and fixed tannins respectively. There is a sharp fall observed between extractions 4 to 16 and then the curve becomes flat up to extraction 34. Page explained that these variations in the shape of the curve should not be considered significant as they represented combined water solubles of different molecular sizes. It was observed that the colour of the solubles removed was becoming progressively darker with the increasing number of extractions which might mean that the molecular size of the solubles increased with successive stages of extraction. The amount of water solubles stripped up to 34 extractions was considered important because this value coincides with that obtained by the method of Wilson and Kern.

The percentage of solubles removed with successive extractions is shown in Fig. 2. Assuming Page's interpretation to be correct, the amounts of different types of tannins present in the leather are: free water solubles, 3·63; combined water solubles, 13·27; and fixed tannins, 13·98 per cent.

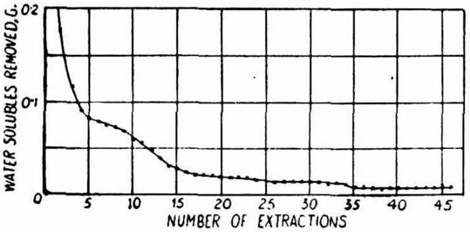

FIG. 1 — EXTRACTION OF WATER SOLUBLES FROM E.I. KIPS

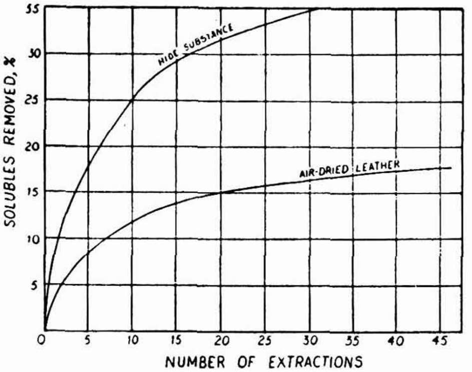

FIG. 2 — WATER SOLUBLES REMOVED FROM E.I. KIPS BY SUCCESSIVE EXTRACTION

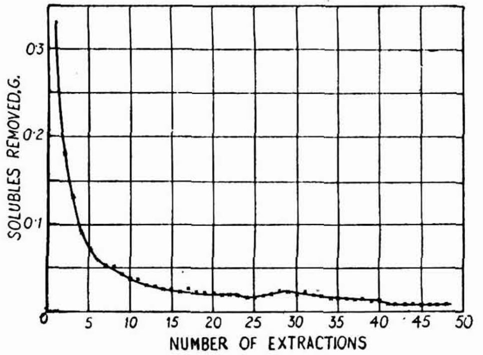

FIG. 3 — EFFECT OF AGITATION ON THE EXTRACTION OF WATER SOLUBLES FROM E.I. KIPS

Extraction by agitation — The static method of Page is time-consuming. Attempts were made to shorten the period of extraction by agitation. Maintaining the same ratio of water to tanned material and using the material in cubes of size 2 mm., successive extractions were carried out by agitating the mixture continuously on a shaker. The results (FIG. 3) were found to be erratic and the time for the extraction of water solubles was not reduced. However, when the water solubles stripped were plotted against the number of extractions, a sharp break was observed in the curve after extraction 41 and the cumulative amount of solubles removed at this point was found to be 16·60 g. which agrees closely with the figure obtained by the static method of extraction (16·9 g.). Page found that agitation did not help to shorten the period of extraction and this is confirmed by our experiment.

However, if leather ground to a powder in a Wiley mill (40 mesh) is used and the material extracted with water in a blender, equilibrium is attained almost immediately. To a 10 g. sample of ground powder, 25 cc. of water were added initially to wet back the material properly. A further 200 cc. of water were added and the whole mass put through a blender for 5 min., filtered in a Buchner flask, transferring the material to the Buchner funnel by an additional 25 cc. of water. The filtrate was made up to a known volume and an aliquot evaporated to determine the solubles content. The residue was carefully collected, transferred back to the blender, 200 cc. of distilled water again added and the mass agitated for 5 min. This process was repeated until a constant value was obtained for the water solubles content. The results are given in Fig. 4. It is observed that the fall in the amount of water solubles removed is rapid up to extraction 6, more gradual up to 17, and ceases more or less during further extractions. A straight line curve obtained in this particular portion is a clear indication of the tannins being more firmly fixed in the tanned leather. It will also be seen that after 17 extractions, the water solubles removed are 16·62 g. which further confirms the earlier results. There is, however, no clear-cut distinction between the free water solubles and combined water solubles. This technique, which has not only confirmed the results obtained by the static technique but is also less time-consuming, has been followed in all other experiments.

Effect of the removal of water solubles on chrome tannage — Ten grams of E.I. tanned kip, cut into 2 mm. cubes, were stripped of free water solubles by 4 successive extractions in one experiment and the combined water solubles by 34 successive extractions in another experiment. The products obtained were tanned with 50 cc. of 33·33 per cent basic sulphur dioxide reduced chrome liquor containing 1·30 per cent chromium for 24 hr. A control was also run using 10 g. of kip pieces without extraction. The material was filtered and the tanned leather washed with water (2 × 50 cc.), air-dried and analysed. The results of these analyses are given in Table 2.

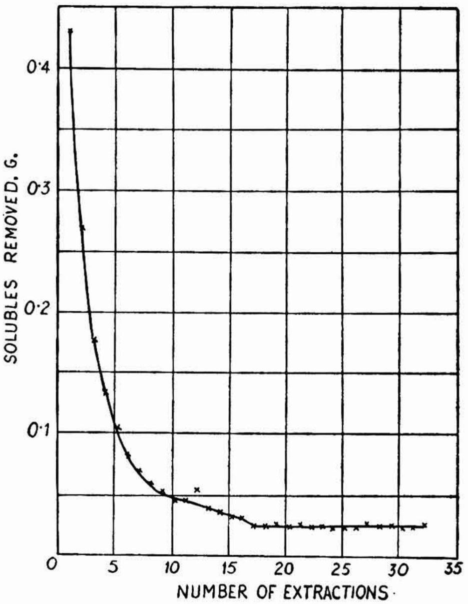

FIG. 4 — EFFECT OF AGITATION IN A BLENDER ON THE EXTRACTION OF WATER SOLUBLES FROM E.I. KIPS

TABLE 2 — EFFECT OF REMOVAL OF WATER SOLUBLES ON FIXATION OF CHROMIUM

SOLUBLES REMOVED ON KIP WEIGHT %	pH OF EXHAUSTED CHROME BATH	AMOUNT OF CHROMIUM FIXED/100 G. H.S.
Nil	3·30	2·37
3·63 (free water solubles)	3·30	2·62
16·9 (combined and free water solubles)	3·45	3·27

It was observed that the greater the amount of water solubles removed the greater is the amount of chromium fixed. This indicates that increased chromium fixation may be due to an increase in the surface area or due to the release of certain active groups. The increase cannot be due to changes in the basicity of the chromium compound, because the pH of the exhaust bath is approximately the same throughout.

To indicate more clearly the effect of the removal of water solubles from E.I. kip leather on the fixation of chromium, 2 g. of material ground in a Wiley mill was extracted with water to remove water solubles to different degrees. The material so obtained was further chrome-tanned with 100 cc. of 33·33 per cent sulphur dioxide reduced liquor containing 0·13 per cent chromium for 48 hr. The powders were filtered on a Buchner funnel, washed with 200 cc. of distilled water for 2 hr., filtered, dried and analysed. The results are given in Table 3. The amount of chromium fixed by the various samples is presented in Fig. 5. It would be observed that, in general, an increase in water solubles removed results in an increase in chrome fixation. When, however, about 15 per cent of the solubles (on hide substance basis) is removed, chrome fixation tends to increase with further removal of solubles. This transition point coincides with the point representing the stage after fourth extraction in Fig. 1 and serves to distinguish free and combined water solubles. The combined water solubles, as represented by the portion of the curve between extractions 4-34 in Fig. 1, were 13·27 per cent and if these combined water solubles are removed, a sharp increase in the chrome fixation is observed. Fig. 5 indicates the occurrence of two sets of reactions: chrome fixation increasing slightly with increasing amount of free solubles removed, and a sharp increase in chrome fixation when combined water solubles are removed. This would mean that the removal of the combined water solubles may create conditions favourable for fixation of chrome by providing reactive groups to fix chrome rapidly. These results also indicate that the increase in chrome fixation is not dependent on a surface phenomenon but actually on the removal of water solubles.

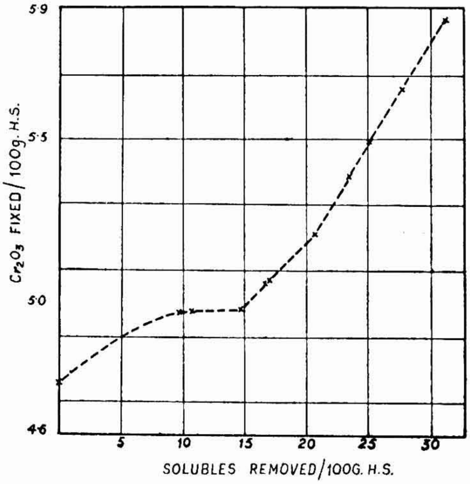

FIG. 5 — FIXATION OF CHROMIUM IN KIP LEATHER

TABLE 3 — EFFECT OF REMOVAL OF WATER SOLUBLES ON FIXATION OF CHROMIUM

WATER SOLUBLES REMOVED		*p*H OF WATER SOLUBLES	FIXED $\frac{Cr_2O_3}{100\ H.S.}$	*p*H OF EXHAUST BATH	*p*H OF WASHINGS
% of air-dried powder	% of hide substance (H.S.)				
Hide powder	—	—	7·55	3·35	3·40
0·000	0·00	—	4·76	3·00	3·10
4·600	9·68	5·00	4·98	3·05	3·20
4·950	10·76	5·00	4·96	3·10	3·20
7·000	14·72	5·10	4·98	2·90	3·10
7·825	16·46	5·10	5·07	2·95	3·10
8·135	17·12	5·10	5·07	2·95	3·20
9·800	20·62	5·10	5·21	2·90	3·10
11·750	23·51	5·10	5·39	2·95	3·20
11·875	25·00	5·10	5·50	2·95	3·20
14·700	30·91	5·10	5·87	3·00	3·20

The increase in the amount of chrome fixed is hardly 4·6 per cent Cr_2O_3 when free water solubles are removed, whereas this increase is 19 per cent when an approximately equal amount of combined water solubles is removed. It is, therefore, reasonable to conclude that the removal of the combined water solubles releases reactive groups favourable for the fixation of chrome.

In the above experiments it has been shown that the removal of the water solubles releases reactive groups to fix additional amount of chrome. Use has been made of the dye technique to determine the groups released by the removal of combined water solubles. Acid magenta (B.D.H.), an anionic dye was used. This dye has a low molecular weight and was chosen because acid dyes of low molecular weight have been shown to get fixed on leather mainly by electrovalent linkages[9]. The colour of the dye solution follows Beers' law closely. Two grams of ground kip powder were taken and the combined water solubles removed. Blanks were run with ground powder without removal of the water solubles. Two grams of the material were treated with 100 cc. of 0·1 per cent dye solution, kept overnight, filtered in a Buchner funnel, washed with 800 cc. of distilled water and the amount of dye determined in the washings. These results are given in Table 4.

The results in Table 4 indicate practically no difference in dye absorption of the stripped and unstripped powder which means that during the course of the removal of water solubles, no basic groups are released to fix additional amount of dye. This is confirmed by a study of the pH of the exhausted dye baths where the pH of the baths was controlled by using 10 per cent acetic acid for dissolving the dye and for subsequent washing.

Effect of removal of the combined water solubles on the fixation of non-cationic chrome complexes — The non-cationic chrome complex was prepared by adding, at boil, sodium oxalate in the ratio of 3 moles to 1 mole chromium oxide to 33·33 per cent basic chromium sulphate, free from neutral salt, according to the method of Shuttleworth[10]. The liquor was found to contain 67 per cent of anionic chrome complexes and 33 per cent of non-ionic chrome complexes; no cationic chrome complexes were present. Stripped and unstripped kip powder (2 g.) were tanned separately in 100 cc. of 0·13 per cent chromium content for 48 hr., filtered, washed with 200 cc. of distilled water for 2 hr., filtered, air-dried and analysed. A control was also run to study the fixation of non-cationic chrome on hide powder. The results of this analysis are given in Table 5.

The results given in Table 5 show that the amount of non-cationic chrome fixed increases with increase in the combined water solubles removed, as in the case of cationic chrome liquors.

In his theory on the mechanism of vegetable tannage, Page[11] contends that the combined water solubles are held by auxiliary valencies and the fixed tannins by principal valencies. The combined water solubles are believed to be held by weaker hydrogen bonding with the carbonyl and imino groups of peptide chains. The rise in the shrinkage temperature of vegetable tanned leather by the removal of combined water solubles and the increase in their fixation by the use of lyotropic agents were given as further evidence to indicate the weak nature of these auxiliary valencies.

TABLE 4 — EFFECT OF REMOVAL OF WATER SOLUBLES (DYE TECHNIQUE)

	EXHAUST DYE BATH	
	pH	Optical density
Unstripped powder	4·70	0·120
Stripped powder	5·00	0·121
Unstripped powder	2·90	0·540
Stripped powder	2·90	0·550

TABLE 5 — EFFECT OF REMOVAL OF WATER SOLUBLES ON FIXATION OF NON-CATIONIC CHROME COMPLEXES

	FIXED Cr_2O_3 / 100 G. H.S. g.	pH OF EXHAUSTED BATH
Unstripped powder	2·65	4·50
Stripped powder	3·19	4·70
Hide powder	3·50	5·30

H.S. = hide substance.

The fact that semi-chrome leather has excellent thermal stability in spite of low fixation of Cr_2O_3 (about 4 per cent on hide substance) indicates that its thermal stability is due to the nature of combination that occurs between chrome and leather rather than due to the amount of chrome fixed. This fact is well established.

Vegetable pre-tannage is known to decrease the fixation of anionic and cationic chrome complexes. Many postulates have been suggested for proper understanding of this mechanism and these have been reviewed in a recent publication[1]. The explanation given is that the vegetable tannins acting as donors through their hydroxy groups react with carbonyl groups of peptide chains on the one hand and behave as acceptors reacting with protein donors like the amino and carboxyl groups of the protein on the other. Thus, vegetable pretannage results in the inactivation of not only the amino but also the carbonyl and carboxyl groups. Successive extractions of vegetable tanned leather with water remove, as shown earlier, free and combined water solubles. The combined water solubles, according to Page, are supposed to be attached to the peptide groups by weak hydrogen bonding. It is also likely that the carboxyl groups are involved in this type of bonding. The removal of combined water solubles may release the carboxyl and peptide groups which have been inactivated by vegetable tannin, and which act as acceptors. The dye technique experiments show that no basic groups are released. It is, therefore, possible that the increased chrome fixation with increase in the combined water solubles removed may be due to carboxyl and carbonyl groups thus released. There is ample evidence for the reactivity of chrome complex through secondary valencies[12-14]. Gustavson[13] pointed out that with hydrated polyamide appreciable amounts of vegetable tannins and non-cationic chrome complexes got fixed at the peptide linkage. Recently Sykes[14] showed that collagen, in which both the amino and carboxyl groups were inactivated, fixed chrome both from cationic and anionic chrome complexes.

One interesting finding from the results given in Table 3 is that the *p*H is lowered in the case of semi-chrome tannage. Compared to *p*H 3·35 for tannage with hide powder, the *p*H of the semi-chrome exhaust tanning bath was found to be 3·00 in the case of E.I. tanned kip and of kip stripped of the water solubles. This lowering of *p*H should, in fact, retard the chromium fixation as the ionization of carboxyl groups is necessary for co-ordination with the chromium complex and would increase with the increase in *p*H. This lowering of *p*H may be taken as an indication that the amino groups are no longer available for fixing the hydrolysed chrome acid and thus act as buffer, facilitating chrome fixation. In other words, the amino groups have been blocked by vegetable tannin. But the acid combining capacity of collagen is shown to be unaffected by its combination with vegetable tannins[15,16]. Gustavson[17] has recently shown that acid binding capacity of vegetable tanned leather at *p*H around the iso-electric point is altered little, indicating that vegetable tannage in these conditions does not involve participation of any amino groups. This is particularly so in the case of tannage with wattle and myrobalan which are mainly used in E.I. tanning. Kip tannage is usually done at the *p*H range 4·5 to 5. The acid binding capacity of the ground kip powder was found to be 0·93 m. eq. per g. hide substance, which is equivalent to 1 g. of collagen. This confirms the observation that vegetable tannage does not involve blocking of amino groups.

On the other hand, there is substantial evidence to show that vegetable tannins, particularly of the pyrogallol type, can enter the chrome complexes[18]. If the vegetable tannin enters chrome complex, displacing the sulphate acid radical, the *p*H of the tanning bath will be lowered. As the dye technique has also confirmed that no amino groups are involved in the removal of the water solubles, it is possible that the vegetable tannin might penetrate the chrome complex shifting the equilibrium and leading to lowering of the *p*H of tanning bath by the acid.

Yet another interesting finding is the reduction of the amount of water solubles in the semi-chrome tanned leather. When 1 g. of the kip powder is treated with 100 cc. of water for 48 hr., the solubles removed are about 20-21 per cent on hide substance. But when the same powder is semi-chromed and subjected to similar treatment with water, the solubles removed are only about 1-2 per cent. The sharp fall in the amount of water solubles in semi-chrome leather may mean that water solubles which are fixed originally by weak auxiliary forces may react with the chrome complex acting as a donor and an acceptor. The other probability may be that in the presence of chromium salts, the water solubles fixed by the weaker bonds of auxiliary valencies may be displaced by chromium solutions for co-ordination with carboxyl and carbonyl groups. The water solubles thus displaced may be fixed more firmly by electro-valent forces to the activated basic groups of the protein.

These postulates have to be taken with caution and more data are required to confirm them.

Conclusion

1. The method of Page was applied to the E.I. tanned kip leather and the results obtained confirmed Page's findings with regard to the classification of free, combined and fixed tannins in the vegetable tanned leather.

2. The removal of combined water solubles has shown to increase the fixation of both cationic and non-cationic chrome complexes.

3. The removal of combined water solubles appears to release peptide and carboxyl groups of the protein and not the basic amino groups.

4. Additional data have been obtained to confirm the postulate that cationic and non-cationic chrome complexes will react with the same group through co-ordination, irrespective of the charge on the chromium complex.

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Preparation of Semolina-like Product from Soft Wheat

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THE principal commercial varieties of wheat fall under the following groups: (1) common hard or soft wheat (*Triticum vulgare*) and (2) durum wheat (*Triticum durum*). Common hard or soft wheat is utilized largely for the manufacture of whole meal flour and white flour used in making bread, biscuits and pastries. Semolina and semolina-like products are generally prepared from durum and common hard wheat[1,2].

Prior to the last war, various grades of semolina and semolina-like products were manufactured in India in large quantities. Considerable quantities of these products are being imported every year from other countries, the import of semolina during 1952-53 costing over twelve lakhs of rupees[3]. The consumption of wheat in rice-eating areas has been mainly in the form of semolina-like products or coarsely ground wheat and to a lesser extent in the form of vermicelli and flour. Of late, the production and import of semolina-like products have considerably decreased while large quantities of wheat (predominantly of the soft variety) are being imported[4]. Soft wheat yields mainly flour and does not lend itself to the preparation of semolina-like products by the usual commercial process applicable to hard wheat. As these products are preferred to flour in the rice-eating areas, the possibility of making such products from soft wheat has been investigated. As a result of these investigations, a process has been developed for the preparation of a semolina-like product from soft wheat. A brief account of this work is reported in this paper.

The process consists in parboiling soft wheat under specified conditions whereby the grains become hard due to the gelatinization of starch. The parboiled wheat is polished in a small rice huller (Engelberg model) to remove the germ and bran and finally converted into semolina-like product by coarse grinding in a disintegrator.

TABLE 1 — EFFECT OF VARIOUS TREATMENTS ON THE YIELD OF SEMOLINA AND FLOUR FROM SOFT WHEAT

(For treatment Nos. 1-7, 1 kg. samples of wheat were soaked in 1,500 cc. water; for treatment No. 8, 1 kg. sample was soaked for 1 min. in 1,500 cc. water and water drained off)

EXPT. No.	TREATMENT	YIELD OF		
-		Semolina-like product %	Bran and germ %	Flour %
1	Untreated wheat	20	14	62
2	Soaked in water at 60°C. for 30 min.	40	16	40
3	Soaked in water at 60°C. for 1 hr.	42	14	42
4	Soaked in water at 60°C. for 2 hr.	40	13	42
5	Soaked in water at 70°C. for 30 min.	41	15	40
6	Soaked in water at 70°C. for 1 hr.	45	14	37
7	Soaked in water at 70°C. for 2 hr.	40	16	41
8	Moist wheat steamed for 30 min.	46	14	35
9	Soaked in water (30°C.) for 30 min.; soaked wheat (after draining off the water) steamed for 30 min.	65	15	18

Some preliminary experiments were conducted in order to find out the optimum conditions of parboiling of soft wheat for obtaining the maximum yield of semolina-like product.

Samples of soft wheat (1 kg.) were subjected to different treatments as indicated in Table 1. The processed wheat was dried in a drier at 45°-50°C. in a current of air. The moisture content of the wheat was determined. The material was conditioned at 45°-50°C. by adding water to bring the moisture content to 15-16 per cent. The conditioned wheat was polished and converted into a semolina-like product in the same way as described below in the final procedure. The effect of various treatments on the yield of semolina is indicated by the results given in Table 1. The results show that while untreated soft wheat gives a very low yield (10 per cent) of semolina-like product, the maximum yield (65 per cent) was obtained from wheat which was soaked in cold water for 30 min., steamed for 30 min. and dried.

Final procedure

The procedure finally adopted for the preparation of semolina-like product from soft wheat consists of the following steps: (1) cleaning and soaking, (2) parboiling and drying, (3) polishing and (4) grinding and grading.

Cleaning and soaking — Soft wheat, freed from grit and other impurities, was soaked in one and a half times its volume of cold water for 30 min. at room temperature (29°-30°C.) and the water drained off.

Parboiling and drying — The moist wheat is transferred to a thick-walled iron vessel with a tight-fitting lid, having an outlet for steam. The vessel is fitted with pipes with perforations through which steam is introduced. The material is parboiled by steaming at atmospheric pressure for 30 min. It is then removed and dried in the sun or in a cabinet drier at 45°-50°C. in a blast of air.

Polishing — The moisture content of the parboiled wheat is determined and the material conditioned at 45°-50°C. by adding water to bring the moisture content to about 15-16 per cent. The wheat is then passed through a rice huller (Engelberg model) when the bran and greater part of the germ are removed in the same way as from brown rice. The yield of the bran and germ is about 13-16 per cent of the wheat.

Grinding and grading—The polished wheat is coarsely ground in a disintegrator using a suitable sieve to obtain the semolina-like product of desired grain size. This is subsequently graded by passing through sieves of three different mesh (40, 30 and 20), when coarse wheat flour, fine and coarse semolina respectively are obtained. The material not passing through 20-mesh sieve is again ground and graded as described above. All the products are finally dried in a drier at 45°-50°C. to a moisture content of 9-10 per cent before being packed. The yield of different products is approximately as follows: fine semolina 60, coarse semolina 10, flour 10 and bran and germ 13-16 per cent.

Semolina was also prepared from Indian hard wheat by the above process except that the wheat was not parboiled before polishing and grinding.

Chemical composition of wheat and quality of semolina

The chemical composition of the samples of soft and hard wheat used in the present investigation and that of semolina prepared from them is given in Table 2. The proximate principles and minerals were determined by the methods of the Association of

TABLE 2 — CHEMICAL COMPOSITION OF SOFT AND HARD WHEATS AND SEMOLINA PREPARED FROM THEM

	SOFT WHEAT	SEMOLINA FROM SOFT WHEAT	INDIAN HARD WHEAT	SEMOLINA FROM HARD WHEAT
Moisture, %	10·8	10·90	10·2	10·50
Protein (N × 6·25), %	10·8	9·40	12·8	11·20
Fat (ether extractives), %	2·0	1·00	2·3	1·20
Fibre, %	1·4	0·50	1·5	0·60
Ash, %	1·5	0·84	1·6	0·95
Carbohydrate (by difference), %	73·5	77·36	71·6	75·55
Calcium (Ca), mg., %	42·0	27·00	51·0	30·00
Phosphorus (P), mg., %	284·0	125·00	312·0	138·00
Iron (Fe), mg., %	5·0	3·10	5·5	3·40
Thiamine (γ/100 g.)	410·0	320·00	520·0	180·00

Agricultural Chemists[5]. Thiamine was determined by the method of Swaminathan[6].

It will be observed that the thiamine content of semolina prepared from parboiled soft wheat is higher than that of semolina obtained from Indian hard wheat. This might be due to a part of the thiamine present in the germ and bran penetrating into the endosperm during parboiling as in the case of rice[7]. Further, a part of the germ and scutellum might have attained a firmer attachment to the rest of the grain during parboiling as reported by Hinton[7] in the case of rice.

Consumer trials — Various sweet and savoury preparations were made from the semolina obtained from soft wheat by the above process. Consumer trials revealed that the products were highly acceptable, the taste and consistency of the preparations being exactly similar to those obtained from semolina prepared from hard wheat.

Summary

A process for the preparation of a semolina-like product from soft wheat has been described. It consists in soaking wheat in water at 30°C. for 30 min., draining off the water, parboiling it by steaming for 30 min. at atmospheric pressure and drying. The parboiled wheat is then milled to remove bran and germ and finally converted into semolina-like product by coarse grinding. The process is simple and can be adopted on a cottage scale.

Acknowledgement

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Asafoetida

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ASAFOETIDA is a gum resin derived chiefly from an umbelliferous plant (*Ferula foetida*) which is indigenous to the plains of Kandahar, Eastern Persia and Western Afghanistan[1,2]. It is obtained as an exudation of the decapitated rhizome or root of a plant about four years old[3]. The stems are cut close to the root and asafoetida exudes in blobs or drops from the part left in the ground. The accumulated exudation is scraped off at intervals, the soft mass sometimes being rendered more convenient to handle by admixture with calcareous or other materials. Of the two kinds of asafoetida known in commerce, one turns red and then brownish when a fresh surface is exposed to air and the other remains white or pale buff. The latter variety is supposed to be derived from *Ferula rubricaulis*. Other species from which asafoetida can be got are *Ferula narthex* and probably *F. scorodorma*[2,4].

The history of asafoetida before the seventh century is obscure. It was probably introduced into India at a later date and there is reference to it as *Hingu* in Ayurveda and in Sanskrit works[3]. The subsequent history is rather difficult to trace, but during the past few centuries it became increasingly popular, especially in the south of India, which still constitutes the major consuming area. At the present time, India is the chief market for the world's asafoetida, and Bombay is the main importing centre where the product is also processed and packed for distribution to other parts of the country. The industry is largely in the hands of a few established trading families who have carried on by traditional methods, handed over from one generation to another.

Uses

As a food adjunct — Asafoetida was used as a condiment by the people of Baluchistan at least as early as the tenth century. Asafoetida is relished as a condiment in India and Persia, and is in demand in France for its use in cookery. In most European and American countries the odour of asafoetida is not much liked and the material is sometimes referred to by them as " Devil's dung"[4]. In contrast to this, quite a large section of people, especially in South India, regard it as a valuable spice without which the food preparation would be incomplete. In the regions of its growth the whole plant is used as a fresh vegetable, the inner portion of the full-grown stem being regarded as a luxury[3]. Asafoetida is an ingredient in Worcestershire sauce[3].

In medicine — Asafoetida is used in medicine as carminative and antispasmodic, as an expectorant in chronic bronchitis, also as an enema in intestinal flatulence[3,4]. Mixed with Cayenne pepper and sweet flag, it is a popular medicine for cholera in India[3].

Pharmacology

Hinsdale[5] reported that the acuteness of the sense of hearing is diminished by continued ingestion of asafoetida. Macht and Ting[6] showed that it exerted a distinct sedative effect as determined with rat as the experimental animal. Boyd[7] studied its pharmacological action on stomach, intestine, bladder, uterus, heart, as also on blood pressure and respiration.

Composition

The chief constituents of asafoetida are resin, gums, volatile oil and traces of umbelliferone[3,8]. The resin consists of asaresinotannol ($C_{24}H_{34}O_5$), both free and combined, with ferulic acid, a constituent which is responsible for the odour and the bitter acrid taste[9,10]. The colourless asaresinol ferulic ester is very labile and is thus responsible for the change of colour to red, reddish violet and brown[11]. The resin gives on distillation (*in vacuo*) umbelliferone. Repeated microsublimation of asafoetida yields pure umbelliferone (m.p. 223°-24°C.), free from ferulic acid. Tschirch and Polasek[9] reported that asaresinotannol, on treatment with nitric acid, yields picric acid. Crystalline asaresene A, $C_{24}H_{32}O_4$, m.p. 172°C., obtained by fractional precipitation of ether solutions with ligroin, and crystalline hydroasaresene B, $C_{20}H_{30}O_5$, m.p. 155°C., obtained from asaresene B by catalytic hydrogenation under pressure at ordinary temperature have been isolated from resene in small quantities[12]. The ester, on saponification with 5 per cent sodium carbonate solution in the cold or by 1 per cent sodium hydroxide solution, yields amorphous asaresinol which is insoluble in ether or sodium carbonate solution but soluble in sodium hydroxide solution. Thus asaresenol is a phenol and not coniferyl alcohol as concluded by Reinitzer[13] from colour reactions. The ester is found stable towards ammonium carbonate which enables its separation from the free acid in ether solution. Asaresinol is sensitive to light and air. Vanillin does not occur in the drug but is formed by oxidation of ferulic acid. This observation was confirmed by Koffler and Kutiak[10] by fractional micro-sublimation of the dried precipitate obtained on pouring the ether extract of 1 g. of asafoetida into petroleum ether.

Asafoetida owes its powerful, characteristic odour to the oil present in it[3]. The oil was examined by Hlasiwetz[9] in 1849, who stated that it was composed of hexynyl sulphide, $(C_6H_{11})_2S$, and hexynyl disulphide, $(C_6H_{11})_2S_2$, and was devoid of any oxygen or nitrogen. According to Brannt[9], asafoetida oil contains allyl sulphide and disulphide. Semmler[9] and Mannich and Fresenius[14], however, found the oil to contain pinene, a sesquiterpene and sulphur compounds having the composition $C_{17}H_{14}S_2$ (about 45 per cent), $C_{10}H_{20}S_2$ (the constituent to which the oil owes its odour, about 20 per cent), $C_8H_{16}S_2$ and $C_{10}H_{18}S_2$ and an oxygenated compound having the formula $(C_{10}H_{16}O)_n$. The volatile oil determined by the method of Clevenger[15] has a sulphur content[16] varying from 15·3 to 28·0 per cent, the refractive index, $n_D^{20°}$, 1·493 to 1·518, $[\alpha]_D^{20°}$, $-9{\cdot}0°$ to $+9{\cdot}3°$ and density at 20°, 0·906 to 0·973. The main fraction of the oil boils at 82°-84°/10 mm.[14].

Purity standards

Small[3] describes the best quality of asafoetida as the one in the form of single, separate drops or tears up to about 0·5 in. diameter. This, he says, is known in Bombay as *Khandahari hing*. The more common form is a mass, sometimes showing on its shape indications of its drops having run together. More usually, the main structural evidence for origin as drops or tears is in the mottled appearance when relatively soft fresh mass is cut. Small[3] has also given microphotographs of cut sections of asafoetida in support of his conclusions and traces the differences in physical form to the methods employed in collection.

According to Hirchsohn[9], good samples of asafoetida should yield not less than 11 per cent of soluble matter with petroleum spirit when the extract is dried at 17°C. and not less than 6 per cent of the dried extract should be lost when heated to 120°C. Pure, tear asafoetida, according to *B.P. Codex*[17], contains from 65 to 75 per cent matter soluble in 90 per cent alcohol and gives about 3 to 5 per cent ash. The *B.P. Codex*[17] lays down the following standards for asafoetida: (1) the ash content should not be more than 15 per cent, and (2) the alcohol (90 per cent) insoluble solids should not be more than 50 per cent.

The regulations of the Bombay Prevention of Adulteration Act (1925) specify that (1) the ash should not be more than 20 per cent, (2) alcoholic (90 per cent) extract should not be less than 25 per cent, and (3) that there should be present no foreign resins like galbanum, colophony, etc.

Analytical

A study of several samples of both false and true asafoetida including the chemistry and the physical aspects has been made by Peyer and Imhof[18]. Baumann[11] found that asafoetida consisted of 69 per cent of resin soluble in acetone, 31 per cent of gum and impurities. Of the resin, 50·1 per cent (calculated on the original material) consisted of resin and ethereal oil, 1 per cent of ether-insoluble matter (apparently free resinol), 16·57 per cent of asaresinol ferulic ester and 1·33 per cent of free ferulic acid. According to Small[3], asafoetida contains 6-17 per cent of volatile oil, about 25 per cent of gum and about 40-64 per cent of resin which consists of asaresinotannol, both free and combined with ferulic acid. Harrison and Self[19] analysed samples of asafoetida for the resin content (variation 19 to 52 per cent), ash (variation from 2·7 to 52·6 per cent), volatile oil (variation from 4·6 to 21 per cent), loss on drying (variation from 7·9 to 32·2 per cent) and sulphur in oil (variation from 8·9 to 31·4 per cent).

On an examination of 41 commercial samples of asafoetida, Clevenger[16] reported that the ethyl alcohol soluble extract varied from 54·5 to 74·7; ethyl alcohol insoluble extract 1·4 to 12·9 ; moisture 2·7 to 11·8 per cent ; volatile oil 7·5 to 12 cc. per 100 g. In determining the alcohol soluble extractives of asafoetida, Christensen[20] recommends that the material reduced to a powder (with the aid of purified sand) be used for extraction, otherwise low results are obtained. Grewal and Kochhar[21] observed that 11 of 13 samples of asafoetida examined by them contained less than 50 per cent of resin soluble in alcohol. Sen Gupta and Das[22] analysed samples of asafoetida from the open market for alcohol extractives, gum, ash, acid value and saponification value of the resin, and also tested the samples for the presence of foreign gums, rosin and galbanum. None of the samples satisfied the specifications of the pharmacopoeia. The alcohol extractable matter varied from 21 to 53, gums from 21 to 56, ash from 6·6 to 59 per cent and saponification value of resin from 138 to 255.

From an examination of 11 samples of asafoetida, Martin and Moor[23] found the ash to range from 26·4 to 63·1 per cent and the ash insoluble in hydrochloric acid to range from 42 to 84 per cent of the total; in one case the ash dissolved readily in HCl with much effervescence, leaving only 3·6 per cent insoluble matter.

For the estimation of ash, Mausch[9] suggested the treatment of the sample with 10-15 times its weight of 60 per cent chloral hydrate in water when the gum and resin slowly dissolve. After filtering and washing the residue with chloral hydrate and subsequently with alcohol, the residue is dried and ignited. This preliminary treatment with chloral hydrate is said to overcome errors arising in normal procedure of ash estimation, wherein the organic sulphur present in asafoetida is fixed by the bases during ashing, while a portion of the sulphate is liable to be reduced by the organic matter.

The U.S. Customs authorities[9] laid down a limit for the " lead number " of genuine asafoetida to be at least 200. The " lead number " is a measure of the constituent (or constituents) of the ether soluble portion of the resin, which forms a lead compound insoluble in alcohol. Parry[24], Rippetoe[25] and Harrison and Self[26] have shown that this test has limitations.

The acid value of the extracted gum resins has been shown[9] to vary from 11 to 82 and the ester value from 82 to 182, while the methoxyl value, as determined by Gregor[9], has been shown to vary from 6·9 to 11·9 and by Bamberger[9] to be 18.

Adulterants

Asafoetida is adulterated with cheaper resins like ammoniacum and galbanum and, more often, an enormous amount of low grade material is present in the form of earthy matter and organic debris. Sechler and Becker[27] detect the presence of ammoniacum and galbanum from colour reactions. When 2 cc. of a 1 in 10 aqueous emulsion of asafoetida diluted with 5 cc. of water is floated on sodium hypobromite solution, an olive green colour results. Galbanum emulsion gives a similar colour but ammoniacum gives a cherry red tint. When 2 cc. of asafoetida emulsion are floated on cold sulphuric acid, no perceptible change occurs. Ammoniacum also gives no marked reaction, while galbanum gives a violet colour. Oil of asafoetida is colourless, while ammoniacum yields dark yellow volatile oil and galbanum light yellow volatile oil.

As umbelliferone is present in the combined state in asafoetida, the latter fluoresces when made alkaline with ammonia only after initial acid hydrolysis, while galbanum which contains free umbelliferone fluoresces without prior treatment[3].

Analysis of samples from Mysore market

Recent analyses by us of samples of asafoetida (purchased from the local market) showed (TABLES 1 and 2) that alcohol soluble portion varied from 21 to 28 per cent; volatile oils from 4·3 to 10 per cent; total ash from 4·4 to 44·3 per cent and gums from 11·7 to 56·3 per cent, apart from differences in the physical appearance. It can be seen that no correlation exists between the values of any two constituents. Sample B, though containing as high as 44·3 per cent of total ash, had an alcohol soluble portion of 26·2 per cent. In the ash from this sample calcium was estimated to be 13·62 per cent (calculated as Ca on the original basis). Sample C had a high nitrogen content and also starch compared to the

TABLE 1 — PROXIMATE ANALYSIS OF SAMPLES OF ASAFOETIDA BOUGHT FROM MYSORE MARKET

Sample	Appearance	Price per lb.	Alcohol (90%) soluble fraction	Proteins	Total ash	Crude fibre	Difference (chiefly gums and starch; *see* Table 2)
			(a)	(b)	(c)	(d)	(e)
		Rs. a. p.	%	%	%	%	%
A	Hard, brown lumps	17 8 0	28·0	4·4	6·5	8·2	52·9
B	Hard, solid mass	6 10 8	26·2	2·5	44·3	2·3	24·7
C	Small lumps, not very hard	4 9 0	21·1	15·6	4·4	4·1	54·8
D	Small, hard lumps	3 12 0	20·8	3·2	9·3	1·4	65·3

(a) Extraction under reflux with 90% alcohol. This extract includes moisture, volatile oil, resins and sugars (sugars being less than 1% in the samples examined); (b) sample triturated with 10% trichloroacetic acid and nitrogen estimated in the residue and expressed as protein (N × 6·25); (d) A.O.A.C., (1945), 540; and (e) this figure does not include sugars soluble in 90% alcohol.

TABLE 2 — ANALYSIS OF ASAFOETIDA FRACTIONS

Sample	Alcohol soluble fraction (*refer* Table 1a)					Carbohydrate fraction* (*refer* Table 1e)		Acid soluble ash	Acid val.	Saponification val.
	Moisture	Volatile oil	Resins	Sugars						
				Free reducing sugars	Total sugars	Gums	Starch			
	(f)	(g)	(h)	(i)	(j)	(k)	(l)	(m)	(n)	(o)
	%	%	%	%	%	%	%	%	%	%
A	7·0	7·5	12·54	0·80	0·96	39·6	13·4	5·7	59·8	281
B	4·8	10·0	11·30	0·08	0·10	11·7	9·6	34·0	42·5	267
C	6·1	4·5	10·27	0·17	0·23	16·1	35·7	4·0	45·0	190
D	8·2	4·3	8·08	0·20	0·22	56·3	8·7	4·9	29·4	252

*Does not include sugars soluble in 90% alcohol.

(f) Loss in weight of sample kept under reduced pressure over calcium chloride till no further loss in weight was observed; (g) by difference: total loss in weight on keeping sample at 120°C. for 14 hr. minus moisture (f); (h) by difference: alcohol (90%) soluble fraction (Table 1a) minus sum of (f), (g) and (j); (i) estimated by Hulme and Narain's modification of Hane's method[28] and expressed as glucose; (j) inverted with 1N HCl for 9 min. at 67°C. and estimated as under (i); (k) 90% *alcohol insoluble* fraction extracted with cold water and gums precipitated from the filtrate by addition of 15 times its volume of 90% alcohol. The dried precipitate weighed, ignited and residue weighed. Difference in weights before and after ignition reported as gums; (l) A.O.A.C., (1945), 540. Lane and Eynon's volumetric method[29] employed for determination of sugars in hydrolysed extract, after clarification; (m) total ash (Table 1c) extracted with hot, dilute hydrochloric acid; (n) *B.P.*, (1948), 759; and (o) *B.P.* (1948), 760.

other samples. All the samples contained very small quantities of free sugars which, by paper chromatography, has been qualitatively shown to be a mixture of rhamnose, glucose and sucrose.

The data presented in Table 1 indicate that none of the brands is genuine according to the *B.P. Codex* standard based on the alcohol (90 per cent) soluble matter. Only sample "A" can be passed as genuine according to the regulations of the Bombay Prevention of Adulteration Act (1925).

The *B.P. Codex* requirement of 50 per cent alcohol soluble solids in asafoetida may be a satisfactory specification for samples meant for medicinal purposes, but may not be a suitable standard for samples meant as a spice for culinary purposes, where flavour is the criterion. Hence, for asafoetida which is sold in the Indian market essentially as a flavouring agent, the quality standards must be based on flavour constituents, like volatile oil and, perhaps, its sulphur content.

There are several outstanding problems relating to asafoetida which are still awaiting solution. In the interests of the millions of consumers, especially in India, specifications should be laid down regarding the types and quantity, if at all, of diluents that may be permitted. At the present time there are no means of knowing as to what has gone into the composition of marketed asafoetida or whether it is sold at a fair price. Further work on the physiological action of asafoetida is also needed. The attributes that it is a powerful intestinal antiseptic and a highly potent carminative also require to be examined. The possible use of asafoetida, especially in treating certain types of heart diseases, deserves further investigation. The quantity of asafoetida that goes into the dietary of people is variable, as it is largely dependent on individual taste. It is difficult to state whether at the levels at which it is normally consumed, it merely serves as a flavouring agent or whether it also exercises any therapeutic action. It is hoped that investigations that are now in progress at the Central Food Technological Research Institute, Mysore, will throw further light on the above and related problems.

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First Oil Refinery in India Goes on Stream

INDIA'S FIRST ONE MILLION TON PER ANNUM petroleum refinery erected by the Standard Vacuum Oil Co. at a cost of Rs. 17·5 crores at Trombay Island (Bombay) went on stream in July 1954.

Work on the erection of the refinery began on a 280-acre site at Trombay in December 1952 and the first phase, viz. clearing work, was over within 75 days. The installation of major equipment, electrification, etc., were accomplished in the short span of 15 months and with the arrival, in June 1954, of the first 110,000 barrels of crude oil from the oil wells of Saudi Arabia, the refinery was ready to go into production.

The Stanvac Refinery will turn out every year more than 300 million gallons of six different fuel products by processing crude oil which will come mostly from the Persian Gulf area. These are (in million gallons): gasoline, 90; kerosene, 40; diesel oils, 59; industrial fuel oil, 58; and bunker fuel, 49. These will supply about one-third of India's needs of petroleum products.

The project, it is estimated, will result in an annual saving of more than Rs. 120 lakhs in India's foreign exchange, and provide, in addition, employment for about 500 technicians and workers.

REVIEWS

THE PHYSICS OF THE EXPERIMENTAL METHOD, by H. J. J. Braddick (Chapman & Hall Ltd., London), 1954, pp. xx + 404. Price 35*s*.

There is a dearth of text-books on the methods of experimental physics suitable for the advanced student. The most up-to-date book on the subject is Strong's *Modern Physical Laboratory Practice*, and the appearance of an excellent companion volume is particularly welcome. Written by a gifted experimentalist who received his training in the great school of experimental physics under Lord Rutherford and who is now a prominent worker in the field of cosmic rays, this book provides guidance and information of immense value in the construction of apparatus. It is thus eminently valuable as a text-book of physics applied to physical experiment.

After a brief introduction, the author devotes a chapter to experimental errors and the treatment of experimental results. The theory of errors and the application of " least squares " methods have been treated admirably and the appendix to this chapter is a good review of the mathematical tools required by the experimentalist.

The next chapter deals with the mechanical design of instruments. The principles of kinematic design are lucidly explained and illustrated by suitable applications. This is followed by a description of the mechanical properties of various key materials, with a view to their proper utilization in the construction of apparatus. This is especially valuable for physicists without engineering training. The next chapter on vacuum techniques deals with the design features of static and kinetic vacuum systems, glass-to-metal seals, and vacuum plumbing.

This is followed by a chapter on electrical measurements, which deals mainly with the use of high sensitivity galvanometers, the techniques of measurement of small currents by the electrometer tube method, and the measurement of magnetic fields. This, in turn, is followed by a chapter on electronics that necessarily has to be brief on account of limitations of space. An excellent discussion, however, is given of the feedback principle and the application of negative feedback to linear amplifiers, and positive feedback to multivibrator circuits.

The next chapter on optics and photography is especially commendable. A very good treatment of illuminating systems is given followed by a lucid account of the construction and adjustment of the optical assembly of the telescope and microscope. A succinct account is also given of photography and photographic and photoelectric photometry.

The next chapter on the natural limits of measurement deals with spontaneous fluctuations of voltage in electrical circuits and their limitations on the ultimate sensitivity of instruments. Typical applications of the theory are given to practical problems, e.g. the alpha-particle ionization chamber, the photocell plus amplifier.

The last chapter describes some of the techniques of nuclear physics. A clear and brief account is given of the constructional techniques of ion chambers, proportional counters and Geiger counters. Some of the ancillary electronic equipment, e.g. stabilized power supplies, discriminators, scaling circuits, are briefly described. In conclusion, a brief account is given of cloud chamber and nuclear emulsion techniques.

A fairly extensive list of references to books and easily accessible papers that give detailed accounts of particular procedures is given at the end. The printing and get-up of the book are quite good.

Every experimental physicist will find the book very useful. It should find a place in every physical laboratory.

R. S. KRISHNAN

INSDOC LIST — CURRENT SCIENTIFIC LITERATURE, Vol. 1, No. 1, Col. 1-28, 1 June 1954, New Delhi (Insdoc, New Delhi 12). Annual subscription Rs. 10

The necessity for a publication listing periodically the literature on sciences has been felt in India for a long time but no sustained effort seems to have been made in this direction. The National Institute of Sciences of India made an attempt to provide a bibliographical service, in 1935; but the publication of the *Indian Science Abstracts* was discontinued after the issue of the first number. The Indian scientists had to remain contented with whatever services were available in foreign countries. The result was that the information was received after considerable delay. This difficulty was somewhat mitigated when the Unesco South Asia Science Co-operation Office in New Delhi began issuing the *Bibliography of Scientific Publications of South Asia* (*India, Burma, Ceylon*) in January 1949. This *Bibliography* is issued twice a year and covers almost all the Indian scientific periodicals. The subjects are classified according to the U.D.C. A similar bibliography is also being published every month since the beginning of 1952 in the *Journal of Scientific & Industrial Research*, though its scope is limited to some branches of pure science and technological research.

The Insdoc which was established in 1952, having surveyed the situation in India, has undertaken the publication every fortnight, of a list of current scientific literature embracing almost the entire field of science, from all countries of the world. This is a very praiseworthy enterprise and is bound to fill a want felt for a long time by scientific workers. The first issue has just appeared. Necessarily, the maiden attempt cannot fulfil the expectations of all concerned. A universal bibliography as attempted here is almost an impossible achievement. The results of scientific research are published in a multitude of periodicals issued in many countries and in different languages. According to a recent computation there are nearly 50,000 scientific periodicals in the world, of which nearly 20,000 are current. It has also been estimated that at least one million scientific articles, reports, patents and books are added to the world's libraries every year [HOLMSTROM, *Research*, 7 (1954), 190]. No single library, even in foreign countries, receives more than a portion of these.

India publishes around 250 scientific periodicals, of which *only* 16 have been noticed in the current issue of the *Insdoc List*. The total number of journals indexed is 126.

Out of the 250 Indian scientific periodicals, only 98 are noticed in different abstracting journals in foreign countries. The scant attention given to Indian scientific work has to be made good by organizing an efficient Indian bibliographical service in which all the Indian scientific periodicals are properly and adequately indexed, not only for the use of Indian scientific workers but also for workers abroad. It is, therefore, obvious that priority should be given to Indian scientific work in any bibliographical service initiated in India.

As regards the current list, the headings have been arranged in broad subject groups according to the Colon classification. The U.D.C. numbers are also given. The reader would find the arrangement more convenient if the contents are also alphabetically arranged and relevant classification numbers given against the entries in the contents list. The interpolation of alphabets in lower case in between the two columns to indicate the position of entries is not particularly helpful.

A novel feature introduced in the entries is the elimination of punctuations, and the adoption of uniform types for the title and reference entries. It is hard to find an authority which prescribes that abbreviations should not be followed by full stops. This is an innovation, the utility of which is doubtful. The *Indian Standards Specification* IS: 18-1949 has not been adopted, nor the rules of the *International Code of Abbreviations for Titles of Periodicals* (Paris, 1930) and *Supplement* (Paris, 1932). The indention or the vertical alignment of the columns is staggered. The Latin names of plants and animals do not conform to the generally adopted rule, namely, that they should be printed in italics.

Does a bibliographer have the option of selecting or rejecting articles of a particular issue of a journal, for noticing in a bibliography? This is one of the issues that poses itself from a perusal of this list. Such a selection is permissible when it is a *selected* bibliography, prepared by an expert on the subject of his choice. But it is not within the scope of a general bibliographer to exclude from his bibliography any article published in a particular journal. To quote an instance, the *Journal of Scientific & Industrial Research*, Vol. 13, No. 4, April 1954, has published 6 articles in Section A of which 4 have been included in the *Bibliography* under notice, and out of 15 articles in Section B only 5 have been included. Letters to the Editor which were 8 in number and which have as much scientific value as a full paper, have been entirely ignored. A scientist who is to depend upon this *Bibliography* will miss some very important information contained in these articles.

It is earnestly hoped that with the passage of time the small defects, as mentioned above, will have disappeared and the *Bibliography* will render very useful service to those for whom it is intended.

K.K.G.R.

CHROMATOGRAPHY — A REVIEW OF PRINCIPLES AND APPLICATIONS, by Edgar Lederer & Michael Lederer (Elsevier Publishing Co., London), 1953, pp. xviii + 460. Price 60*s*.

The book is primarily meant for the industrial and research chemist. One of the authors, Edgar Lederer, was an early leader in the field of chromatography. He first applied the idea of chromatographic column technique of Tswett while working in Kuhn's Laboratory in 1931. He has, thereafter, never lost interest in chromatographic analysis. This book coming from such a master is a marvellous exposition of the technique of chromatographic analysis which today covers a very wide field of utility. A particularly desirable feature of this book is its emphasis on description of the experimental details. The arrangement of chapters is also very welcome and this book will be extremely useful for a busy chemist desiring to use chromatographic technique in his own sphere without having to take the trouble of going through the entire field of chromatographic literature for which he might not have the necessary time. A considerable part of this present volume is devoted to inorganic chromatography which is especially welcome. Bibliography, at the end of the volume, is quite exhaustive containing about 1,900 references, and an addenda containing reference to important works on matters discussed chapter-wise is also very handy. The book is very fine reading and contains no errors or misprints.

This volume by two masters in chromatography will be a very useful addition to any chemical library and an indispensable reference book to a library attached to any analytical or preparative laboratory.

A. N. GHOSH

SELECT METHODS OF METALLURGICAL ANALYSIS, by William Archibald Naish, John Edward Clennell & Victor S. Kingswood (Chapman & Hall Ltd., London), Second Edition (Revised), 1953, pp. xii + 660. Price 75*s*.

The second edition of this is the result of a thorough revision of the previous edition by a panel of experts and deals with many types of metallurgical analysis, including those of metals, alloys, ores and refractories.

The book is divided into six parts. Part I deals with the sampling, standard methods of solution, separation and qualitative analysis. It would have been an advantage if the wet methods of separation, qualitative tests and confirmatory tests had been dealt together. The drying and ignition of precipitates should have been treated after the discussion of various filtering media. A chapter on common laboratory apparatus in the analytical room would have been welcome.

Part II deals with the various methods of quantitative analysis for the individual elements arranged in alphabetical order. This account will be very useful to both students and analysts as it deals with the occurrence of the metal, source of standard sample and recommended methods of analysis. The chemistry of the methods included has been given in full detail with the reactions indicated by the liberal use of equations. Reference to new methods has also been included which will be very useful for those desiring full information.

Part III deals with the analysis of commercial metals and ferrous and non-ferrous alloys. The presentation is sound, but it is felt that more information should have been given on the analysis of oxygen and hydrogen in metals and information on the determination of aluminium and magnesium when present in traces in iron and steel should have been included.

Part IV deals in outline with the analysis of a few typical ores and slags. Part V includes the analysis of refractory materials and of coal and coke, though the analysis of fuel gases is conspicuously absent.

Physical methods of analysis have been included in Part VI and a brief mention is also made of micro-chemical methods. Our only comment is that the mercury cathode electrolytic cell described is not very convenient to work and the other cells recently mentioned in the literature should have been included.

In spite of these minor limitations, the book is strongly recommended to analysts and students of metallurgy.

T. BANERJEE & P. P. BHATNAGAR

PRINCIPLES OF SUGAR TECHNOLOGY, edited by P. Honig (Elsevier Publishing Co., Amsterdam, Houston, New York & London), 1953, pp. xxii + 767. Price 80*s*.

The book is edited by Dr. Honig, who is well known for his contribution to sugar technology, and the 18 chapters comprising it are contributed by 13 specialists who are actively engaged in sugar research in different parts of the world. The treatment of the subject matter is, therefore, authoritative and up to date.

The aim of the book, as stated in the preface, is to present an account of the physico-chemical principles as applied to sugar technology and to help the sugar technologist appraise new developments and inventions in the field. In this publication, the topics have been carefully selected and the theoretical considerations underlying the various processes in sugar technology have been presented in a lucid manner. These features amply justify the publication of this book which is really a useful addition to the existing list of outstanding books on the subject.

The book is divided into two parts. The first part, comprising 11 chapters, deals with the physical and chemical properties of sugars and non-sugars and the second part, comprising 7 chapters, deals with the purification of technical sugar solutions.

Chapter I describes, among other things, the formation of sucrose in plants, sucrose-salt addition compounds, metal saccharates, decomposition of sucrose, etc. Chapter II gives the physical properties of sucrose including 26 elaborate tables. The physical and chemical properties of reducing sugars given in chapter III explain the formation of colouring matter in sugar solutions, crystallizability of sucrose and exhaustibility of molasses. The principles underlying some analytical methods are also presented. In section 10 of this chapter it would have been useful to include analytical methods for the estimation of glucose, fructose and other reducing sugars which could be adopted in the factory. Chapter IV describes non-nitrogenous organic acid of sugarcane, their importance as buffers and their influence on clarification, titratable acidity, scaling and crystallization. The importance of the study of the nitrogenous non-sugar constituents (free amino compounds and proteins) in sugar solutions has been emphasized in chapter V and the application of chromatographic technique in these studies has been reviewed. In chapter VI the complex organic non-sugars of high molecular weight in sugarcane have been described and their commercial and technological importance is indicated. Chapter VII deals with the three main constituents of sugarcane lipids in the light of old and recent researches, and future lines of research have been indicated. The treatment of colour and coloured non-sugar constituents given in chapter VIII is exhaustive, and further lines of work in this field have been indicated. In chapter IX the scattered material on inorganic non-sugars has been brought together and the behaviour of these constituents at various stages of sugar manufacture has been described with the object of stimulating further study in this rather meagrely explored aspect of sugar technology. The behaviour of many secondary reagents used in cane juice clarification and of various compounds used in feed water and evaporator scale treatment is not always properly understood and hence its treatment in a separate chapter (X) is justified. Temperature, density and *p*H, the three variables defining a set of conditions of sugar factory materials, have been treated in chapter XI which, however, could perhaps be more appropriately assigned a place in Part II.

Chapter XII deals with the history and development of the technology of sugar manufacture and the one following is devoted to chemical and technical aspects of sugar technology. Auxiliary defecants have also been reviewed to cover juices of unusual characteristics. Chapter XIV deals with the fundamentals of lime treatment and its effects on the constituents of the juice have been lucidly brought out. The technology of sulphitation forms the subject of chapter XV, which provides a clear insight into the sulphitation technique. In chapter XVI is given a masterly treatment of the technology of the carbonation process explaining the significance of all the operational procedures involved, as also such important aspects as changes in *p*H, causes of irregularity, etc. Chapter XVII describes the middle juice carbonation process suggested by Dr. Honig in 1934. This process has since been tried in the factory and has been found more effective for removal of non-sugars. The lines on which further work has to be carried out is also indicated. The ion-exchange technique for the removal of non-sugars, though limited in its application at present by economic considerations, offers enormous possibilities in the manufacture of white sugar as a result of the rapid advances in the development and manufacture of synthetic resins. Chapter XVIII explains the principles and possibilities of this technique.

The reviewer has observed some overlapping in the different chapters. While excisions here and there would have avoided overlapping and saved space for inclusion of more useful information, this feature has the advantage that each chapter is complete in itself and makes for easy reference, particularly for the worker in the factory.

The title of this book might be misleading to the sugar technologist. It not only serves his needs admirably but also meets the requirements of the research worker. The extensive bibliography at the end of each chapter will be of immense value to the research worker.

The reviewer is of the opinion that this book should find a place on the shelves of every sugar factory library and should be a constant companion of every progressive sugar technologist.

J. M. SAHA

INDUSTRIAL ORGANIZATION, by Bimal C. Ghose (Oxford University Press, Bombay), 1954, pp. 250. Price Rs. 8

In the face of a vast literature that already exists on the major industries of India, the publication of yet another book on the subject could, normally, hardly be justified. A perusal of *Industrial Organization* by Bimal C. Ghose, however, would convince a careful reader of the desirability of such a book. The existing books on the subject usually stopped at the Industrial Policy Statement of the Government of India (1948), and a student pursuing a course of study on industrial organization of India was obliged to refer to official statistics and a number of other publications for up-to-date facts and figures. And in spite of much literature hunting, the result was not satisfactory and the conclusions remained unco-ordinated. The one merit of the present book is that it is up to date; it takes note of the major developments in the field of industries in India right up to the end of 1953.

The book is divided into two parts: the first part, dealing with general principles of industrial organization, is elementary, but the author deserves credit for having summarized in a small space the two standard works of Mr. E. A. G. Robinson, viz. *The Structure of Competitive Industry* and *Monopoly*. The second part aims at a presentation of the current problems of India's six major industries, viz. textile, jute, sugar, iron and steel, coal and tea, from a new angle and, although the exposition is just introductory, it would be of value to the university student pursuing a course of study on industrial organization of India.

S. P. SAWHNEY

PUBLICATIONS RECEIVED

THE MICROSCOPY OF METALS (The Institution of Metallurgists, London), 1954, pp. 132, price 16*s*. 6*d*.

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PHYSICS AND APPLICATIONS OF SECONDARY ELECTRON EMISSION, by H. Bruining (McGraw-Hill Book Co. Inc., New York), 1954, pp. xii+178, price $ 5.50

QUALITATIVE INORGANIC ANALYSIS, by G. Charlot (Methuen & Co. Ltd., London), 1954, pp. xi+354, price 42*s*.

TEXT BOOK OF METALLURGY, by A. R. Bailey (Macmillan & Co. Ltd., London), 1954, pp. viii+560, price 30*s*.

MINERALS FOR THE CHEMICAL AND ALLIED INDUSTRIES, by Sydney J. Johnstone (Chapman & Hall Ltd., London), 1954, pp. 692, price 75*s*.

GLASSCHMELZ-WANNENOFEN, by Rudolf Gunther (Verlag Der Deutschen Glastechischen Gesellschaft, Untermainkai 12), 1954, pp. 52, price 15.75 marks

BIBLIOGRAPHY OF SOIL SCIENCE AND FERTILIZERS WITH REFERENCE TO INDIA, compiled by K. K. Guha Roy (Manager of Publications, Delhi), 1954, pp. iv+131

PROBLEMS RELATING TO THE DEVELOPMENT OF INTERNAL COMBUSTION ENGINE INDUSTRY IN INDIA (Proceedings of the Symposium held at the Indian Institute of Science, Bangalore, April 5-6, 1952) (Council of Scientific & Industrial Research, New Delhi), 1954, pp. viii+242, price Rs. 12

SURVEY OF RESEARCH PROBLEMS IN PLASTICS WITH SPECIAL REFERENCE TO THE DEVELOPMENT OF PLASTICS INDUSTRY IN INDIA (Council of Scientific & Industrial Research, New Delhi), 1954, pp. 155, price Rs. 5

NOTES & NEWS

Cation exchange resin from myrobalan nuts

AS TANNIN MATERIALS ON SULPHONATION and subsequent condensation with phenol and formaldehyde yield cation exchange resins, sulphonated myrobalan nut powder was condensed with resorcinol and paraformaldehyde in alkaline medium. The resin obtained compares favourably with other cation exchange resins. Myrobalan nuts are available in plenty and their use in the large-scale preparation of cation exchange resins appears promising.

Powdered myrobalan nuts (50 g.) were sulphonated with about 2½ times their weight of concentrated sulphuric acid. The black mass obtained on washing yielded a granular product. The product was dissolved in excess of caustic soda, filtered and boiled with 5 g. of paraformaldehyde for 1 hr. Resorcinol (30 g.) was then added to the solution and the volume reduced to about one-third. The product was cooled, and a further 5 g. of paraformaldehyde were added with stirring and heated, when it turned into a gel. The gel was broken up and kept at the water-bath temperature till the mass was dry. The dry product was crushed, washed with water and leached with dilute hydrochloric acid for 24 hr. Finally the resin was washed free of acid and dried at 105°C. The yield of the resin was 80 g.

The resin has been found to be particularly suitable for the removal of Ca, Ba, Mg, Co and Ni ions. The exchange capacity of the dry resin was 1·4 m. eq./g.; with cobalt and nickel chlorides the exchange capacity was 1·5 m. eq./g. of dry resin.

The details of this work will be published elsewhere.—A. N. DHAR, *Provincial Industrial Research Laboratory, Government of Bihar, Patna*

Optical cement

AN IMPROVED OPTICAL CEMENT, plasticized cellulose caprate, developed at the U.S. Naval Research Laboratory, is capable of withstanding the extreme temperature variations and other rigours of naval service and is suitable as a replacement for Canada balsam in all types of optical instruments. This synthetic resin is an improvement over the unplasticized material, which has been the standard in the navy for over five years for airborne optical instruments, in that it is sufficiently fluid to be cemented at a temperature of less than 250°F., permitting the cementing of large camera lenses [*J. Franklin Inst.*, **257** (1954), 346].

Stainless steel powders

A RECENT TECHNIQUE WHICH IS gaining importance in the manufacture of stainless steel powders is water disintegration of prealloyed molten metal. Steel of the desired composition is melted in induction furnaces and is transferred to a tundish lined with zirconium-silicate refractory and heated electrically to control and maintain the temperature of the molten metal. The liquid metal flows through a small zirconia nozzle (hole diam. $\frac{3}{16}$-$\frac{7}{32}$ in.) into the disintegrator, where the thin stream is blasted to powder by water jets emerging from a hollow rapidly rotating disc. The disc is attached to the top of a hollow shaft through which water flows at low pressure, and the centrifugal action of the revolving disc builds up pressure sufficiently high to supply the required disintegrating energy. The mixture of water and powder is then pumped to a dewatering and classifying unit, in which sorting of powder according to particle size and final annealing are carried out.

Among the applications for which parts made from these powders have been successfully used are small driving arms in intermediate gear trains of water meters, sleeve bearings and bushings working under corrosive conditions, guides for fishing rods, small gears and levers. Other uses include porous sheets used in de-icing equipment, filters and spray coatings [*Nickel Bull.*, **27** (1954), 75].

Pelletizing fine iron ores

THE PROBLEM OF PROCESSING IRON ore fines and concentrates before charging to the blast furnace has assumed considerable importance in the U.K. where the imported fines now constitute the bulk of the material which the British iron and steel industry has to deal with. Laboratory and pilot-scale experiments conducted by the British Iron & Steel Research Association on the pelletizing of haematite concentrates from Sierra Leone have led to the development of a successful pelletizing process.

Sierra Leone concentrates employed had the following typical analysis: Fe, 66 (Fe_2O_3, 94); SiO_2, 4; Al_2O_3 0·6 per cent.

The ore, as received, being too fine for sintering and much too coarse for balling (about 60 per cent lay between 40 and 100 mesh), was ground in a high speed mill (atritor) swept with hot air which serves to dry the feed, and the product collected in a cyclone. The size grading of the product gave a range of −200 mesh fraction from 40 to 90 per cent.

Laboratory experiments carried out with concentrates balled with water alone gave a critical limit at about 50 per cent in the proportion passing through 200 mesh below which pelletizing became difficult and slow. The optimum moisture content for pelletizing this ore was 8-10 per cent.

Pellets were fired in batches in a Nernst-Tammann carbon-tube resistor furnace which would readily attain 1,300°C. in 20 min. Pellets heated to 1,270°C. had the same strength as those dried out at 100°C., a 1 in. pellet failing under compression at about 300 g. Binding agents were, therefore, tried. Organic binders were not helpful since they were burnt out long before recrystallization bonding began. Inorganic salts proved more effective and the most important effect occurred with alkaline materials of which sodium carbonate was the most advantageous.

Tests were carried out with the addition to concentrates of fines and slimes from British low grade ores. Mixtures of ground concentrates with Sierra Leone fines (Fe, 60·25; SiO_2, 6·4; Al_2O_3, 3·4 per cent) were freed from fraction larger than ⅛ in. Addition of fines in the range 0-50 per cent showed significant improvements in dry and wet strength. Maximum wet strength was recorded with 15 per cent of fines, but dry strength increased up to 50 per cent of fines when 1 in. diam. pellets withstood a crushing load of 20 kg. Pilot-scale tests using 75 per cent of ground concentrates and 25 per cent of fines were successful; but in comparison with 100 per cent concentrates, the operation was less stable and rather more difficult to control.

A number of experiments carried out in the pilot plant under gas-fired and solid fuel-fired conditions using a variety of raw materials point to the desirability of establishing a suitably located pelletizing plant to deal with the bulk of the present imports in the U.K. rather than supplementing of sintering facilities in a number of works with less economic units.

Allethrin synthesis

THE FIRST FULLY INTEGRATED plant for the production of synthetic allethrin has been completed by the U.S. Industrial Chemical Co. Ltd. at Baltimore. An 18-step batch process (FIG. 1) is employed and the capacity of the plant is 6,250 lb. per month. The process involves the use of 130 reactors and more than 35 different raw materials and 20 intermediates, byproducts and solves are analysed as a standard procedure.

There are two important phases in the production of allethrin: (1) preparation of allethrone and (2) preparation of chrysanthemum acid chloride. Allethrin is then produced by reacting allethrone and chrysanthemum acid chloride.

Preparation of allethrone — Allyl chloride and crude ethyl acetoacetate are allowed to react and unreacted ethyl acetate stripped off at atmospheric pressure. The initial fraction from the still contains mainly allyl chloride and the subsequent fraction consists of ethyl acetate free of allyl chloride and contains *c.* 10 per cent ethyl alcohol.

The allyl chloride stripped off ethyl acetate is next treated with 5 per cent sodium hydroxide to produce sodium α-allyl acetoacetate and ethyl alcohol. After saponification, the material is acidified with 50 per cent sulphuric acid to convert the sodium α-allyl acetoacetate to allyl acetoacetate to allyl acetone, with the simultaneous formation of sodium bisulphate and carbon dioxide. The allyl acetone is then purified by distillation and treated with diethyl carbonate to form ethyl-3-oxo-6-heptenoate and ethyl alcohol.

The crude ethyl-3-oxo-6-heptenoate is fractionated in a still under a 14 mm. vacuum. The initial fraction consists of a small amount of diethyl carbonate, in addition to some ethyl α-allyl acetoacetate formed in a side reaction during the synthesis of ethyl-3-oxo-6-heptenoate. The ethyl α-allyl acetoacetate collected in the heads receiver is subsequently returned to the process for conversion to allyl acetone.

Ethyl-3-oxo-6-heptenoate from the above step is saponified with an excess of 10 per cent potassium hydroxide to produce potassium-3-oxo-6-heptenoate and ethyl alcohol. Carbon dioxide in the presence of water is used to convert the potassium-3-oxo-6-heptenoate to 3-oxo-6-heptenoic acid and potassium bicarbonate. In the next step 37-43 per cent pyruvaldehyde is treated with sodium bicarbonate to raise its *p*H from 3 to 8. This pyruvaldehyde is added to the 3-oxo-6-heptenoic acid resulting in the formation of 3-hydroxy-8-nonene-2, 5-dione. After the reaction is complete, the mixture is acidified with 35 per cent hydrochloric acid. Next, 50 per cent sodium hydroxide is added to raise the *p*H to a minimum of 10·0. The caustic converts the dione to 2-allyl-3-methyl-2-cyclopenten-4-olone, or allethrolone, which is one of the two major intermediates in the allethrin process. At the completion of the reaction, the solution is acidified with hydrochloric acid, and allethrolone salted out of solution.

The crude allethrolone is distilled at 0·4-0·7 mm. vacuum and after the low boiling material has distilled over, the product is collected in a separate receiver within a 6°C. temperature range. The product contains 90-95 per cent allethrolone.

Preparation of chrysanthemum acid chloride—The preparation of chrysanthemum acid chloride requires the prior synthesis of 2, 5-dimethyl-2, 4-hexadiene and ethyl diazoacetate.

The initial step in the production of 2, 5-dimethyl-2, 4-hexadiene involves the formation of 2, 5-dimethylhexyne-2, 5-diol. In the synthesis of 2, 5-dimethylhexyne-2, 5-diol, acetylene reacts with potassium hydroxide to form potassium acetylide which, in turn, combines with acetone to form the potassium salt of 2, 5-dimethylhexyne-2, 5-diol. The free 2, 5-dimethylhexyne-2, 5-diol is then obtained by treatment of the potassium salt with hydrochloric acid.

The next step involves the catalytic hydrogenation of 2, 5-dimethylhexyne-2, 5-diol to 2, 5-dimethylhexane-2, 5-diol. The synthesis of 2, 5-dimethyl-2, 4-hexadiene involves the catalytic dehydration of 2, 5-dimethylhexane-2, 5-diol in a Dowtherm-heated catalyst tube. The reaction products flow into a receiver, from which the water layer is separated and discarded. The organic phase is then distilled. The initial distillate contains the decomposition products of 2, 5-dimethylhexane-2, 5-diol in addition to a small amount of water. The product cut, collected in a separate receiver, contains the 2, 5-dimethyl-2, 4-hexadiene.

The next series of steps involves the preparation of ethyl diazoacetate through the intermediate formation of ethyl glycine hydrochloride. Through a mixture of glycine and anhydrous alcohol, dry hydrogen chloride gas is bubbled and the reactants are heated under reflux until the reaction is complete. The material is then cooled to 20°-25°C. Ethyl glycine hydrochloride is washed twice with anhydrous ethyl alcohol, dried and then reacted with nitrous acid to form ethyl diazoacetate. On completion of diazotization, the mixture is agitated for 30 min., and the organic phase, containing most of the ethyl diazoacetate, is sent to a vacuum stripping still. Because of the instability of this compound, it is immediately reacted with 2, 5-dimethyl-2, 4-hexadiene to form ethyl chrysanthemumate with the evolution of nitrogen.

Ethyl chrysanthemumate is distilled at 10 mm. pressure and the distillate is saponified with potassium hydroxide to form potassium chrysanthemumate and ethyl alcohol. The reaction mixture is cooled to 20°C. and 50 per cent sulphuric acid is added. The acid converts the potassium chrysanthemumate to chrysanthemum acid. The product is treated with heptane when chrysanthemum acid goes into solution in the heptane layer, while the potassium sulphate remains dissolved in the water layer. The two phases are allowed to settle for 30 min., water

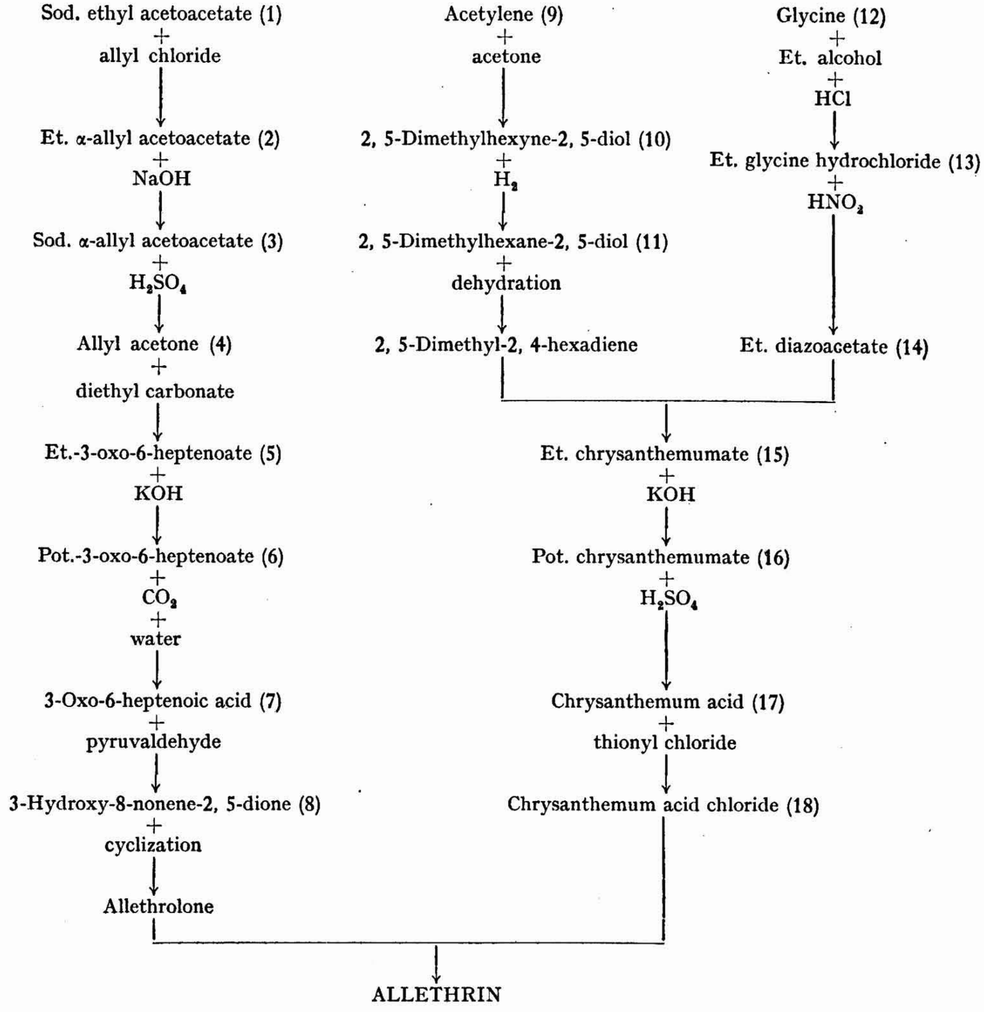

FIG. 1 — MATERIAL FLOW SHEET FOR THE SYNTHESIS OF ALLETHRIN

layer drained and the organic layer separated.

The organic layer is stripped of water by distillation at atmospheric pressure and to the water-free material containing *c.* 30 per cent chrysanthemum acid and 70 per cent heptane, purified thionyl chloride is added to convert the chrysanthemum acid to chrysanthemum acid chloride. After the reaction is complete, the heptane is stripped off at 90 mm. pressure. The pressure is then lowered to 10 mm. and chrysanthemum acid chloride is distilled over at 93°-100°C.

Production of allethrin — To a mixture of allethrolone, pyridine and benzene, chrysanthemum acid chloride dissolved in benzene is gradually added. The reaction occurs almost instantaneously with the formation of allethrin and hydrogen chloride. After all the chrysanthemum acid chloride is charged, the reaction mixture is washed with water to remove the solid pyridine hydrochloride formed and then treated three times with sodium carbonate solution to remove free acid. The organic layer, containing the allethrin, is washed twice with water to remove salts and reduce the *p*H. Benzene is then distilled off under vacuum at a temperature below 50°C.

The allethrin is passed through a polishing filter to remove solid impurities and then stored in aluminium drums.

About 2 weeks are required for all 18 steps in the allethrin process to be completed [*Industr. Engng. Chem.*, **46** (1954), 414].

Thermenol — a new alloy

AN IRON-ALUMINIUM ALLOY TO which small amounts of vanadium and molybdenum are added is a recent discovery of the U.S. Naval Ordnance Laboratory. The alloy has high resistance to heat and corrosion, an electrical resistivity 50 per cent greater than that of metals now used in heating elements, is 20-25 per cent lighter than stainless steel, and is cheaper to make [*Chem. Age*, **70** (1954), 825].

Manganese from low grade ores

Two new features — a high temperature autoclaving step and a sintering operation — characterize a sulphur dioxide process developed in the U.S.A. for the recovery of manganese from low grade ores. The study applies particularly to the treatment of 20·2 per cent manganese concentrates in a plant for making 303 tons/day of manganese as sintered oxide.

Leaching is accomplished in a number of vertical, cylindrical vessels provided with agitation, operating in parallel, and sulphur dioxide gas is introduced under pressure below the lowest impeller. The slurry after absorption of sulphur dioxide is pumped under pressure to be oxidized in autoclaves — horizontal, cylindrical tanks, divided into compartments by internal baffles. Air under pressure is introduced under the agitator in each compartment to promote the oxidation to sulphur trioxide. The sulphur dioxide previously dissolved as sulphites or sulphurous acid is oxidized and the free sulphuric acid generated is partially used to transform soluble non-manganese oxides to sulphates.

Aluminium, iron and magnesium sulphates so produced are rendered relatively insoluble at the high temperatures. The oxidation slurry effluent under high temperature and pressure is flashed in two stages to a final temperature of 160°F.

The cooled slurry is then decanted to produce a relatively clear manganese sulphate solution and the underflow treated in a counter-current-staged dilution washing system to recover the manganese sulphate.

The solution is evaporated in two stages. In the first, vacuum stage, the liquor from the decantation is partially evaporated and some of the manganese sulphate is precipitated into the magma as a monohydrate. Magma is recirculated through a heat exchanger. Manganese sulphate liquor is added and magma withdrawn at constant rates. The second effect is operated at approximately 260°F., evaporation being effected by submerged combustion. By returning mother liquor after filtration, a magma density of approximately 40 per cent solids and a liquid phase of 60 per cent sulphuric acid is maintained in this vessel.

After filtering through vacuum filters, the filter cake, which consists of 80 per cent manganese sulphate, 5 per cent sulphuric acid, plus water and other ingredients, is conveyed to covered storage.

Weighed batches of sulphate, powdered coal and powdered recycled oxide are transported to a rotating drum where water is added and small spherical pellets are produced. These pellets are dumped on to the grate of a three-compartment sintering machine. In the first compartment, hot air generated by drawing air through the bed of the third compartment to cool the sinter is passed through the layer of pellets to dry them. The pellets are ignited in the second compartment and a small portion of the carbon of the coal is used to reduce the manganese sulphate. The balance is burnt to carbon dioxide and furnishes the heat to raise the bed to sintering temperature.

A good grade, hard porous sinter is formed which is rough ground and screened to furnish a +¼ in. hearth layer. The balance is ground to −50 mesh in a ball mill to furnish the recycled oxide. The 7-8 per cent sulphur dioxide from the centre compartment of the sintering machine is compressed and absorbed.

This 100,000 tons/year plant is estimated to cost $ 16½ million, and the direct operating cost would amount to $ 41.33 per ton of manganese [*Industr. Chem.*, **30** (1954), 190].

New synthesis gas process

A new synthesis gas process, developed jointly by Babcock & Wilcox, the Bureau of Mines and Du Pont, if successful, will replace the costly, air-polluting coke ovens and water-gas generators. The process could also open the way for use of low grade, non-coking coals of any particle size. The first demonstration unit is to be completed this year.

The new process continuously burns pulverized coal in an atmosphere of steam and oxygen to produce a synthesis gas which normally consists of about 40 per cent hydrogen, 40 per cent carbon monoxide, 15 per cent carbon dioxide, less than 1 per cent methane and *c.* 4 per cent of inert gases. The amount of oxygen used varies with the coal analysis but is of the order of 8-10 cu.ft./lb. of coal.

The gasifier consists of a two-chamber, refractory-lined furnace with a waste-heat boiler, superheater and economizer. In many respects it uses the basic design fundamentals of conventional pulverized coal-fired, slag-tap steam boiler furnaces.

A proposed full-scale design, which resembles the demonstration unit in size, comprises 88 ft. high gasifier, 15 ft. in diameter, with a capacity of *c.* 17 tons of coal per hour, equivalent to 25 m. cu. ft. of synthesis gas per day.

Since the gasifier works best with highest temperatures in the primary (exothermic) reaction zone, and as these temperatures are above usual ash-fusing temperatures under reducing conditions, the slag-tap type of operation was employed. The only disadvantage is that some coals with extremely high ash-fusing temperatures cannot be used. The furnace is divided into primary and secondary zones, and the burners are fired in the general direction of the tap hole.

To minimize heat losses due to absorption by the furnace, a full-scale gasifier which would reduce the losses to about 200 B.t.u. per lb. is operated. The lower chamber of the gasifier will have a layer of liquid slag covering the walls and would be subject to the chemical and erosive action of the slag.

The design calls for a generator built of boiler tubes with metal studs and plastic chrome ore applied as a monolithic structure. This type of construction has been widely used in boiler furnaces and has been able to withstand continuous operation with slag flowing over the chrome ore surface. The entire gasifier is enclosed in a pressure-tight casing [*Industr. Chem.*, **30** (1954), 241].

Manufacture of ammonium nitrate

The new continuous, vapour-phase process for the manufacture of ammonium nitrate that is being operated on a 225-tons-a-day plant by the Commercial Solvents Corporation at their Sterling Louisiana works is described.

Nitric acid is pumped into the reactor through a stainless steel nitric acid preheater and a tantalum heater. The preheater is a shell and tube type exchanger with the acid flowing through the tubes and 150 lb./sq. in. steam on the shell side. The tantalum heater consists of three identical tube bundles in series; the tubes are of tantalum and the heads are stainless steel lined with tantalum.

Ammonia vapour from the charge tanks also flows through two heat exchangers before going into the reactor at 290°-300°F.

The reaction between ammonia and nitric acid vapours takes place in a packed tubular reactor with no water added other than that contained in the nitric acid, the packing serving both as a reaction and condensation surface. Molten ammonium nitrate flows out of the reactor through a separator which removes steam and any unreacted ammonia. The ammonium nitrate drops through a packed column with a heated air stream passing counter-currently. This serves to reduce the moisture content to any desired level. The molten salt is then flaked on a water-cooled stainless steel belt, ground, screened, coated and bagged. Safety is assured by the fact that the molten nitrate is blanketed by steam during the whole of its stay in the reactor separator, and by the fact that the amount of material in the equipment at any one moment is very small. As an extra safety precaution, the reactor and separator are placed in a concrete barricade [*Chem. Tr. J.*, **134** (1954), 1213].

Mould growth in optical instruments

THE PROBLEM OF DETERIORATION of optical instruments in tropical areas has been receiving increasing attention since World War II and extensive investigation of preventive and control measures has been undertaken in America, Great Britain, Australia and India in recent years. In an investigation conducted at Pitman-Dunn Laboratories, Philadelphia, an attempt has been made to protect more complex optical instruments containing prisms with radioactive materials. In order to protect the optical elements, certain binocular parts were treated with a gold foil containing radium, a radioactive lacquer and plated with polonium. The effectiveness of the three radioactive treatments in eliminating fungus fouling of the treated instruments after 5 months' exposure in a tropical chamber is described.

The decreasing order of susceptibility to fungus growth of the optical elements in the untreated telescopes was as follows: reticle, hypotenuse surface of upper and lower prisms, field lens, eye lens, objective lens and right-angle surfaces of the prisms. Of the telescopes treated with the radioactive foil, the eye lens and objective lens were completely protected, the field lenses and reticles had only traces of growth at the edges in some cases, and the prisms were only partially protected. However, the mould growth on the prisms was confined to the edges or areas not protected by the radioactive gold foil. In both the treated and untreated instruments, in many cases, mould growth started not on the optical glass but on the metallic rings used to keep the optical elements in place in the telescope. In the rings protected with the radioactive materials, mould growth started in back of the radioactive surface and grew on to the edge of the optical glass until inhibited by the alpha radiation. This fact may be one of the limiting factors in the use of radioactive materials to prevent mould growth in optical instruments.

The radioactive lacquer offered little protection to any of the optical elements. Either the lacquer shielded the radium to such an extent that the alpha particles did not escape from the lacquer film or the radium settled out prior to application to the optical parts.

The polonium-treated binocular parts gave complete protection to all the optical elements, with the exception of a trace of mould growth on one of the prism surfaces.

However, mould growth occurred on all surfaces which were not adequately protected, and on non-glass surfaces, such as metallic parts (retaining and reticle rings), cork pads, grease and sealing compounds. The growth of fungi from non-glass surfaces to the margins of optical glass elements protected with radioactive materials offers a serious drawback to their use. Because alpha radiation is stopped by 39 microns of fungus tissue, it is conceivable that sufficient growth could occur at the edges of the glass to stop the radiation.

Radioactive emanations would not prevent the entrance of animal vectors such as mites. The mites would die on the glass surfaces and could serve as centres of mould growth. The dead organism would shield any germinating fungus spores from the alpha radiation.

It is concluded that owing to the difficulty in protecting binoculars with radioactive materials and the potential health hazards in their application to the instruments, other methods for the prevention of the deterioration of these instruments should be considered. However, for the protection of simple optical instruments not containing prisms or for special instruments which cannot be protected by other means, the use of radioactive materials may be desirable. The internal surfaces of binoculars may also be sterilized periodically by ionizing radiation from high-voltage machines. In order to use this external source of radiation, the optical glasses now used will have to be replaced with glasses that do not darken when exposed to the high energy radiation [*Industr. Engng. Chem.*, **46** (1954), 778].

Determination of orthophosphate

A RAPID ONE-STEP PROCEDURE FOR orthophosphate determination, which is both simple and precise, has been developed at the U.S. National Bureau of Standards. The method is based on the yellow complex (molybdivanadophosphate) formed when phosphate reacts with a mixture of molybdic and vanadic acids. Solutions of the yellow complex are made up to high absorbency (less than 1 per cent transmission) in the near ultraviolet, and their absorbency is compared with that of solutions containing known amounts of phosphate. While the absorbency of the yellow solutions changes measurably with standing, this source of error is eliminated by comparing solutions developed simultaneously.

The procedure employs the Beckman DU spectrophotometer with an incandescent lamp, a wavelength setting at 390 mμ and a slit opening of about 1 mm.

Aqueous solutions of ammonium molybdate and ammonium metavanadate and a standard phosphate solution containing perchloric acid are prepared in advance and kept on hand. When a phosphate determination is to be made, the unknown material, ordinarily dissolved in hydrochloric acid, is diluted with water. Aliquots of this solution are taken which contain amounts of phosphate varying over a small range — say 4·5 to 5·5 mg. of P_2O_5 per 100 cc. of final volume. Standard phosphate solution is simultaneously used to make up two or three standard solutions covering this range. A solution containing the appropriate amounts of ammonium molybdate, ammonium vanadate and perchloric acid is then added quickly to each flask which holds the unknown or standard solution, and the remaining volume is made up with water. A 1 cm. absorption cell is filled with the lightest coloured solution, and all the other solutions are successively placed in a second cell and compared spectrophotometrically with the first solution. The phosphate content of the unknown solutions is interpolated from the absorbencies and known phosphate contents of the standards. Under optimum conditions phosphate concentrations can be compared by this method with a precision of 1 part in 3,000 [*J. Franklin Inst.*, **257** (1954), 231].

Fuels for high speed diesel engines

RECENT STUDIES ON THE POSSIBILITIES of running high speed diesel engines on cheaper light diesel oil conducted at the Indian Institute of Science, Bangalore, have shown that it is not advisable to run such engines on light diesel oil since, in the long run, this leads to increased wear, ring sticking, valve burning and pitting of valve seats. In an emergency, however, light diesel oil can be used for short periods without adverse effects.

The wear of the engines running on either of these fuels is appreciably reduced when fitted with chromium-plated top compression rings instead of plain cast iron rings.

For experimental work, three high speed diesel engines were chosen which were identical in every respect except for the combustion chambers and the compression ratio. Two of them had precombustion chambers and a compression ratio of 19 : 1, and the third had an open combustion chamber and a compression ratio of 16·75 : 1. All of them had the same bore and stroke and were rated to develop 5 b.h.p. at 1,500 r.p.m. These engines were run under identical test conditions but on two different fuels. One precombustion chamber engine was run on high speed diesel oil for 2,000 hr. and the other on light diesel oil for 2,000 hr. The open combustion chamber engine was also run on light diesel oil for 1,500 hr. Both precombustion chamber engines were fitted with plain cast iron top compression rings during the first 1,000 hr. of test and chromium-plated top compression rings during the second 1,000 hr. The third engine was fitted with a chromium-plated top ring throughout the test [*J. Indian Inst. Sci.*, **36** (1954), 59].

Peroxides from gum turpentine

A RAPID AND ECONOMICAL PROCESS for the production of pinane hydroperoxide in good yield and concentration from gum turpentine developed in the U.S.A. and considered commercially feasible will make pine gum a potential source of organic peroxides suitable for use in a number of industrial processes, especially as polymerization catalysts in the production of synthetic rubber, resins and plastics.

The process involves four main steps: hydrogenation of the turpentine to give pinane; purification of pinane by simple distillation; oxidation of pinane with molecular oxygen to a peroxide content of about 50 per cent; and stripping the oxidate under vacuum to recover unoxidized pinane, leaving pinane hydroperoxide as a residue. Starting with 8 lb. turpentine, this process yielded 4 lb. of peroxides of 80-90 per cent purity [*J. Franklin Inst.*, **257** (1954), 260].

Projection welding

PROJECTION WELDING IS A method of resistance welding mild steel in which current flow and heating during welding are localized by the form of the parts being welded rather than by the electrodes in contact with the work-piece. This is usually accomplished by a projection on one or both of the work-pieces, and it is from this that the process derives its name. The projection may be formed by pressing in the case of sheet metal, by forging or machining from solid pieces, or on the edge of strip by using special shears or punches.

The advantages of projection welding over spot welding include: more uniform results; ability to make several welds simultaneously; longer electrode life and lower electrode maintenance; improved finished appearance; and possibility of making welds which could not be made otherwise.

Projection welding is mostly carried out on steel with carbon content not exceeding 0·1 per cent, and if the carbon content is higher than this, particularly if it is associated with high percentages of manganese and minor constituents such as nickel, chromium, molybdenum, etc., hard and brittle welds may cause difficulty. Generally, the thicker the material being welded, the higher the carbon content which can be tolerated (British Welding Research Association, London, Booklet No. T. 30).

Wheat Breeding Station, Simla

A NEW LABORATORY OF THE SIMLA Wheat Breeding Station of the Indian Agricultural Research Institute, Pusa, New Delhi, was opened on 18 June 1954 by the Union Minister for Agriculture, Dr. Panjabrao Deshmukh. Built at a cost of Rs. 55,000, the laboratory has as its objective the study of new rust-resistant races that may arise from time to time and the maintenance in pure culture of the known races. An 8·5 acre agricultural farm for field experiments on wheat and barley has been provided and a glass house for testing wheat material under controlled conditions is under construction.

The laboratory, which has been set up under the co-ordinated wheat-rust control scheme, is one of a chain of laboratories that have been established on a regional basis in different parts of India for fulfilling the long-felt need of the country to evolve disease-resistant varieties of wheat. The more important varieties evolved so far are NP (New Pusa) 710, 718, 761, 770 and 775. Of these five strains, NP710, 718, 761 and 775 have been found suitable for different regions in the plains, while NP 770, which was released through the Simla substation, has proved its worth in the hilly tracts.

Development of small-scale industries

THE GOVERNMENT OF INDIA HAVE examined the recommendations made by the Ford Foundation International Planning Team on Small-scale Industries and have decided to implement the following recommendations as early as possible: (1) The establishment of four Regional Institutes of Technology for Small-scale Industries which would act as service agencies and would assist small-scale industries in improving their technique of production and management, in obtaining credit and finance, in securing proper raw materials, in marketing their goods to the best possible advantage, and in promoting patterns of development calculated to make small-scale industries ancillary to large-scale industries by bringing about co-ordination of production programmes; (2) the establishment of a Marketing Service Corporation which would later integrate its activities with those of the institutes; and (3) the establishment of a Small-scale Industries' Corporation to organize production for meeting Government orders.

The Government have also decided to appoint a Director of Small-scale Industries and to constitute a Small-scale Industries' Board of which he would be the *ex officio* Chairman, and which would consist of representatives of the Ministries concerned in the Government of India and of State Governments. The functions of the Director and the Board would be to control and co-ordinate the activities of the organizations mentioned above and also to frame and implement programmes generally for the development of small-scale industries in this country. It is proposed to expand the Board in due course to include representatives of both large-scale and small-scale industries and other interests concerned.

Utilization of agricultural wastes

THE UTILIZATION AND DISPOSAL OF nutshells and fruit pits which accumulate in quantity about cracking plants, canneries and similar food-processing plants have been studied at the Northern Regional Research Laboratory in order to explore the possibilities of converting them into profit to the processors.

The agricultural residues included in the study comprised the pits of apricots, cherries, peaches and dates and the shells of almonds, coconuts, filberts, peanuts and black walnuts. It is estimated that more than one billion pounds of these are available annually within the United States.

A 39-page bulletin, *Nut Shells and Fruit Pits — Their Composition, Availability, Agricultural and Industrial Uses* by T. F. Clark and E. C. Lathrop, issued by U.S. Department of Agriculture, describes the methods of processing these residues for such diverse uses as animal and poultry feeds, fertilizers, insecticides and pesticides, fur cleaning and polishing, soft grit blasting, hand soaps, fillers, bricks, ceramics and clay products, plastics, plywood adhesives, rubber compounding, cork substitutes, industrial explosives, etc.

Code of Practice for Concretes

A STANDARD CODE OF PRACTICE for plain and reinforced concrete for general building construction has been published by the Indian Standards Institution. This Code deals with the general structural use of cement concrete and reinforced cement concrete and lays down detailed specifications for materials, concrete mix, design, workmanship, inspection and testing.

With necessary modifications to suit special conditions, the general provisions of this Code are also purported to apply to such structures as tanks, reservoirs, chimneys, bridges, shell structures, etc. The Code, however, does not apply to special types of concrete constructions such as pre-stressed concrete construction.

Bulletin of the Quality Control Association

WE WELCOME THE FIRST BULLETIN [1 May 1954, price Re. 1] of the Quality Control Association, Bangalore. The application of statistical quality control (SQC) techniques in all manufacturing and productive sectors has given a considerable fillip to research on SQC theory and practice in India. The bulletin will thus act as a forum for pooling knowledge, for exchanging views and for disseminating the accumulated experience in this comparatively new field.

Corrosion Prevention and Control

A NEW JOURNAL — *Corrosion Prevention and Control: Engineering — Equipment — Technology* — devoted exclusively to the subject of corrosion has now started publication from London. The aim of the journal is to present accounts of new developments in a form suitable for rapid appraisal by engineers, chemists and metallurgists who are concerned with the practical application of corrosion knowledge. Articles in the first number (**1**, No. 1, March 1954) refer to cathodic production, zirconium, metal pre-treatment and protection by paints and resistant plastics.

The journal carries a subscription of 30*s*. or $ 5 per annum and 75*s*. or $ 12.50 for three years.

Chemische Industrie

CHEMISTS AND TECHNOLOGISTS not well conversant with the German language will welcome the appearance of the English edition of the German monthly *Chemische Industrie*. The English edition will appear twice a year in April and October and will present a cross-section of the German and European chemical industries.

The first issue [**1E**, No. 1 (1954)] contains reports and news items and includes world surveys on the production and consumption of the more important industrial chemicals such as Searchlight on Europe's Chemical Industry, Poland's Progress on Large-scale Chemical Synthesis, Economic Aspects of Phenol Syntheses.

The English edition carries an annual subscription of Rs. 15 and is available in India from J. P. De Sousa, C19 Sitaram Building, Hornby Road, Bombay 1.

Lac in India

A NEW PUBLICATION, ENTITLED *Lac in India* — 1951-52, brought out by the Directorate of Economics and Statistics, Government of India, presents, within a brief compass, an integrated picture of production, imports, exports, prices and wages of labour employed in this industry during the years 1939-40 to 1951-52.

The publication will be of interest to the trade and to all those interested in understanding the lac situation and formulating proposals and policies in the future and will remove a great lacuna in the available literature on the industry. It is the first issue of the series which is proposed to be brought out every year.

Analysis of vegetable oils

THE DIRECTORATE OF MARKETING and Inspection, Government of India, has issued a publication, *Methods of Sampling and Testing Vegetable Oils and Fats under Agmark*, containing detailed information about the sampling of vegetable oils, the size of the samples, their marking and despatch and instructions to chemists for carrying out specific tests which form the basis of gradation under the Agmark scheme.

Though primarily intended for the use of chemists working in the Agmark grading scheme, the publication should have a wider appeal and be also of use to chemists working in oil mills throughout the country.

Discrete Sources of Galactic Noise

A SPECIAL REPORT ENTITLED *Discrete Sources of Extra-Terrestrial Noise* just published by the Union Radio-Scientifique Internationale (U.R.S.I.) gives a brief account of established experimental data and techniques developed up to 1954. The report is priced 11*s*. and is available at the General Secretariat of the U.R.S.I., 42 Rue des Minimes, Brussels.

Properties of Tin

The Properties of Tin (TIN RESEARCH Institute, Middlesex), 1954, pp. 35, price 2*s*. 6*d*., is the fourth edition of a booklet originally compiled and issued in 1934. Apart from having been brought up to date, the present edition follows a more convenient arrangement in the presentation of data which have been completely revised. The aim has been to give one recommended value for each property under stated conditions rather than a choice of constants with appropriate references, leaving the ultimate selection to the reader.

Hydrogen Peroxide

THE STORY OF THE DEVELOPMENT of hydrogen peroxide and its properties and applications are described in a 35-page monograph (*Hydrogen Peroxide* by W. S. WOOD, Lectures, Monographs and Reports, 1954, No. 2) published recently by the Royal Institute of Chemistry, London. A comprehensive bibliography listing over 100 references to relevant literature from 1818 to 1954 is included.

New colorimeter

A NEW COLORIMETER — THE TYPE A Colorimeter — has been designed by Electronic Machine Co., England, to discriminate between fine shades of colour, which are imperceptible to the eye; it may be used for testing powders, inks, paints, plastics and coloured liquids.

The instrument comprises a box type galvanometer and test head, which latter functions by means of a photocell and a light source fed through interchangeable narrow band colour filters. The resulting reflections pass to the galvanometer reading panel.

The chief use of the instrument is to test materials against standards. Further, by means of a range of colour filters on the wheel in the test head, it can be ascertained in which colour or colours the test paper is deficient.

The operation is simple and quick, and graphs may be taken to record spectrum curves of standards for future reference and comparison [*Industr. Chem.*, **30** (1954), 186].

Improved centrifuge

A NEW CENTRIFUGE MODEL FOR throughput capacities in excess of 1,000gal./hr. developed by Sharples Centrifuges Ltd. incorporates a tubular bowl type of rotor which makes for high efficiency, simplicity of construction and ease of cleaning. It consists of a hollow cylinder containing a three-wing impeller; the bowl rotates at 15,000 r.p.m. and impurities in the fluid being treated are subjected to an accelerated settling force in excess of 13,000 G. The bowl can be stopped, cleaned and put back into service in less than 15 min.

The equipment is particularly designed for the regeneration of insulating oil, the purification of all types of fuel oil, lubricating oil and cutting oil, and the treatment of such materials as rolling mill oil, wire drawing lubricant, etc. The basic design, however, is such that the machine can be applied to almost any problem where it is desired to separate two immiscible liquids or to remove particles of contaminating solids from a liquid or mixture of liquids.

The machine is available with two basic types of bowl —the separator bowl and the clarifier bowl — depending upon the purification duty [*Chem. Age*, **60** (1954), 794].

Portable X-ray unit

A PORTABLE X-RAY UNIT USING radioactive thulium has been developed by the U.S. Atomic Energy Commission. The unit weighs less than 10 lb. and produces rays comparable to a 100,000 V. X-ray machine without the need of a power source.

The active component of the instrument is a radioactive thulium particle mounted in a source holder and shield equipped with the shutter mechanism operated by a standard photographic cable release [*Science Newsletter*, Indian Scientific Liaison Office, London, No. 159 (1954), Item No. 3059].

Announcements

Dr. K. S. Krishnan, Director, National Physical Laboratory of India, has been re-elected Vice-President of the International Union of Pure and Applied Physics for 1954-55.

The Kalinga Prize for 1954 has been awarded to Mr. Waldemar Kaempffert, Science Editor of the *New York Times*. The award, which is of the value of £1,000, is made every year for popular writing in science by Unesco on the basis of a grant by Mr. B. Patnaik of India. Mr. Kaempffert has had a distinguished career in science writing for over a quarter of a century. His books include: *The New Art of Flying, The A.B.C. of Radio, Invention and Society, Science Today and Tomorrow, Explorations in Science*, etc.

Corrosion Congress — The Working Party on Corrosion, Frankfurt (Main), which held its last meeting as an international body in 1943, has resumed its activities.

This body is organizing the World Corrosion Congress on 11-12 Nov. 1954 in Frankfurt (Main). The Annual General Meeting of the Deutsche Gesellschaft für chemisches Apparatewesen (DECHEMA) will also be held on the same dates.

Further details about the Congress may be obtained from DECHEMA, Frankfurt (Main), W. 13 Post fach, Rheingauallee 25 (Dechema-Haus).

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Progress Reports

TECHNOLOGICAL RESEARCH ON COTTON

A NOTABLE FEATURE OF THE ACTIVITIES OF THE Technological Laboratory of the Indian Central Cotton Committee during the year 1952-53 was the running of a second shift by the Spinning and Testing Laboratories to cope up with the increasing amount of material received for testing. The total number of spinning tests carried out during the year was 4,121 as against 2,761 during the previous year. The small-scale spinning test, recently introduced by the laboratory, has been found to be useful to the breeders, and as many as 497 samples were received for testing. In all 1,894 samples of all types were received for testing and 517 reports were issued during the year. Most of the testing work related to new strains and improved varieties to help agricultural officers from different States in the selection of suitable strains for further propagation.

Testing — Tests on (Co2 × S1) F1 hybrid samples from (a) ratooned crop raised from seeds, (b) ratooned crop raised from cuttings and (c) summer sown crop at Surat showed that the ratooned crop from cuttings gave better spinning performance than that from seeds; the summer sown crop was inferior to both the ratooned crops.

Sea Island cotton grown in the West Coast of Madras State was found to compare favourably with imported varieties. The cotton was suitable for the manufacture of sewing threads up to 6/60s counts.

Technological research — Experiments carried out to ascertain the differences in trade valuation and spinning quality between samples of lint obtained by (1) ginning *kapas* without cleaning, (2) precleaning *kapas* and ginning, and (3) ginning *kapas* and cleaning the lint in a crighton opener, showed that it was not generally profitable to get the lint crightoned before baling. It would, therefore, be an advantage to give this treatment when a mill gets its supply of cotton through its own ginning factories.

A quick method of determining the maturity count by differential dyeing with an acid colour, Carbolan Violet 2RS, was developed. In this test the use of a microscope and swelling of the fibres are not necessary. Immature fibres are deeply dyed by this dye whereas the mature ones are lightly dyed. The difference in shade between cottons differing in maturity by 5 per cent is easily discernible.

Tests carried out to find out the influence of different length-groups of fibres on yarn-strength indicated that fibres of 21-25 mm. length and longer directly contribute to yarn-length.

The count to which a cotton could be spun could be estimated as accurately by using Pressley strength index as by intrinsic strength when it is done in conjunction with mean fibre length and fibre weight per unit length. From a study of the relationships between single thread strength and chief fibre properties, it was found that mean fibre length and fibre weight per unit length contributed most towards single thread strengths of 20s and 30s yarns; the mean fibre length is of greater significance than fibre weight per unit length for 20s, while both these are of equal importance for 30s.

An investigation on the formation of neps due to ginning showed that the lint separated from seed-cotton by hand gave the least number of neps and saw-ginned lint the highest; roller-ginned lint gave an intermediate value.

INDIAN CENTRAL OILSEEDS COMMITTEE, ANNUAL REPORT, 1952-53

THE AREA UNDER MAJOR OILSEED CROPS, I.E. groundnut, rape and mustard, sesamum, linseed and castor, was 1,75,11,000 acres yielding 46,35,000 tons of oilseeds. The total amount of oil produced including *mohua*, cottonseed, niger and other oils was 5,34,563 tons. The quantity of oilseeds, oils and oilcakes exported was 50,610, 1,43,207·8 and 5,485 tons respectively, valued at Rs. 27,83,05,526.

Twenty-six agricultural schemes and 9 technological schemes were running during the year. Eight new agricultural and 4 technological research schemes were sanctioned.

A survey of minor oilseed resources was initiated in Uttar Pradesh, Bhopal, West Bengal, Vindhya Pradesh, Punjab, Mysore, Bombay and Madhya Bharat. The object of the survey is to estimate the availability of *neem*, *mohua*, *pungam* (*karanj*), niger, tobacco, safflower, cashew nut, poppy seed, *kamala*, pissa and bhilawan oilseeds and to suggest ways and means for bringing about a fuller utilization of these sources of vegetable oils.

A draft Five-Year Plan has been prepared by the Committee for increasing the production of the five major oilseeds by *c.* 12 lakh tons. The increased production is proposed to be achieved by multiplication and distribution of improved seeds and adoption of intensive cultivation methods and not by increasing the acreage under oilseeds. The expenditure to be incurred for implementing the plan is estimated at Rs. 40 lakhs.

Breeding investigations — Breeding experiments on castor carried out in Hyderabad have yielded significant results of interest to the breeder. They are: (1) The stigma was receptive 12 hr. before the opening of the flower; (2) the stigma was capable of fertilization 72 hr. after opening of the flower; (3) the pollen was viable from 60 to 66 hr. under field conditions and 66-72 hr. under laboratory conditions; (4) staminate flowers begin to open by 11 p.m. with a maximum opening at 5 a.m., while the pistillate flowers open between 4.30 and 5.00 a.m.

Manurial trials — In manurial trials carried out with different doses of nitrogen, viz. 0, 10, 20, 30, 40 and 50 lb. as ammonium sulphate per acre, all the doses increased the yield of groundnut crop significantly. The highest yield (25·89 md. per acre) was obtained with the application of 50 lb. (control, 22·88 md.); from the economic point of view, application of 20 lb. of nitrogen per acre gave the highest net income. In N.-P. cum spacing experiment, closer spacing (9 in.) from plant to plant gave significantly higher yield per acre than wider spacing (18 and 27 in.). The average yields from 9, 18 and 27 in. plant spacings were 14·77, 11·82 and 8·8 md. per acre respectively.

Diseases and pests — Surveys carried out in Mahboobnagar, Raichur, Gulberga, Hyderabad, Warrangal, Nalgonda, Bidar and Osmanabad districts revealed that *Tikka* on groundnut crop was virulent in all these districts. Both the species of *Tikka* (*Cercospora personata* and *Cercospora arachidicoia*) were common. In addition to *Tikka, Sclerotium* sp., *Rhizoctonia* sp. were noted. Eight varieties of groundnut collected from various parts of India were tried for their resistance to leaf spots. Varieties KOP1, Samrala and H.G.6 were found to be moderately resistant; H.G.6 gave poor yields. Seed-dressing trials with a number of fungicides were tried to control leaf spots of groundnut. Although treated seed gave higher germination rate the results were not statistically significant.

Large-scale trials with various insecticides revealed that *Surul* pest (*Stomopteox nerteria*) could be effectively controlled by dusting twice with 5 per cent DDT; *Tikka* by spraying with $\frac{3}{4}$ per cent Bordeaux mixture or dusting fine sulphur thrice at monthly intervals at the rate of 20 lb. per acre.

As a result of the analysis of a large number of rust collections, four new physiologic races are reported. Pure cultures of these races have been established and maintained in a viable condition in the laboratory at Simla.

RADIO RESEARCH IN BRITAIN

THE ANNUAL REPORT OF THE RADIO RESEARCH Organization, D.S.I.R., London, for the year 1953 reveals considerable amount of work on radio wave propagation over a wide band of frequencies.

The development of a new phase-measuring system was completed and preliminary trials over short land paths were undertaken. The new system employs an ultra high frequency radio link for the transmission of a reference signal. For obtaining detailed knowledge of ground conductivity under various conditions, an earth resistivity meter has been constructed and a programme of systematic measurements started.

From a series of phase measurements connected with the determination of the effects of a coastline on the radial paths, it was concluded that there is a definite path disturbance at a coastline similar to that observed over land at marked boundaries in the geological structure.

Ground conductivity — An instrument for determining the electrical conductivity of the ground has been constructed. A low frequency alternating current is passed through the ground between two earth rods and the potential difference between a second pair of rods located between the first pair is measured. The conductivity is calculated from the values of potential difference, current and rod spacing.

Surface waves — Measurements at a wavelength of 3·2 cm. on a corrugated metal guide showed that the surface reactance varies with the dimensions of the corrugation and with the number of corrugations in a free-space wavelength. It was found that provided there were more than three corrugations to the wavelength, the guide supported an almost pure surface wave.

Forecasting of radio transmission conditions — A new type of forecasting chart, the British Zone Chart, depicting the conditions six months in advance for an area of the ionosphere at a radius of 2,000 km. from London, has been prepared.

Radio wave propagation — Valuable information about the influence of solar radiations on the properties of the ionosphere was obtained as a result of analysis of the data collected during the solar eclipse of February 1952. It has been established that the component of the solar radiation responsible for ionization in the E layer was not emitted uniformly from the solar disc, but was particularly intense from the eastern and western limbs where radiation of the green coronal line was also enhanced. An improved system for measuring the angle of elevation of downcoming signals at high frequencies has been devised and calibrated. For the frequency band 13-18 Mc./s., the variation with angle of elevation of the ratio of the signal amplitudes in the two aerials agreed closely with the theoretical variation.

A study of the echo patterns observed from pulse signals transmitted from Colombo has revealed that propagation takes place mainly by multiple reflections from the F layer and that two-hop to six-hop modes are present although not necessarily simultaneously. Each reflection mode appears as a complex group of echoes.

The rotating 17 Mc./s. Yagi aerial system and plan position indicator were completed during the year.

High frequency direction finding — It has been shown that the nature of the earth's surface midway between the transmitter and the receiver affects the magnitude of the rapidly varying component of bearing fluctuation in the case of second-order reflections from the ionosphere. Signals reflected from land showed larger rapid fluctuations than those from the sea, indicating that the land behaves as a more irregular reflector than the sea.

Materials for telecommunication — Studies on alloy junction germanium diodes have provided a critical junction diode theory and have also enabled a satisfactory equivalent circuit to be devised. This circuit consists of a resistance R_n representing the bulk properties of the *n*-type germanium water in series with a shunt combination of an ionic space-charge capacitance C_i and a hole admittance Y_p. The zero-voltage value of R_n can be approximately obtained from the resistivity and thickness of the germanium and the area of the alloyed region, and is of the order of 100 ohms. When a forward current flows, holes are injected into the *n*-region and the enhanced conductivity so produced results in R_n decreasing to the order of a few ohms. The ionic capacitance is of the type which occurs in metal rectifier theory and it is found that as expected $1/C_i^2$ is a linear function of the reverse voltage V; the slope and the intercept of the plot enable the donor ion density in the *n*-region and the potential step of the junction to be determined. The hole admittance Y_p can be assumed to have the form $G_o (1+j\omega\tau)^{\frac{1}{2}}$ where G_o is the low frequency conductance associated with hole diffusion from the *n*-region and τ is the hole lifetime. From the dependence on temperature of the zero voltage admittance, it is possible to deduce the energy level of the traps responsible for hole generation and recombination.

INDIAN PATENTS

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

Chemicals, plastics, rubber, paints and allied products

48661. Separating one or more solid substances, such as solid hydrocarbons or complex hydrocarbon compounds, from a mixture thereof with oil: *A part of the used auxiliary phase is brought into contact with oil or a mixture of oil and solid substance still to be treated, preferably in counterflow* — N. V. De Bataafsche Petroleum Maatschappij

49550. Manufacture of new polycyclic compounds and insecticidal compositions prepared therewith: *By reacting cyclopentadiene and hexahalogenated polycyclic diene to produce two to five linearly fused bicyclo-*(2-2-1)*-heptane ring* — Arvey Corporation

50202. Manufacture of cuprous compounds, particularly cuprous chloride and cuprous oxide: *Reacting together acid sodium sulphate, sodium chloride and copper either yielding oxygen or with oxidizing agent* — Hindle

50203. Manufacture of basic copper chloride: *Reacting a mixed mass of sodium and copper sulphates with acid sodium sulphate and copper or copper oxide with reagent to bring chlorine* — Hindle

50497. A method of making a paint and other solutions: *Filling the colouring matter into a receptacle made of a material which is soluble in a solvent or dispersion medium and introducing the receptacle into said solvent or dispersion medium* — Eckart Werke Standard Bronzepulver-Werke Carl Eckart

50546. A combination process for the distillation of crude oil: *The reduced crude is introduced into a fractionation zone and stripped to remove hydrocarbon constituents of the gas oil boiling range, with hydrocarbon vapours produced in a catalytic cracking operation, the gas oil fraction is segregated and cracked to produce at least a portion of vapours used for stripping* — Standard Oil Development Co.

49764. Manufacture of insecticidal composition: *Treating essence of turpentine with* H_2SO_4 *neutralizing the liquid with alkali collecting the produced terpene and incorporating it in benzene hexachloride* — Huidobro & Escobar

49234. Preparation of titanium tetraiodide: *By reacting titanium dioxide with aluminium triiodide* — Council of Scientific & Industrial Research

50864. Preparation of 2-hydroxy-3 : 6-dimethoxy acetophenone: 2, 5-*Dihydroxy*-6-*methoxy acetophenone is fully methylated to the trimethoxy ketone and subsequently partially dimethylated with aluminium chloride to yield* 2-*hydroxy*-3, 6-*dimethoxy acetophenone* — Council of Scientific & Industrial Research

51226. Process for the continuous manufacture of phenol: *Circulating through reaction chamber a stream of solid reaction residue and continuously adding starting mixture thereto in amount to give a stream of solid material containing* 10-15 *per cent by weight of starting mixture* — Stamicarbon N.V.

48609. Process for preparing naphthalene derivatives and product resulting therefrom: *Heating* 2-(β-*dialkylaminopropionyl*)-6-*alkoxynaphthalene with an alkyl ester of acetoacetic acid and converting the cyclohexenone ring in the resulting product to cyclohexanone, cyclohexanol or cyclohexenol* — Merck & Co. Inc.

48809. Process for the preparation of new phenoxyacetic acid compounds and herbicidal compositions prepared therefrom: *Comprising aqueous solution of* 2: 4-*dichloro*-5-*methylphenoxyacetic acid obtained by condensing monochloroacetic acid with* 2: 4-*dichloro*-5-*methylphenol in alkaline solution* — Monsanto Chemicals Ltd.

49555. Boron-free enamels: *Comprising quartz with or without felspar and titanium oxide and one or more of soda ash,* $CaCO_3$, $MgCO_3$, $NaNO_3$, *fluorspar,* ZnO *with a potassium carbonate or nitrate* — Council of Scientific & Industrial Research

50483. Soft iodobromide positive emulsions: *Using indigenous gelatine which has been subjected to washing followed by swelling for* 4-5 *hr. in a* 0·5-0·6 *per cent potassium bromide solution at* 25°-28°*C.* — Council of Scientific & Industrial Research

Chemical processes, engineering and equipment

48807. Improvements in regulating throttle devices for use in hydraulic installations: *A throttle member of circular cross-section having a greater diameter than the vertical nozzle opening is supported to swing laterally* — Etablissements Neyrpic

50739. Improvements in rotary chamber mills: *Rotary mill driven simultaneously about two axes of rotation, which cross within the chamber* — Limb

51442. Improvements relating to driers for fluent solid material and to mixing plants including such driers: *The feed means and discharge means rotate with hollow drum in which the material is dried* — Frederick Parker Ltd. & F. W. Parker

49635. A process for the recovery of elemental sulphur from copper pyrites: *Reacting copper pyrites with cupric chloride* — Council of Scientific & Industrial Research

51144. Heat exchanger for fluids: *Heat exchanger is constructed as a double-sided rotatable fan and* *constitutes a wall between the spaces for fluid exchanger* — SWENDSEN

Physics — general

49210. Improvements in cold-gas refrigerating machines having at least two spaces, the volumes of which vary continuously with a substantially constant phase difference: *Providing a filler for the regenerator which comprises elements through which at least a portion of the gas which passes is in thermal contact with a medium independent of the cycle* — N. V. PHILIPS' GLOEILAMPENFABRIEKEN

49296. A flasher for lighthouse lamps or electrically operated sound signals: *Comprising lighthouse lamps or sound signal apparatus connected in series with a transformer and saturable reactor, the d.c. coil of the reactor being connected in series with a rectifier and a cam-operated switch so arranged that when current passes through the d.c. coil the effective reactance of its a.c. coils is diminished* — ENGINEER-IN-CHIEF, LIGHTHOUSE DEPARTMENT, MINISTRY OF TRANSPORT, GOVERNMENT OF INDIA

Drugs and pharmaceuticals

48918. Manufacture of new methyl steroids: *Preparing 14, methyl steroids having in 3- and 17- or 20-positions free or functionally converted hydroxyl or oxo-group by methods known per se*— CIBA LTD.

48823. Process for the manufacture of new quinoxaline compounds: *Substituted quinoxalinium salts and the corresponding pseudo-bases are made by quaternating a suitable quinoxaline by converting a 2-oxo-di- or tetrahydro-quinoxaline or by other known methods from an ortho-disubstituted ring compound* — CIBA LTD.

49543. Manufacture of new amides: *Reacting N-methyl-trimethyl colchicinic acid with ammonia, primary or secondary amines* — CIBA LTD.

Metals and metal products

51604. Smelting of lead-containing ores: *Air blast and a part of charge are preheated to maintain temperature at the top of furnace at 700°-900°C. and a reducing atmosphere is maintained in off-take vapours*—THE NATIONAL SMELTING CO. LTD.

49498. Porous mould for the continuous casting of metals: *Metal is passed through a sleeve having a labyrinth of capillary pores filled by a lubricant*— GOSS

51071. Improvements in or relating to the smelting of tin: *Tin ores are smelted in a blast furnace together with zinc ores* — THE NATIONAL SMELTING CO. LTD.

Glass and ceramics

49524. Foam glass: *Mixing together a pulverized reducing agent and a powdered glass comprising reactive oxygenated sulphur compounds other than sulphates such as sulphites, thiosulphates or dissolved gases comprising lower oxides of sulphur such as SO_2*— COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

49837. Production of pink enamels: *Manganese dioxide is used as colourant* — COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

Leather and leather products

50782. Improvements in tanning liquors: *Comprises reducing a bichromate with a metal like aluminium or iron in presence of an acid such as sulphuric or hydrochloric acid* — COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

48815. A process for the production of improved tan liquors from vegetable tanstuffs: *Soaking the vegetable tanstuffs in water, leaching to obtain tan liquor and adding to said liquor or stuff during leaching, oxalic acid and sodium bisulphite with or without the addition of formic acid* — COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

50067. Synthetic tanning materials (syntans) for making leather: *Condensing formaldehyde with a mixture of calophony and phenols or cresols and sulphonating the condensed product* — COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

50863. Synthetic tanning materials: *Sulphonated and condensed phenolic coal-tar distillation products are hydroxylated with condensed resorcinol*— COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

Building materials and methods

48711. A self-supporting structural element, of reinforced concrete such as a roofing, joist, wall element or the like: *Two reinforced concrete slabs between which one light insulating slab preferably of cellular concrete is interconnected by means of reinforced concrete bars* — RINGDAHL

Miscellaneous

50981. Cement batching plant: *Comprising an upper storage hopper, a lower feed hopper, an archimedian screw elevator and feed hopper, the feed hopper having means for aerating* — EONIT ENGINEERING CO. LTD.

49126. Reinforced waterproof paper: *Consists of two layers of paper wherein reinforcing threads of jute or cotton are laid between the layers in a manner extending across the paper in both the crosswise and lengthwise directions* — WARDEN

50994. Process for decorticating fibrous materials: *Conducting suspended fibre bundles in a moving fluid stream, while repeatedly bending said bundles* — S.I.S. SOCIETE D'INVESTISSEMENTS COLLECTIFS

51012. A method of producing an electro-luminescent powder: *Photo or cathodoluminescent particles are made from a crystalline substance, the crystal lattice of which is made up from at least one element of each of the groups:* (1) *zinc and cadmium,* (2) *sulphur and selenium,* (3) *silver, copper, lead, manganese and the like, the number of atoms of groups being arranged in a predetermined ratio* — N.V. PHILIPS' GLOEILAMPENFABRIEKEN

50574. A magnetic fluid for crack detection: *Suspending in a mineral oil vehicle of density between* 0·78 *and* 0·85 *g./cc. a finely ground magnetic material from which non-magnetic materilas have been removed* — COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH

Journal of
Scientific & Industrial Research

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NEW DELHI

J. sci. industr. Res., Vol. 13B, No. 8, Pp. 527-594. August 1954

Two Useful Laboratory Accessories

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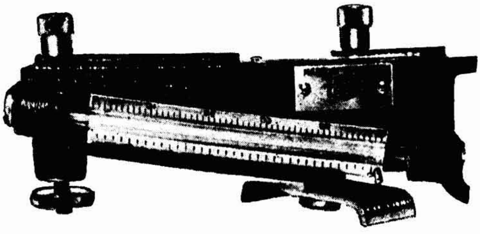

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On the Efficiency of Large Area Liquid Scintillation Counters for Cosmic Rays

G. H. VAZE
Tata Institute of Fundamental Research, Bombay

A single 1P21 photomultiplier was used to view the scintillations produced in a large area liquid counter by cosmic rays, and the efficiency data obtained with the instrument are presented. The difficulties and limitations of using a single photomultiplier are discussed.

THE scintillation method for radiation detection is one of the earliest in nuclear research. In its modern version a scintillation counter consists of a fluorescent substance capable of emitting light when traversed by an ionizing particle, and a photomultiplier that transforms the light pulse into an electric pulse. After suitable amplification the pulse is either displayed on an oscilloscope or recorded by a suitable device.

Some of the chief advantages of the scintillation detector over the other types, such as the G.M. counter, are high sensitivity to gamma rays, the rapid response time and high resolution which is very advantageous for coincidence measurements. In addition, the detecting phosphor has the property of emitting a light pulse proportional to the energy dissipated in the phosphor by the radiation. Thus the scintillation counter has the combined advantages of the G.M. and the proportional counter.

The usefulness of scintillation counters for cosmic ray research has been recognized recently. The proportional response of anthracene crystal of size $1\frac{1}{4} \times 1\frac{1}{4}$ in. diam. to mesons has been indicated by the results of Roser and Bowen[1]. However, because of the low counting rates encountered in cosmic ray observations, it is necessary to employ counters of large sensitive area. In general it is difficult to grow large and clear crystals, and as such limitations do not apply to clear solutions, liquid counters were tried for such work.

Kallmann[2] has reported that some of the organic liquids exhibit the scintillation property when bombarded by ionizing radiation. When such liquids are mixed with a small quantity of suitable " fluorescent molecules ", the effect is intensified. Thus, pure xylene alone gives a relative output of 0·012, which is increased to 0·46 by the addition of a few grams of terphenyl per litre. Toluene when mixed with terphenyl gives similar results. It was decided to use toluene solutions in our counters, as toluene was available more easily than xylene.

Attempts have already been made to develop liquid counters of sensitive area much larger than that of crystal scintillators. A pyrex glass counter of $\frac{1}{2} \times 1 \times 6$ in. size was used by G. T. Reynolds[3] to investigate the advantage of solutions as compared to crystals. His observations show that pulse heights comparable to those obtained with stilbene crystals could be obtained with solutions. Harrison[4] has described a liquid counter of size $1 \times 12 \times 12$ in. He has used four 1P21 photomultipliers, two on each of the two parallel sides of the glass tray, to view the scintillations.

Since the detecting device is a photomultiplier, the extensiveness of the counter will largely depend upon how far the photomultiplier can see the scintillations produced in the liquid by cosmic rays. The ionization loss in one centimeter of the liquid by cosmic rays is of the order of 1-2 Mev, and the sensitivity at a desired distance from the detector in the liquid can be estimated by placing a beta source at that point. The source should have the energy of 1-2 Mev, comparable with the energy lost by cosmic rays. As regards direct efficiency for cosmic rays, it can be determined with the help of G.M. counters.

In June 1951, a start was made under the guidance of Dr. Halban, at Oxford to study the usefulness of large area liquid counters. In the experimental arrangement an EMI photomultiplier was placed at the bottom of a liquid tank of size 1×6×12 in. The inside of the tank was silver plated for efficient light collection. The liquid in the tank was directly in contact with the photomultiplier, in order to avoid the loss due to refraction. The solution used was xylene and a beta source contained in a thin glass bulb was inserted from the top into the liquid and was placed at various distances from the detector. The bias curve was taken for each position of the source from the detector.

The results recorded in Fig. 1 indicate that the counts due to a source placed at 30-40 cm. are higher than the noise at zero bias, showing thereby that the solution is not only transparent for light pulses created at 30-40 cm. but the detector is sensitive enough to pick up the pulses. The beta source used for the above observations being P^{32} of 1·2 Mev, the rays had a range less than 1 cm. in the liquid. The curve termed background includes dark current noise, plus counts due to cosmic and other radiations.

The observations were carried out here mainly with the intention of exploring the possibilities of using large area liquid counters for cosmic ray work. As the cosmic ray rate is very low, the dark current noise counts of the photomultiplier will completely mask the counts due to cosmic rays. It is necessary, therefore, to adopt some method which will respond to cosmic ray counts and eliminate the dark current counts. This can be achieved conveniently by using a liquid counter in coincidence with two G.M. counters. The coincidence arrangement eliminates the noise background of the photomultiplier, and the G.M. counter assembly responds to cosmic rays. The G.M. counter assembly plays the important part of defining the sensitive area in an extensive liquid counter.

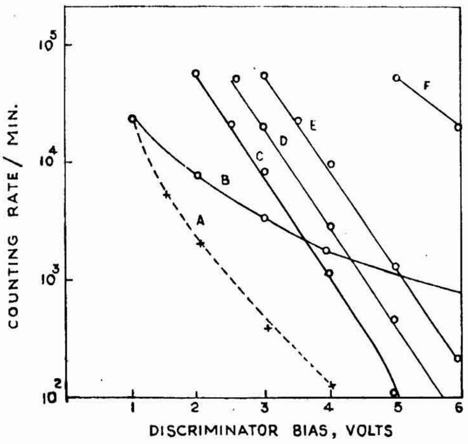

FIG. 1 — BIAS CURVE FOR THE BETA SOURCE INSIDE THE LIQUID SCINTILLATION COUNTER [A, noise; B, background with the liquid; C, D, E, F, counting rates, after subtracting the background, with the source at 20, 15, 10 and 5 cm. from the photomultiplier]

In the experiments carried out in this Institute the liquid counter was made out of aluminium and had a rectangular shape. It had a sensitive area of 10 × 30 cm. with a depth of 6 cm. The inside of the rectangular counter was lined with nickel-plated copper and was filled with toluene solution; a single photomultiplier 1P21 was used to look directly into the sensitive area from the shorter side. Initial observations were made with a gamma source placed at different distances from the detector, at different multiplier voltages. The results give only a rough idea, as it is not possible to define accurately the geometry of the gamma source. The results indicate that the relative counting rate decreases as the distance of the source from the detector is increased, but the relative rate can be improved by increasing the multiplier voltage.

Further experiments were carried out in coincidence with G.M. counters. In the experimental arrangement the liquid counter formed the central element in a triple coincidence assembly, the other two end elements being G.M. counters. In this case, as mentioned previously, the sensitive area was defined by the end G.M. counters, the source being cosmic rays. The experimental arrangement is shown in Fig. 2.

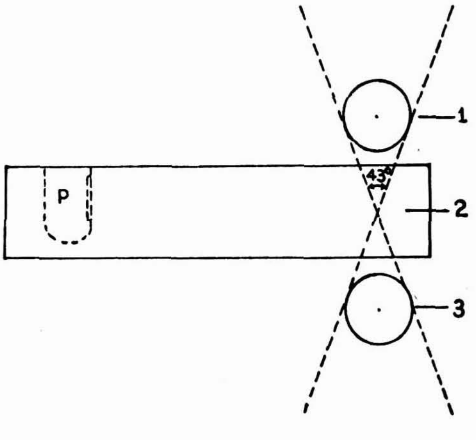

FIG. 2 — EXPERIMENTAL ARRANGEMENT [1, 3, G.M. counters; 2, liquid scintillation counter; P, photomultiplier]

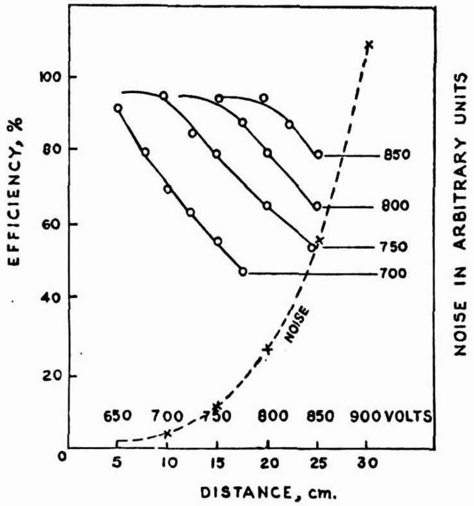

FIG. 3 — EFFICIENCY OF THE LIQUID SCINTILLATION COUNTER ALONG ITS LENGTH FOR COSMIC RADIATION AT VARIOUS PHOTOMULTIPLIER VOLTAGES, AND NOISE AT DIFFERENT PHOTOMULTIPLIER VOLTAGES

Observations were made by placing the G.M. counter assembly at different distances from the photomultiplier and recording the double and the triple rates. The triple and the double rates were simultaneously recorded on two different channels. The double to triple ratio is a measure of the efficiency of the central liquid counter. The results shown in Fig. 3 indicate that the efficiency drops as the sensitive area determined by the G.M. counter assembly is moved further away from the detector.

The results recorded in Fig. 3 indicate that it is possible to increase the efficiency of the counter by increasing the multiplier voltage, but the increase in the voltage results in a rise of the dark current noise rate. The voltage cannot be increased indefinitely, because the increased multiplier noise may give some chance counts in the triple rate, thus affecting the ratio. It was observed by a separate experiment that the effect of the dark current noise is about 1 per cent at 800 V. and is about 3 per cent at 850 V., the background rate at these voltages being 150 and 500 counts per second. The noise background at different voltages is also shown on the same curve. For convenience, the noise rate at different voltages is shown in terms of the noise rate at 650 V. The rate at this voltage is five counts per

TABLE 1 — SUMMARY OF RESULTS

BIAS V.	NOISE BACKGROUND	EFFICIENCY AT			
		25 cm.	20 cm.	15 cm.	10 cm.
0·0	150	96	96	96	96
0·5	90	92	95	95	95
1·0	60	72	82	94	94
1·5	32	48	65	92	95
2·0	25	20	42	75	86
3·8	18	—	30	65	—

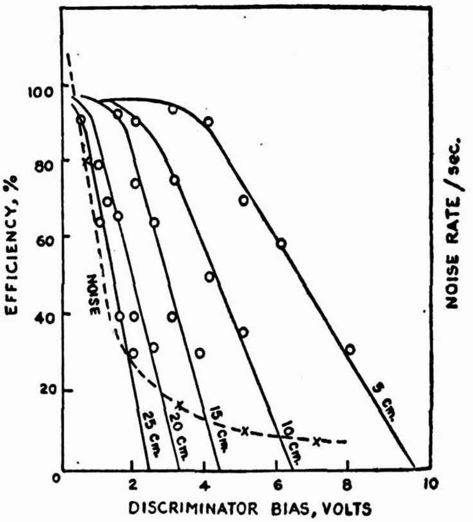

FIG. 4 — EFFICIENCY OF THE LIQUID SCINTILLATION COUNTER ALONG ITS LENGTH FOR COSMIC RADIATION AT VARIOUS BIAS VOLTAGES, AND BIAS CURVE FOR NOISE

second. It can be seen at once that the percentage increase in the noise due to change in the voltage is much more than the corresponding increase in the efficiency. The bias of the discriminator for the above observations was set at two volts. As the voltage was reduced to zero, it naturally increased the noise background, which was compensated by decreasing the multiplier voltage. The multiplier voltage was reduced to 750 volts to give the same background noise rate of 150 counts per second. The efficiency improved almost to 95 per cent even up to 25 cm., and that too at the same background rate, indicating that some of the signal pulses were eliminated by bias setting of two volts.

In order to come to a definite conclusion regarding the use of a single photomultiplier as a detector in an extensive liquid counter, bias curves were taken for different distances of the sensitive area from the detector. The results are recorded in Fig. 4.

Table 1 summarizes the results of the observations.

It shows that the noise rate increases much more rapidly at a bias setting of 1·5 volts and so, for good results, this bias setting should be used, giving a background rate of 30-40 counts per second. The useful sensitive area then extends up to 15 cm. from the detector. Further investigations on the proportional property of the counter, the proper geometrical shape of the container for good light collection, etc., are necessary in order to make optimum use of this type of counter.

Acknowledgement

I wish to express my thanks to Dr. Bhabha for suggesting the problem and Dr. Halban under whose guidance the work was initiated at Oxford. I also wish to thank Dr. Phadke for his helpful suggestions throughout the work.

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A Crystal Comparator

B. R. V. VARDAN & H. D. KRISHNA PRASAD
Radio Development Unit, Civil Aviation Department, New Delhi

A crystal comparator for quick and accurate measurement of the difference in frequency of a number of crystals ground for a certain frequency has been developed. The instrument can also be used as a frequency meter to measure any frequency in the range 0-60 kc./s.

THE necessity for grinding a number of crystals to exactly the same frequency values arises when preparing crystals for aircraft transmitters, air ground channels and point to point channels of ground network, etc. When mass manufacture of crystals for the same spot frequency is undertaken, it is necessary to check the frequency of one crystal accurately, and the frequency of the subsequent crystals can be determined by the use of a comparator utilizing the first crystal as a standard.

The crystal comparator described in this paper indicates the frequency difference between the two crystals under comparison on a meter. The maximum difference in frequency between the crystals compared should be within 60 kc./s. To facilitate measurement of very small frequency differences, an aural indication on a loud speaker is also provided. A provision has been made for determining the sign of the difference in frequency. By using a substandard crystal of the required frequency the frequency of crystals ground for the required frequency can be accurately determined.

This instrument would be particularly useful when mass manufacture of crystals for spot frequencies is undertaken, and can also be used as a frequency meter in the range 0-60 kc./s.

Principle of operation

The comparator consists of two separate crystal oscillator circuits, the associated R.F. amplifiers and a frequency measuring circuit (FIG. 1). A crystal which is used as the reference is plugged into one crystal oscillator stage and the crystal under comparison is plugged into the other crystal oscillator. The R.F. signals from the two amplifier stages are mixed at the mixer stage. The output from the mixer consisting of the individual R.F. signals, their sum and difference frequencies, is fed on to a wideband amplifier with low pass characteristics. At the output of the wideband amplifier only the difference frequency or the beat frequency of these two R.F. signals is obtained. This difference frequency signal is amplified in the next amplifier limiter stage. If the signal is sufficiently large, it is also peaked at this stage. This output is fed on to a limiter. Here the signal is shaped to rectangular pulses. These pulses are then fed on to a measuring circuit where the difference in frequency is measured and indicated on a meter. An audio amplifier and loud speaker are provided for monitoring the difference frequency when it is in the audible range.

A mains rectifier supplies the plate and screen potential to all the stages. Only the limiter tube derives its plate supply through a voltage regulator.

Circuit description (FIG. 2)

R.F. oscillator — A conventional oscillator circuit with 6C5 tube has been employed. The tuned circuit is inserted in parallel with the oscillator and the output is coupled to the grid of the R.F. amplifier. The tuned stages for the R.F. amplifier and oscillator are ganged. The frequency range from 500 kc./s. to 13 Mc./s. is covered in 4 bands.

All the coils except those for the highest frequency range are provided with trimmer capacitors for purposes of alignment. The coils for the highest frequency range are mounted by the side of the main tuning condenser and are well shielded. All the coils have been wound on phenolic formers. The single pole toggle switch on the front panel brings in a trimmer condenser in parallel with the crystal, thus decreasing the oscillator frequency.

R.F. amplifier — A tuned R.F. amplifier using a 6SK7 tube is used primarily to eliminate the harmonics of the crystal frequency and at the same time to amplify the fundamental R.F. signal before it is fed to the mixer tube. This also serves as an isolating stage between the two oscillators.

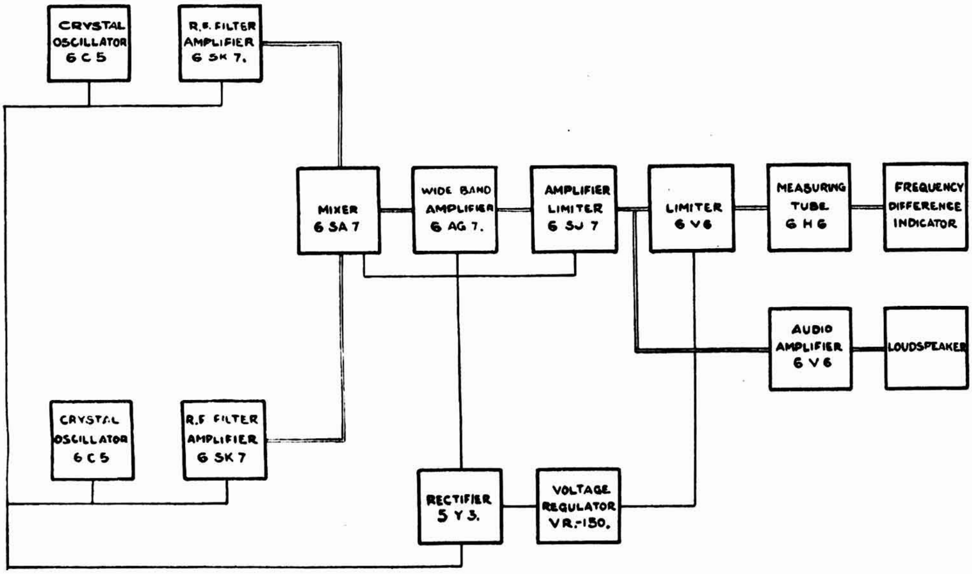


FIG. 1 — BLOCK DIAGRAM OF CRYSTAL COMPARATOR

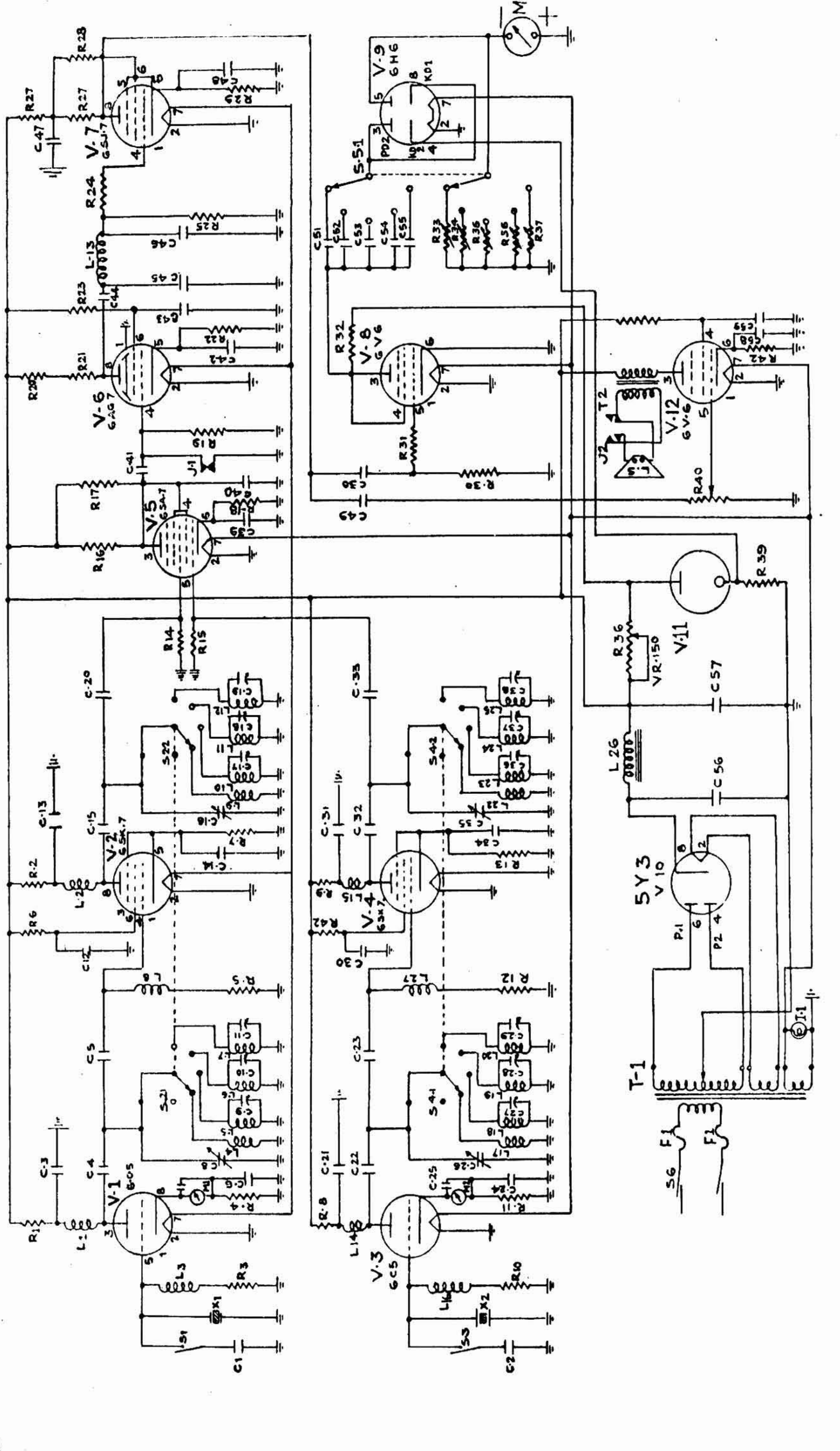


FIG. 2 — CRYSTAL COMPARATOR — COMPLETE SCHEMATIC CIRCUIT DIAGRAM

Mixer — A 6SA7 mixer tube is used for mixing the two R.F. signals. The output of the mixer is coupled to the grid of the wideband amplifier.

Wideband amplifier — This provides fairly equal amplification for all frequencies below 60 kc./s. and sharply attenuates frequencies above 60 kc./s. The R.F. signals are eliminated by the low pass pi filter network in the plate circuit of this amplifier.

Amplifier limiter (*clipping and shaping amplifier*) — The detected signal is fed into an over driven 6SJ7 amplifier wherein a combination of grid current and cut-off limiting takes place for signals above a level determined by the self bias. Limiting does not take place at this stage when the signal is below 0·75 volts amplitude at the 6AG7 grid.

Limiter (*over driven amplifier*) — The 6V6 amplifier works with zero bias and a low plate potential, thereby introducing plate current limiting. The minimum signal required at the 6AG7 grid to give a perfectly square-shaped wave at the limiter plate is 400 mV.

Frequency measuring circuit — The square wave from the plates of the 6V6 is fed to a 6H6 measuring circuit. The measuring circuit consists of double diode 6H6 which separates the charging and discharging currents and a d.c. meter in the cathode circuit of one of the diodes indicates the frequency of the square waves. Figs. 3-6 show the oscillograms at the various stages. The lower curve in each oscillogram indicates the voltage input at the grid of the wideband amplifier and the upper curve is the oscillogram at the particular stage. Different combinations of C and R are used for the five ranges.

When a square wave of repetition frequency N is applied to a resistance and condenser series combination and the discharging is averaged, then the average current

$$I_{av}=ECN\left(1-e^{-\frac{1}{2NCR}}\right)$$

where E is the amplitude of the pulse; C, capacitance of the condenser; N, P.R.F.; and R, resistance.

The square-shaped pulses at the plate of 6V6 charge the capacitor in the plate circuit of the first section of the diode. The cathode

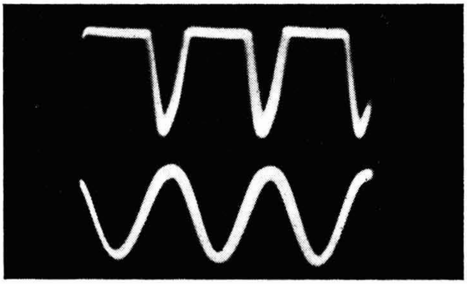


FIG. 3 — WAVE FORM AT THE GRID OF LIMITER AMPLIFIER SHOWING GRID CURRENT LIMITING

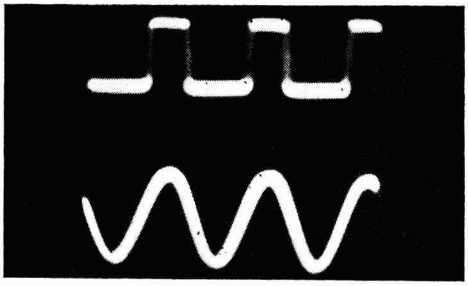


FIG. 4 — WAVE FORM AT THE PLATE OF THE LIMITER TUBE SHOWING THE SHAPED, RECTANGULAR PULSES

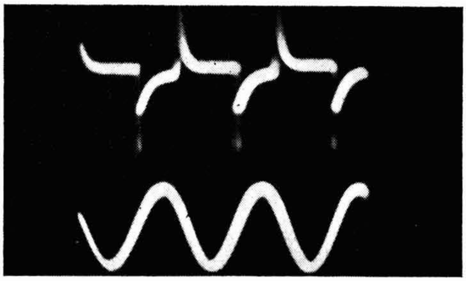


FIG. 5 — WAVE FORM AT THE PLATE OF THE FIRST SECTION OF THE MEASURING TUBE SHOWING THE CHARGE AND DISCHARGE OF THE MEASURING CAPACITY

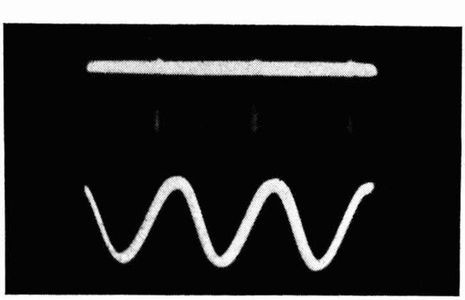


FIG. 6 — WAVE FORM AT THE PLATE OF THE SECOND SECTION OF THE MEASURING TUBE SHOWING A COUNTING PULSE FOR EVERY CYCLE OF INPUT VOLTAGE

of this diode is maintained at a positive potential of 4-5 V., so that there is no conduction due to hum and stray voltages and only strong pulses due to the mixer output charge the measuring capacitor. The discharge path for the capacitor is provided through the other section of the diode and the calibrating potentiometer which are in series. The milliammeter is connected in parallel with the calibrating potentiometer. The linearity of indication with respect to the frequency is maintained by suitable choice of C and R for each range. The meter dial is marked in cycles and the frequency can be read off directly. There are five ranges divided as follows:

0-300 c./s.; 0-3,000 c./s.; 0-15 kc./s.; 0-30 kc./s. and 0-60 kc./s.

A 6V6 audio amplifier provides audio monitoring.

Power supply — A d.c. potential of 260 V. is available for all the tubes except the 6V6 limiter tube for which a regulated supply of 150 volts is provided. The cathode of the regulating tube VR150 is returned to earth through a resistor so that the drop across the resistor is available as a positive bias for the first section of the 6H6 diode tube.

Construction

The equipment is built on a $\frac{1}{16}$ in. copper sheet chassis supported by a $\frac{1}{2} \times \frac{1}{2}$ in. angle iron frame work. Complete shielding of all the components is provided by the aluminium panels covering all the sides. The overall size of the equipment is 19 × 30 × 15 in.

The front panel is in two pieces. The top panel houses the 5 in. loud speaker. On the bottom panel the various controls and the meters have been mounted. The universal type crystal mounts have been fixed at the bottom corners. This enables frequency comparison of crystals with holders of all the common types, like two pin 10x and 110XN, three pin FT-249, and octal, etc. The front panel is black crackle finished.

The R.F. amplifier and oscillator are shielded from one another to prevent direct pick up and hence self-oscillation. Five calibration potentiometers with slotted shafts are mounted inside the chassis and are accessible for adjustments from the front.

Adjustment and operation — The frequency meter range switch is initially kept in the 60 kc./s. position. The two crystals to be compared are plugged into the two crystal oscillator sockets. The R.F. band switches are set to the required range and the main tuning dial is adjusted for stable oscillations as indicated by the milliammeters. Calibration charts are provided to avoid tuning to harmonics of the crystal frequency. The frequency meter range switch is placed on the appropriate range and the frequency difference between the two crystals is read off. By the operation of either of the trimmer switches the sign of the frequency difference can be easily determined.

Acknowledgement

The authors are grateful to the Civil Aviation Department, Government of India, for permission to publish this article.

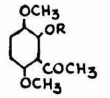
Synthetic Experiments in the Benzopyrone Series: Part XLIX—A Convenient Synthesis of Flavones of the Primetin Series

P. S. KOHLI, S. K. MUKERJEE & T. R. SESHADRI
Department of Chemistry, Delhi University, Delhi

A convenient synthesis of 2-hydroxy-3 : 6-dimethoxy acetophenone by partial demethylation of 2 : 3 : 6-trimethoxy acetophenone is described. The condensation of this ketone with esters of aromatic acids in presence of metallic sodium has been studied. It proceeds with good yield with ethyl benzoate, but with other esters the yields are poor. For the preparation of higher members of the primetin series the Baker-Venkataraman method is found to be quite suitable.

THE most convenient method for the synthesis of primetin is the nuclear oxidation of 5-hydroxy flavone (primuletin), but it is not found to be suitable for the preparation of the higher members of the series. Baker *et al.*[1] noted that the yield went down in the oxidation of 5-hydroxy-4′-methoxy flavone. In the recent work of Ahluwalia *et al.*[2], it was found that this method is unsuitable for the higher members, the yields rapidly dwindling down. Consequently attempts were made to use 8-hydroxy flavone derivatives for nuclear oxidation. Though better yields were secured thereby, the yields were not altogether satisfactory, and further the preparation of the required ketone intermediate was difficult.

Among possible alternatives, improvements in the method of Baker[3] have now been explored. 2-Hydroxy-3 : 6-dimethoxy acetophenone (Ib) was the important intermediate and it was originally converted into primetin dimethyl ether by adopting the Baker-Venkataraman procedure. The difficulty of demethylation of the dimethyl ether of primetin was overcome by Rao, Rajagopalan and Seshadri[4] using aluminium chloride in benzene solution as the demethylating agent. Hence, the important stage that required improvement was the preparation of the ketone. It was originally made by Baker[3] starting from γ-resacetophenone and using among other steps partial benzylation, oxidation, methylation and subsequent debenzylation. The yields were very poor and the steps somewhat difficult. The present method consists in the preparation of 2 : 3 : 6-trimethoxy acetophenone[5] (Ia) and its partial demethylation to 2-hydroxy-3 : 6-dimethoxy acetophenone (Ib).



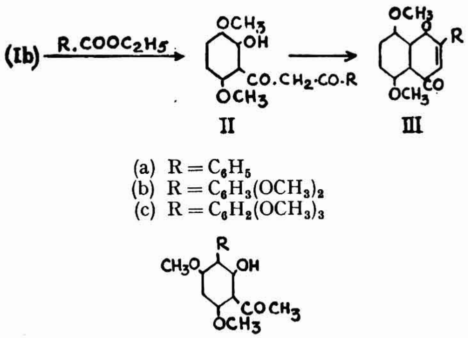
I

(a) $R = CH_3$
(b) $R = H$

The discovery of the suitability of this partial demethylation is based on analogy with the behaviour of 2 : 3 : 4: 6-tetramethoxy acetophenone[6] which under the same conditions suffers partial demethylation in the 2-position and not in the 6. Considerable amount of earlier work indicates that a methoxyl in the 6-position is more readily formed and less readily demethylated as compared with that in the 2-position (*see* for discussion[7]). With minor modifications in the experimental procedure the yield of 2 : 3 : 6-trimethoxy acetophenone (Ia) itself has now been considerably improved. Since the subsequent partial demethylation is quite smooth, the required intermediate for the primetin synthesis can now be made in quantity.

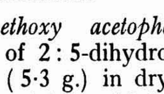
As mentioned earlier, the conversion of the above ketone (Ib) to the corresponding ω-benzoyl derivative was originally carried out by Baker *et al.*[3]. A good yield of this diketone could now be obtained by condensation with ethyl benzoate in the presence of metallic sodium.

This method of preparation seems to be more convenient for this particular compound. The ester method of diketone synthesis was originally adopted by Kostanecki *et al.*[8], but they felt it was necessary to protect all the phenolic hydroxyl groups by methylation. Consequently there was need to effect demethylation before flavone ring closure. In the present case the use of hydriodic acid was objectionable because of the possibility of isomeric change. Experiments have now been made to adopt this ester method even with 2-hydroxy-3 : 6-dimethoxy acetophenone (Ib) and quite good yields of primetin-dimethyl ether (IIIa) have been obtained. However, when applied to other cases the method has not been uniformly efficient. The yields are less with 2-hydroxy-3 : 4 : 6-trimethoxy acetophenone (IVb) and considerably diminished in the case of 2-hydroxy-3-methyl-4: 6-dimethoxy acetophenone (IVa). Actually even with the original ketone (Ib) when esters of veratric and trimethyl gallic acids were used poor yields of the diketones were obtained. For these diketones the Baker-Venkataraman technique seems to be far more satisfactory; a detailed description of these products is given in the experimental part.



II III

(a) $R = C_6H_5$
(b) $R = C_6H_3(OCH_3)_2$
(c) $R = C_6H_2(OCH_3)_3$



IV

(a) $R = CH_3$
(b) $R = OCH_3$

Experimental procedure

2 : 3 : 6-*Trimethoxy acetophenone* (Ia) — To a solution of 2 : 5-dihydroxy-6-methoxy acetophenone[5] (5·3 g.) in dry acetone (200 cc.) dimethyl sulphate (8·5 cc.) and anhydrous potassium carbonate (30 g.) were added and the mixture refluxed for 15 hr. Acetone was then distilled off and water (150 cc.) added to the residue. The mixture was heated on a boiling water bath for 1 hr. to destroy the excess of dimethyl sulphate. It was then cooled and extracted with ether. The ether solution was washed with aqueous sodium hydroxide (10 per cent) and then with water and dried over anhydrous sodium sulphate. Ether was then distilled off and the residue crystallized from petroleum ether when 2 : 3 : 6-trimethoxy acetophenone was obtained as silky needles melting at 41°-42°; yield 4·8 g. Baker[5] prepared this compound by the wet methylation method and reported the same melting point.

2-*Hydroxy*-3 : 6-*dimethoxy acetophenone* (Ib)—To a solution of anhydrous aluminium chloride (11·4 g.) in dry ether (50 cc.) cooled in an ice bath to 0° was added slowly with shaking a solution of 2 : 3 : 6-trimethoxy acetophenone (6 g.) in dry ether (50 cc.). The mixture was then allowed to stand at room temperature for 48 hr. with occasional shaking. The aluminium chloride complex was then decomposed with ice (150 g.) and concentrated hydrochloric acid (12 cc.). The decomposition was completed by heating the mixture on a water bath at 70°-80° for 30 min., ether being allowed to distil away. It was then cooled and extracted with ether and the ether solution extracted with aqueous sodium hydroxide (5 per cent). The combined alkaline extract was acidified with dilute hydrochloric acid and extracted again with ether. On evaporation of the ether solution a brownish oil was left behind which solidified on cooling. It crystallized from petroleum ether as lemon-yellow big rhombic plates melting at 62°-63° and giving a bluish green colour with ferric chloride in alcoholic solution; yield 4·8 g. Baker, Brown and Scott[3] reported the melting point as 61°.

2-*Hydroxy*-3: 6-*dimethoxy dibenzoyl methane* (IIa) — An ice-cold solution of 2-hydroxy-3: 6-dimethoxy acetophenone (2 g.) in ethyl benzoate (10 cc.) was added to powdered sodium (2 g.) just covered with a layer of dry ether. The mixture was continuously stirred, allowed to warm up gradually and then left at room temperature overnight. Next day the brownish semi-solid mass was treated with a little methanol to decompose any unreacted sodium, the sodium salts were dissolved in ice-cold water (150 cc.) and the solution extracted with ether to remove excess of ethyl benzoate.

Acidification of the aqueous solution with glacial acetic acid resulted in the separation of a pale yellow oil which solidified in the refrigerator overnight. This was collected and washed with a little ether-petroleum ether mixture to remove oily impurities. The diketone crystallized from benzene as deep yellow rhombic prisms melting at 165°-66°; yield 0·8 g. Baker *et al.*[3] gave the melting point as 165°.

5:8-*Dimethoxy flavone* (IIIa) — A solution of the above diketone (0·4 g.) in glacial acetic acid (7 cc.) was treated with fused sodium acetate (0·5 g.) and the mixture heated on a boiling water bath for 2 hr. It was cooled and diluted with water when a colourless product separated. It crystallized from alcohol as colourless needles melting at 145°-46° with earlier sintering at 120°C.; yield 0·3 g.

5:7:8-*Trimethoxy flavone* — A mixture of 2-hydroxy-3:4:6-trimethoxy acetophenone (IVb) (1·5 g.), ethyl benzoate (10 cc.), dry ether (10 cc.) and powdered sodium (2g.) was kept at room temperature for 12 hr. with occasional shaking. It was then worked up as given earlier when an yellowish brown oil was obtained which could not be crystallized and was, therefore, used directly for cyclization. It was dissolved in glacial acetic acid (6 cc.) containing fused sodium acetate (1 g.) and the mixture was gently refluxed for 4 hr. and then diluted with water. The precipitated flavone was collected and crystallized from dilute alcohol twice when it was obtained as colourless long narrow rectangular plates melting at 166°-67°. Mixed melting point with an authentic sample of 5:7:8-trimethoxy flavone was undepressed.

5:7-*Dimethoxy-8-methyl flavone* — A solution of 2-hydroxy-3-methyl-4:6-dimethoxy acetophenone (IVa) (2 g.) in ethyl benzoate (10 cc.) was added to powdered sodium (2 g.). The mixture was gently warmed to start the reaction and then cooled in an ice bath at the same time shaking vigorously. After 4 hr. more ethyl benzoate (5 cc.) and dry ether were added to keep the mass in a pasty condition. It was then left in the ice chest for 24 hr. with occasional shaking. On working up the product in the usual way a yellow oil was obtained which could not be crystallized and was, therefore, subjected to cyclization using glacial acetic acid (15 cc.) and fused sodium acetate (2 g.). After crystallizing twice from dilute alcohol 5:7-dimethoxy-8-methyl flavone was obtained as pale yellow long narrow rectangular prisms melting at 231°-32° alone or when mixed with an authentic sample; yield 0·1 g.

2-*Veratroyloxy-3:6-dimethoxy acetophenone* — To a mixture of 2-hydroxy-3:6-dimethoxy acetophenone (1 g.) and veratroyl chloride (2 g.), dry pyridine (10 cc.) was added. The solution was heated on a boiling water bath for 1 hr. and then poured on to crushed ice and dilute hydrochloric acid (25 cc.). After 4 hr. the aqueous layer was decanted off, the sticky solid residue washed with water by decantation and then macerated thoroughly with cold alcohol (15 cc.). The resulting colourless solid was filtered and crystallized from alcohol when 2-veratroyloxy-3:6-dimethoxy acetophenone came out as colourless small prisms melting at 124°-25°; yield 1·5 g. (found: C, 63·5; H, 5·7; $C_{19}H_{20}O_7$ requires: C, 63·3; H, 5·6 per cent).

2-*Hydroxy-3:6:3′:4′-tetramethoxy dibenzoyl methane* (IIb) — Sodamide (7 g.) was powdered under dry toluene (25 cc.) and 2-veratroyloxy-3:6-dimethoxy acetophenone (1·7 g.) added in small lots with shaking. The sides of the flask were washed with some more toluene (10 cc.) and the mixture heated at 100° in an oil bath for 6 hr. with occasional shaking, then filtered and the solid residue washed thrice with hot benzene. It was dried and decomposed by adding in small lots to crushed ice. The pale yellow solution was filtered to remove some slimy impurities and saturated with carbon dioxide. The yellow precipitate was filtered, dried and crystallized from acetone twice. The dibenzoyl methane separated out in the form of deep yellow rectangular tablets melting at 170°-71°; yield 0·6 g. It gave a brown colour with alcoholic ferric chloride. It was sparingly soluble in alcohol and benzene and more readily in acetone and ethyl acetate (found: C, 63·4; H, 5·5; $C_{19}H_{20}O_7$ requires: C, 63·3; H, 5·6 per cent).

5:8:3′:4′-*Tetramethoxy flavone* (IIIb) — (i) The above diketone (0·5 g.) was dissolved in glacial acetic acid (30 cc.) and heated with fused sodium acetate (4 g.) for 3 hr. The solution was then cooled, diluted with water (50 cc.) and the acetic acid neutralized with dilute alkali. On leaving overnight in the refrigerator, a colourless solid separated. It was filtered, dried and crystallized from ethyl acetate. 5:8:3′:4′-Tetramethoxy flavone was obtained in the form of colourless fibrous needles melting at 168°-70°; yield 0·4 g. Ballio and Pocchiari[9] obtained this compound by the selenium dioxide oxidation of the corresponding chalkone and reported the same melting point.

(ii) An ice-cold solution of 2-hydroxy-3: 6-dimethoxy acetophenone (1 g.) and methyl veratrate (8 g.) in dry ether (50 cc.) was added to powdered sodium (1 g.). After 2 hr. the mixture was gently refluxed for an hour, left overnight at room temperature and then worked up in the usual way. The resulting oily diketone was cyclized as mentioned in (i) above. The yield of the tetramethoxy flavone obtained in this case was 0·1 g.

2-Trimethyl galloyloxy-3: 6-*dimethoxy acetophenone* was prepared in the usual way from 2-hydroxy-3: 6-dimethoxy acetophenone (1 g.), 3 : 4 : 5-trimethoxy benzoyl chloride (1·8 g.) and pyridine (12 cc.). A colourless solid was obtained which crystallized from alcohol as colourless rectangular plates and needles melting at 111°-13°; yield 1·7 g. (found: C, 61·0; H, 6·0; $C_{20}H_{22}O_8$ requires: C, 61·5; H, 5·6 per cent).

2-Hydroxy-3: 6: 3′: 4′: 5′-*pentamethoxy dibenzoyl methane* (IIc) — The above aroyloxy ketone (1 g.), powdered sodamide (4 g.) and dry toluene were heated at 100° for 8 hr. The mixture was then worked up as described earlier and the diketone crystallized from alcohol when it was obtained as bright yellow rectangular plates and needles melting at 145°-47°; yield 0·5 g. It gave a brown colour with alcoholic ferric chloride (found: C, 61·3; H, 5·7; $C_{20}H_{22}O_8$ requires: C, 61·5; H, 5·6 per cent.).

5: 8: 3′: 4′: 5′-*Pentamethoxy flavone* (IIIc) — (i) The above diketone (0·5 g.) was cyclized by heating a solution of it in glacial acetic acid (35 cc.) with fused sodium acetate (3 g.) for 4 hr. Acetic acid was then neutralized with dilute alkali and the precipitated pentamethoxy flavone was collected and crystallized from ethyl acetate when it formed colourless thick rectangular plates melting at 208°-9°; yield 0·3 g. It was easily soluble in alcohol and less easily in ethyl acetate (found: C, 64·7; H, 5·7; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4 per cent).

(ii) A solution of 2-hydroxy-3 : 6-dimethoxy acetophenone (1·5 g.) and methyl 3 : 4 : 5-trimethoxy benzoate (12 g.) in dry benzene (75 cc.) was refluxed for 3 hr. with powdered sodium (1·2 g.). After 24 hr., benzene was distilled off and the product worked up in the usual way. In this case, an oil mixed with some crystals was obtained. Further purification was not, however, possible and, therefore, it was cyclized to the flavone as described under (i) above. The yield of the pentamethoxy flavone was 0·1 g.

5 : 8 : 3′: 4′: 5′-*Pentahydroxy flavone* — The above pentamethoxy flavone (IIIc) (0·6 g.) was dissolved in dry benzene (35 cc.) and powdered anhydrous aluminium chloride (3·5 g.) added. The mixture was refluxed for 2 hr. Benzene was distilled off and the residual complex decomposed with ice and hydrochloric acid. The yellow precipitate of the pentahydroxy flavone was collected and crystallized from a large volume of alcohol. It separated as bright yellow short needles and thin plates which did not melt below 350°. It gave a greenish brown ferric chloride reaction in alcohol. It dissolved in dilute sodium hydroxide to give a yellow solution which turned rapidly orange and then bright red; on heating, the colour slowly faded and changed to permanent yellow; yield 0·25 g. (found: C, 59·2; H, 3·8; $C_{15}H_{10}O_7$ requires: C, 59·6; H, 3·3 per cent).

The acetate of the pentahydroxy flavone was prepared by the acetic anhydride-pyridine method and crystallized from a mixture of chloroform and alcohol. The pentaacetate was obtained in the form of long colourless fibrous needles melting at 254°-55° (found: C, 59·0; H, 4·0; $C_{25}H_{20}O_{12}$ requires: C, 58·6; H, 3·9 per cent).

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Synthetic Experiments in the Benzopyrone Series: Part L—Nuclear Methylation of Quercetin*

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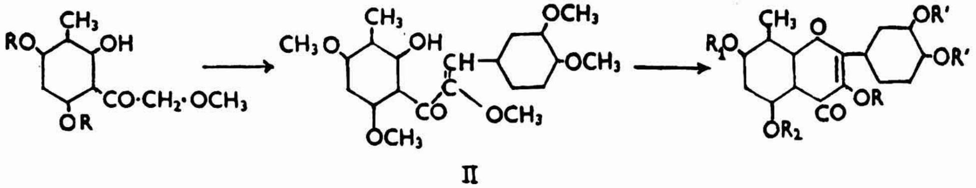
It is shown that nuclear methylation of quercetin yields 6-C-methyl quercetin derivative. For purposes of comparison authentic samples of 8-C-methyl and 6-C-methyl quercetins and their derivatives have been prepared. C-Methylation in the 8-position can be effected by initial formylation and subsequent reduction.

IN the methylation of quercetin using a large excess of methyl iodide and methyl alcoholic potash, Perkin[1] noticed that besides the usual *o*-pentamethyl ether (yield 50 per cent) and *o*-tetramethyl ether (very small quantity), C-methylated products could be obtained in an overall yield of 12 per cent. Of these the major product melting at 184°-85° was considered to be C-methyl quercetin tetramethyl ether and the minor product melting at 213°-15° the corresponding C-methyl pentamethyl ether. He studied in detail their fission with alkali, but not their demethylation. Their constitutions were not investigated.

For purposes of comparison authentic samples of 6-methyl and 8-methyl quercetins and their derivatives were needed. Employing 2-hydroxy-3-methyl-ω : 4 : 6-trimethoxy acetophenone (I), 8-methyl quercetin pentamethyl ether (III) has been made in two ways: (1) Condensation with veratraldehyde and dehydrogenation of the resulting chalkone (II) with selenium dioxide; and (2) Allan-Robinson condensation using the anhydride and sodium salt of veratric acid. During the second reaction, no demethylation of the 5-methoxy group occurs as has been recorded in some other cases[2-4]. The resulting pentamethyl ether undergoes demethylation with hydriodic acid under ordinary conditions to yield 8-methyl quercetin (IV). That there was no isomeric change in this process has been confirmed by remethylation to the original pentamethyl ether (III). Partial methylation yields the tetramethyl ether (V).

When C-methyl-ω-methoxy phloracetophenone (VI) is subjected to Allan-Robinson condensation, two isomeric products are obtained. The major product (75 per cent) is found to be 8-methyl-3 : 3′ : 4′-*o*-trimethyl quercetin (VII) because on complete methylation it forms the above-mentioned 8-methyl-*o*-pentamethyl quercetin (III) and on partial methylation 8-methyl-*o*-tetramethyl quercetin (V). The minor component (25 per cent) should, therefore, be the corresponding 6-methyl quercetin derivative (VIII) which



II

I, $R = CH_3$
VI, $R = H$

III, $R = R_1 = R_2 = CH_3$
IV, $R = R_1 = R_2 = H$
V, $R = R_1 = CH_3$; $R_2 = H$
VII, $R = CH_3$; $R_1 = R_2 = H$

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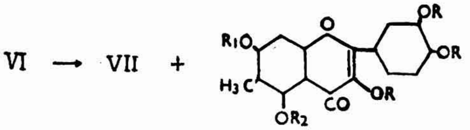
*See " Nuclear Methylation of Flavonols ", *J. sci. industr. Res.*, **12B** (1953), 564.

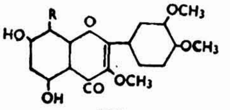
yields on complete methylation the corresponding pentamethyl ether (IX) and on partial methylation the tetramethyl ether (X). On demethylation 6-methyl quercetin (XI) is obtained in good yield.



VIII, $R_1 = R_2 = H$; $R = CH_3$
IX, $R = R_1 = R_2 = CH_3$
X, $R = R_1 = CH_3$; $R_2 = H$
XI, $R = R_1 = R_2 = H$

Nuclear methylation of quercetin has now been carried out under the conditions adopted by Perkin[1] but the products have been separated using an improved method. The major product (50 per cent) is found to be quercetin pentamethyl ether. C-Methyl quercetin tetramethyl ether is obtained in 12 per cent yield together with a small amount of quercetin tetramethyl ether. The properties and derivatives of the C-methyl compound agree with those recorded by Perkin and also observed in the course of the present work for 6-methyl quercetin tetramethyl ether (X). It is, therefore, established that as in similar cases nuclear methylation of quercetin takes place in the sixth position. In the course of the present experiments on nuclear methylation, C-methyl quercetin pentamethyl ether has not been obtained. The m.p. of 213°-15° reported by Perkin for this substance does not agree with the melting point of 164°-65° obtained for the authentic 6-methyl quercetin pentamethyl ether (IX) prepared in the course of the present work.

Nuclear methylation under strongly alkaline conditions leads invariably to the 6-C-methyl compounds. As an alternative method which will introduce a methyl group in the 8 position, formylation followed by subsequent reduction is found to be quite convenient. Using quercetin-3: 3′: 4′-trimethyl ether (XIIa), the corresponding 8-aldehyde (XIIb) and 8-methyl derivative (VII) have been obtained. The identity of the C-methyl compound is established by comparison with the authentic sample already prepared using Allan-Robinson condensation.



XII

a, R = H
b, R = CHO

Experimental procedure

2-Hydroxy-ω : 4 : 6-trimethoxy-3-methyl acetophenone (I)* — ω-Methoxy phloracetophenone (2 g.) was refluxed with methyl iodide (8 cc.) and anhydrous potassium carbonate (14 g.) in acetone solution (50 cc.) for 3 hr. The acetone solution was filtered from the potassium salts, evaporated, the residue taken up in ether leaving behind brown impurities, the ether solution washed with water and concentrated. The residue was thrice crystallized from methyl alcohol when it formed long colourless needles melting at 141°-42°; yield 0·5 g. It contained water of crystallization and, after drying at 100°, it melted at 176°-77°. It dissolves easily in dilute alkali to give a yellow solution and gives a reddish brown colour with alcoholic ferric chloride (found in sample dried at 110°: C, 60·3; H, 6·9; $C_{12}H_{16}O_5$ requires: C, 60·0; H, 6·7 per cent).

The alcoholic mother liquor from which the above C-methyl compound had been recovered was diluted with water when it precipitated a crystalline substance which was identified as 2-hydroxy-ω: 4: 6-trimethoxy acetophenone melting at 104°-5°.

2-Hydroxy-3-methyl-ω-4 : 6 : 3′ : 4′-pentamethoxy chalkone (II) — An alcoholic solution of 2-hydroxy-3-methyl-ω: 4: 6-trimethoxy acetophenone (I) (1·2 g.) and veratraldehyde (0·85 g.) was treated with a solution of potassium hydroxide (3 g. in 3 cc. of water) and left at room temperature for 48 hr.; it was diluted with water when some turbidity appeared which was cleared up by ether extraction. On acidification and cooling in ice, a bright yellow product separated out. It was filtered, washed first with aqueous sodium bicarbonate solution and then with water and crystallized from methyl alcohol when the chalkone (II) formed lemon yellow rectangular prisms melting at 146°-47°; yield 0·9 g. (found: C, 65·3; H, 6·7; $C_{21}H_{24}O_7$ requires: C, 64·9; H, 6·2 per cent).

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*This compound was first prepared in collaboration with V. Venkateswarlu.

It is sparingly soluble in aqueous sodium hydroxide. It yields a golden yellow solution when treated with an acetone solution of dry boric-citric acid mixture. Its solution in concentrated sulphuric acid is crimson red. It imparts a brown colour to alcoholic ferric chloride.

8-*Methyl-o-pentamethyl quercetin* (III) — (i) The above chalkone (II; 0·5 g.) was mixed with dry selenium dioxide (0·5 g.) and the mixture heated under reflux with dry amyl alcohol (5 cc.) at 140° for 15 hr. After cooling, it was filtered and the selenium residue on the filter paper was washed with boiling rectified spirit. Amyl alcohol was removed by distillation under reduced pressure, the last traces by passing a current of steam. The residue was twice crystallized from ethyl acetate-acetone mixture when the flavonol methyl ether (III) was obtained as colourless small rectangular prisms melting at 220°-21°; yield 0·3 g. (found: C, 64·8; H, 6·0; $C_{21}H_{22}O_7$ requires: C, 65·3; H, 5·7 per cent). It is insoluble in alkali and does not give any colour with alcoholic ferric chloride.

(ii) An intimate mixture of 3-methyl-ω: 4: 6-trimethoxy-2-hydroxy acetophenone (I) (3 g.), sodium veratrate (3 g.) and veratric anhydride (20 g.) was heated for 4 hr. under reduced pressure. The product was refluxed with 8 per cent alcoholic potash (100 cc.) for half an hour. After removal of alcohol under vacuum, water was added to the residue and the colourless solid that separated out was filtered, washed with water and dried. It crystallized from a mixture of ethyl acetate and acetone as colourless small rectangular prisms melting at 220°-21° which was undepressed when mixed with the sample prepared by method (i); yield 2·5 g.

8-*Methyl quercetin* (IV)—8-Methyl-*o*-pentamethyl quercetin (III) (0·5 g.) was refluxed with hydriodic acid (d, 1·7; 15 cc.) for 3 hr. and the mixture cooled and poured into sodium bisulphite solution. The yellow precipitate was filtered, washed with water and macerated with 5 per cent aqueous sodium carbonate. The small undissolved portion was filtered off and the clear filtrate after neutralization with hydrochloric acid was extracted with ether. The ether solution was dried over anhydrous sodium sulphate, evaporated and the yellow residue was crystallized from ethyl acetate; yield 0·35 g. It was purified further by acetylating it in the usual way. The acetate was twice crystallized from ethyl acetate-petroleum ether mixture when it was obtained as colourless flat needles melting at 179°-80°. It (0·25 g.) was then refluxed with alcoholic hydrochloric acid (1: 1, 16 cc.) for 1 hr. and when the solution was diluted with water it yielded a yellow precipitate. It was filtered, washed with water and dried. It crystallized from ethyl acetate as pale yellow small prisms melting at 304°-5° (found: C, 60·0; H, 4·6; $C_{16}H_{12}O_7$ requires: C, 60·7; H, 3·8 per cent). It readily dissolves in sodium carbonate or sodium hydroxide solution and gives a green colour with alcoholic ferric chloride.

In order to confirm that no isomerization had taken place during demethylation with hydriodic acid the above product (100 mg.) was completely methylated by refluxing for 75 hr. with excess of dimethyl sulphate (0·5 cc.) and dry potassium carbonate (1 g.) in acetone medium. The potassium salts were filtered off and washed well with hot acetone. The combined filtrate was concentrated and excess of dimethyl sulphate was removed by washing with petroleum ether. The white solid product was filtered and crystallized from ethyl acetate-acetone mixture when it separated as colourless rectangular prisms melting at 220°-21° which was undepressed when mixed with an authentic sample of 8-methyl-*o*-pentamethyl quercetin (III).

3 - *Methyl* - ω - *methoxy phloracetophenone* (VI) — To an ice-cooled solution of C-methyl phloroglucinol (5 g.) and methoxy acetonitrile (3 cc.) in dry ether (60 cc.) was added freshly fused zinc chloride (2 g.) and a rapid stream of dry hydrogen chloride gas was passed through it for 3 hr. On leaving overnight, the ketimine hydrochloride separated as a yellow crust. The ethereal layer was decanted off, the hydrochloride washed with dry ether and heated with water (75 cc.) for 2 hr. on a boiling water bath. On cooling to 0°, a yellow solid separated out. It was filtered and washed with a little water. It came out as a colourless solid and crystallized from a mixture of ether and petroleum ether as colourless small prisms melting at 206°-7°; yield 2·4 g. (found: C, 50·5; H, 5·9; $C_{10}H_{12}O_5$, $1\frac{1}{2}H_2O$ requires: C, 50·2; H, 6·2 per cent). It is highly soluble in alcohol, acetone and ether but sparingly so in petroleum

ether. It gives a bluish violet colour with alcoholic ferric chloride.

6-*Methyl and* 8-*methyl*-3: 3′: 4′-*o-trimethyl quercetins* (VIII *and* VII) — A well-powdered mixture of 3-methyl-ω-methoxy phloracetophenone (VI) (4 g.), veratric anhydride (25 g.) and sodium veratrate (4 g.) was heated under reduced pressure at 180°-84° for 4 hr. The cooled product was powdered and dissolved in ethanol (150 cc.) and water (10 cc.) containing potassium hydroxide (12 g.) and the resulting solution boiled under reflux for 20 min. The solvents were then removed under reduced pressure and the residue dissolved in water (250 cc.). A rapid passage of carbon dioxide through this solution separated a pale yellow solid (3·5 g.) which was filtered and washed with water. It was dissolved in rectified spirit (150 cc.), treated with animal charcoal and filtered.

(a) *First fraction*: 6-*C-methyl derivatives* — The clear alcoholic solution, on cooling, separated a bright yellow crystalline solid melting between 215° and 245°. It was dissolved in boiling methyl alcohol and allowed to cool slowly. The crystals which separated out were filtered and then thrice crystallized from methyl alcohol when straw yellow plates were obtained, m.p. 263°-64°; yield 0·6 g. (found: C, 63·5; H, 5·0; $C_{19}H_{18}O_7$ requires: C, 63·7; H, 5·0 per cent). It gives a green colour with alcoholic ferric chloride. It (100 mg.) was acetylated by refluxing with acetic anhydride (5 cc.) and a few drops of pyridine. The acetate crystallized from ethyl acetate-petroleum ether mixture as colourless fibrous needles melting at 202°-3°. Another 100 mg. of the compound was completely methylated by refluxing with dimethyl sulphate (0·9 cc. in 3 lots) and potassium carbonate (2 g.) in acetone solution until it gave no ferric reaction (150 hr.). The filtered acetone solution was evaporated and the dark red viscous liquid was stirred with aqueous sodium hydroxide. The solid so obtained was repeatedly crystallized from methanol when the complete methyl ether (IXa) was obtained as colourless stout rectangular prisms melting at 164°-65° which is far below that of 8-methyl quercetin pentamethyl ether (III) (220°-21°) (found: C, 65·1; H, 5·9; $C_{21}H_{22}O_7$ requires: C, 65·3; H, 5·7 per cent).

(b) *Second fraction*: 8-*methyl derivatives* — The methyl alcoholic mother liquors, on concentration, deposited a yellow crystalline solid (2·5 g.) which melted between 221° and 235°. It was acetylated in the usual way. The acetate was thrice crystallized from ethyl acetate-petroleum ether mixture when it melted at 192°-93°. The acetate (2·5 g.) was refluxed with alcoholic hydrochloric acid (1: 1; 120 cc.) for 45 min. on a boiling water bath. On dilution with an equal volume of water and cooling, a yellow crystalline product was obtained. It was filtered, washed with water and twice crystallized from methyl alcohol when it formed yellow needles melting at 236°-38°; yield 1·6 g. It gives a green colour with alcoholic ferric chloride (found: C, 60·7; H, 5·5; $C_{19}H_{18}O_7.H_2O$ requires: C, 60·6; H, 5·3 per cent). Complete methylation of this as in the previous case yielded 8-methyl quercetin pentamethyl ether (III) identical with the one prepared earlier.

6-*Methyl quercetin* (XI) — 6-Methyl-3: 3′: 4′-*o*-trimethyl quercetin (VIII) (100 mg.) was refluxed with hydriodic acid (d, 1·7; 5 cc.) for 3 hr., and the yellow solid obtained by pouring the cooled reaction mixture into saturated sodium bisulphite solution was collected and thrice crystallized from methyl alcohol when 6-methyl quercetin (XI) formed yellow tiny prisms melting at 285°-86°; yield 50 mg. (found: C, 57·4; H, 4·4; $C_{16}H_{12}O_7.H_2O$ requires: C, 57·5; H, 4·2 per cent). It gives a light green colour with alcoholic ferric chloride. The acetate obtained from this (20 mg.) by refluxing with acetic anhydride and a few drops of pyridine for 5 hr. was crystallized twice from ethyl acetate-petroleum ether mixture when it separated out as colourless shining flat needles melting at 203°-4°.

6-*Methyl*-3 : 7 : 3′ : 4′-*o-tetramethyl quercetin* (X) — The trimethyl ether (VIII) (150 mg.) was dissolved in dry acetone (150 cc.) and heated under reflux with dimethyl sulphate (0·5 cc., 1 mole) and dry potassium carbonate (0·5 g.) for 12 hr. Acetone was distilled off and water added to dissolve potassium salts. The white solid which separated out was filtered, washed with water and then with a little petroleum ether. It was repeatedly crystallized from methyl alcohol when it was obtained as colourless thick rectangular plates and prisms melting at 183°-84°; yield 100 mg. (found: C, 63·0; H, 4·8; $C_{20}H_{20}O_7$, $\frac{1}{2}H_2O$ requires: C, 63·0; H, 5·5 per cent). It is sparingly soluble in aqueous sodium hydroxide and imparts a green colour to alcoholic ferric chloride.

The acetate prepared by acetylation with acetic anhydride and pyridine crystallized from alcohol as colourless long rectangular plates melting at 178°-80°.

8-*Methyl*-3 : 7 : 3′ : 4′-*o-tetramethyl quercetin* (V) — The trimethyl ether (VII) on methylation with 1 mole of dimethyl sulphate and 8-methyl quercetin (IV) with 4·4 moles of dimethyl sulphate and working up the products as described in the case of the 6-methyl derivative gave 8-methyl-3: 7: 3′: 4′-*o*-tetramethyl quercetin (V) which crystallized from methyl alcohol as yellow needles and rectangular rods melting at 158°-59°. It gives a green colour with alcoholic ferric chloride (found: C, 64·6; H, 5·8; $C_{20}H_{20}O_7$ requires: C, 64·5; H, 5·4 per cent).

Nuclear methylation of quercetin — The method of Perkin[1] was followed with modifications. Pure quercetin (10 g.) was treated with methyl alcohol (120 cc.) and methyl iodide (60 cc.) and gently refluxed with a solution of potassium hydroxide (20 g.) in methyl alcohol (75 cc.), added in the course of 16 hr. The yellow creamy mass of potassium quercetin at first formed disappeared; after about 6 hr. a clear solution resulted and at the close of the operation, the addition of fresh alkali gave no change in colour. After removal of methyl iodide and methyl alcohol by distillation, the residue was diluted with water, the mixture extracted with ether containing a little chloroform and the ethereal solution washed with 2 per cent alkali and alkaline washings (A) were reserved for examination.

The ether solution was evaporated and the resulting solid (nearly 2 g.) was dissolved in absolute alcohol and potassium hydroxide (0·25 g.) added when an orange solution resulted. Alcohol was removed as quickly as possible and the residue was exhaustively extracted with dry benzene (benzene solution B). The potassium salt remaining insoluble in benzene was decomposed with dilute hydrochloric acid and the product was repeatedly crystallized from methyl alcohol. The sparingly soluble fraction (1·2 g.) melted at 175°-79° (methyl alcoholic mother liquor C). It was acetylated and the acetate was crystallized twice from ethyl acetate when it melted at 179°-80°. When hydrolysed with 50 per cent alcoholic hydrochloric acid, it yielded a compound melting at 184°-85° and identical with 6-methyl quercetin 3: 7: 3′: 4′-tetramethyl ether (X). Identity was further confirmed by complete methylation and comparing the ether with synthetic 6-methyl quercetin pentamethyl ether (IX). The benzene solution (B) did not give any C-methyl product, but yielded only a small quantity of quercetin pentamethyl ether (m.p. 151°-52°). The methyl alcoholic mother liquor (C) yielded a small amount of quercetin tetramethyl ether (m.p. 156°). The alkaline solution (A) on saturation with common salt yielded a curdy precipitate which crystallized from acetone as colourless needles melting at 150°-51° identical with quercetin pentamethyl ether; yield 5 g.

3 : 3′: 4′-*o-Trimethyl quercetin*-8-*aldehyde* (XIIb) — Quercetin 3: 3′: 4′-trimethyl ether[6] (1 g.) (XIIa) and hexamine (4 g.) were heated in glacial acetic acid solution on a steam bath under dry conditions for 6 hr.; dilute hydrochloric acid (1: 1, 40 cc.) added and the heating continued for half an hour, the solution diluted with water and then cooled. A yellow solid (0·6 g.) separated out. It was filtered and repeatedly crystallized from glacial acetic acid when the aldehyde separated as pale yellow tiny needles and prisms melting at 260°-61°. It gives a reddish brown colour with alcoholic ferric chloride and does not dissolve in aqueous alkali (found: C, 59·8; H, 4·1; $C_{19}H_{16}O_8$, $\frac{1}{2}H_2O$ requires: C, 59·8; H, 4·4 per cent). The 2: 4-dinitrophenyl hydrazone crystallized from glacial acetic acid as red aggregates of small prisms melting at 273°-74° with decomposition.

Reduction — A solution of the above flavonol aldehyde (0·5 g.) in glacial acetic acid (500 cc.) was treated with palladium charcoal (2 g.) and the whole mixture was shaken well in an atmosphere of hydrogen until it absorbed exactly 2 moles of pure hydrogen gas. The catalyst was filtered off, washed well with hot glacial acetic acid and the filtrate was distilled under reduced pressure to remove the solvent. The residue was then treated with water and the whole mixture extracted with ether. The ether solution was exhaustively extracted with 5 per cent sodium carbonate. The alkaline solution on acidification yielded a pale yellow solid which crystallized from methyl alcohol as pale yellow needles melting at 236°-37°, alone or when mixed with the synthetic sample of 8-methyl quercetin-3: 3′: 4′-trimethyl ether described earlier; yield 0·3 g.

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Hydroxy Ketones: Part I—Fries Rearrangement of the Phenyl & Isomeric Cresyl Esters of 1-Naphthoic Acid

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The Fries migration of the phenyl and isomeric cresyl esters of 1-naphthoic acid have been studied at 120° and 160°C. With one exception in which the para-ketone was formed from phenyl-1-naphthoate at the higher temperature, all the others conform to the general pattern of migration of acyl groups.

WHILE considerable amount of work has been done on the synthesis of hydroxy ketones from esters of phenols by Fries reaction, not much work has been done on the esters of polyhydric phenols, long chain unsaturated acids and aromatic acids.

The precise position taken up by the migrating group in polyhydric phenols is affected by the nature of the phenol, the reaction temperature, the acyl group and the amount of aluminium chloride. The effect of temperature on the course of the Fries reaction has been studied by a number of workers[1,2]. Rosenmund and Schnur[3] developed two general procedures for preparing para- and ortho-hydroxy ketones by employing lower temperatures for the former and higher temperatures for the latter. Cox[4] employed aromatic acids and pointed out that the method has distinct advantages over Friedel and Crafts reaction for the preparation of benzoyl cresols. The migration of the differently substituted phenolic esters has also been studied[2], and it was found that nitro, acetyl and carboxyl groups in the phenolic ring have a profound influence on the nature of the product.

A perusal of the literature revealed that hardly any work has been done on the migration of the phenolic esters of condensed ring system acids, though this migration has of late been studied with the esters of simple substituted aromatic acids[5].

Work was, therefore, started in these laboratories to study the behaviour of these complex esters and the present paper deals with the migration of the phenyl and isomeric cresyl esters of 1-naphthoic acid[6].

The reactions have been studied in the absence of any solvent at two different temperatures, viz. 120° and 160°C. At higher temperatures ortho-hydroxy ketone was obtained and at lower temperatures para-hydroxy ketones. It was observed, contrary to the predictions of Baltzly and Bass[7], that the bulky naphthyl group had a tendency to occupy the para position even under conditions favourable for ortho migration. Our observations support the findings of previous workers as regards the influence of the presence of the alkyl group in the phenolic part of the molecule and the effect of temperature on the course of the migration.

However, there was one departure where the formation of para-hydroxy ketone from phenyl-1-naphthoate was observed at 160°C.

Experimental procedure

1-*Naphthoic acid chloride* required for the preparation of the phenolic esters was prepared according to the method described in *Organic Synthesis*[8].

Preparation of the esters — To the acid chloride (1 mole) contained in a conical flask (100 cc.) phenol (1·1 mole) was added followed by the addition of a solution of sodium hydroxide (10 per cent) till alkaline. The reaction mixture was cooled in ice and the solid separating out on shaking was filtered, washed and crystallized from dilute alcohol to give the pure ester.

Fries rearrangement of the esters of 1-*naphthoic acid and the formation of the hydroxy ketones* — The ester (1 mole) was intimately mixed with powdered anhydrous aluminium chloride (1·3 mole) in a round bottom flask (100 cc.) fitted with an air condenser and a calcium chloride tube and the contents heated in an oil bath for 2 hr. at 120° and 160°C. The dark red crystalline mass obtained on cooling was hydrolysed with ice-cold hydrochloric acid (1:1) and extracted with ether.

The aqueous layer was shaken up with ether (twice) and the combined ethereal extracts were washed successively with sodium bicarbonate solution (2 per cent), sodium carbonate solution (1 per cent) and finally with water. The ethereal solution was dried over anhydrous sodium sulphate. The residue was triturated with petroleum ether containing a few drops of benzene, which on warming effected the separation of the isomeric hydroxy ketones. Finally, the two ketones were crystallized from dilute alcohol or petroleum ether.

The sodium carbonate extract, on acidification, in some cases furnished the para-hydroxy ketones in a pure form. The ketones were characterized through their 2: 4-dinitrophenylhydrazones. The results of analysis are given in Table 1.

The *o*-hydroxy ketones gave a violet colouration with ferric chloride and were identified as 2: 4-dinitrophenylhydrazones with the following characteristics: (1) dark red needles, m.p. 286°-87°; (2) orange needles, m.p. 260°-61°; (3) dark red needles, m.p. 290°; and (4) red plates, m.p. 222°.

TABLE 1 — ANALYSIS OF KETONES

Ester	M.P. °C.	Mol. formula	Found % C	Found % H	Required % C	Required % H	Reaction temp. °C.	Ketone	Appearance	M.P. °C.	Found % C	Found % H	Required % C	Required % H
Phenyl-1-naphthoate	106	$C_{17}H_{12}O_2$	81·8	4·9	82·2	4·8	120	4-Hydroxyphenyl-(1)-naphthyl ketone	Yellow needles	165-66	81·7	4·6	82·2	4·8
							160	do	do	165-66	81·7	4·6	82·2	4·8
o-Cresyl-1-naphthoate	90	$C_{18}H_{14}O_2$	81·9	5·2	82·4	5·3	120	4-Hydroxy-3-methyl-phenyl-(1)-naphthyl ketone	Light brown rectangular plates	165	81·8	5·2	82·4	5·3
							160	No ketone was formed and free acid was obtained						
m-Cresyl-1-naphthoate	72	$C_{18}H_{14}O_2$	82·4	5·8	82·4	5·3	120	4-Hydroxy-2-methyl-phenyl-(1)-naphthyl ketone	Gummy solid characterized through 2: 4-dinitrophenylhydrazone	—	—	—	—	—
p-Cresyl-1-naphthoate	73	$C_{18}H_{14}O_2$	82·8	5·8	82·4	5·3	160	2-Hydroxy-5-methyl-phenyl-(1)-naphthyl ketone	Yellow needles	145	82·4	5·4	82·4	5·3

Acknowledgement

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Chemical Examination of the Root Bark of *Melodinus monogynus* Roxb.: Part I

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A bitter β-glucoside and two sterols have been isolated from the root bark of *Melodinus monogynus* Roxb. The glucoside, provisionally named melodin, $C_{25}H_{36}O_8.H_2O$, yields on hydrolysis the aglucone, melodinidin, $C_{19}H_{26}O_3$.

MELODINUS monogynus Roxb. [syn. *Nerium piscidium* Roxb.; N.O. *Apocynaceae*; vern. (Sylhet and Khasia): *sadulkou, echalat*] is a tall climber, growing in Sikkim Himalayas, Assam, Sylhet and Khasia mountains up to an altitude of 4,000 ft. Like many other Apocynaceae plants, its bark has long, tough fibres which are used locally as a substitute for hemp. The roots of the plant are thick and bitter, the bitter principle being particularly concentrated in the root bark. The plant is poisonous to fish[1,2] and is reported to possess hypnotic properties. It is also used locally as an antimalarial drug.

No work is reported on this plant in the literature and in view of its important physiological properties, it was considered of interest to carry out a systematic chemical examination of the root bark. As a result of the present study, the following crystalline products have been isolated.

1. A bitter β-glucoside, provisionally named melodin, $C_{25}H_{36}O_8.H_2O$; m.p. 128°; $[\alpha]_D^{18} = +40°$; yield 0·1 per cent on the weight of the dried root bark.

2. A sterol, provisionally named monogynol A, $C_{28}H_{48}O_2$; m.p. 238°; $[\alpha]_D^{18} = +24°$; yield 0·7 per cent on the weight of the dried root bark.

3. Another sterol, designated monogynol B, $C_{28}H_{46}O$; m.p. 208°; $[\alpha]_D^{18} = +34°$; yield 1·7 per cent on the weight of the dried root bark.

The total petroleum ether extracts of the root bark gave, on concentration, a mixture of the sterols, monogynol A and B, which were effectively separated through repeated fractional crystallization from acetone. Attempts at further purification through sublimation in high vacuum (10^{-4} mm.) resulted in the transformation of the higher melting monogynol A into the lower melting monogynol B. This was established through a comparison of their analytical data, and melting point and mixed melting point determinations. This transformation could take place through the elimination of a molecule of water from a tertiary hydroxyl group present in monogynol A leading to the formation of the unsaturated monogynol B. Monogynol B gives Liebermann-Burchardt reaction, adds bromine and absorbs one mole of hydrogen on catalytic reduction, while monogynol A does not respond to this colour reaction and does not absorb bromine or hydrogen. These two sterols yield the same mono-acetyl derivative, indicating the ease with which the tertiary hydroxyl of monogynol A is eliminated as a molecule of water.

The alcoholic percolates of the defatted drug powder gave a brown viscid mass which, on purification in the manner detailed in the experimental part, was obtained as an orange bitter viscous residue. It failed to crystallize from single or mixed solvents and was finally chromatographed in chloroform solution over an alumina column using ether, ethyl acetate and mixtures of ethyl acetate and methanol as the successive eluants. The ethyl acetate methanol eluates fractions gave a greyish residue which, on keeping in dilute alcohol, yielded the glucoside, melodin, in colourless, silky needles melting at 128°. The mother liquors, although bitter in taste, failed to crystallize.

Melodin analysed to the molecular formula $C_{25}H_{38}O_9$. It was soluble in acetone and ethyl acetate, and insoluble in water. It is hydrolysed by emulsin and with dilute acids; it gives the aglucone, melodinidin, $C_{19}H_{26}O_3$, and glucose. The apparent discrepancy between the molecular formula of melodin, $C_{25}H_{38}O_9$, arrived at on the basis of its analytical data, and $C_{25}H_{36}O_8$ calculated on the basis of the hydrolytic products, melodinidin and glucose, however, indicates a difference of H_2O. This is due, obviously, to the retention of a molecule of water by the glucoside, which could not be removed by drying the glucoside at $100°/10^{-1}$ mm. over phosphorus pentoxide. A similar observation was made by Rastogi, Sharma and Siddiqui[3] in the case of the glucoside, kutkin, isolated from *Picrorhiza kurrooa*.

The aglucone melodinidin, m.p. 148° and $[\alpha]^{25}_{D} = -60°$ (in pyridine solution), does not give any colouration with ferric chloride, and is insoluble in dilute alkali and sodium bicarbonate. It gives a positive Legal's test. On acetylation it yields a mono-acetyl derivative; m.p. 82°. Further work on the elucidation of its constitution is in progress.

Experimental procedure

The powdered root bark (375 g.), obtained from Shillong, Assam, was soxhleted with petroleum ether. The pale yellow extract was concentrated and kept in the cold when a solid deposit (8·4 g.; 2·4 per cent on the weight of the air-dried bark) was obtained which was filtered. It was fairly soluble in petroleum ether, ether, benzene, acetone and alcohol and insoluble in water, dilute acids or alkalies. On repeated fractional crystallization from acetone, monogynol A (0·7 g.) was finally separated from the more soluble monogynol B.

Monogynol A crystallizes from acetone in colourless needles; m.p. 232°; $[\alpha]^{18}_{D} = +24°$ (chloroform). It is soluble in acetone, ether and alcohol, sparingly so in petroleum ether and chloroform and insoluble in water, dilute acids and alkalies. It does not give any colouration with ferric chloride and does not absorb bromine in carbon tetrachloride solution. Its chloroform solution does not give any colouration with a mixture of sulphuric acid and acetic anhydride. A deep blood-red colouration is, however, obtained by the addition of sulphuric acid to its chloroform solution (found: C, 80·55; H, 11·5; $C_{28}H_{48}O_2$ requires: C, 80·7; H, 11·5 per cent).

On sublimation in high vacuum ($160°$-$66°/10^{-4}$ mm.), monogynol A gave a crystalline sublimate melting at 208°. The melting point of this product on recrystallization or vacuum sublimation did not rise any further. It did not give any depression in melting point on admixture with monogynol B (found: C, 84·07; H, 12·0; $C_{28}H_{46}O$ requires: C, 84·4; H, 11·6 per cent).

Monogynol A (0·5 g.) gave a monoacetyl derivative (0·35 g.) on heating with acetic anhydride and fused sodium acetate, and working up the reaction product in the usual manner. This was crystallized from dilute alcohol and obtained in colourless needles; m.p. 206°; $[\alpha]^{29}_{D} = +42°$ (benzene) (found: C, 81·56; H, 11·2; sap. equivalent, 438; $C_{28}H_{45}O.COCH_3$ requires: C, 81·8; H, 10·9 per cent; sap. equiv., 440).

Monogynol B was obtained in the form of colourless needles from its acetone solution; m.p. 208°; $[\alpha]^{18}_{D} = +34°$ (dioxan). It is soluble in chloroform, benzene, ether and petroleum ether, sparingly so in alcohol, and insoluble in water, dilute acids and alkalies. It does not give any colouration with ferric chloride, absorbs bromine in the cold in carbon tetrachloride solution and gives a purple-violet colouration with Liebermann-Burchardt reagent. Its chloroform solution gives a blood-red colouration with sulphuric acid (found: C, 84·1; H, 12·0; $C_{28}H_{46}O$ requires: C, 84·4; H, 11·6 per cent).

It is recovered unchanged on sublimation in high vacuum (10^{-3} mm.). The corresponding acetyl derivative prepared in the usual manner, m.p. 206° (yield 90 per cent); $[\alpha]^{29}_{D} = +42°$ (benzene), does not give any depression in melting point on admixture with the acetyl derivative of monogynol A (found: C, 81·5; H, 11·1; sap. equivalent, 437; $C_{28}H_{45}O.COCH_3$ requires: C, 81·8; H, 10·9 per cent; sap. equiv., 440).

Monogynol B (0·4 g.) was catalytically hydrogenated in the presence of platinum black in dioxan solution. After 3 hr., when the uptake of hydrogen had ceased, the mixture was filtered and freed of the solvent. The reduced product was crystallized from acetone; m.p. 165°; $[\alpha]^{29}_{D} = +40°$ (dioxan); hydrogen absorbed at N.T.P., 26 cc.; requires: for one double bond, 22·4 cc.

Melodin — The defatted powdered root bark was repeatedly percolated with alcohol at room temperature, and the combined percolates concentrated under reduced pressure. The dark brown bitter residue (15 g.) gave, on keeping in alcoholic solution in the cold, a crystalline deposit consisting mainly of sodium chloride and a small quantity of monogynol B. The filtrate was freed of the resinous impurities by partial precipitation with ether and petroleum ether. This gave a bitter orange-coloured alcohol-ether-petroleum ether solution. The precipitated water-soluble, non-bitter, dark-coloured viscous mass was not pursued further. On concentration of the bitter solution on the water bath and finally *in vacuo*, an orange-coloured residue was obtained which was insoluble in water, petroleum ether, ether and benzene, but soluble in other organic solvents. It, however, failed to crystallize from single or mixed solvents. A chloroform solution of this residue was then passed through an alumina column and the chromatogram successively eluted with ether, ethyl acetate and mixtures of ethyl acetate-methanol (9: 1, 4: 1, 3: 1 and 1: 1) and finally with methanol. The ether eluates gave some monogynol B and traces of an essential oil. The ethyl acetate eluate yielded a residue which was crystallized from dilute alcohol in colourless silky needles (50 mg.); m.p. 128° (melodin). The residues from ethyl acetate-methanol and methanol eluates, which were bitter in taste and which failed to crystallize from any of the solvents, were combined and purified through fractional precipitation of the impurities with ether. The final purified solution, on concentration and keeping in the cold, deposited more of the glucoside, which was crystallized from alcohol (300 mg.) (found: C, 62·1; H, 7·8; $C_{25}H_{38}O_9$ requires: C, 62·2; H, 7·8 per cent).

Melodin is insoluble in water, benzene or petroleum ether, sparingly soluble in ether, but soluble in ethyl acetate, acetone and alcohol. Its dilute acid hydrolysate reduces Fehling's solution.

An aqueous solution of emulsin (2 per cent) was added to a solution of the glucoside (2 per cent) in dilute alcohol, and the mixture incubated at 35° for 24 hr. The resultant mixture reduced Fehling's solution readily.

Hydrolysis of melodin (melodinidin) — The glucoside (100 mg.) was refluxed on the water bath with alcoholic hydrochloric acid (10 cc.; 1·5 per cent) for 2 hr. The reaction mixture was diluted with water and repeatedly extracted with ether. The ethereal solution was washed with water, dried over anhydrous sodium sulphate and freed of the solvent. The brown oily residue (60 mg.) so obtained failed to crystallize from solvents. It was chromatographed over alumina in benzene solution and subsequently eluted with ether and ether-ethanol (9: 1, 4: 1, 2: 1 and 1: 1) mixtures. The final ether-ethanol eluate (1: 1) yielded a yellow crystalline residue which, after repeated crystallizations from dilute alcohol, was obtained in colourless plates, m.p. 148°. It is insoluble in water and petroleum ether, sparingly so in benzene and ether, and soluble in other organic solvents. It does not give any colouration with ferric chloride and is insoluble in sodium bicarbonate and caustic soda solution [found: C, 75·4; H, 8·9; mol. wt. (Rast), 313; $C_{19}H_{26}O_3$ requires: C, 75·3; H, 8·6 per cent; mol. wt., 302].

Acetyl melodinidin — Melodinidin (40 mg.) was treated with acetyl chloride in dry pyridine solution at 0° and worked up in the usual manner. The acetyl derivative (30 mg.) so obtained was crystallized from dilute ethanol; m.p. 82° (found: C, 73·09; H, 8·75; acetyl value, 12·3; $C_{19}H_{25}O_3COCH_3$ requires: C, 73·2; H, 8·14 per cent; acetyl value, 12·49).

Identification of the sugar moiety — The sugar moiety of the glycoside was identified as glucose by ascending and descending paper partition chromatography of the hydrolysate, using water-saturated phenol and butanol-acetic acid-water (4: 1: 5) respectively and aniline hydrogen phthallate as the spraying reagent[4].

After removal of the aglucone, the acid hydrolysate was diluted with an equal volume of water, buffered by the addition of sodium acetate[5], and heated on the water bath for 45 min. with a mixture of phenyl hydrazine hydrochloride and sodium acetate (0·75 g. each). After 20 min. golden yellow crystals separated out which were filtered. The osazone was recrystallized from hot water, m.p. 206°. It gave no depression in melting point on admixture with an authentic sample of glucosazone.

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Changes in Ascorbic Acid Metabolism in Guinea Pigs During Fracture

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Fracture of the tibia and fibula in guinea pigs causes a decrease of ascorbic acid in the blood and urine of the animals. A similar decline is observed in most of the organs, except brain, lung and liver. Adrenal glands are the most affected.

IN recent years considerable attention has been paid to the changes in ascorbic acid metabolism of the adrenals during stress conditions. However, comparable studies on other tissues have been meagre. In acute stress conditions like fracture, there are losses of N, S, P, K and creatine in the urine due to damage of tissue and disuse atrophy of muscle and thereby the resistance of the body is decreased[1,2]. In view of the possible role of ascorbic acid in the defence mechanism of the body, the changes in its metabolism during stress conditions merit special consideration. Besides, this vitamin seems to play an important role in the focus of injury as its deficiency is known to disturb callus formation of broken bones[3]. But the extent to which such a local effect might contribute to the disturbance of ascorbic acid metabolism in the system has received little attention.

The present paper is the outcome of an attempt to investigate the alteration in the total ascorbic acid content of blood, urine and various tissues of guinea pigs during fracture of both tibia and fibula. It is expected that this study might lead to a better understanding of the biochemical changes observed during this condition.

Experimental procedure

Methods and materials — Male albino guinea pigs from the Central Drug Research Institute Colony, weighing between 400 and 500 g., were throughout maintained on a normal mixed diet of green grass and germinated gram. Before starting the experiment the animals were kept on this diet for a preliminary period of six days in order to attain constant level of ascorbic acid. Both tibia and fibula were then fractured by bending them suddenly with a pair of pliars and without breaking the skin. The blood, urine and tissues were collected from the animals after they had been made to fast for 24 hr. The determinations of the total ascorbic acid were done by the colorimetric method of Bessey, Lowry and Brock[4] using a Klett-Summerson photoelectric colorimeter (520 mμ filter).

Results

Blood — In order to study the effect of fracture on the ascorbic acid content of blood, four groups of guinea pigs, each consisting of 4 animals, were used. Two groups were used as controls and in the other two the bones were fractured. The purpose of using two groups simultaneously was to give rest and food to one group while the other was fasting. Blood from the heart of the guinea pigs was taken out alternately from two fractured groups at 24 hr. interval up to 168 hr. after fracture. Before fracturing the bones, the initial ascorbic acid content in the blood of each animal was determined. The ascorbic acid content was determined from 2 cc. oxalated blood, after precipitation of the protein by 5 per cent trichloroacetic acid. The values for the average ascorbic acid content (8 animals) for a period of 7 days are recorded in Table 1.

Table 1 shows that there was a progressive decrease in ascorbic acid content of blood up to the fourth day, and thereafter there was a slight rise. In order to show the rate of fall of ascorbic acid level of fractured animals, the average figures along with those of control were best fitted into a straight line represented by the equation $Y = a + bx$ where x and y represent days and ascorbic acid content respectively. From this, theoretical values corresponding to each day

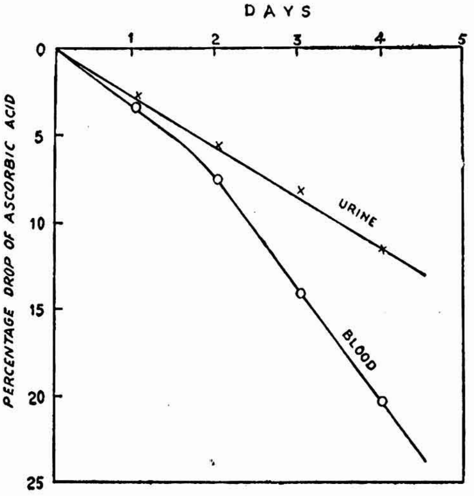

FIG. 1 — COMPARATIVE DROP IN ASCORBIC ACID LEVEL

TABLE 1 — CHANGES IN BLOOD ASCORBIC ACID OF NORMAL AND FRACTURED ANIMALS

(*γ ascorbic acid/100 cc. blood*)

CONDITION	DAYS							
	0	1	2	3	4	5	6	7
Normal	608	592	582	600	578	597	582	580
S.E. ±	7·3	11·1	13·2	11·5	8·1	2·5	8·6	8·1
Fracture	611	616	541	531	500	535	548	558
S.E. ±	8·1	15·6	33·6	22·2	26·4	12·2	11·5	11·1

S.E. = standard error.

TABLE 2 — ASCORBIC ACID EXCRETED IN THE URINE DURING 24 HR. PER GUINEA PIG

(*Ascorbic acid expressed in γ*)

CONDITION	DAYS							
	0	1	2	3	4	5	6	7
Normal	800	690	755	770	820	875	840	763
S.E. ±	66·6	63·5	74·4	11·5	80·2	25·0	10·0	69·0
Fracture	611	752	636	645	536	723	670	763
S.E. ±	59·8	88·0	13·3	40·4	16·6	95·0	20·0	40·7

S.E. = standard error.

were calculated. The extent of drop from the zero day value is expressed in percentages. This is illustrated in Fig. 1.

Urine — From the same fasting animals of the two groups, two at a time (one normal and one fractured) were kept in separate metabolic cages and 24 hr. sample of urine was then collected over sufficient quantity of glacial acetic acid. The washing of the cage and the funnel was done in such a way that the final concentration of acetic acid remained near about 10 per cent. The combined urine and washings were made up to 200 cc. with distilled water. Four cc. of the acidulated dilute urine after precipitation of protein with 5 per cent trichloroacetic acid was used for determining total ascorbic acid content. The values for average ascorbic acid content (8 animals) of urine from zero to seventh day are given in Table 2.

It would appear from the results given in Table 2 that both under normal and fractured conditions, an irregular fluctuation is observed in day-to-day urinary excretion of ascorbic acid; a maximum fall was observed in the fractured animals on the fourth day. The two straight lines obtained by fitting each point of the graph in case of normal and fractured animals represent the actual trend of ascorbic acid excretion in the urine during the first 4 days. The theoretical values and the extent of drop from the zero day were calculated as in the case of blood ascorbic acid and are given in Table 3 and Fig. 1 respectively.

Tissues and organs — Similar experiments were carried out with other groups of guinea pigs in order to determine the total ascorbic acid content of the tissues and organs like adrenal, spleen, brain, testes, liver, lungs, kidney, heart and thigh muscle of the control and fractured animals at 24, 48, 72, 96, 120, 144 and 168 hr. intervals. Every day following fracture till 7 days the animals were sacrificed from normal and fractured groups and the samples of various organs and tissues removed for analysis. The weighed organs and tissues were ground with acid-washed sea sand and extracted with acetate buffer (*p*H 4·8). The ascorbic acid content was determined in 4 cc. aliquot of the protein-free filtrate. The average values for ascorbic acid in the organs and tissues of normal and fractured animals are given in Table 4.

It appears from Table 4 that except for a few organs it is very difficult to draw any conclusion as to the changes of ascorbic acid content observed. In order to obtain a straight

TABLE 3 — CALCULATED VALUES OF ASCORBIC ACID IN BLOOD AND URINE

DAYS	CONDITION			
	Ascorbic acid/100 cc. blood γ		Ascorbic acid excreted in urine per day per guinea pig γ	
	Normal	Fracture	Normal	Fracture
0	602·4	621·2	763·0	687·7
1	592·0	590·5	755·0	662·1
2	586·8	559·8	747·0	636·5
3	596·8	529·8	739·0	610·9
4	581·6	498·4	731·0	583·3

TABLE 4 — AVERAGE VALUES FOR ASCORBIC ACID IN FRACTURED ANIMALS UP TO THE SEVENTH DAY

(*Ascorbic acid expressed in γ*)

ORGAN OR TISSUE	NORMAL VALUES MEAN*	VALUES AFTER FRACTURE†, DAYS						
		1	2	3	4	5	6	7
Adrenal	936	550	560	630	590	425	550	550
S.E. ±	32·5	25·3	—	—	—	—	—	40·8
Spleen	450	335	215	375	330	374	365	360
S.E. ±	10·8	11·5	—	—	—	—	—	11·5
Brain	253	200	235	257	245	230	236	233
S.E. ±	27·8	8·1	—	—	—	—	—	2·03
Testes	251	230	240	240	250	170	175	230
S.E. ±	3·6	2·8	—	—	—	—	—	17·3
Lungs	235	—	245	290	200	230	210	247
S.E. ±	17·7	—	—	—	—	—	—	1·07
Kidney	180	98·7	98·7	130	140	115	130	200
S.E. ±	10·1	2·2	—	—	—	—	—	5·7
Liver	157	130	—	182	140	165	165	150
S.E. ±	4·15	4·08	—	—	—	—	—	4·6
Heart	100	60	80	82	—	65	94	110
S.E. ±	3·1	2·8	—	—	—	—	—	4·5
Muscle	97	80	65	65	88	67	72	83
S.E. ±	3·2	3·5	—	—	—	—	—	3·6

*Average of 5 guinea pigs. †Average of 7 guinea pigs.

line relation ($Y = a + bx$) or curve of ascorbic acid variations through seven days, values for ascorbic acid for every day, for all the organs, were obtained by the method of least squares. The straight line curve was extrapolated to meet the Y-axis. This gave the calculated theoretical initial ascorbic acid level after 24 hr. From the slope of this theoretical curve it was easy to calculate the final ascorbic acid content after 7 days. Taking this calculated initial and final ascorbic acid level (i.e. first day and seventh day values), a histogram, in descending order in respect of the organs, has been drawn. For comparison the mean normal values are also included side by side (FIG. 2).

The histogram shows that in the case of adrenal gland, there was *c.* 38 per cent reduction in the total ascorbic acid content 24 hr. after fracture, and during the 7 days the ascorbic acid concentration remained at a low level and there was a tendency to decrease further. A marked change in ascorbic acid content was observed in the spleen. The percentage decrease on the first and seventh day was 34 and 16 per cent respectively. Similar difference between normal and fractured animals was also observed in kidney, heart and muscle; the percentage decrease on the first day from normal was 45·4, 35·3 and 34·6 respectively. In all these cases the tendency to regain the normal value is marked on the seventh day. The relatively small difference in the ascorbic acid level of brain, lungs and liver appears to be insignificant although in each case there is slight decrease on the first day followed by a similar increase on the seventh day. Testes also undergoes a decrease which is maximum on the seventh day after fracture, i.e. *c.* 21 per cent of the normal.

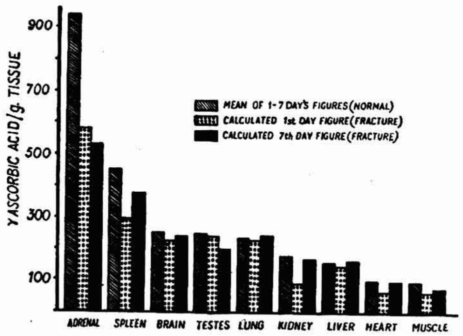

FIG. 2 — HISTOGRAM SHOWING LEVEL OF ASCORBIC ACID

Discussion

The data presented in this study clearly indicate that the fracture of the tibia and fibula of guinea pigs causes a decrease in the total ascorbic acid content of the system. The plasma ascorbic acid decreases initially and then rises approximately to the normal level. The urinary elimination of ascorbic acid also decreases during fracture condition; the percentage drop is lower than that in blood. This increased tolerance may be due to increased need for ascorbic acid by the tissues and its direct utilization by the injured tissues.

Of all the glands and tissues examined, the adrenal gland is the most affected. This finding confirms the observed fall in ascorbic acid or cholesterol content and secretion of adrenal corticoid during stress conditions other than fracture.

The changes which take place in the spleen may be due to the release of ascorbic acid into the general circulation in states of emergency.

Whether the loss in ascorbic acid suffered by the kidney is due to the elimination of vitamin in urine or due to its return to the blood (as it is one of the threshold substances) cannot be definitely ascertained from this study. It is difficult to say whether the changes in kidney due to fracture is a direct or an indirect effect. Similar significant decrease observed in the ascorbic acid concentration in the testes, heart and muscle may be due to disturbed or disordered tissue metabolism which is a common feature during general adaptation syndrome where profound disturbance of bodily function occurs[6]. On the other hand, brain, liver and lung appear to be unaffected. It may be presumed that these organs are capable of resisting any change following fracture. It seems from this study that, as the animal recovers, the demand for ascorbic acid is less and the concentration of ascorbic acid during this period is restored to near about normal level in all tissues except in adrenals and testes.

Although the actual mechanism involved in the metabolism of ascorbic acid under stress conditions is not known, according to Deane and Morse[7], the decline in ascorbic acid level is associated with the inability of the cortical cells to synthesize steriod hormones. How far this type of injury impairs the function of the cortical cells requires further investigation.

Summary

1. The fracture of the tibia and fibula of guinea pigs causes a diminution of ascorbic acid in the system.
2. There is an initial fall in the ascorbic acid content of blood first which later rises to near about normal level.
3. There is a decrease in the amount of ascorbic acid excreted in urine during this condition.
4. A decrease in ascorbic acid level was observed in adrenal gland, spleen, testes, kidney, heart and muscles of the fractured animals whereas in brain, lung and liver it is not significantly affected.

Acknowledgement

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A Phosphate Titrimetric Procedure for the Estimation of Magnesium, Zinc, Manganese & Cadmium

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The method of titrating phosphates by bismuthyl perchlorate in presence of diallyldithiocarbamido-hydrazine in chloroform as indicator has been extended to the estimation of magnesium, zinc, manganese and cadmium. These metals are precipitated as their double ammonium phosphates and titrated with bismuthyl perchlorate after dissolution in dilute perchloric acid. From the phosphate contents of the precipitates the stoichiometric equivalents of the metals are computed. Besides being equally reliable, the titrimetric method is simpler and more elegant than its gravimetric counterpart.

THOUGH many metals are precipitated as insoluble phosphates under specific conditions, only a few of the latter are finally weighed as such in quantitative estimations. Thus zirconium, which precipitates as the zirconyl phosphate in strongly acid solution, is weighed as the pyrophosphate. Aluminium forms a normal orthophosphate in buffered, slightly acid solution, and is weighed as such. Zinc, cadmium, manganese and magnesium, which form double ammonium phosphates, are usually weighed as their pyrophosphates. Beryllium, cobalt and nickel may also be precipitated as their double ammonium phosphates under specified conditions though they are seldom used in their quantitative estimation since better methods are available. Despite the fact that the gravimetric estimations of some of these metals as their pyrophosphates are standard procedures, the ignition of a double ammonium phosphate precipitate to the pyrophosphate is admittedly a difficult job. An element of uncertainty exists in the composition of the final product to be weighed. The estimation of magnesium[1] is a typical example. It would, therefore, seem desirable to eliminate the "ignition procedure" by estimating the phosphate content of the precipitate directly and calculating the metal equivalent therefrom.

The author has shown in a recent paper[2] that orthophosphates in solution can be satisfactorily titrated with bismuthyl perchlorate using diallyl-dithiocarbamidohydrazine as internal indicator. This method has been used with advantage in estimating the phosphate content of several metal phosphates which are precipitated quantitatively. The phosphate precipitates are dissolved in dilute perchloric acid and directly titrated with bismuthyl perchlorate, provided the metals in question do not induce co-precipitation of phosphate by precipitating with bismuth phosphate. The results obtained in the earlier studies[2] indicate that only aluminium in appreciable amounts co-precipitates with bismuth phosphate. Cadmium, which was not included in the previous studies[2], has since been found not to co-precipitate. In this paper the applicability of the proposed titrimetric procedure has been studied with respect to the double ammonium phosphates of magnesium, zinc, manganese and cadmium.

Experimental procedure

Indicator and standards — Diallyl-dithiocarbamido-hydrazine indicator (a saturated solution in chloroform), standard bismuthyl perchlorate solution (7·8 g. of Bi_2O_3 in a litre) and standard phosphate solution (4·536 g. of KH_2PO_4 in a litre) were prepared as described in the earlier paper[2].

Standard magnesium solution — One gram of ignited A.R. magnesium oxide (which was tested for its purity by standard methods) was dissolved in dilute hydrochloric acid and made up to 250 cc.

Standard zinc solution — One gram of ignited A.R. zinc oxide (which was tested for its purity by standard methods) was dissolved in dilute hydrochloric acid and made up to 250 cc.

Standard manganese solution — Half gram of pure manganese metal was dissolved in dilute nitric acid and made up to 250 cc. Its strength was checked by estimating manganese in an aliquot by the well-known bismuthate method.

Standard cadmium solution — Half gram of pure cadmium metal was dissolved in dilute hydrochloric acid containing a few drops of nitric acid and made up to 250 cc. The purity of the cadmium metal was ascertained by testing for metallic impurities, particularly for zinc, and finally weighing as cadmium sulphate.

Estimation of magnesium — An aliquot of the standard magnesium solution was pipetted out into a 400 cc. pyrex beaker, 10 g. of ammonium chloride added and diluted to about 150 cc. with distilled water. Twenty cc. of a 10 per cent solution of diammonium phosphate were added, followed by 1: 1 ammonia till a precipitate just formed. After stirring vigorously for a few minutes, 10 cc. of concentrated ammonia liquor were added, and the precipitate allowed to settle for 4 hr. It was then filtered through quantitative filter paper and washed free of chloride with 1: 9 ammonia. The precipitate was transferred to a 500 cc. conical flask, 7 cc. of 7 per cent perchloric acid added and shaken. The precipitate should dissolve to give a clear solution. It was diluted to about 100 cc. with distilled water and 10 cc. of the indicator diallyl-dithiocarbamido-hydrazine in chloroform added. Standard bismuthyl perchlorate solution was then slowly run in from a burette keeping the contents of the flask well shaken till the indicator layer at the bottom acquires an orange tinge. The titre gives the phosphate content of the magnesium ammonium phosphate precipitate from which magnesium was calculated assuming the formula of the precipitate to be $MgNH_4PO_4$. The results of estimations with pure magnesium chloride solutions are given in Table 1.

Magnesium in presence of other cations — While a prior separation of practically all the bases except the alkalies is normally necessary before precipitating magnesium ammonium phosphate, the interference of metals like aluminium, iron and titanium is sometimes overcome by complexing them with ammonium citrate. In Table 2 the results of such estimations obtained after a double precipitation are compared against those obtained in the gravimetric pyrophosphate method under similar conditions. Five grams of ammonium citrate are added in the first precipitation. In the reprecipitation, 0·5 g. of ammonium citrate is added and the excess of the precipitant is limited to 3 cc. of 10 per cent diammonium phosphate.

TABLE 1 — ESTIMATION OF MAGNESIUM BY THE TITRIMETRIC PROCEDURE

MgO TAKEN mg.	MgO FOUND mg.
20·0	19·8
40·0	39·9
60·0	60·1
80·0	79·8
100·0	99·9
150·0	150·2

TABLE 2 — ESTIMATION OF MAGNESIUM IN PRESENCE OF ELEMENTS COMPLEXED WITH CITRATE

SALT ADDED	MgO TAKEN mg.	MgO FOUND BY TITRATION mg.	MgO FOUND BY PYROPHOSPHATE PROCEDURE mg.
Ferric alum, 0·2 g. Fe	60·0	60·2	60·4
Aluminium nitrate, 0·2 g. Al	60·0	60·3	60·5
Titanium sulphate, 0·2 g. Ti	60·0	60·3	60·5
Fe+Al+Ti, 0·05 g. each	30·0	30·2	30·2

TABLE 3 — ESTIMATION OF MAGNESIUM IN PRESENCE OF ALKALI SALTS

SALT ADDED	MgO TAKEN mg.	MgO FOUND BY TITRATION		MgO FOUND BY PYROPHOSPHATE PROCEDURE	
		Single precipitation mg.	Double precipitation mg.	Single precipitation mg.	Double precipitation mg.
NaCl, 10 g.	60·0	61·6	59·7	62·5	60·1
KCl, 10 g.	60·0	60·6	59·8	64·1	60·8
NaCl+KCl, 5 g. each	60·0	61·4	59·8	63·6	60·6

Magnesium in presence of alkali metals — Appreciable amounts of alkali metals may often be present in solutions prepared for magnesium estimations, particularly when the sample is opened up by an alkali fusion. This gives rather high values for magnesium in the gravimetric pyrophosphate method, especially when double precipitations are not made[3]. To study their effect in the proposed method, several estimations were carried out after adding known amounts of alkali salts. In Table 3 a few of the results obtained by single as well as double precipitations are compared against those obtained in parallel estimations by the usual gravimetric method.

Estimation of zinc, manganese and cadmium — Taking an aliquot of the standard solutions of these elements, their double ammonium phosphates are precipitated and washed free of the precipitant by standard procedures. The dissolution of the precipitates in dilute perchloric acid and subsequent titration with bismuthyl perchlorate are carried out as described under magnesium. On the basis of the formula $MNH_4PO_4 \cdot xH_2O$ for the double ammonium phosphate precipitates, where M represents the above divalent metals, the respective metal equivalents are calculated from the phosphate content. The results are summarized in Tables 4, 5 and 6 respectively.

Results and conclusions

It is obvious from the results presented in Table 1 that the proposed titrimetric procedure of estimating magnesium from the phosphate content of its double ammonium phosphate yields results comparable with those obtained by any standard method. In the presence of interfering elements like aluminium, iron and titanium kept in solution with citrate, the titrimetric method gives results which are even slightly better than those obtained by the gravimetric pyrophosphate method under similar conditions (TABLE 2). Finally, the estimation of magnesium in presence of considerable amounts of potassium, where even a double precipitation does not ensure satisfactory results by the gravimetric method[3], the new titrimetric procedure gives more reliable

TABLE 4 — ESTIMATION OF ZINC BY THE TITRIMETRIC PROCEDURE

ZnO TAKEN mg.	ZnO FOUND mg.
20·0	20·1
40·0	39·6
60·0	60·1
100·0	100·3
130·0	129·8
160·0	160·3

TABLE 5 — ESTIMATION OF MANGANESE BY THE TITRIMETRIC PROCEDURE

Mn TAKEN mg.	Mn FOUND mg.
20·0	20·1
40·0	40·1
60·0	59·8
100·0	100·2
140·0	139·7
160·0	159·6

TABLE 6 — ESTIMATION OF CADMIUM BY THE TITRIMETRIC PROCEDURE

Cd TAKEN mg.	Cd FOUND mg.
20·0	20·1
40·0	39·7
60·0	59·7
100·0	99·6
140·0	139·4
160·0	159·3

values (TABLE 3). This is because the high results in the pyrophosphate method are partly due to the substitution of the ammonium radical by potassium or sodium in the magnesium ammonium phosphate. When such a precipitate is ignited, the alkali metals, unlike the combined ammonia, are retained by the precipitate even at high temperatures. But this substitution does not affect the accuracy of the titrimetric procedure, since it does not alter the ratio of phosphate to metal M in the precipitate. The somewhat high values obtained in single precipitations by the titrimetric method are probably caused by surface adsorption of soluble phosphates by magnesium ammonium phosphate precipitate.

Besides alkali substitution, there are other factors which are likely to affect the accuracy of the ignition procedure. The filter paper, which is used in preference to asbestos in filtering the strongly alkaline phosphate solutions, sometimes gets fire-proofed while igniting, and leaves behind a black and difficultly oxidizable residue[4]. Heating a phosphate precipitate with carbon at high temperatures may result in the loss of phosphorus by volatilization[5]. All such uncertainties are eliminated in a direct titrimetric procedure.

The same procedure can be adopted for estimating zinc, manganese and cadmium with equally satisfactory results as shown by data presented in Tables 4-6.

Acknowledgement

The author expresses his grateful thanks to Dr. J. Gupta for suggesting the problem and for his keen interest and guidance in the investigation.

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Carbohydrates for Fermentation Industries: Part III—Chemical Examination & Saccharification of Sugarcane Bagasse

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Samples of Indian sugarcane bagasse have been chemically analysed for their chief constituents. Saccharification of bagasse has been carried out by a method now used in commercial wood hydrolysis. By successive extraction of different batches of bagasse with cold concentrated hydrochloric acid, an extract of high sugar content was obtained. Crystalline glucose in good yields has been prepared from the concentrated acid extract.

INDIA'S sugar factories produce about 3½ million tons of sugarcane bagasse per annum[1]. It is chiefly used at present as a fuel in the factory boilers and attempts are continuously being made to convert it into useful products. Saccharification of the cellulose material in bagasse for the production of alcohol has frequently been suggested[2,3] in analogy with the utilization of wood sugar for fermentation. Wood hydrolysis was till recently of practical importance only under conditions of special emergency such as existed in Germany during the two world wars when, due to shortage of raw materials for fermentation and of protein foods and feeds, wood sugar was used for the production of alcohol and of food and fodder yeast. However, as a result of recent developments[4,5] the production of fermentable sugar and crystalline dextrose from wood waste appears to have reached the stage of successful exploitation in normal times.

Three methods have in general been used for the saccharification of cellulose in lignified tissues: (1) extraction with dilute acids by pressure percolation at temperatures of about 170°C. as in the Scholler[6] process; (2) extraction with cold concentrated sulphuric acid followed by dilution and heating after standing, as in the laboratory method of preparing glucose from cellulose; and (3) extraction with concentrated hydrochloric acid first initiated by Willstätter[7] and now used in the Rheinau process of Bergius.

For large-scale commercial operation the last method alone is considered to be of practical importance (for an authoritative discussion, *see* Hägglund[8]). The dilute acid treatment yields only very dilute sugar solutions; further at the high temperature used there is considerable destruction of sugars so that the yields are low. Treatment with concentrated sulphuric acid involves the use of large quantities of acid, which cannot be recovered as it is removed as calcium sulphate; on account of prohibitive cost this method has not found application on a commercial scale. Cold concentrated hydrochloric acid brings about the conversion of cellulose of woody tissues quantitatively into glucose[7] but its practical application in wood saccharification had to await the construction of suitable equipment from corrosion resistant material in which extraction of wood waste with concentrated hydrochloric acid and the recovery of the latter by vacuum distillation could be economically carried out. A feature of the process which has been of great importance for its commercial success is that concentrated hydrochloric acid, which has reached the limit of its extractive power on a batch of wood is capable of solubilizing more sugar when brought into contact with fresh material. By carrying out the extraction in a battery of diffusers with the fresh acid coming first into contact with the nearly extracted wood, and last with unextracted material, extracts containing high concentrations of sugar are obtained. A recent improvement introduced in the Rheinau process[9] is ar petreatment of wood with warm dilute acid for the removal of the hemicelluloses and pentosans, thus facilitating the crystallization of dextrose from the main hydrolysate.

In applying this method to the saccharification of bagasse it became necessary as a preliminary to carry out a chemical analysis of the material. A reasonably complete analysis comparable to those on woods is not available, although there are several references in the earlier literature[10] on the estimation of individual products obtainable from bagasse by different treatments. The two best known analyses[11] differ widely with respect to the values for important constituents.

This paper describes the chemical examination of bagasse with special reference to the constituent sugars, their extraction, identification and determination, and the preparation of crystalline dextrose from the bagasse hydrolysate.

Experimental procedure

Preparation of sample — Bagasse was obtained from four sugar factories: Ravalgaon Sugar Factory, Nasik; Saswad Mali Sugar Factory, Saswad; Walchandnagar Industries, Walchandnagar; and Modinagar Sugar Factory, Modinagar.

Large quantities of air-dried bagasse from each source were first passed through a Wiley mill and thoroughly homogenized. Each sample (in kg. lots) was then ground to pass through 60-80 mesh sieves and stored in airtight containers for analysis.

Moisture and ash were determined according to the standard method of A.O.A.C.

Alcohol-benzene extractives — Bagasse (2 g.) was extracted with an alcohol-benzene mixture (1 : 2) for 6-8 hr. and the extracted residue weighed after evaporation of the solvent and drying in a vacuum desiccator.

Pentosans were determined by conversion to furfural according to the method of Schorger[12].

About 1-2 g. of sample was distilled with 12 per cent hydrochloric acid, the distillate containing furfural being collected at the rate of 30 cc. in 10 min. The distillation was continued till the distillate gave a positive spot test with aniline acetate. The furfural was then precipitated from the distillate with a slight excess of phloroglucinol solution and the precipitate filtered after standing for 16 hr., washed with water and dried at 105°C.

TABLE 1 — ANALYSIS OF BAGASSE

SAMPLE	MOISTURE %	% DRY WEIGHT							
		Ash	Alcohol-benzene extractives	Pentosan	Cellulose	Pentosan in cellulose	Lignin	Uronic acid	Methoxyl
Ravalgaon Sugar Factory, Nasik	5·67	2·11	3·35	23·10	49·63	13·65	21·52	4·56	3·5
	5·70	2·04	3·40	23·00	49·89	13·77	21·72	4·61	3·7
Saswad Mali Sugar Factory, Saswad	5·36	2·05	3·50	24·15	47·54	12·75	20·80	4·61	3·3
	5·38	2·00	3·67	23·90	48·54	13·10	21·00	4·60	3·4
Walchandnagar Industries, Walchandnagar	5·38	2·42	4·23	23·53	49·93	14·08	21·00	4·50	3·3
	5·28	2·51	4·65	22·00	49·71	13·92	21·20	4·40	3·2
Modinagar Sugar Factory, Modinagar	6·37	3·16	2·40	23·20	47·58	12·34	23·82	4·12	2·9
	6·28	3·17	2·52	23·58	47·09	12·54	23·62	4·13	3·1

The dried precipitate was repeatedly extracted with hot alcohol to remove phloroglucides of substances other than furfural and then again dried and weighed. The pentosan was calculated from the weight of furfural phloroglucide using Krober's table[13].

Cellulose — The determination of cellulose was carried out according to Ritter and Mitchell[14], using a modified Cross and Bevan[15] method, which, according to Freeman[16], combines the most desirable feature of numerous modifications of the original method.

About 5 g. of sample was extracted with alcohol-benzene mixture (1: 2), washed successively with alcohol and water and the material chlorinated for 2-5 min. The residue was washed with 2 per cent sodium sulphite solution and the residue was again chlorinated. This process was repeated till the sodium sulphite washing was colourless indicating complete removal of lignin. Four to six chlorinations were usually found necessary. The cellulose residue was digested on a steam bath with distilled water to remove acids and salts, filtered, dried and weighed.

Pentosans in cellulose — Furfural was determined in the cellulose prepared as above and expressed as " pentosans in cellulose ", although the source of furfural in Cross and Bevan cellulose is uncertain.

Lignin was determined according to Goss and Phillips[17]. Bagasse (2 g.), after being successively extracted with alcohol-benzene mixture (1: 2), hot water and 1 per cent HCl, was suspended in ice-cold fuming hydrochloric acid saturated with dry hydrogen chloride gas. The contents after keeping at 8°-10°C. for 24 hr. were diluted, boiled, filtered, washed free of acid, dried at 105°C. and weighed.

Uronic acid was determined according to Dickson, Ottersen and Link[18], the carbon dioxide produced on treatment of 5 g. of bagasse with 12 per cent hydrochloric acid being absorbed in barium hydroxide and determined by titration.

The corrected percentage of carbon dioxide multiplied by four equals the percentage of uronic acid anhydride in the sample.

Methoxyl was estimated by the Zeissl method[19]. Results of the analysis are given in Table 1.

Saccharification and identification of sugars

Extraction with dilute acid — Bagasse (10 g.) was taken in a 100 cc. centrifuge bottle and kept at 60°-70°C. with 70-75 cc. of 4 per cent hydrochloric acid for 4-5 hr. with occasional stirring. The contents were centrifuged and the residue again treated with fresh acid. The process was repeated till the extract gave positive test with Bial's reagent for pentoses. Six to seven extractions were found necessary.

The combined centrifugate was hydrolysed by refluxing on a steam bath for 2 hr., decolourized with charcoal and filtered hot. The solution was then repeatedly evaporated *in vacuo* to a syrup with the addition of water to remove most of the hydrochloric acid and the residual syrup made up to volume. Aliquots were used for the identification and determination of the sugars.

The sugars present in the hydrolysate were identified by paper chromatography by the method of Partridge[20] using butanol-acetic acid as the developing solvent. The paper was irrigated for about 48 hr. and sprayed with aniline oxalate. Xylose and arabinose were found to be the main components present but the presence of small amounts of glucose and of uronic acid was also indicated (FIG. 1).

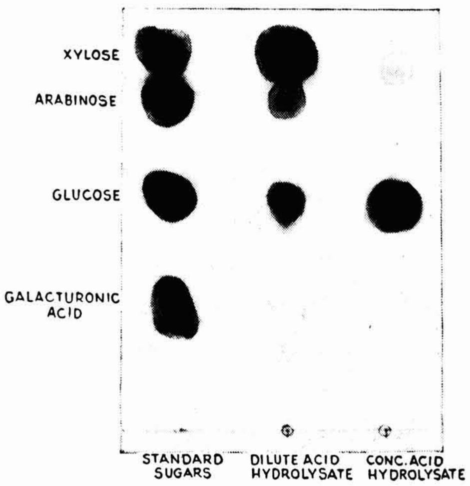

FIG. 1 — CHROMATOGRAM OF BAGASSE HYDROLYSATES

The total reducing sugar in the hydrolysate was estimated according to Bertrand[21], Glucose was determined by glucose oxidase[22] and the pentose value obtained by difference from the total reducing sugar as described by the method of Willstätter and Schudel[23] which has the advantage over other reduction methods for sugars in that the reaction involved is a stoichiometric one.

The fermentable sugar in the hydrolysate was determined by the method of Somogyi[24], as carried out by Saeman, Harris and Kline[25], the yeast used being prepared from a strain of baker's yeast, N.C.I.M. 3059. The reducing sugar was estimated before and after fermentation by Shaffer and Somogyi's method[26] using " reagent 50 ".

Extraction with concentrated acid — The bagasse extracted as described above with dilute acid was dried in a draught oven at 45°-55°C. to less than 10 per cent moisture content. To a weighed amount (6·4 g.) seven times the quantity of fuming hydrochloric acid was added and the mixture shaken overnight at 15°C. After filtering off the extract through a sintered glass funnel, the residue was again subjected to fresh acid as before. This process was repeated till the cellulose was completely hydrolysed as shown by the absence of reducing sugar in the extract. Four extractions were found necessary.

From the combined extracts hydrochloric acid was removed as far as possible by repeated evaporation *in vacuo* with the addition of water. The syrupy residue was taken up with water to give an acid strength of less than 2 per cent, heated for 30 min. at 120°C. in an autoclave to reconvert any polymerized sugars to the monomeric form[4] and then made up to volume.

Paper chromatography of the solution showed the presence of glucose and a trace of xylose (FIG. 1).

Reducing sugar, fermentable sugar and glucose were estimated by the methods already mentioned.

The results of the analysis of the sugars obtained by saccharification with dilute and concentrated hydrochloric acid are given in Table 2.

Preparation of crystalline dextrose — Bagasse (250 g.) was repeatedly extracted with warm dilute (4 per cent) hydrochloric acid to remove pentosans and the residue dried and extracted with cold fuming hydrochloric acid as described before. However, with the object of obtaining an acid extract with high sugar concentration, which is a necessary condition for success in commercial wood sugar production, the dry residue obtained above was extracted in small batches (10-15 g.) with the same lot of fuming hydrochloric acid. By this means acid solutions containing 18-20 per cent reducing sugar were obtained. In wood sugar hydrolysis, according to Hägglund[8], extracts containing over 30 per cent sugar have been obtained. This, however, includes

TABLE 2 — SACCHARIFICATION OF BAGASSE

HYDROLYSATE	% DRY WEIGHT				
	Extractable material	Reducing sugar (as glucose)	Fermentable sugar (as glucose)	Glucose (by glucose oxidase method)	Pentoses
Dilute acid (4%)	37·05	33·44	13·54	6·25	21·89
Concentrated acid	41·94	36·19	35·44	34·43	4·65
Total	78·99	69·63	48·98	40·68	25·54

the pentoses which in the present case had been removed by the previous extraction with warm dilute acid.

This hydrolysate, after removal of most of the acid and short hydrolysis for conversion of polymerized sugar as described before, was diluted to an acidity of less than 1N and passed through a column of anion exchange resin Amberlite IR-4B regenerated by the usual treatment with hydrochloric acid and sodium carbonate. The hydrochloric acid free effluent was acidified (*p*H 4·5) with a little acetic acid and evaporated under reduced pressure to a thin syrup. On leaving in the cold room with the addition of small amount of alcohol and inoculation with glucose crystals the material separated out in crystalline form. From a solution containing 18·5 g. sugar the first crop of crystals gave a yield of 11·2 g. of glucose of 92 per cent purity. On repeating the process with the mother liquor a second lot of 6·5 g. of glucose of 91 per cent purity was obtained.

Summary and conclusions

1. Samples of Indian sugarcane bagasse have been analysed for their chief constituents. The results indicate that the composition of bagasse is more similar to that of hard woods than soft woods; the cellulose content is slightly lower and the lignin content slightly higher than that of hard woods.

2. Saccharification of bagasse has been carried out by a method now used in commercial wood hydrolysis.

Warm dilute acid extracts about 37 per cent of the dry weight of bagasse, the reducing sugar formed consisting mainly of the pentoses, xylose and arabinose.

A further 40 per cent of the dry matter is extracted by cold concentrated hydrochloric acid, the sugar formed being almost entirely glucose.

By successive extraction of different batches of bagasse with the same hydrochloric acid, a solution of high sugar content was obtained.

3. Crystalline glucose in good yields has been prepared from the concentrated acid hydrolysate by evaporation of the de-ionized solution.

4. It is concluded that bagasse saccharification stands on the same footing as wood hydrolysis for the production of alcohol (from the glucose present), of food yeast (from glucose and the pentoses), and of crystalline glucose.

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Studies in Reduction of Powdered Haematite: Part I—Batch Reduction

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High grade powdered haematite has been reduced in hydrogen by a batch process and the effect of various operating variables on the rate of reduction has been studied. Various factors such as the amount of hydrogen passed, its linear velocity, particle size of the ore have also been studied with respect to their effect on the efficiency of reduction.

IRON powder employed in powder metallurgy is made chiefly by decomposition of iron carbonyl and by electrolytic decomposition or reduction of its oxide. Of these the reduction process is probably the most interesting and the most promising application of this method is in the production of metal powder parts on a commercial scale[1]. For the production of sintered ferrous metals both sponge iron and iron powder are used. Sponge iron is produced by reduction directly from the ore and generally has an iron content not exceeding 96 per cent[2]. It is suitable for moulding powdered metal parts only when pulverized fine. Besides it is found that sponge iron powder is not sufficiently pure for its use in the fabrication of a number of iron base products and in such cases iron powder made by the reduction of rolling or drawing scale or from synthetic oxides is employed. This, however, makes the process more expensive. The price factor could be controlled by mixing high purity iron powder (made by reduction of synthetic oxide or by other production methods) with powder made by direct reduction of oxide ore of sufficiently high purity. A gaseous reducing agent is preferred for reduction of the oxide as it does not affect the purity of the oxide. Thus it may be possible to employ directly reduced iron ore in powder metallurgy[3]. It may also be possible in this way to control the plasticity of the products as well as their dimensions.

India has extensive deposits of high grade haematite[4] whose iron content is *c.* 66 per cent[5]. Silica and alumina are less than 1 per cent each and phosphorus is as low as 0·015 per cent. Such ores are well suited for the production of iron powder, and the purity of the powder obtained will be adequate for a number of powder metallurgical applications[6]. Preliminary experiments carried out have shown that by simple caustic soda digestion a haematite ore of about 95 per cent oxide content could be brought to about 99 per cent oxide content. The iron powder made from this will be 98·5 per cent pure which is adequate for powder metallurgical purposes[7].

The present work was carried out with a view to studying the reduction characteristics of powdered haematite of high purity. The haematite as received had the following average composition: Fe, 67·86; Al_2O_3, 2·3; SiO_2, 0·38; and MnO_2, 0·20 per cent. On digestion with caustic soda for 1 hr. the total impurities in the ore were *c.* 1·0 per cent. It was found that the digested ore behaved exactly in the same way as the undigested ore as regards its reduction characteristics. The conclusions drawn from these investigations hold good for haematite ores of very high purity as well as for those in which the total impurities do not exceed *c.* 3-4 per cent.

Studies on the reduction of haematite by the batch process have been carried out with a view to making use of the results obtained for carrying out the reduction in a rotary kiln. Hydrogen was used as the reducing agent as it does not affect the purity of the iron powder obtained.

Earlier workers[8-18] have concentrated more on the mechanism of reduction and the best temperature of reduction than on the correlation of the different variables involved in the process. Their aim was not so much to make iron powder and in a number of cases pure Fe_2O_3 was used. All the experiments described in this paper were carried out with powdered Indian haematite.

Apparatus

The apparatus used for reduction (FIG. 1) consists of the main reduction furnace (A) in which is placed a high grade fireclay tube carrying the porcelain boat (F) which contains the oxide powder to be reduced. An auxiliary furnace (B) filled with copper turnings (600°C.) is used for removing any oxygen present in hydrogen used for reduction, and the water vapour formed in the above furnace is removed by two drying towers (C) containing anhydrous calcium chloride. A thermocouple (D) connected to a Cambridge regulator controls the temperature of the reduction furnace. A gas meter was employed to measure the rate of gas flow. The boat is placed in the zone of uniform temperature which is controlled within ±2°C.

A weighed amount of –200 mesh ore contained in a boat is introduced into the furnace and, after switching on the furnaces, nitrogen gas is passed through the system until the temperature of the reduction furnace reaches the desired value and remains constant. At this stage hydrogen is turned on instead of nitrogen. It is found that about 2 min. are required to displace all nitrogen. The flow of hydrogen is continued for a known period after which hydrogen is again replaced by nitrogen, which passes through the system while the furnace cools to room temperature. The powder is then removed, weighed, sampled and analysed for metallic iron, $Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ content by the usual methods of analysis.

The reduced sample was analysed for (1) total iron, (2) iron present as $Fe^{\cdot\cdot\cdot}$ – (Fe_2O_3), (3) iron present as $Fe^{\cdot\cdot}$ – (FeO) and (4) iron present as metallic iron. The percentage of total iron reduced to metallic iron is represented as percentage reduction to metallic iron. The total percentage reduction to metallic iron and lower oxides is obtained by dividing the amount of oxygen removed by the amount of removable oxygen in the ore. The latter is computed from the results of analysis of the reduced sample on the assumption that all the iron in the ore is present as Fe_2O_3 (percentage of FeO in the ore is negligible, being less than 0·1 per cent).

For simplicity in presenting and interpreting data, the following notations are used:

L = litres of hydrogen equivalent to stoichiometric requirement for complete reduction

t = reduction time in min.

Y = proportion of total reduction to metallic iron or to a lower oxide achieved in t min.:

$$\frac{\text{proportion of hydrogen converted to water} \times \text{rate of flow of hydrogen} \times t}{L}$$

where rate of flow of hydrogen is expressed in l./min.

$$X = \frac{\text{rate of flow of hydrogen} \times t}{L}$$

$$\frac{\Delta X}{\Delta t} = \frac{\text{rate of flow of hydrogen}}{L}$$

$$\frac{\Delta Y}{\Delta t} = \frac{\text{proportion of hydrogen converted into water} \times \text{rate of flow of hydrogen}}{L}$$

$$\frac{\Delta Y}{\Delta X} = \frac{\text{hydrogen converted to water}}{\text{hydrogen supplied}}$$

= efficiency of conversion

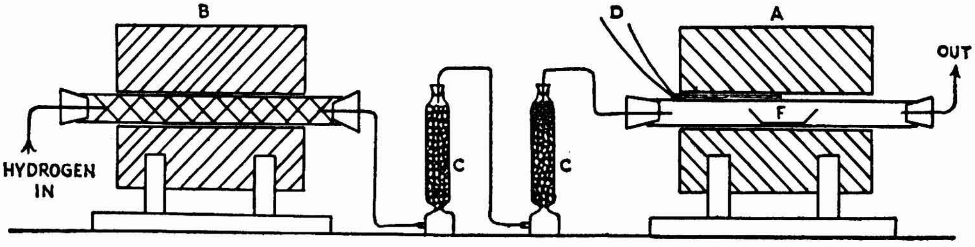

FIG. 1 — APPARATUS FOR REDUCTION OF POWDERED HAEMATITE

Results and discussion

Effect of temperature — Fig. 2 shows the relation between temperature and the time necessary for 80 per cent reduction of ore. Under the conditions of experiment, the rate of reduction increases on an average by 1·8 times when the temperature increases from 550° to 650°C., and 1·35 times for every 100° rise above 650°C. It will be seen that at lower temperature such as 550°C. the time required for reduction becomes too long for technical purposes and 650°C. may be taken as the lowest temperature at which complete reduction is practicable within a reasonable time (FIG. 3 and TABLE 1). Higher rates of reduction obtained above 750°C. are of little practical utility as the reduced material forms a hard solid cake difficult to break.

Effect of time — Fig. 3 shows the relation between time and total percentage reduction (percentage of total oxygen removed) at different temperatures. The reduction curves are exponential in character. If, in any reaction, a is the initial concentration of the reacting substance and c the amount transformed in time t, then the concentration of a after time t will be (a—c). For a first order reaction the following relation holds:

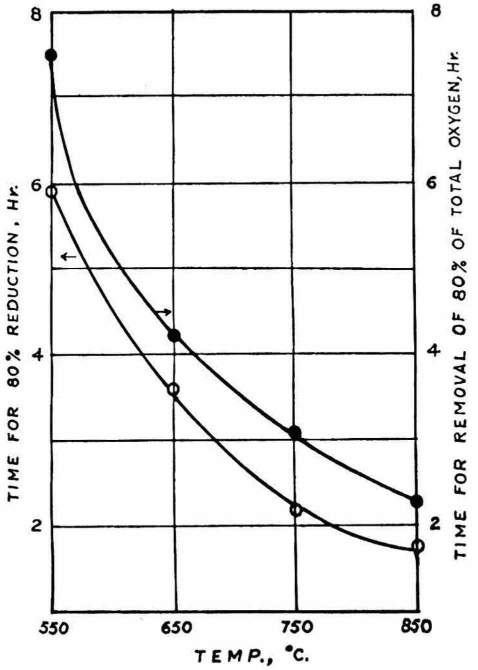

FIG. 2 — EFFECT OF TEMPERATURE ON THE REDUCTION OF HAEMATITE

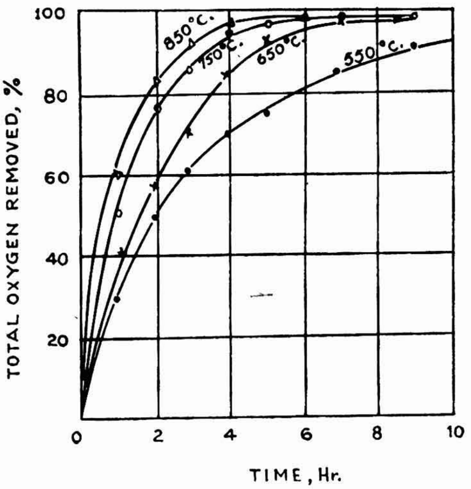

FIG. 3 — EFFECT OF TIME ON THE REDUCTION OF HAEMATITE

TABLE 1 — EFFECT OF TIME ON REDUCTION OF HAEMATITE

(Temp., 650°C.; particle size of the ore, —200 mesh; wt. of ore, 10·18 g.; rate of gas flow, 0·38 l./min.; linear gas velocity, 0·2 ft./min.)

REDUCTION TIME hr.	PERCENTAGE REDUCTION TO METALLIC IRON	TOTAL PERCENTAGE REDUCTION (% OF TOTAL OXYGEN REMOVED)	LOG_{10} (% OXYGEN NOT REMOVED)	$\frac{\Delta Y}{\Delta X}\times 100$	X
1	18·0	41·2	1·7964	7·95	5·3
2	36·0	56·9	1·6345	5·21	10·6
3	55·1	69·8	1·4800	4·26	15·9
4	76·2	83·9	1·2068	3·82	21·2
5	91·3	94·0	0·7782	3·45	26·5
7	95·7	96·7	0·5185	2·53	37·1
9	95·7	96·7	0·5185	1·93	47·7
12	95·5	96·7	0·5185	1·47	63·6

$$\frac{1}{t}\log_{10}\frac{a}{a-c} = 0{\cdot}4343K$$

$$\text{or}\quad \frac{1}{t}\log_{10}\frac{(a-c)}{a}100 = 2-0{\cdot}4343K$$

In the reduction reaction, if the initial and the final concentration be computed in terms of the amount of oxygen present, then the above expression reduces to $\frac{1}{t}\log_{10} =$ constant. Thus the plot of time t vs. $\log_{10}$ (percentage of total oxygen not removed) should be a straight line for each temperature.

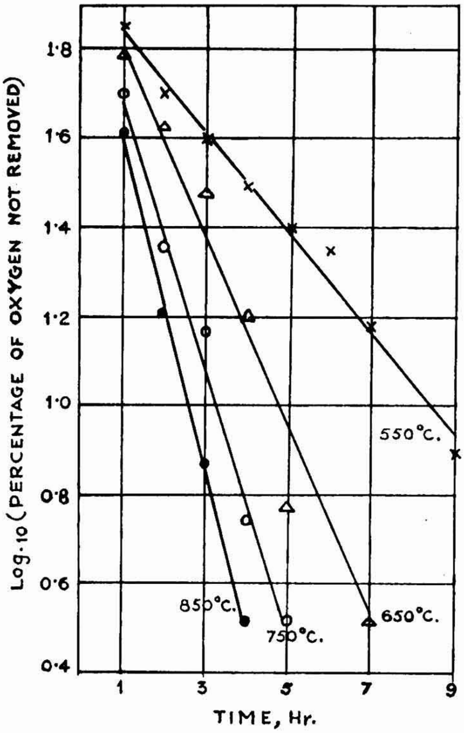

FIG. 4 — TIME OF REDUCTION VS. LOG PERCENTAGE OF OXYGEN NOT REMOVED

The curves in Fig. 4 provide sufficient indication of the tendency of the reduction reaction to behave as first order reaction.

Extent of reduction — The difficulty experienced in effecting the removal of more than 97 per cent oxygen in the ore may be attributed to two factors: (1) Incomplete removal of moisture from the reducing gas (sufficient care was taken as regards this), and (2) slow oxidation which inevitably occurs due to exposure of the powder, after reduction, to humid atmosphere.

The total iron content of even electrolytic iron powders is not more than 98·5-99 per cent, as shown by recent investigations[19]. The oxygen content of these powders obtained six weeks after preparation is about 1 per cent, the increased percentage of oxygen being attributed to slow spontaneous oxidation during storage.

Konrad and Hoffmann[9], and Jane Nash[20] claim to have obtained 100 per cent reduction at such low temperatures as 500°C. and in 20-40 min. This may be attributed to the fact that they used as raw material pure oxide of iron (prepared by chemical methods) which is much more easily reduced than haematite. However, the investigations of Luyken and Kirchberg[21], who used haematite as raw material, corroborate our observations. They found that the reduced material contained 1·9 per cent oxygen even after drastic treatment of the ore with hydrogen for 13 hr.

Effect of rate of gas supply — Increase in the rate of supply of gas increases the linear velocity of the gas as well. Keeping the volume rate of the gas constant, linear velocity of the gas can be varied by changing the diameter of the tube containing the ore boat. The reduction obtained at the end of 3 hr. at different linear velocities is given in Table 2. The results given in Table 2 show that at constant volume rate of flow, increase in linear velocity has no effect on the rate of reduction. Thus any increase or decrease in the rate of reduction observed when the rate of gas supply is changed can be attributed to the alteration in volume rate only.

The effect of varying the volume rate of flow of the gas on the rate of reduction can be summarized as follows: all the other factors remaining constant, the higher the volume rate the shorter the time required for reduction. Fig. 5 shows the variation in reduction with time at different gas rates, and the reduction obtained at the end of definite intervals of time with a change in volume rate. There is a sudden increase in the rate of reduction when the volume rate is increased from 0·19 l./min. to 0·285 l./min. Beyond this the rate of increase is very slow.

Effect of the weight of ore and its particle size — It is obvious from weight vs. percentage reduction curves (FIG. 6) that at constant volume rate of gas for a given interval of time, increased reduction can be

TABLE 2 — EFFECT OF LINEAR VELOCITY ON REDUCTION

(*Temp.*, 650°C.; *reduction time*, 3 *hr.*; *volume rate of gas flow*, 0·38 *l./min.*; *wt. of ore*, 10·18 *g.*; *particle size of ore*, −200 *mesh*)

LINEAR GAS VELOCITY ft./min.	TOTAL IRON %	METALLIC IRON %	PERCENTAGE REDUCTION TO METALLIC IRON
1·58	87·5	48·2	55·1
0·61	88·0	48·3	55·0
0·27	87·4	48·2	55·1
0·20	87·4	48·2	55·1

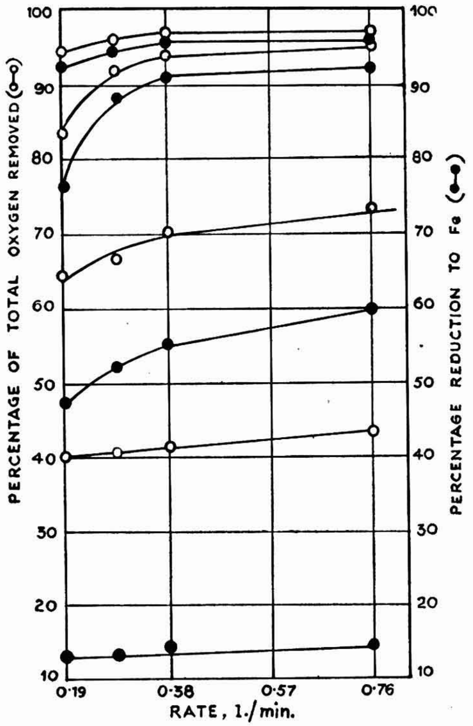

FIG. 5 — EFFECT OF RATE OF FLOW OF HYDROGEN ON REDUCTION OF HAEMATITE (TEMP. 650°C.)

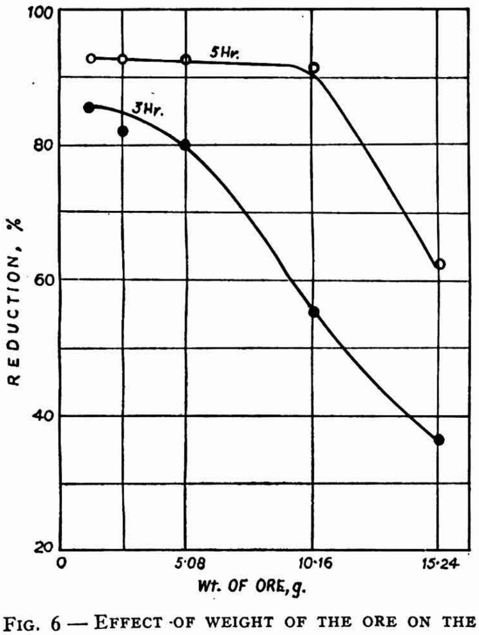

FIG. 6 — EFFECT OF WEIGHT OF THE ORE ON THE REDUCTION OF HAEMATITE

TABLE 3 — EFFECT OF PARTICLE SIZE ON THE REDUCTION OF HAEMATITE

(*Temp.*, 750°C.; *reduction time*, 4 *hr.*; *wt. of ore taken*, 10·18 *g.*; *rate of gas flow*, 0·38 *l./min.*; *linear gas velocity*, 0·2 *ft./min.*)

PARTICLE SIZE OF ORE	TOTAL IRON %	METALLIC IRON %	PERCENTAGE REDUCTION TO METALLIC IRON	IRON PRESENT AS Fe·· %	IRON PRESENT AS Fe··· %
−200	96·5	88·7	93·0	1·0	6·8
−150+200	96·5	91·7	95·0	0·6	4·2
−100+150	96·8	92·0	95·2	1·0	3·8
−65+100	96·2	91·0	94·8	1·0	4·2
−48+65	96·4	91·3	94·6	1·0	4·1
−28+48	95·5	77·1	81·0	1·0	16·6

obtained by decreasing the weight of the ore taken for reduction. However, a stage is always reached beyond which any decrease in the weight of the ore taken does not result in greater reduction.

Particle size of the ore seems to exert little influence on the rate of reduction except when the particle size greater than 48 mesh is encountered (TABLE 3).

Controlling variable or variables — With decrease in the weight of the ore taken or increase in the volume rate of flow there is a corresponding increase in the amount of hydrogen passed over that stoichiometrically required for complete reduction. This adds one more variable to the number of variables already taken into account. In order to determine the effect of different variables on the rate of reduction of iron ore shown by this mass of data it was necessary to evolve a method of treatment that would show the true controlling variable or variables.

It is clear that if the proportionalities mentioned above hold, identical curves should be obtained for a given temperature, by plotting the percentage of hydrogen converted to water against the amount of hydrogen fed/L rather than against reduction time, i.e. by plotting $\Delta Y/\Delta X \times 100$ against X. Such a relationship serves to eliminate from the plot the variables such as linear velocity and weight of ore, and reduces the time taken for reduction in terms of the amount of hydrogen supplied up to any given time. The values of

$$\frac{\Delta Y}{\Delta X} \times 100 = \text{percentage efficiency of conversion}$$

$$= \frac{\text{hydrogen removed as water}}{\text{hydrogen supplied}} \times 100$$

$$\text{and } X = \frac{\text{rate of flow} \times t}{L}$$

are calculated from the results of analysis for each experimental point and all the data (TABLES 1, 4 and 5) are plotted in Fig. 7. The data plotted in this way show that points obtained from samples taken during widely varying conditions map out as a single curve. The existence of this curve means that the rate of reduction depends on the mass rate of flow of hydrogen and that the efficiency of reduction depends only on the amount of hydrogen passed and not on the linear velocity or the weight of the ore taken. Consequently the rate of reduction can be increased proportionately by increasing the volume rate of gas (by using higher linear velocity) or reduction in weight of the ore taken at constant linear velocity.

TABLE 4 — EFFECT OF TIME ON THE REDUCTION OF HAEMATITE AT DIFFERENT RATES OF GAS FLOW

(*Temp.*, 650°C.; *particle size*, −200 *mesh*; *wt. of ore*, 10·18 *g.*)

RATE OF GAS FLOW l./min.	REDUCTION TIME hr.	PERCENTAGE REDUCTION TO Fe	TOTAL PERCENTAGE REDUCTION	$\frac{\Delta Y}{\Delta X} \times 100$	X
0·19	1	15·8	40·0	14·60	2·65
0·19	3	47·2	64·1	7·30	7·95
0·19	5	75·8	83·5	6·10	13·20
0·19	7	92·5	94·5	4·95	18·55
0·285	1	16·0	40·4	9·94	3·98
0·285	3	52·0	66·5	5·51	12·00
0·285	5	88·6	91·8	4·49	19·80
0·285	7	94·7	95·7	3·34	27·82
0·76	1	18·5	43·3	3·97	10·60
0·76	3	59·2	72·9	2·23	31·80
0·76	5	92·3	95·2	1·74	52·80
0·76	7	95·7	96·7	1·27	74·20

TABLE 5 — EFFECT OF WEIGHT OF ORE ON REDUCTION RATE

(*Rate of gas flow*, 0·38 *l./min.*; *linear gas velocity*, 0·2 *ft./min.*; *temp.*, 650°C.; *particle size*, −200 *mesh*)

REDUCTION TIME hr.	WT. OF THE ORE TAKEN g.	PERCENTAGE REDUCTION TO Fe	TOTAL PERCENTAGE REDUCTION (PERCENTAGE OF TOTAL O_2 REMOVED)	$\frac{\Delta Y}{\Delta X} \times 100$	X
3	1·27	85·4	91·0	0·70	136·2
3	2·54	82·0	86·7	1·32	63·6
3	5·09	77·9	84·3	2·57	31·8
3	10·18	55·1	69·8	4·26	15·9
3	15·27	36·6	56·5	5·18	10·6
5	2·54	92·5	95·2	0·87	105·6
5	5·09	92·6	95·0	1·74	52·8
5	10·18	91·3	94·1	3·45	26·4
5	15·27	62·2	74·2	4·08	17·6

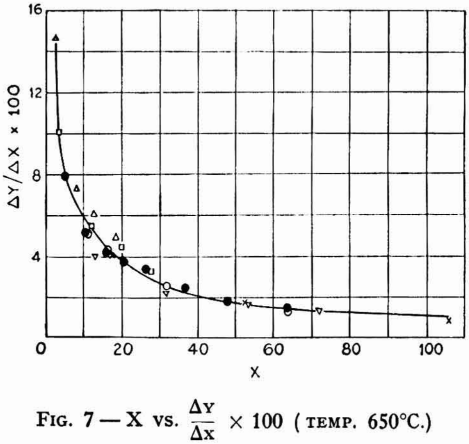

FIG. 7 — X vs. $\frac{\Delta Y}{\Delta X} \times 100$ (TEMP. 650°C.)

The scattered points are due to experimental error in determining the exact time of reduction, a short but finite time being required to replace hydrogen from the reaction tube by nitrogen. It is also possible that pockets of nitrogen are left at the beginning of each run and of hydrogen at the end of the run, and this fact may vitiate the results to a certain extent.

In view of the scattered points several trends are attributable to $\Delta Y/\Delta X$ vs. X curve. In any case, any such trends in this curve are insignificant as compared to the variations observed in the rate of reduction as a function of reduction time by varying the rate of flow of gas (expressed as percentage of stoichiometric requirement) by linear velocity or weight of the ore.

Each temperature will have a characteristic $\Delta Y/\Delta X$ vs. X curve which, however, will be similar in nature to that obtained at 650°C.

It will also be observed (TABLE 4), that variation in particle size, so long as it is less than 48 mesh, will have little effect on this curve.

Reducibility index is for comparing the reducibility of different ores. Joseph[22] employed the reciprocal of time for 90 per cent reduction as a measure of reducibility whereas Philbrook[23] used "slope index" which is obtained by determining the slope of the reduction curve at the end of 20 min. (slope A) and 60 min. (slope B) respectively. The expression is

$$\text{Slope index} = \log_{10} \frac{\text{slope A}}{\text{slope B}}$$

The advantage of the slope-index method, according to Philbrook, is that a reduction experiment can be completed in an hour to obtain the necessary data for an ore sample.

The disadvantages of both the methods are obvious. Joseph's "reducibility index" as well as Philbrook's "slope index"

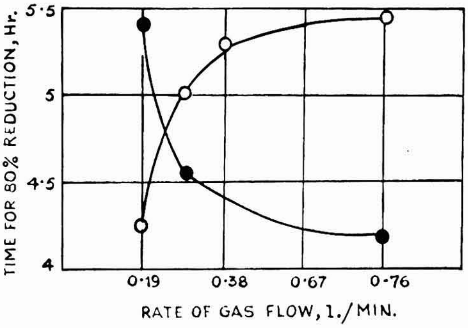

FIG. 8 — RATE OF GAS FLOW VS. JOSEPH'S REDUCTION RATIO (TEMP. 650°C.)

methods are dependent on the rate of gas flow, composition of the gas, weight of the ore used and temperature. The effect of rate of gas flow on Joseph's " reducibility index " is shown graphically in Fig. 8.

On the contrary, ΔY/ΔX vs. X curve is independent of all these factors except temperature and, therefore, may be regarded as a better index of comparison, provided the reduction experiment is carried out at the same temperature. It simplifies the comparison of results obtained under different conditions of gas composition, gas velocity, weight of ore, etc., and thus helps to correlate the data on the reduction of different ores.

Conclusions

1. The reduction of haematite by hydrogen follows a first order reaction.

2. The lowest temperature at which complete reduction is practicable is 650°C. At lower temperatures the time required for reduction is too long whereas at higher temperature the reduced material forms a hard mass.

3. At a given temperature, the rate of reduction at any stage is proportional to the rate of supply of hydrogen. Hence the time taken to bring the ore to any stage of reduction is inversely proportional to the volume rate of supply of hydrogen. The efficiency of conversion is a function of the amount of hydrogen passed (expressed as proportion of stoichiometric requirement), and not of the linear velocity, weight of the ore taken or of particle size, if smaller than 48 mesh. Consequently the rate of reduction can be increased by increasing the rate of flow of hydrogen.

4. ΔY/ΔX vs. X curve seems to be a better reducibility index than that suggested either by Joseph or Philbrook.

Acknowledgement

Our thanks are due to Messrs Tata Iron & Steel Co. Ltd., Jamshedpur, for supplying the high grade haematite ore.

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Studies in Reduction of Powdered Haematite: Part II—Continuous Reduction in a Rotary Kiln

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Conditions for obtaining iron powder without sintering and cake formation, when powdered haematite is reduced continuously in a rotary kiln, have been examined.

LUYKEN and Kirchberg[1] were the first to use a rotary furnace for the reduction of haematite. Recently several processes have been patented for the continuous reduction of granular or powdered iron oxides. In a Swedish patent by Tanner[2] the oxide is introduced in a granular form into a furnace supplied with a reducing gas, so that the granules sinter together and are immediately reduced. The oxide continues to fall on the sintered heap so that eventually a mass of spongy metallic iron is obtained. In the British patent by Planiol[3] the iron oxide is heated in a non-reducing atmosphere to produce Fe_3O_4, which is then dispersed in a finely divided form by grinding in hydrogen at 900°-1,500°C. to form dense metallic iron and finally cooled in a reducing atmosphere. The process is continuous. In another Swedish patent[4], metal oxides, particularly finely crushed ores, are passed through a furnace counter-currently to a stream of reducing gas which is caused to circulate through the furnace. The object of the present investigation is to make iron powder without sintering and formation of cake by reducing haematite continuously in a rotary kiln and to determine the effect of the various operating variables.

Experimental procedure

The assembly used in this case is similar to that used in batch reduction[5] except that the reduction furnace is replaced by a rotary kiln (internal diam., $1\frac{3}{4}$ in.; length, 32 in.). The rotary kiln consists of a stainless steel cylinder (lined with a refractory tube) inclined slightly from the horizontal and rotating about its axis with a speed of 3 r.p.m. Rotation is imparted by a pair of aluminium pulleys connected by belts to a speed reducing unit driven by a $\frac{1}{2}$ h.p. motor. The stainless steel shell fits loosely into a cast iron stationary housing at each end, each unit serving as a bearing for the rotating shell. Each chamber is fitted with a removable lid thus facilitating the cleaning operation after each run. The stationary housing is provided with a packing space which could be fitted with $\frac{1}{4}$ in. serpent-type packing. A sleeve supported on studs fixed to the housing served to keep the packing in place and to make the gland between the stationary and rotary parts sufficiently tight and leak-proof. The chamber at the upper end is provided with a feeding mechanism and an outlet for the gas, and that at the lower end, with a bottom hopper for the removal of reduced powder, and an inlet for the gas. The feed is introduced into the upper end of the kiln by a screw conveyer type of device. This serves also as an efficient seal to prevent any gas leakage when the conveyer is in operation. The entire mechanism, i.e. the kiln, the reduction gear and the motor, was mounted on a single wooden platform and could be given any desired slope by lifting the platform with the help of the screw-jack.

The same ore previously used for batch operation[5] was used. However, for use in rotary kiln −200 mesh ore was found to be unsuitable as it formed a cohesive mass which adhered to the lining of the kiln forming a ring. The thickness of the layer increases continuously and finally blocks the flow of the material completely. Different types of scraper arrangements were tried but all of them were found to be ineffective. A coarser feed was, therefore, used in the kiln and this showed no tendency to adhere to the lining if the temperature is kept well below 700°C. In most of these experiments −100 +200 mesh size was used for reduction.

The operation of the kiln was as follows: the furnace was heated and nitrogen gas passed through the system until the desired temperature was attained. The flow of nitrogen was then stopped and hydrogen introduced. When all the nitrogen was displaced (which took about 2 min.), the rotation of the kiln was started and the feed introduced. The flow of hydrogen and the feeding of the ore were continued until equilibrium conditions were established, i.e. until the rate of discharge and the analysis of the ore were constant over a considerable period of time. The screw conveyer mechanism is operated every 5 min., thus introducing the feed in known lots spread over the entire period of operation.

When equilibrium conditions were established, the experiment was continued and 50-100 g. of the reduced powder were collected. The kiln was then stopped and cooled to room temperature in an atmosphere of nitrogen. The hold up in the kiln was collected and weighed.

Discussion

In the batch process[5], the reduction of the oxide is influenced mainly by four factors, viz. (1) temperature, (2) time of reduction, (3) percentage excess of hydrogen and (4) particle size. The variation due to the particle size of the ore, however, is eliminated by using a narrow range of particle size. The interdependence of the remaining factors and their simultaneous variation by altering a single kiln variable so complicates the reduction mechanism in the rotary kiln that it is almost impossible to evaluate the effect of each of the factors individually. An attempt has been made to explain the effect of kiln variables in the light of the results obtained in the batch reduction.

Effect of slope — Friedmann and Marshall[6] have shown that a direct relationship exists between the time of retention, feed rate and hold up of the ore. They have shown that:

$$T = \frac{LW}{100F} \quad \ldots\ldots\ldots\ldots (1)$$

$$W = \frac{0{\cdot}294F}{S_d N^{0{\cdot}9} D} \quad \ldots\ldots\ldots (2)$$

$$T = \frac{0{\cdot}00294L}{S_d N^{0{\cdot}9} D} \quad \ldots\ldots\ldots (3)$$

$$\text{Also } W = W_a - KG \quad \ldots\ldots\ldots (4)$$

where T is average time of passage (hr.); L, length of the kiln (ft.); D, diameter of the kiln (ft.); W, hold up without air flow, per cent of kiln volume; W_a, hold up with air flow; F, feed rate (cu. ft./hr. sq. ft.); K, constant; G, mass velocity (cu. ft./hr.) (this term has been referred to as volume velocity in the following discussion); S_d, kiln slope; and N, r.p.m.

The equations 1-4 have been derived for rotary driers where no chemical reaction takes place; therefore, no attempt has been made to apply this equation quantitatively to the rotary kiln wherein chemical reaction constantly changes the physical and, hence, the flow properties of the material. However, at a given temperature, all other conditions (viz. feed rate, length, diameter, and r.p.m.) remaining constant, there is ample justification to assume, for purposes of comparison, that at definite feed rate, the time of retention is directly proportional to the ratio (hold up/slope) from equations 1 and 3. Fig. 1 shows the variation in this ratio due to changes in slope.

The results obtained by carrying reductions at 550° and 650°C. and varying the slope of the kiln are plotted in Fig. 2. The curve for 650°C. shows that as the slope is increased the percentage reduction of the ore to iron decreases initially and then increases, attains a maximum value and finally decreases sharply. This behaviour which appears anomalous at first sight may be explained by considering the factors brought into play by varying the slope of the kiln. Increase in slope decreases the ratio (hold up/slope, i.e. time of retention) but at the same time decreases the weight of the material exposed to the same mass of hydrogen

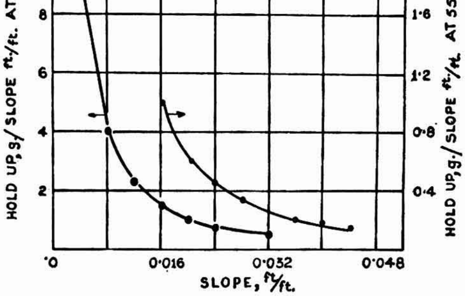

FIG. 1 — EFFECT OF SLOPE ON THE TIME OF RETENTION

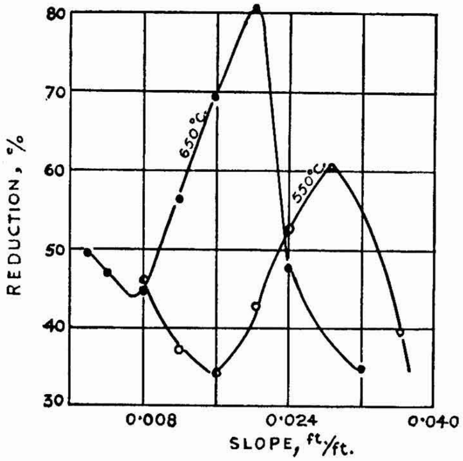

FIG. 2 — EFFECT OF SLOPE ON REDUCTION

with a constant increase in the percentage excess of hydrogen per unit weight of hold up. Initially, the former factor, viz. the time of retention, is the predominant effect with the resultant decrease in the percentage reduction as the slope is increased. Decreased reduction due to reduced time of passage is only partially off-set by increase in the percentage excess of hydrogen. As the slope is increased a state is reached when the effect due to these factors become nearly equal. This explains the bottom hump of the curve.

With further increase in the slope of kiln, the effect of the second factor, viz. percentage excess of hydrogen, becomes more prominent. Increased reduction can thus be attributed to increased excess of hydrogen, i.e. to the thinner and smaller layer of the material exposed to the same volume of hydrogen or to the increase in the mass of hydrogen passed expressed as a proportion of stoichiometric requirement for complete reduction.

The results obtained in batch reduction process[5] show that a stage is always reached beyond which any further increase in the percentage excess of hydrogen does not result in more reduction. This is also true for reduction by the continuous process. In this case there is an optimum slope at which maximum reduction is obtained, any further increase in the slope resulting in a sharp fall in the reduction as the effect of decreased time of retention is not off-set by increased percentage excess of hydrogen.

The results of the experiments at 550°C. lend additional support to this view.

Effect of temperature — The effect of increasing the temperature of reduction is to increase the overall reduction. This explains the increased rate of reduction at 650°C. The results given in Table 2 show that under identical conditions, the weight of the hold up is greater at higher temperatures. When the slope is 0·02 and the feed rate 30 g./hr., the weight of the hold up at 550°C. is 12 g. whereas it is 26 g. at 650°C. Thus increased reduction at 650°C. includes the increase due to longer retention time at 650°C. as well as a decrease due to a comparatively greater weight of the material exposed to the same volume of hydrogen.

At temperatures higher than 650°C. even −100 +200 mesh ore tends to form a cohesive mass on reduction and adheres loosely to the lining of the kiln. Therefore, 650°C. is the best temperature for carrying out reduction of the ore in the rotary kiln.

Effect of feed rate — For a given slope, the time of retention may be taken, for comparison, to be proportional to weight of hold up/feed rate, when the feed rate is varied. As the rate of feeding is decreased, there is a decrease in the weight of the hold up with a consequent rise in the percentage excess of hydrogen. The ratio weight of hold up/feed rate shows that with decreased feed rate the time of retention increases continuously (TABLE 1 and FIG. 3). Fig. 4 shows the relation between percentage reduction of ore to iron and feed rate.

The increased reduction of ore may thus be attributed to longer retention time and to the increase in the percentage excess of

TABLE 1 — EFFECT OF VARYING FEED RATE

(*Temp., 650°C.; rate of gas flow,* 0·38 *l./min.; r.p.m.,* 3)

SLOPE OF THE KILN	FEED RATE (F) g./hr.	WT. OF HOLD UP (X) g.	X/F	PERCENTAGE REDUCTION TO METALLIC IRON
0·008	30·0	32·5	1·08	44·5
	20·0	23·8	1·19	63·9
	15·0	19·5	1·30	68·4
	10·0	15·2	1·52	88·1
	7·5	30·5	4·06	92·4
0·02	60·0	36·0	0·60	37·8
	40·0	28·0	0·70	64·0
	30·0	26·0	0·87	80·3
	20·0	23·2	1·16	93·4
	15·0	19·5	1·30	94·5
	12·0	16·0	1·33	94·4
	10·0	13·2	1·32	94·6
	7·5	12·5	1·67	93·5

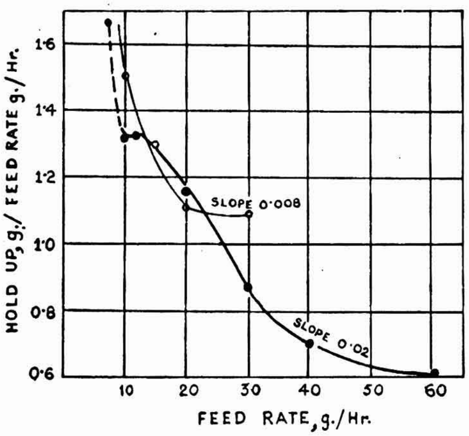

FIG. 3 — EFFECT OF FEED RATE ON TIME OF RETENTION (TEMP. 650°C.)

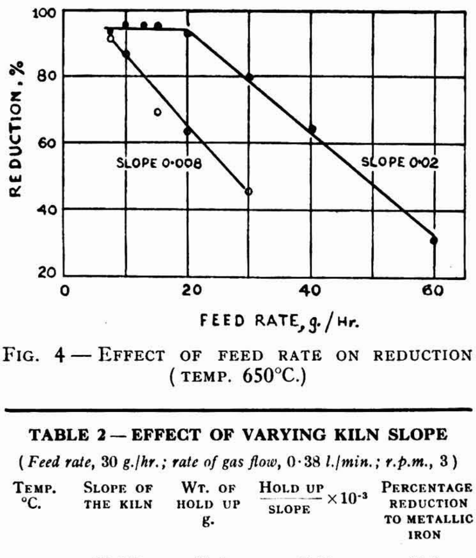

FIG. 4 — EFFECT OF FEED RATE ON REDUCTION (TEMP. 650°C.)

TABLE 2 — EFFECT OF VARYING KILN SLOPE

(*Feed rate*, 30 *g./hr.*; *rate of gas flow*, 0·38 *l./min.*; *r.p.m.*, 3)

TEMP. °C.	SLOPE OF THE KILN	WT. OF HOLD UP g.	$\frac{\text{HOLD UP}}{\text{SLOPE}} \times 10^{-3}$	PERCENTAGE REDUCTION TO METALLIC IRON
550	0·012	28·5	2·68	46·0
	0·016	17·0	1·06	37·5
	0·020	12·0	0·60	34·3
	0·024	10·0	0·46	42·3
	0·028	9·5	0·34	52·7
	0·032	8·0	0·25	59·8
	0·036	7·3	0·20	56·2
	0·040	7·5	0·19	39·8
	0·044	7·3	0·16	26·8
650	0·002	50·0	25·00	49·3
	0·004	37·5	9·40	47·0
	0·008	32·5	4·06	44·5
	0·012	27·5	2·30	53·4
	0·016	24·0	1·50	69·0
	0·020	21·0	1·05	80·3
	0·024	18·6	0·77	47·4
	0·032	15·9	0·50	34·8

hydrogen. Probably the latter factor does not play a prominent part (TABLE 2) because any increase in the percentage excess of hydrogen beyond a certain level is not particularly effective.

It is apparent from Fig. 4 and Table 1 that for each slope there is a minimum feed rate at which maximum reduction is obtained. Further decrease in the feed rate decreases the output without a corresponding gain in efficiency.

The results for the lowest feed rate (TABLE 2) show an abnormal rise in retention time. The feed rate is probably inadequate for efficient functioning of the kiln.

The optimum operating conditions for the kiln are: r.p.m., 3; temperature, 650°C.; kiln slope, 0·02; and feed rate, 20 g./hr.

Conclusions

1. Haematite ore (—200 mesh) when reduced shows a tendency to adhere to the kiln lining at all temperatures; —100 +200 mesh ore is more suitable for use in a rotary kiln.
2. The highest temperature at which continuous reduction is satisfactory and practicable is 650°C. At temperatures above 650°C. even —100 +200 mesh ore adheres to the lining of the kiln.
3. There is an optimum kiln slope for a given feed rate and a minimum feed rate for a given kiln slope at which the reduction of the ore is maximum.

Acknowledgement

Our thanks are due to Mr. M. V. Joshi for the valuable help rendered in the construction of the rotary kiln. Thanks are also due to Messrs Tata Iron & Steel Co. Ltd., Jamshedpur, for supplying high grade haematite ore.

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Recovery of Nickel & Fat from Spent Hydrogenation Catalysts

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Optimum conditions for the large-scale recovery of nickel and fat from commercial spent hydrogenation catalyst residues are reported and the economics of the process evaluated. A method is described for the removal of iron from the spent catalyst.

THE Indian hydrogenated vegetable oil (vanaspati) industry is the second major food-processing industry in the country. In 1950, there were 42 factories working producing 1,72,000 tons of vanaspati. The present installed capacity is estimated at 3,92,000 tons per year.

Large amounts of nickel catalyst are employed in the hydrogenation of oils. The spent catalyst which contains considerable quantities of nickel and fat finds little use in India and is generally discarded as waste. Recovery of nickel from the spent catalyst is of special interest to the Indian hydrogenated oil industry as there are no known sources of nickel in the country.

Bhasin *et al.*[1] have worked out a method for the recovery of nickel and fat from spent nickel catalysts. The present investigation was undertaken to develop this process for large-scale recovery of nickel and fat from the spent catalyst and to assess its economic possibilities.

The analyses of spent nickel catalyst samples obtained from three vanaspati factories are given in Table 1. Nickel and iron in the samples were estimated by dimethyl glyoxime and colorimetry respectively. Fat was determined by extraction with petroleum ether (b.p. 60°-80°C.).

Recovery of nickel by acid digestion

Bhasin *et al.*[1] digested the spent catalyst thrice with hot commercial hydrochloric acid. The acid dilutions employed in the successive digestions were 1: 1, 1: 2 and 1: 3 respectively. Belekar *et al.*[2], using 15 per cent sulphuric acid for digestion (single) and 10 g. of spent catalyst, obtained a nickel recovery of 71·2 per cent. Employing a mixture of 20 per cent sulphuric acid and 70 per cent nitric acid (2 digestions) with 100 g. of catalyst, they achieved a recovery of 94·9 per cent.

In the present investigation, the acid concentration was kept as low as possible consistent with a satisfactory overall recovery of nickel to minimize deterioration of fat. The effect of different concentrations of acids on nickel recovery was studied in the case of spent catalyst No. II and the results are recorded in Table 2. The spent catalyst was digested thrice with the acid, the mixture being mechanically agitated during digestion.

Sulphuric acid (1N, 5 per cent w/v) gave a satisfactory recovery of nickel with a digestion time of 2 hr. per digestion (TABLE 2). Reducing the amount of acid from 2 l./kg. of catalyst per digestion to 1·5 l./kg. did not significantly affect the recovery of nickel. Consequently, in subsequent digestions 1·5 l. of 5 per cent sulphuric acid were used per kg. of the catalyst per digestion.

TABLE 1 — ANALYSIS OF SPENT NICKEL CATALYSTS

CATALYST No.	Ni %	FAT %	Fe %	SILICEOUS MATTER %	CARBON AND MOISTURE %
I	2·80	48·80	0·16	42·90	5·34
II	5·37	64·90	0·19	9·71	19·83
III	14·00	47·10	0·37	32·80	5·73

TABLE 2 — RECOVERY OF NICKEL USING VARYING STRENGTHS OF ACIDS

(*Weight of catalyst used, 1 kg.; vol. of acid used, 2 l./kg. per contact*)

ACID	DIGESTION No.	DIGESTION TIME AT BOIL PER DIGESTION hr.	ACID STRENGTH	NICKEL RECOVERED %
HCl	1 2 3	1	4N 2·5N 2N	86
HNO_3	1, 2 and 3	1	2N	85
H_2SO_4	1, 2 and 3	1	2N	72
H_2SO_4	1, 2 and 3	1	1N	77
H_2SO_4	1, 2 and 3	2	1N	90

Counter-current multiple digestion

To study relative recoveries by simple and counter-current digestions, a three-stage counter-current battery of mechanically agitated acid digesters was set up, each vessel having a capacity of 5 l.

The spent catalyst sample No. III containing 14 per cent nickel was used for these experiments. The conditions of operation were as follows: amount of catalyst, 1 kg.; amount of acid, 1·5 l. of 5 per cent H_2SO_4; temperature of extraction, 90°-100°C.; digestion time, 2 hr. per stage.

An average nickel recovery of 53·8 per cent was achieved and it was calculated that 5 extractions were necessary for a 90 per cent recovery.

The spent catalyst sample No. III was also subjected to three simple digestions with sulphuric acid under the same conditions. The results are given in Table 3.

From these results it is clear that for catalyst No. III both methods gave poor recoveries of nickel, the triple digestion procedure proving somewhat superior.

Spent catalyst sample No. III has an unusually high nickel content, and, therefore, requires more acid and/or a longer digestion time than the average for greater recovery.

In general, with the usual spent catalysts having a nickel content in the range 3-10 per cent, a three to four stage simple or counter-current digestion will result in recoveries of more than 90 per cent. The main advantage of the counter-current procedure for large-scale operations is that it effects almost a 60 per cent economy in the acid requirements and thereby produces a more concentrated nickel solution which in turn reduces the size of process equipment for subsequent steps.

The triple extraction procedure was, therefore, used in all subsequent experiments.

Removal of iron

The iron contained in the spent catalyst goes into solution along with nickel and must be removed. Belekar *et al.*[2] used precipitated calcium carbonate for removing iron. Bhasin *et al.*[1] have recommended both precipitated calcium carbonate and ammonia for the purpose.

Precipitated calcium carbonate was employed to precipitate iron present in the acid digests from catalyst No. II. The concentrations of nickel and iron in the solution were 0·63 per cent (w/v) and 0·035 per cent (w/v) respectively.

TABLE 3 — NICKEL RECOVERY BY MULTIPLE SIMPLE DIGESTIONS

(*Wt. of spent catalyst III used, 1 kg.; wt. of nickel in the catalyst, 140 g.*)

DIGESTION No.	NICKEL RECOVERED g.	NICKEL RECOVERY %
1	49·0	35·0
2	32·6	23·3
3	32·0	22·8
	113·6	81·1

TABLE 4 — REMOVAL OF IRON BY PRECIPITATED CALCIUM CARBONATE

$CaCO_3$ ADDED g./100 cc.	NICKEL IN SOLUTION % (w/v)	IRON IN SOLUTION % (w/v)
0	0·63	0·035
2	0·57	0·016
4	0·23	0·003
5	0·32	0·001

To the acid digest (100 cc.), carefully neutralized with sodium carbonate, known amounts of precipitated calcium carbonate were added (2, 4 and 5 g. in three successive experiments), the mixture stirred for 15 min. at 90°-100°C., and allowed to cool and settle. The solid matter was filtered off and washed. Nickel and iron were estimated in the filtrate to which the washings had been added. The results are presented in Table 4.

While precipitated calcium carbonate removes most of the iron from the acid digest it also brings down with it as much as 50 per cent of the nickel (TABLE 4). This method, therefore, is unsatisfactory.

Among several alternative procedures tried for the removal of iron, the following was found to be effective and most economical. The acid digest (100 cc.) was partially neutralized (*p*H 5) with sodium carbonate and a stream of air bubbled through to oxidize the ferrous iron. The solution was heated to 90°-100°C. and solid sodium carbonate added in amount equal to that required to neutralize the solution plus that equivalent to the iron present. The solution was cooled and the solid mass filtered off.

In another experiment, hydrogen peroxide solution (3 per cent) was used as the oxidizing agent. The rest of the procedure was the same. The results obtained are given in Table 5.

It may be observed from the results given in Table 4 that almost all the iron in the acid digest can be removed by this method

TABLE 5 — REMOVAL OF IRON BY SODIUM CARBONATE & HYDROGEN PEROXIDE

(*Original solution: Ni,* 0·63%; *Fe,* 0·035%)

OXIDIZING AGENT	WT. OF OXIDIZING AGENT USED PER 100 CC. OF ACID DIGEST	NICKEL IN SOLUTION % (w/v)	IRON IN SOLUTION p.p.m.
Air	—	0·59	<1
H_2O_2	5 cc. of 3% solution	0·57	<1

TABLE 6 — CHARACTERISTICS OF RECOVERED FAT

SAMPLE No.	ACID VAL.	IOD. VAL.	SAP. VAL.	COLOUR	ODOUR
I	31·04	75·5	205·5	Dark	Rancid
II	1·52	63·3	188·0	Normal	Normal
III	0·91	65·9	192·3	do	do

without appreciable loss of nickel. Sodium carbonate acts as a precipitating as well as neutralizing agent and is cheaper than precipitated calcium carbonate and ammonia.

Recovery of fat

Fat was recovered from the washed and dried solid mass remaining after acid digestion by solvent extraction with petroleum ether (b.p. 60°-80°C.).

The characteristics of the fat recovered are given in Table 6.

Large-scale operation

For economic and large-scale operation the process reported by Bhasin *et al.*[1] has been modified in the light of the results obtained in the above investigations.

The spent catalyst as received was digested with 5 per cent sulphuric acid at 90°-100°C. under vigorous agitation in a simple three stage or a three to four stage counter-current digestion. The acid : catalyst ratio was about 1·5 l. to 1 kg. per digestion for simple digestion and about 1·5-2·0 l./kg. for counter-current digestion. The total digestion time was 6 hr. Water was added occasionally to make up the losses due to evaporation. Jacketed and lead-lined mild steel or cast iron vessels with lead-lined anchor type stirrers may be used as digesters.

In order to separate effectively the liquid and solid portions in the acid digest, cold water was circulated in the jacket after each digestion. This solidifies the solid matter, making it easy to drain off the liquid.

The acid digests were stored in a lead-lined vessel provided with steam coils for heating and a blade type agitator. Enough sodium carbonate was added to the liquor to bring the *p*H to *c.* 5, and a stream of compressed air bubbled through to oxidize the ferrous iron. The temperature was then raised to 90°-100°C. by admitting steam, and solid sodium carbonate, in an amount sufficient to neutralize the solution and precipitate all the iron present, was added under agitation. The solution was allowed to cool and filtered in a wooden plate and frame filter press to remove the precipitated iron. The addition of filter aids is helpful and necessary. The filtered, iron-free liquid was fed to a jacketed stainless steel pan provided with means for agitation. Sodium carbonate was added at boil to precipitate all the nickel in solution as nickel carbonate. The slurry was pumped through a plate and frame filter press to remove nickel carbonate.

The precipitated nickel carbonate was treated with the requisite amount of dilute sulphuric acid to convert it to nickel sulphate. This may be done in a jacketed lead-lined pan with suitable means for agitating the mixture. Nickel sulphate was crystallized out from the hot concentrated solution in a jacketed agitated batch crystallizer. The crystals of nickel sulphate were centrifuged free of mother liquor and dried in a hot air cabinet drier at 40°-50°C. Iron-free nickel sulphate thus obtained can be used in the electroplating industry.

The solid residue, after the removal of the acid liquor, was thoroughly washed with water. This can be done in the digester itself. It was dried in a hot air drier, and then extracted with petroleum ether (b.p. 60°-80°C.) using, on an average, *c.* 3 l. of solvent per kg. of solids. The fat was recovered from the oil extract by distillation. The loss of solvent does not exceed about 3 per cent. A standard solvent extraction cum vacuum distillation unit of copper is suitable for recovering the solvent.

Recoveries of nickel and fat

Table 7 gives data on the recoveries of nickel and fat from the three spent catalyst samples, when working with 1 kg. batches.

TABLE 7 — RECOVERIES OF NICKEL AND FAT

SAMPLE No.	NICKEL RECOVERED %	FAT RECOVERED %
I	94·8	95
II	90·8	87
III	81·4	94

Economics of the process

Table 8 presents cost figures relating to the recovery of nickel and fat from catalyst No. 1 (2·8 per cent nickel). The net profit per cwt. of catalyst is Rs. 10/3/-. Similarly catalyst Nos. II (5·37 per cent nickel) and III (14 per cent nickel) yield net profits per cwt. of Rs. 25/8/- and Rs. 45/13/- respectively.

TABLE 8 — COST DATA FOR RECOVERY OF NICKEL AND FAT FROM SPENT CATALYST

(*Basis:* 1 *cwt. of spent catalyst processed*)

ITEM	QUANTITY	RATE	RS.	AS.	P.
Spent catalyst	1 cwt.	Rs. 50 per cent nickel content per ton	7	0	0
Chemicals					
Sulphuric acid (98%)	30·2 lb.	Rs. 280 per ton	3	12	0
Soda ash	29·4 lb.	Rs. 560 per ton	7	5	0
Petroleum ether (make-up solvent)	1 gal.	Rs. 3 per gallon	3	0	0
Processing costs and overheads			15	0	0
		TOTAL	36	1	0
Credit from recoveries					
Nickel sulphate	13·5 lb.	Rs. 1/8/- per lb.	20	4	0
Fat	52·0 lb.	As. -/8/- per lb.	26	0	0
		TOTAL	46	4	0
		NET PROFIT	10	3	0

From the commercial view point, it would be profitable to process spent catalysts with a nickel content of *c.* 5 per cent or above. Since the bulk of spent catalysts from Indian vanpasati factories is not likely to contain less than 5 per cent nickel, the recovery of nickel from this material merits serious consideration by the industry.

Acknowledgement

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Stabilization of Hydrogen Peroxide

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The decomposition of 3-30 per cent hydrogen peroxide solutions in the presence of various stabilizers has been investigated. Among the stabilizers examined, tartaric acid and sodium salicylate mixture, sulphanilamide, 8-hydroxyquinoline, Nipagin, acetanilide and phenacetin possess greater stabilizing power than the rest. The activity of these stabilizers is attributed to their ability to deactivate the decomposition catalysts of hydrogen peroxide by complex formation or chelation.

HYDROGEN peroxide is thermo-chemically unstable; its decomposition into water and oxygen is exothermic (23,450 cal./g. mol.). However, pure hydrogen peroxide solution keeps well at ordinary temperatures and the rate of decomposition is extremely slow. The decomposition is accelerated by traces (one part per billion) of contaminants such as copper, iron, manganese, lead, etc., which act as catalysts. One way of stabilizing hydrogen peroxide solution would be to render it free from all contaminants, which in commercial practice is difficult to achieve. Therefore, stabilization of hydrogen peroxide solutions by using stabilizers is a matter of commercial importance, especially in the hot climate obtaining in India.

A good stabilizer must completely deactivate contaminants which catalyse the decomposition of hydrogen peroxide and afford protection for the period it is stored. Another reason for the use of stabilizers is to furnish protection against explosion of airtight glass containers during distribution and storage.

Earlier work on the stabilization of hydrogen peroxide has been reviewed by Bailey[1] and Kaush[2]. Most of the commercial stabilizers are acids or substances which slowly liberate acids in solution, e.g. sulphuric

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TABLE 1 — STABILIZATION OF HYDROGEN PEROXIDE SOLUTION (3% H_2O_2 OR 10 VOL. OXYGEN)

(Acidity of the solution = cc. of 0·1N NaOH required for neutralizing 100 cc. H_2O_2 solution using phenolphthalein as the indicator; non-volatile residue of unstabilized solution at 110°C., 17-19 mg. per 100 cc.; residue on ignition, 0·2 mg./100 cc.)

No.	ADDITIVE	ACIDITY	% DECOMPOSITION OF HYDROGEN PEROXIDE								
			1 day	15 days	1 month	2 months	3 months	6 months	12 months	18 months	24 months
1	Hydrogen peroxide without stabilizer	4	2	53	92	—	—	—	—	—	—
2	Acetanilide[3] (0·02%)	4	nil	6	12	43	98	—	—	—	—
3	Acetanilide (0·02%) + H_3PO_4[4] (0·01%)	5	nil	3	3	4	4	9	12	23	—
4	Acetanilide (0·02%) + H_2SO_4 (0·02%)	5	nil	nil	3	5	5	—	16	28	—
5	Acetic acid (0·02%)	6	nil	11	47	65	82	—	—	—	—
6	Acetamide (0·02%)	5	nil	2	20	40	55	—	—	—	—
7	Aspirin (0·02%)	4	nil	nil	2	8	—	18	63	85	—
8	Aspirin (0·02%) + H_3PO_4 (0·01%)	4	nil	nil	20	35	68	100	—	—	—
9	Adipic acid (0·02%)	5	1	—	31	—	58	85	—	—	—
10	Barbituric acid[5] (0·01%)	6	nil	6	18	40	44	78	—	—	—
11	Barbitone (0·02%) + $Na_4P_2O_7$ (0·02%)	5	nil	—	3	—	21	—	58	—	—
12	Barbitone (0·02%) + H_3PO_4	4	nil	—	10	30	47	80	97	—	—
13	Benzoic acid[6] (0·2%)	6	nil	nil	16	32	—	52	—	—	—
14	Benzanilide (0·2%)	6	nil	nil	18	42	—	60	—	—	—
15	Benzamide (0·2%)	4	nil	1	22	50	—	76	—	—	—
16	Calcium orthophosphate[7,8] (0·1%)	4	nil	—	27	54	67	82	—	—	—
17	Calcium dibasic phosphate (0·1%)	4	2	—	63	83	—	—	—	—	—
18	Calcium tribasic phosphate (0·1%)	4	2	—	41	77	—	—	—	—	—
19	Ethyl alcohol (abs.)[9], 1% by vol.	4	nil	4	7	20	32	84	—	—	—
20	Ethyl glycol (0·2%)	4	nil	nil	1	25	64	100	—	—	—
21	Ether	4	1	6	44	75	—	—	—	—	—
22	Glycerine[9], 1% by vol.	4	nil	nil	nil	15	48	95	—	—	—
23	Glycerine (0·5%) + H_3PO_4 (0·01%)	4	nil	22	35	58	90	99	—	—	—
24	8-Hydroxyquinoline[10] (0·001%)	5	nil	3	11	23	41	64	—	—	—
25	(a) 8-Hydroxyquinoline (0·001%) + $Na_4P_2O_7$ (0·05%)	4	nil	nil	4	8	17	18	20	25	56
	(b) 8-Hydroxyquinoline (0·01%) + $Na_4P_2O_7$ (0·05%)	4	nil	nil	nil	nil	4	4	4	10	25
26	Hydroquinone[11] (0·01%)	4	4	10	36	94	100	—	—	—	—
27	Malic acid	4	2	26	45	—	—	—	—	—	—
28	Mepacrine	4	nil	nil	nil	6	6	28	—	—	—
29	Malonic acid	4	1	30	70	—	—	—	—	—	—
30	α-Naphthylamine (0·01%)	4	nil	1	5	33	39	77	—	—	—
31	Nipagin (methyl *p*-hydroxybenzoate)[12,13] (0·05%)	6	nil	3	3	4	6	10	21	25	—
32	Nipagin (0·1%)	6	nil	nil	nil	nil	1	8	10	15	—
33	Nipagin (0·2%)	6	nil	nil	3	4	6	12	13	23	—
34	Nipagin (0·1%) + $Na_4P_2O_7$ (0·1%)	6	nil	7	—	—	16	34	76	84	—
35	*m*-Phosphoric acid (0·02%)[14]	7	nil	nil	10	39	46	100	—	—	—
36	*o*-Phosphoric acid (0·2%)	7	nil	15	37	—	87	100	—	—	—
37	Phenyl barbitone (0·01%)	—	—	—	16	19	19	32	41	—	—
38	Phenacetin[14,15] (0·005%) (aceto-*p*-phenetide)	5	nil	3	3	—	8	24	44	70	—
39	Phenacetin (0·025%)	5	nil	nil	3	3	3	13	34	40	—
40	Phenacetin (0·05%)	5	nil	5	6	—	10	—	60	97	—
41	Phenacetin (0·075%)	5	nil	nil	6	—	6	—	52	79	—
42	Phenacetin (0·1%)	5	nil	6	6	—	7	—	54	78	—
43	Phenacetin (0·1%) + H_3PO_4 (0·01%)	6	nil	nil	nil	nil	nil	nil	38	60	—
44	Phenacetin (0·02%) + $Na_4P_2O_7$ (0·02%)	5	nil	nil	nil	4	—	—	24	35	—
45	Phenacetin (0·02%) + H_3PO_4 (0·01%)	6	nil	nil	nil	—	—	—	16	20	—
46	Phenacetin (0·035%) + acetanilide (0·002%) + H_3PO_4 (0·01%)	5	nil	nil	nil	—	nil	—	6	16	18
47	Phenyl cincoline (0·05%)	4	nil	nil	nil	nil	nil	31	64	—	—
48	Phenyl salicylate (0·02%) (salol.)	5	nil	49	88	98	—	—	—	—	—
49	Quinine sulphate[16] (0·02%)	4	nil	3	14	14	17	74	98	—	—
50	Quinine glycerophosphate (0·02%)	4	nil	2	—	8	11	22	—	—	—
51	Quinine salicylate (0·02%)	4	nil	nil	—	3	6	11	54	—	—
52	Salicylic acid[14] (0·02%)	6	nil	26	53	58	98	—	—	—	—
53	Sodium salicylate (0·01%)	6	nil	30	62	78	100	—	—	—	—
54	(a) Sodium stannate[17] (0·01%)	4	nil	nil	10	—	53	100	—	—	—
	(b) Sodium stannate (0·01%) + H_3PO_4 (0·01%)	5	nil	nil	nil	10	18	75	—	—	—
55	(a) Sodium pyrophosphate[8,18] (0·1%)	4	nil	nil	10	37	62	92	—	—	—
	(b) Sodium pyrophosphate (0·02%)	—	nil	nil	nil	20	48	62	86	—	—
56	Sodium glycerophosphate (0·008%)	4	nil	5	10	10	—	—	21	62	—

TABLE 1 — STABILIZATION OF HYDROGEN PEROXIDE SOLUTION (3% H_2O_2 OR 10 VOL. OXYGEN) — *contd.*

(*Acidity of the solution = cc. of* 0·1*N NaOH required for neutralizing* 100 *cc.* H_2O_2 *solution using phenolphthalein as the indicator; non-volatile residue of unstabilized solution at* 110°C., 17-19 *mg. per* 100 *cc.; residue on ignition,* 0·2 *mg.*/100 *cc.*)

No.	Additive	Acidity	% decomposition of hydrogen peroxide								
			1 day	15 days	1 month	2 months	3 months	6 months	12 months	18 months	24 months
57	Sodium glycerophosphate (0·08%) + $Na_4P_2O_7$ (0·04%)	4	nil	9	13	28	49	70	83	—	—
58	Sodium phosphate acidified by H_3PO_4	7	nil	17	22	39	56	75	—	—	—
59	(a) Sulphuric acid[19] (0·29%)	6	nil	3	6	10	13	68	—	—	—
	(b) Sulphuric acid (0·25%)	5	nil	5	21	36	55	90	—	—	—
	(c) Sulphuric acid (0·2%)	4	nil	nil	7	26	46	85	—	—	—
60	Succinic acid[19] (0·02%)	5	nil	6	30	55	—	—	—	—	—
61	Sulphanilamide (0·02%)	4	nil	nil	nil	nil	nil	nil	4	8	20
62	Tartaric acid (0·02%)	7	3	21	51	84	—	—	—	—	24
63	Tartaric acid (0·02%) + sodium salicylate (0·01%) + sodium *m*-phosphate (0·01%)[20]	7	nil	nil	nil	nil	nil	nil	6	6	14
64	Uric acid[21] (0·001%), max.	—	nil	40	81	100	—	—	—	—	—
65	Urea (0·02%)	5	3	17	54	100	—	—	—	—	—
66	Urea (0·02%) + sodium pyrophosphate (0·02%)	5	nil	—	13	26	50	72	—	—	—

acid, phosphoric acid, phosphates and pyrophosphates. A large number of organic substances have been suggested as general stabilizers. Amides and imides, including ureas, acetyl derivatives of aromatic bases, esters of aromatic hydroxy acids, hydroxy quinoline, phenacetin and acetanilide, have been reported as good stabilizers even in the presence of an active catalyst like copper, but no comparative data on the effectiveness of different substances in stabilizing hydrogen peroxide are available.

Materials and methods

Stability tests — The hydrogen peroxide solution used in the tests was obtained by distilling the solution in an all-pyrex glass distillation unit.

There are two methods for determining the stability of hydrogen peroxide solutions. In the first method (ageing method) the percentage of hydrogen peroxide in the solution is determined after storing the solution for two years in the presence of various stabilizers. Merck's porcelain cap, airtight glass bottles were used for storing the hydrogen peroxide solutions. Table 1 gives the results obtained with various stabilizers by this method.

In the second method [boiling point (b.p.) method], hydrogen peroxide solution with added stabilizer is boiled in a flask fitted with a reflux double surface condensor. The percentage of hydrogen peroxide in the solution is determined at 1, 3 and 6 hr. intervals. The decomposition of hydrogen peroxide solution at b.p. for 1 hr. is approximately equal to the decomposition of the solution stored for one year at room temperature. This equality is based on the evaluation by the ageing method. The b.p. method promises a rapid means of determining the effectiveness of stabilizers. The result of b.p. tests are given in Tables 2-3.

TABLE 2 — STABILITY OF HYDROGEN PEROXIDE BY B.P. METHOD

No.	Additive	Acidity	% decomposition of H_2O_2 at 95°C.		
			1 hr.	3 hr.	6 hr.
1	Pure hydrogen peroxide	4	86	—	—
2	Phenacetin (0·02%) + $Na_4P_2O_7$ (0·02%)	5	2	14	27
3	Phenacetin (0·02%) + $Na_4P_2O_7$ + H_3PO_4 (0·01%)	6	nil	4	11
4	Phenacetin (0·02%) + $Na_4P_2O_7$ + H_3PO_4*	36	1	11	—
		24	0	8	—
		12	0	2	—
5	Tartaric acid (0·02%) + sodium salicylate (0·01%) + *m*-sodium phosphate (0·01%)	0	0	—	8
6	8-Hydroxyquinoline (0·01%) + $Na_4P_2O_7$ (0·05%)	—	0	3	12
7	Urea (0·02%)	5	0	83	98
8	Nipagin (0·1%)	6	4	8	10
9	Sodium pyrophosphate (0·02%) + H_3PO_4 (0·01%)	5	0	50	80 (4 hr.)

*Acidity of solution varied by adding requisite amount of phosphoric acid.

Results and discussion

The following is the stabilizing power of the organic stabilizers tested in the order of their decreasing effectiveness (TABLE 1): Deutsche Gold und Silber Scheide-Anstalt (Degussa) stabilizer, sulphanilamide, 8-hydroxyquinoline, nipagin, acetanilide and phenacetin. These compounds are more

TABLE 3 — STABILIZATION OF 30 PER CENT (100 VOL. O) HYDROGEN PEROXIDE SOLUTION

(*Non-volatile solid residue of unstabilized solution at* 110°C., 120·60 *mg.*/100 *cc.*)

No.	Additive	Acidity	% decomposition				
			At room temp.			At 95°C.	
			3 months	6 months	12 months	1 hr.	3 hr.
1	Phenacetin (0·02%) + $Na_4P_2O_7$ (0·02%) + H_3PO_4 (0·01%)	28	8	14	17	8	12
	H_2O_2, %		(27·6)	(26·8)	(24·9)		
2	8-Hydroxyquinoline (0·01%) + $Na_4P_2O_7$ (0·05%)	28	—	6	9	2	4
	H_2O_2, %			(28·2)	(27·3)		
3	Tartaric acid (0·02%) + sodium salicylate (0·01%) + *m*-sodium phosphate (0·01%)	32	Not observed			4	6
4	Nipagin (0·1%)	28	Not observed			6	9

effective than the others tested. The results obtained with phenacetin, acetanilide and nipagin show that use of high concentrations of stabilizers is worse than using no stabilizer at all and there seems to be no simple relationship between concentration of stabilizer and the rate of retardation of decomposition of hydrogen peroxide. The optimum concentration of these substances are 0·025, 0·02 and 0·10 per cent respectively, and any increase in their concentration beyond these levels renders them less effective. Acetanilide has greater stabilizing power than phenacetin. Hydrogen peroxide solutions stabilized with acetanilide can be used for all general purposes such as bleaching, dyeing and for external use in medicine. Phenacetin stabilized solutions become slightly pink on storage; this can be avoided by using pyrophosphate or phosphate in combination with phenacetin.

A mixture of phenacetin, acetanilide and phosphoric acid preserves hydrogen peroxide solution for two years and the loss of hydrogen peroxide was only 18 per cent, i.e. the strength of a 3 per cent (10 vol. of oxygen) hydrogen peroxide solution was reduced to 2·46 per cent. The mixed stabilizer of Deutsche Gold und Silber Scheide-Anstalt is superior to all the other mixtures of stabilizers tried. The acidity of the hydrogen peroxide solution containing this stabilizer is 7 but this cannot be a contributory factor for its better performance, as metaphosphoric acid, sulphuric acid or tartaric acid individually does not stabilize the solution at this acidity. Tartaric acid, sodium salicylate and metaphosphoric acid individually are effective only for short periods.

Nipagin, 8-hydroxyquinoline and sulphanilamide are of special interest since they individually exhibit high stabilizing power. 8-Hydroxyquinoline and tartaric acid mixture are better than phenacetin or nipagin for stabilizing high strength hydrogen peroxide solutions. The low stabilizing power of barbituric acid and uric acid is probably due to their low solubility in hydrogen peroxide solutions.

The decomposition of hydrogen peroxide solution at boiling point in 1 hr. has been assumed to be equal to the decomposition undergone by the solution stored for one year at room temperature. However, it was observed in the case of phenacetin stabilized solution that the extent of decomposition undergone by storing the solution for one year at room temperature was 16 per cent, whereas no decomposition was noticed in the solution according to the b.p. method. The results (TABLE 3) show that the solution is less stable than indicated by the b.p. method. The extent of decomposition undergone by hydrogen peroxide solutions stored in a cold climate is not the same when stored under tropical conditions, and it may be assumed that the percentage decomposition undergone by hydrogen peroxide solutions in 6 hr. at 95°C. is approximately equivalent to the decomposition undergone by the solution stored for one year under tropical conditions.

Stabilization data obtained for 30 per cent hydrogen peroxide by the b.p. method (TABLE 3) show that the extent of decomposition in 3 hr. is approximately equal to that undergone by the solution stored for 6 months at room temperature. The results are in agreement with those obtained according to the other relationship.

Various theories have been put forward to explain the mode of action of the stabilizers. According to one theory, the stabilizers owe their action to the removal or deactivation of substances which catalyse the decomposition of hydrogen peroxide. In general, hydrogen peroxide is stabilized by acids and Lemoine[22] explains the stabilizing action of acids as due to their greater affinity for the water molecules formed during decomposition of hydrogen peroxide. This theory seems untenable in view of the fact that acids exert a pronounced stabilizing effect even in a system in which the ratio of acid to water molecules is very small. Clarens[23] is of the opinion that the stabilizing action of acids is due to their solvent action on metallic oxides. While this possibility may exist, it is certain that this is not the main factor involved. Another view held is that hydrogen peroxide forms a stable compound with the stabilizer. Evidence is available in support of this theory from the fact that hydrogen peroxide forms addition compounds with acetanilide, urethane, succinimide and urea. Urea peroxide $[CO(NH_2)_2H_2O_2]$ is of special significance in this context. Similarly, hydrogen peroxide is known to form stable compounds with certain salts, e.g. ammonium sulphate, sodium sulphate, phosphate and acetate. Sodium perborate $NaBO_2.H_2O_2.3H_2O$ is one such compound and is sold commercially as a carrier of hydrogen peroxide. The stabilization of phosphate has also been explained[24] as due to the formation of stable salts, such as $Na_4P_2O_7.\frac{1}{2}H_2O_2$.

The above theory cannot be accepted as final since the amount of the stabilizers present is small and all substances which form additive compounds do not act as stabilizers, e.g. sodium and ammonium sulphate.

It is well known that the rate of decomposition of carefully purified hydrogen peroxide is extremely slow and is accelerated by a wide variety of catalysts. Among the more active and commonly encountered catalysts are copper, iron, manganese and lead. Inactivation of these metallic ions is accomplished by the addition of suitable complex formers. This suggests that the stabilizers owe their stabilizing activity to complex-forming ability which serves to remove the metal ions from the solution. Martell and Calvin[25] cite many examples of such " negative catalysts " and are of the opinion that in many cases powerful chelating agents are needed to deactivate these metal ions. For example, ethylene diamine tetra-acetic acid is a good stabilizer for ascorbic acid which delays the copper-catalysed oxidation of this substance by forming a stable copper chelate.

Sodium phosphates (metaphosphates and pyrophosphates) form complex salts with Ca, Mn, Fe and other heavy metal ions, e.g. phosphoric acid with ferric salt gives ferriphosphoric acid complex, $H_3[Fe(PO_4)_2]$[26]. Sodium pyrophosphate forms two complexes with copper salt[27] having the formula $[Cu(P_2O_7)]Na_2$ and $[Cu(P_2O_7)]Na_6$. The metaphosphate is the most effective of these compounds in its ability to form complexes. Complex tartrate ions[28] are formed with Mn, Co, Ni, Pb, Cu, etc., e.g. ferric tartrate, $[Fe(C_4H_3O_6)_3]Na_6$, and cupric tartrate, $[Cu(C_4H_4O_6)]$, are typical internally complex salts. It is well known that the presence of tartrates inhibits many of the reactions of Fe, Al and Cu due to the formation of internally complex compounds. Aromatic hydroxy acids in particular form inner complexes, e.g. salicylic acid forms inner complexes with Al, Fe(ic), Cu, Pb, Mn, Ni, etc. The violet colour observed when ferric salts are mixed with salicylic acid[29] is due to the formation of the complex $[Fe(C_7O_4O_3)_3]H_3$. Of the stabilizers tested, the best is the one used by Deutsche Gold und Silber Scheide-Anstalt and which is a mixture of these complex-forming substances.

Acetanilide and phenacetin have been reported to be good stabilizers even in the presence of active catalysts[3] (copper) and it is probable that their action is also due to the formation of internally complex compounds. In addition to complex-forming ability, phosphates and phosphoric acid have a specific peptizing effect[30] on complex metal organic compounds and stability of hydrogen peroxide solutions is thus found to be increased by the addition of phosphates along with the organic stabilizers.

8-Hydroxyquinoline (oxine)[31] forms a stable chelate of five-membered ring with Cu, Ag, Ni, Co, Cd, Zn, Pb, Mg, etc.

Sulphanilamide[32], which is another good stabilizer reported here, is also known to form a complex compound with copper. The chelate complexes are most stable when they contain five or six members in the ring including the metal ion. Many of the stabilizers reported here contain the chelate groups and exhibit ability to form complexes with metal ions. One can extend this explanation to the other chelated substances which have not been listed here. For example, oxalic acid is a good stabilizer although its use is prohibited. Another example is α-nitroso-β-naphthol[33] which forms an internal complex with Co, Cu and Fe in its tautomeric ortho-quinoidal forms and has been reported to be a good stabilizer[34].

Each stabilizer is specific to a particular metallic ion and forms complexes whose stability depends on the *p*H of the hydrogen peroxide solution, storage temperature and duration. A single stabilizer may not inactivate all the metal ions present and in such instances, the use of a mixture of stabilizers would be more effective. Oxine is an exception; it forms stable chelate complexes with many metal ions and its use singly is better than using it in admixture with other stabilizers.

The existence of a large variety of organic compounds and groups containing auxiliary valencies indicates that possibilities of obtaining new stabilizers more effective than those known at present have not been exhausted and other chelate forming compounds will be discovered which may even permit the marketing of stable high strength hydrogen peroxide (50-80 per cent H_2O_2) solutions. The complex formation or chelation (with organic stabilizers) seems to be one of the more important requisites of a good stabilizer.

Acknowledgement

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Letters to the Editor

EFFECTS OF UNIDIRECTIONAL RUBBING OF CUPRIC OXIDE FORMED ANODICALLY

AN INTERESTING PHENOMENON WAS OBSERVED when a layer of one-degree orientated cupric oxide[1], produced by the anodic oxidation of copper and brass in a 10 per cent solution of sodium hydroxide at about 10 mA/sq. cm. for 10 min. at 80°C., was given a light unidirectional rubbing with cotton wool. It was found that this treatment transformed the one-degree orientation of monoclinic CuO (FIG. 1) into an approximately two-degree orientation, the second degree of orientation being related to the direction of rubbing, and that the matt jet black surface was simultaneously changed to a reflecting one. The specimen yielded an asymmetric electron diffraction pattern (FIG. 2) when the beam was perpendicular to the rubbing direction, and a symmetrical pattern (FIG. 3) when the beam was along the rubbing direction. If the unidirectionally rubbed surface was further rubbed at right angle to the previous rubbing direction, a similar though less intense asymmetrical pattern related to the new rubbing direction was again obtained. When the same specimen rotated through 180° was examined by electron diffraction, a similar asymmetric arc pattern was obtained, though the positions of the arcs were reversed with respect to the plane of incidence and were on the other side of the photographic plate. This reversal of the pattern amounts to the change of abrasion direction by 180° to the previous one.

Similar asymmetric electron diffraction patterns but less prominent were also obtained by the unidirectional rubbing of CuO formed on heating copper in air.

Thus the unidirectional rubbing has modified the crystal orientation in such a way that a new crystal plane has been brought in the plane of incidence as can be seen in Fig. 2. The appearance of the $11\bar{1}$ and $22\bar{2}$ arcs with medium intensity in the plane of incidence in the asymmetrical pattern, together with the long arcs in the symmetrical pattern, shows that the CuO crystals were so orientated that a principal lattice row in the $(11\bar{1})$ plane was closely parallel to the rubbing direction. On the other hand, the elongated and diffuse nature of the asymmetric arcs in the pattern show that there was considerable disorientation due to rotation about this lattice row as the axis. The asymmetrical pattern is thus equivalent to a partial rotational pattern of the cupric oxide crystals about an axis lying on the $(11\bar{1})$ plane, parallel to the specimen surface

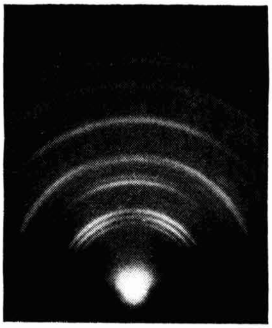

FIG. 1—ELECTRON DIFFRACTION PATTERN OF ONE-DEGREE ORIENTATED CuO, FORMED ANODICALLY AT 10 MA/SQ. CM. AT 80°C.

FIG. 2—ELECTRON DIFFRACTION PATTERN OF UNIDIRECTIONALLY RUBBED ONE-DEGREE ORIENTATED CuO; BEAM NORMAL TO THE RUBBING DIRECTION

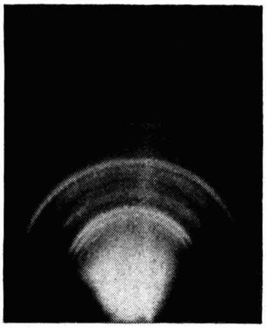

FIG. 3—ELECTRON DIFFRACTION PATTERN OF UNIDIRECTIONALLY RUBBED ONE-DEGREE ORIENTATED CuO; BEAM ALONG THE RUBBING DIRECTION

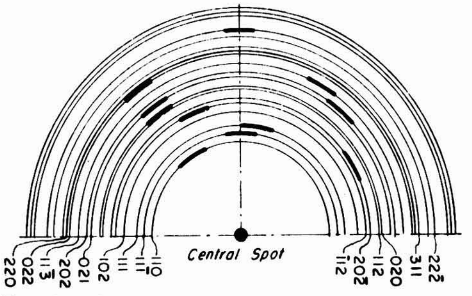

FIG. 4 — ASYMMETRIC PATTERNS OF CUPRIC OXIDE AFTER UNIDIRECTIONAL RUBBING

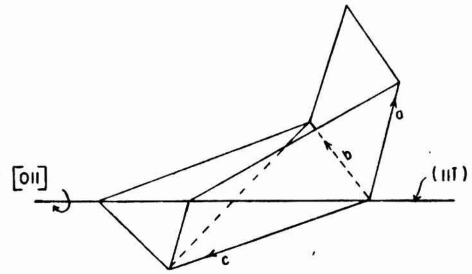

FIG. 5 — CUPRIC OXIDE CELL AND RUBBING DIRECTION

but normal to the beam direction. Since [101], $[1\bar{1}0]$ and [011] are the principal lattice rows in the $(11\bar{1})$ plane, the indices of the rubbing direction can be fixed by the trial and error method in the following way.

If [101] were the rotation axis, a rotation of about 40° is required to bring the (020) plane into the reflecting position, but this plane is then parallel to the surface and would therefore give a Bragg reflection arc in the plane of incidence. This is contrary to the observed pattern (FIG. 2). Further evidence of its incorrectness is obtained from the consideration of the diffraction expected from the planes such as (110) and $(1\bar{1}0)$.

Similarly taking $[1\bar{1}0]$ as the axis, a rotation of about 20° brings the (110) plane parallel to the surface, and it should therefore give a strong arc in the plane of incidence; but this is not in agreement with our result. At the same time the 020 reflection should appear to the left of the plane of incidence as observed at about 40° from this plane, but a $\bar{1}10$ reflection should also appear low down near the shadow edge; this is again not the case. Thus $[1\bar{1}0]$ also cannot be the rotation axis.

On the other hand, a trial with the [011] axis gives good agreement with the pattern. A little rotation brings {110} planes into the reflecting position and the 110 arc would then be about 34° to the left of the plane of incidence. Further rotation by about 30° brings (020) plane into the reflection position. This gives an arc at about the same angle as the 110 arc from the plane of incidence. Rotation in the opposite direction brings the (202) and $11\bar{3}$ planes into the reflecting position on the opposite side of the plane of incidence and 021 and $1\bar{1}2$ reflections should occur on the left side of the plane of incidence. These expectations also agree with Fig. 2. The only discrepancy appears to be the occurrence in the pattern of what might be the $20\bar{2}$ arc of medium intensity to the right of the plane of incidence, whereas it should have been on the left, though requiring about 90° rotation from the initial $(11\bar{1})$ orientation of the surface.

Fig. 4 indicates the positions of the arcs in the asymmetric pattern, if the orientation by the unidirectional abrasion would have been perfect. Fig. 5 shows the cupric oxide cell and its rubbing direction.

Now, that the [011] axis should be the common orientation of the crystals, can be easily understood in relation to the known $(11\bar{1})$ cleavage plane and the usual {100} plate and lath habit of CuO[2]. When such CuO crystals are rubbed, the raking action due to abrasion would cleave them into lath-shaped fragments and align them with their length along the [011] axis in the $(11\bar{1})$ cleavage plane. Such actions would also produce considerable disorientations about the abrasion direction. Since translational slip directions of CuO are not yet known, it is not clear whether an alternative interpretation in terms of slip is possible.

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ELECTRODE SEPARATION AS A DETERMINANT OF THE OPTIMUM PRESSURE FOR MAXIMUM NEGATIVE JOSHI EFFECT

MOHANTY AND KAMATH[1] HAVE SHOWN THAT the negative Joshi effect — Δi in oxygen, under conditions of constant current in dark i_D and reduced potential $V_r = (V - V_m)/V_m$ (where V_m is the "threshold potential" and V that applied), initially increases with the gas pressure p to a maximum, and diminishes thereafter. That the optimum p for maximum $-\Delta i$, i.e. $p_{-\Delta i \text{ max}}$, is not the same for various tubes, observed for the first time by Mohanty and Kamath,[1] has now been traced to difference in the electrode separation δ.

Three soft soda glass Siemens' ozonizers A, B and C were prepared with tubes (wall thickness, 1·2 mm.) from the same batch. The inner tubes were of the same dimensions (outer diameter, 17·0 mm.). The electrode separation δ was respectively 2·8, 4·6 and 5·8 mm. The tubes, carefully cleaned and vacuum dried, were filled with pure oxygen at different p in the range 50-500 mm. Hg (26°-28°C.), and $-\Delta i$ observations made, on a thermal junction-galvanometer system, at various applied V (1-10 kV. rms, 50 ~). The length of the discharge column was 12·0 cm. in each case.

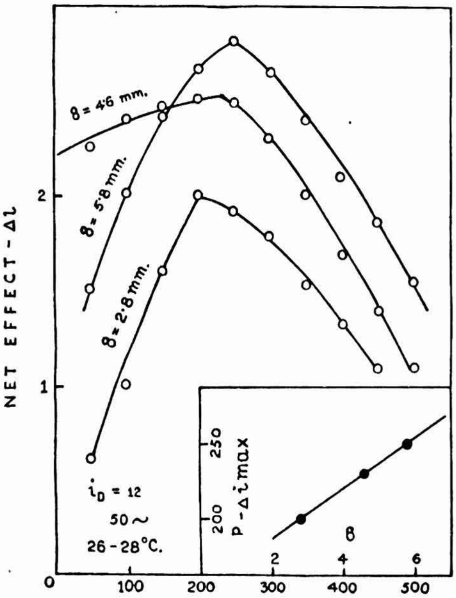

FIG. 1 — THE OPTIMUM PRESSURE FOR MAXIMUM NEGATIVE JOSHI EFFECT AS A FUNCTION OF THE ELECTRODE SEPARATION

It will be seen from Fig. 1 that, under constant i_D conditions, $p_{-\Delta i \text{ max}}$ increases linearly with δ. Thus, values for $p_{-\Delta i \text{ max}}$ at $\delta = 2{\cdot}8$, 4·6 and 5·8 mm. are respectively 200, 230 and 250 mm. Identical results are obtained under conditions of constant V_r.

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A NOTE ON THE "THRESHOLD POTENTIAL" OF OZONIZER DISCHARGE & ITS DEPENDENCE ON ELECTRODE SURFACE

IN A RECENT COMMUNICATION, MOHANTY[1] reported an interesting observation that the threshold potential (V_m) of a low-frequency (50 c./s.) electric discharge in oxygen decreased with deposition of a potassium chloride film on the annular (glass) walls of the discharge tube, viz. a Siemens' ozonizer. Similar results were obtained in water vapour.[2] An attempt is made in this note to explain this finding from a few theoretical considerations[3-5] which are established to be applicable to d/c discharges, and may tacitly be assumed to be so for a/c discharges especially when features occurring, under simple enough conditions such as in the absence of accumulation of space charges, in one half cycle of the alternating potential, are taken into consideration[6].

For a discharge to take place, an initial or triggering electron is necessary. Over a fixed potential range below V_m, akin to the familiar Geiger region of counters, external radiation like cosmic, radio active rays and the like supply the initial electron(s). In this region, the field is large enough to cause ionization by collision (Townsend α-mechanism), but not so to generate secondary electrons by the familiar β-processes.[3] This region may, for convenience, be referred to as the non-selfmaintained or Geiger region of the a/c discharge, which under ordinary conditions such as in the absence of large external resistance is characteristically of narrow potential width in ozonizer discharges. At the threshold potential V_m, which roughly corresponds to the onset potential of a selfmaintained discharge[7], the field is strong enough to produce agencies such as positive ions, photons, etc. which generate sufficient number of electrons from a favourable portion of the discharge tube, chiefly the cathode[3]. In systems with metallic electrodes, " free " electrons forming the Fermi gas constitute these secondary electrons, while in ozonizers with glass electrodes the same is incomprehensible.

It may be postulated that ionization of the adsorbed layers like oxygen, water vapour, etc., or the inherent properties of deposited films like potassium chloride are responsible for the secondary electrons in the ozonizer discharges. It is instructive to note that in an ozonizer of known geometry and of which the adsorbed layers were removed by suitable methods, the discharge in mercury vapour could not be struck even at as large a potential as 10 kV., while it could be initiated in the same vessel with adsorbed water vapour layers on the electrodes at 900 V. Thus the existence of the adsorbed layers aids the liberation of secondary electrons at low voltages. From the above, one expects that in systems containing varied materials with different ionization potentials (V_i) on the electrode surface and in the homogeneous gas phase, e.g. water vapour ($V_i = 12{\cdot}56$ V.) in the adsorbed state on the glass walls and iodine vapour ($V_i = 9{\cdot}7$ V.) in the bulk, the non-selfmaintained or Geiger region would be of marked potential width, while in the absence of adsorbed water vapour layers, i.e. with iodine vapour both in the bulk and on the electrode walls, it should be inappreciable. Experimental data in iodine vapour enclosed in degassed and non-degassed vessels were in good agreement with this deduction (RAMAIAH, unpublished data). Further, from the above view one anticipates that unlike in nitrogen ($V_i = 15{\cdot}5$ V.), the breakdown potential V_m in oxygen ($V_i = 12{\cdot}5$, cf. V_i of water vapour $= 12{\cdot}56$ V.[5]) would be roughly the same in degassed and ordinary ozonizers containing adsorbed water vapour layers; these studies are in progress in these laboratories.

The decrease of V_m, due to deposition of potassium chloride film on the walls of the ozonizer, is of marked significance, and is explained by the following:

(a) Deposited films like potassium chloride alter the nature of the electrode surface due to a change in the corresponding adsorption. Thus, potassium chloride was found to increase sorption on glass of electronegative radicals like OH in water vapour discharge[2,8,9]. This leads, on general theoretical grounds, to an increase in the work function of the surface and, therefore, a rise in the threshold potential which depends, *inter alia*, upon the work function of the surface.

(b) Potassium chloride is also known to behave, under normal conditions of temperature, as a metallic conductor[10]. In coated discharge tubes, the cathode surface acts roughly as a metal to aid the liberation of secondary electrons by bombardment thereon of positive ions or/and photons, at relatively lower fields than in blank vessels wherein the secondary electrons originate, as assumed above, from the adsorbed layers (or in the extreme case as in their absence, from the glass wall).

It is probable that the decrease of V_m due to potassium chloride film is the resultant of (a) and (b).

The above view explains all the observed facts on the influence of " ageing "[11], temperature[12], films like aluminium powder[13], etc., on the thre sholdpotential, and will be reviewed in detail at a later date.

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EQUILIBRIUM FLASH VAPORIZATION OF PETROLEUM FRACTIONS

The process design of equipment for equilibrium flash vaporization involves the determination of bubble and dew points, flash curve and composition of products. The normal method of determining these for mixtures containing a finite number of components is given by Brown[1]. This method cannot be applied to multicomponent systems as petroleum fractions whose individual components cannot be easily identified and estimated. Further, phase equilibrium data of the individual components is not generally available.

A method that may be used to get the process design data for petroleum fractions is to get the data experimentally with a laboratory unit such as that used by Leslie and Good[2], Othmer, Ten Eyck and Tolin[3], and Okamoto and Van Winkle[4]. But laboratory units generally give divergent results due to thermal losses, inaccuracies in measurement, thermal cracking, etc.

Another method is to use the empirical correlations such as those of Piroomov and Beiswenger[5], Obryadchikov[6], Edmister and Pollock[7], and Okamoto and Van Winkle[4]. But empirical equations generally lack a basic approach to the problem.

The method now proposed involves the use of hypothetical components and their relative volatilities. The True Boiling Point (T.B.P.) curve of a petroleum fraction is split into " hypothetical " components using the chord area method. A hypothetical component is thus a mixture of components and is designated by its normal boiling point given by the T.B.P. curve. The volume percentage read on the T.B.P. curve is converted to mole percentage using the method of Watson, Nelson and Murphy[8]. Relative volatility charts of hypothetical components, 0-750, are prepared for 0,100 and 200 lb./sq. in. pressures, with n-octane as the reference substance, using the phase equilibrium constants presented by Hadden[9]. The basic equations given by Brown[1] are suitably transformed so that relative volatilities may be used instead of equilibrium constants.

The following transformed equations give the bubble and dew points:

$$\Sigma Y = \Sigma(\alpha X)\,K_R = 1 \text{ for bubble point} \quad . \; . \quad (1)$$

$$\Sigma X = \Sigma(\alpha Y)/K_R = 1 \text{ for dew point} \quad . \; . \; . \quad (2)$$

For the determination of flash curve, a hypothetical component C whose equilibrium constant is nearest to unity at the assumed conditions is chosen. The basic equations are transformed as follows:

$$V/L = \alpha/\alpha_{CR}.V_c/L_c \quad \ldots\ldots\ldots\ldots \quad (3)$$

$$L = F/\frac{V}{L}+1 \quad \ldots\ldots\ldots\ldots \quad (4)$$

$$\alpha_c = K_c/K_R = V_c/L_c.\Sigma L/\Sigma V \quad \ldots\ldots \quad (5)$$

where X and Y are mole fractions of a hypothetical component in the liquid and vapour phases;

V, L and F are moles of a component in the vapour and liquid phases and feed;

V_c and L_c are the moles of C component in the vapour and liquid phases;

K_c and K_R are the equilibrium constants of C component and reference component;

α and α_c are relative volatilities of any component and C component referred to n-octane; and

α_{CR} is the relative volatility of C component referred to n-octane.

The composition of the products may be determined using equations (3) to (5), but in this determination the pressure and temperature being fixed, the trial is for agreement between the assumed and calculated values of V_c/L_c.

The results obtained by following the proposed procedure are in good agreement with the actual values obtained in the flash runs of petroleum fractions.

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ON THE MECHANISM OF DEPRESSION OF PYRITE

THE MECHANISM OF DEPRESSION OF PYRITE by alkali cyanide in the presence of ethyl xanthate as collector in froth flotation has been attributed by the author in a recent communication[1] to the reduction of ferric ions on the mineral surface to ferrous ions by cyanide ions, so that the insoluble coating of ferric xanthate, which is a prerequisite to the formation of a water-repellent film, may not form. It is suggested that the same mechanism holds good in all cases of depression in presence of ethyl xanthate as collector, and to prove it a few evidences are brought forward in this paper from other sources.

Sulphite ions are used to a limited extent in place of cyanide ions for depression of pyrite. Levine[2] found that sulphite ions prevent bubble attachment to pyrite with ethyl xanthate and destroy bubble attachment at a pyrite surface originally xanthate coated. Although he concluded that in depressing pyrite the mineral surface is closed by a coating of ferric sulphite in the *p*H range 6·4-8·2, and by a basic ferric sulphite at higher *p*H, the author finds this example as an instance where the mechanism proposed also fits in.

It is also reported[3] that depression of pyrite by cyanide ions is greatest in a reducing atmosphere, e.g. ferrous sulphate or sulphur dioxide. It has also been reported that oxidizing agents also depress pyrite, which apparently goes against the mechanism proposed above. Gaudin[4] reports that sodium dichromate depresses pyrite. Potassium permanganate and ferric sulphate also depress pyrite in presence of ethyl xanthate. In order to account for the depressing action of oxidizing agents, the action of potassium dichromate on ethyl xanthate in different concentrations has been investigated. For this purpose 25 cc. of dichromate solution was mixed with 25 cc. of ethyl xanthate solution in a 250 cc. pear-shaped separating funnel for 10 min. and the xanthate content was analysed. The method of analysis was the same as described in the earlier paper[5]. The factor 0·775 was used in the calculations instead of the theoretical value 0·711 to arrive at the weight of K-ethyl xanthate from the weight of Pb-ethyl xanthate. Benzene solution was evaporated by infra-red heating since the lead xanthate decomposed even when water bath was used for evaporation. All chemicals used were of analytical grade (Baker's); ethyl xanthate used was obtained from Dow Chemical Co. and purified by crystallization from ethyl alcohol.

TABLE 1 — EFFECT OF DICHROMATE ON THE STABILITY OF ETHYL XANTHATE

[*Values refer to weights of salts present in* 50 *cc. of solution*]

Potassium dichromate g.	Potassium ethyl xanthate at start g.	Potassium ethyl xanthate after 10 min. g.	Decomposition %
0·02	0·0200	0·0159	20·5
0·02	0·0200	0·0158	21·0
0·02	0·0100	0·0060	40·0
0·02	0·0100	0·0059	41·0
0·02	0·0050	0·0027	46·0

The results obtained, as given in Table 1, show that dichromate definitely decomposes ethyl xanthate. In the very low dilution of xanthate usually used in flotation, it may be inferred that practically the whole quantity of xanthate is decomposed. The mechanism of depression of pyrite by oxidizing agents may, therefore, be traced to the decomposition of the collector itself.

The author is grateful to Principal R. P. Sinha for his interest in the problem.

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EFFECT OF THICKNESS OF THE IONOSPHERIC LAYER ON THE MULTIPLE SPLITTING & SCATTERING OF RADIO WAVES

THE MAGNETO-IONIC DOUBLE SPLITTING OF a downcoming radio wave into ordinary and extraordinary components is of common occurrence. Besides such simple type of split echoes, triple and even quadruple splitting have been observed in vertical incidence radio sounding of the ionosphere, particularly at places of high geomagnetic latitude. Triple splitting of ionospheric waves was first reported by Eckersley[1] in 1933. Soon after Toshniwal[2] from India and Harang[3] from Norway reported similar observations. Ten years later Meek[4] observed triple splitting of the ionospheric echoes in Canada. In 1948 Newstead[5] observed multiple splitting of F_2 echoes at Hobart, Tasmania. In the same year records of triple splitting were obtained by Seaton[6] in Alaska, and by Gipps, Gipps and Venton[7] at Brisbane, Australia. Rydbeck[8] also reported that triple splitting, both in E and F layers, had been frequently observed at Kiruna, Sweden, since 1948. Landmark[9] and Hogarth[10] have recently made experimental investigations on the sense of polarization of the split components.

From the observations made by various workers at different places it will be seen that the multiple splitting of echoes may be obtained even at lower latitudes under suitable conditions of the ionosphere. We have observed multiple splitting on several occasions during our experiments on the scattering of radio waves and found that the thickness of the ionospheric layer plays an important part both on the production of scattered radio signals and the multiple split echoes. Triple splitting of echoes both from the E and F layers has been observed by us in vertical incidence experiments with a low-power pulse transmitter. The split echoes from the E layer have been found to occur only in presence of a strong sporadic E. They are rather infrequent and continue for a very short duration with the intensity of the various split components varying rapidly. Multiple splitting of F echoes, however, is comparatively frequent and a typical oscillographic record of quadruple splitting from the F layer is reproduced in Fig. 1. Such types of splitting are observed usually just before and during the sunset hours in the absence of scattered signals. A brief account of the theory of multiple splitting as advanced by various investigators is given in this paper and the influence of the thickness of the ionosphere in producing these split echoes is also discussed.

The magneto-ionic theory of splitting of radio waves reflected from the ionosphere into two components was theoretically established by Appleton[11], Goldstein[12], and Hartree[13]. The possible existence of a third component in the case of a layer having a sharp vertical gradient of ionization was first shown by Mary Taylor[14]. Later various other workers[15,16] have discussed the mechanism of excitation of the third component or the so-called " z-trace ". The presence of the fourth component in quadruple splitting, however, did not find a ready explanation as it was generally assumed that reflection of waves took place from the point where refractive index was zero. Booker[17], however, has shown in his generalized treatment of the magneto-ionic theory that the wave is totally reflected at the point where the change of complex refractive index per vacuum wavelength is considerable, i.e. when the general condition of reflection of waves is given by $\frac{d\mu}{dz} = \infty$, for vertical propagation. Again, when Booker's generalized wave function is substituted in the Maxwellian equations[18], we get a quartic equation in μ which incidentally brings out that at the point of reflection $\frac{d\mu}{dN} = \infty$. From this condition Bajpai[19] had shown in a different manner that the ordinary ray could

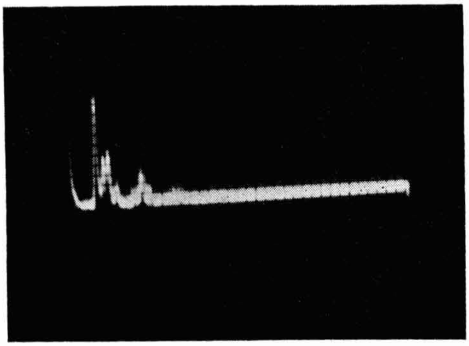

FIG. 1 — OSCILLOGRAPHIC RECORD OF QUADRUPLE SPLITTING: 21 JAN. 1954, 16.30 HR. I.S.T., 7·4 Mc./s.

be reflected from only one concentration of electrons, while the extraordinary wave had in general three conditions of reflection when the pulsatance of the wave was greater than the gyro-frequency. The above two conditions represent the same physical phenomenon in an ionosphere supposed to be horizontally stratified with the electron density increasing with height.

The above conditions of reflection are possible only in the case of a thin layer of the ionosphere when the vertical gradient of ionization is sharp, and thus, during the occurrence of quadruple splitting, the thickness of the ionospheric layer has to be necessarily small. On the other hand, the favourable condition for the occurrence of scattering of radio waves is obtained when the thickness of the layer is large, due to higher concentration of energy of the waves towards the ground, which happens to be the source of scattering. This is in accord with our observations with a low-power pulse transmitter[20]. Hence, it is seen, the requirements for the occurrence of scattered signals and multiple splitting are opposite in nature, as far as the thickness of the ionospheric layer is concerned. In order to verify this the semi-thicknesses of the ionospheric layer, both during the occurrence of scattered signals and the multiple split echoes, have been calculated from the following equation given by Appleton and Beynon[21]

$$h' = h_o + \frac{Y_m}{2} \cdot \frac{f}{f_c} \cdot \log_e \left[\frac{f_c + f}{f_c - f} \right]$$

where h' is the equivalent height of the layer, h_o the height of the lower boundary of the layer above the ground, Y_m the semi-thickness of the layer, f the frequency of transmission, and f_c the critical frequency at vertical incidence. A typical value of Y_m during the evening hours when scattered signals are obtained is found to be 105 Km., and the same is found to be only about 35 Km. when multiple split echoes are obtained. It is interesting to note here that on the occasions when the multiple splitting is observed, the scattered signals are invariably absent. The thinness of the ionospheric layer at the time of multiple splitting is thus confirmed by the absence of scattering on such occasions. It may, however, be added that sometimes multiple splitting may not be observable even when the ionospheric layer is thin, either due to the lack of suitable vertical gradient of ionization or proper magnetic field at the point of reflection in the ionosphere.

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SUPER WIDE-BAND FREQUENCY MODULATION

IT HAS BEEN SHOWN BY RAKSHIT AND SARKAR[1] that the three-phase R-C oscillator due to Rakshit and Bhattacharyya[2] is capable of producing F.M. oscillations if one of the oscillator stages is shunted by a triode having the modulating voltage on its grid. The schematic arrangement of the modulated stage is shown in Fig. 1. The modulating voltage causes a variation of the mutual conductance g and hence of the plate resistance r_p of the modulator. The effective load resistance of this stage, therefore, varies in accordance with the modulating voltage and thus produces frequency modulation. When the load resistance is large enough, *c.* 1,000 ohms or more, the variation of r_p produces large change in frequency and the linear variation is much greater than what is needed for producing wide-band F.M. When the load resistance is small, a few hundred ohms or so, as is necessary for producing oscillations of sufficiently high frequency, the variation in r_p will not obviously produce large frequency deviation as for larger load resistances. Frequency deviation required for normal wide-band operation is, of course, realizable with the simple arrangement of Fig. 1 on carrier frequencies up to about 10 Mc./s.

In some cases, as for example for multi-channel V.H.F. communication using F.M., it would be highly advantageous if super wide-band frequency modulation could be directly impressed on a sufficiently high carrier frequency.

It has been found that the performance of the modulator can be considerably improved by making only slight changes in the circuit arrangement as shown in Fig. 2. The modulating signal is now applied through a resistance R_g which is high in comparison to the reactance of the grid-cathode capacitance C_{gk} at the operating radio frequency. To satisfy this condition C_{gk} may, if necessary, be shunted externally by a suitable capacitance. It will be noticed in Fig. 2 that a fraction of the r.f. voltage V developed across the oscillator load is automatically applied on the modulator grid. Due to this r.f. voltage the modulator can be shown, as a first approximation, to behave as an extra resistance R shunting the oscillator load. The magnitude of R varies also with g as the variation of modulator r_p. The effect of the modulator is thus a parallel combination of R and r_p, the magnitude of R being approximately given by

$$R = \frac{X_1 + X_2}{g.X_2}$$

where X_1 and X_2 are the reactances of C_{ag} and C_{gk} respectively. In general, when R_g is not very large compared to X_2, the effect of the modulator is equivalent to R shunted by a capacitance. In any practical case the value of R is very much smaller than r_p. For type 9002 triode, for example, $R \simeq 1{,}000$ ohms, while $r_p \simeq 11{,}000$ ohms. The variation of R with g due to modulating voltage thus affects the oscillator load and hence frequency to a far greater extent than the variation of r_p. The arrangement shown in Fig. 2 is, therefore, capable of producing super wide-band frequency modulation even when the oscillator load resistance is fairly small, i.e. for high radio frequencies. It may be noted that the effect of the modulator on change in oscillator frequency can be controlled by one of the three circuit parameters C_{ag}, C_{gk} or g. The results showing the effect of the modulator on change in oscillator frequency under different operating conditions are given in Table 1 and plotted in Fig. 3. The minimum frequency f_m corresponds in each case to -10 V. on modulator grid.

FIG. 1 — SCHEMATIC ARRANGEMENT OF THE MODULATED STAGE OF THE OSCILLATOR

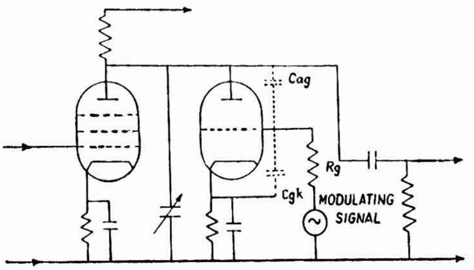

FIG. 2 — MODIFIED CIRCUIT ARRANGEMENT OF THE MODULATOR

The values given in columns 2 and 3 (FIG. 3, curves 1 and 2) correspond to carbon load resistances of 11,000 ohms with total tuning capacity, including stray, of 160 μμF. The values in columns 4, 5 and 6 (FIG. 3, curves 3, 4 and 5) are for 270 ohms; those in columns 4 and 5 are for total tuning capacity of 230 μμF while those in column 6

TABLE 1 — EFFECT OF MODULATOR ON OSCILLATOR FREQUENCY, KC./S.

MODULATOR GRID BIAS ($-$Ve) V.	INCREASE IN OSCILLATOR FREQUENCY				
	$f_m = 150$ kc./s.	$f_m = 186$ kc./s.	$f_m = 4 \cdot 3$ Mc./s.		$f_m = 15 \cdot 5$ Mc./s.
	Modulation as in Fig. 1	Modulation as in Fig. 2; C_{ag} shunted by 30 μμF and C_{gk} shunted by 60 μμF.	Modulation as in Fig. 1	Modulation as in Fig. 2; C_{ag} shunted by 30 μμF.	Modulation as in Fig. 2; C_{ag} shunted by 30 μμF.
10	0	0	0	0	0
9	4·4	41	0	9	27
8	11·3	106	1·5	36	120
7	19·0	177	5·7	102	340
6	26·0	239	15·0	242	657
5	32·7	—	26·0	419	1027
4	37·5	—	33·0	570	1300
3	41·5	—	36·0	682	1485
2	45·7	—	31·5	773	1670
1	49·3	—	28·0	823	1830

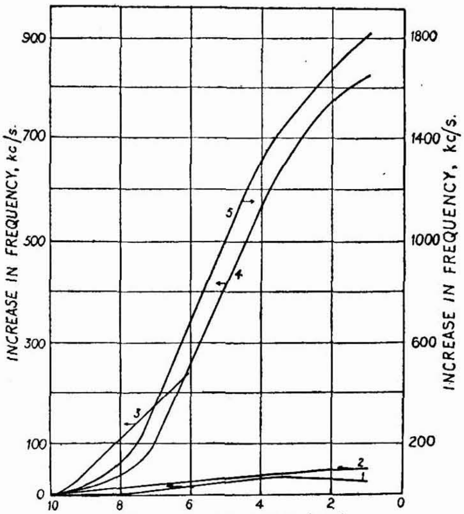

FIG. 3 — EFFECT OF MODULATOR ON CHANGE IN OSCILLATOR FREQUENCY

are for total tuning capacity of 60 μμF. With circuit conditions as in column 3, oscillations stop when the modulator grid bias is 5 V. or less due to insufficient gain in the modulated stage. The tendency of the oscillator frequency to decrease at very low values of modulator grid bias as is shown in column 4 is presumably due to increase in anode-cathode capacity of modulator.

It may be noted that an increase in the percentage variation of oscillator frequency is invariably associated with greater amplitude modulation. The amplitude modulation corresponding to the conditions in column 6 has been measured and found to be about 3 per cent, which can, of course, be easily eliminated with the help of a suitable limiter. For the conditions given in column 3 the percentage frequency variation is comparatively larger and the amplitude modulation is also greater.

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MIXED ADSORPTION OF CARBON MONOXIDE & HYDROGEN BY A COBALT FISCHER-TROPSCH CATALYST*

THE INTERACTION BETWEEN ADSORBED CARbon monoxide and hydrogen on a Fischer-Tropsch catalyst was investigated by determining the simultaneous adsorption of the two gases in the temperature range 53°-97°C. The catalyst used was the same 3·73 g. sample of reduced cobalt-thoria-kieselguhr (100 Co: $18ThO_2$: 200 kieselguhr) used in previous experiments[1]. The adsorption isotherms of carbon monoxide and hydrogen were determined from the pure gases as well as from mixtures of the approximate initial compositions 1CO: $1H_2$

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* The experimental part of this work was carried out in the General Chemistry Section, Indian Institute of Science, Bangalore, and formed part of the M.Sc. thesis of T. S. Viswanathan accepted by the University of Madras in 1952.

TABLE 1 — ADSORPTION OF HYDROGEN AND CARBON MONOXIDE

TEMP. °C.	ADSORPTION OF HYDROGEN AT PARTIAL PRESSURE 30 CM., ML. NTP			ADSORPTION OF CARBON MONOXIDE AT PARTIAL PRESSURE 15 CM., ML. NTP		
	H_2	1CO: $2H_2$	1CO: $1H_2$	CO	1CO: $2H_2$	1CO: $1H_2$
53	7·25	4·35	4·90	7·30	11·20	9·45
76	7·20	4·90	6·15	6·10	10·20	9·65
97	7·20	10·15	9·20	6·80	10·35	9·95

and 1CO: $2H_2$ at 53°, 76° and 97°C. The gas at equilibrium with the catalyst was analysed by means of a built-in thermal conductivity meter[2]. It was verified that there was no detectable reaction at 97°C. between the gases in the presence of the catalyst.

Table 1 gives the values of adsorption from the pure gases and mixtures.

At 53° and 76°C., the adsorption of hydrogen from mixtures is lower than that from the pure gas at the same partial pressure. The adsorption at 97°C., however, is distinctly higher from mixtures than from the pure gas. The amount of hydrogen adsorbed seems to be determined by the resultant of two factors: (1) a suppression of hydrogen adsorption by the blocking up of a part of the surface by carbon monoxide, and (2) an enhancement of hydrogen adsorption caused by complex formation between adsorbed carbon monoxide and hydrogen[1]. The second factor increases with temperature as seen by the progressive rise in the adsorption of hydrogen from mixtures. This is in accordance with the expectation that complex formation between carbon monoxide and hydrogen would be associated with an activation energy and hence would take place to a greater extent at higher temperatures. It is noteworthy that at 53° and 76°C., the adsorption of hydrogen is more from the mixture poorer in hydrogen (1CO: $1H_2$) than from the other, at the same partial pressure of hydrogen.

The adsorption of carbon monoxide from mixtures is, at all temperatures, higher than that from the pure gas at the same partial pressure. This enhancement is due probably to the considerable amounts of hydrogen simultaneously present on the surface, a behaviour which has been indicated in the presorption experiments[1]. In the case of carbon monoxide also, the adsorption is more from a mixture poorer in carbon monoxide than from the one richer in it, at the same partial pressure of the gas.

When the amounts of hydrogen and carbon monoxide adsorbed concomitantly from the mixtures at the various temperatures were plotted against each other, the curves, which are all almost linear, seemed to originate from a common point corresponding to an adsorption of 3·75 ml. of CO and 2·75 ml. of H_2, indicating that a substrate complex of the approximate composition 1CO: $1H_2$ was first formed on the catalyst surface at each of the temperatures investigated. The subsequent increase in the relative amounts of CO and H_2 adsorbed varied with the temperature. At the lowest temperature (53°C.), the CO adsorption increased by 3 ml. for every ml. increase in the hydrogen adsorption. This ratio of the relative uptakes changed to 2CO: $1H_2$ at 76°C. and to approximately 1CO: $1H_2$ at 97°. Further, while at each of the lower temperatures these curves were practically coincident for the two mixtures, the curves for 97°C. indicated a greater ratio of H_2 to CO adsorption from the 1CO: $2H_2$ mixture than from the other. These results, which are similar to those reported earlier on a more complex cobalt catalyst[2], suggest that the CO-H_2 complex initially formed on the surface takes up hydrogen from the gas phase at a rate that increases with temperature.

Further work is in progress on these lines and a more detailed paper will be published elsewhere. We are thankful to Dr. Sir Jnan Chandra Ghosh for his keen interest in this investigation.

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ROLE OF BIOTIN IN THE BIOSYNTHESIS OF RIBOFLAVIN IN *ASPERGILLUS ORYZAE*

IN A STUDY OF THE VARIOUS BIOCHEMICAL functions of biotin[1], it was found that riboflavin synthesis in *Aspergillus oryzae* was inhibited by γ-hexachloro-cyclohexane, and that this inhibition was overcome by biotin and not by inositol. It had also been reported from this laboratory[2], and elsewhere[3-5], that biotin is able to stimulate production of enzymes in *Neurospora* which are capable of oxidatively deaminating amino acids of both the *l*- and *d*-configurational series. Since these amino acid oxidases depend on flavin-adenine-nucleotide for their activity, and in view of our observation connecting biotin with riboflavin[1], it was thought desirable to study if biotin has by itself any influence on the biosynthesis of riboflavin in *Aspergillus oryzae*. Using two compounds which have been known to have potent anti-biotin activity, we have been able to establish a relation between biotin and riboflavin in this organism by the technique of inhibition analysis.

The organism *Aspergillus oryzae*, Culture No. 534, obtained from *N.C.T.C.*, Poona, was cultured on a modified Czapek-Dox medium of the following composition: *d*-glucose, 20 g.; potassium monohydrogen phosphate, 1 g.; sodium nitrate, 3 g.; potassium chloride, 1 g.; magnesium sulphate, 0·5 g.; trace elements (mg.): molybdenum, 0·04; iron, 0·4; copper, 0·2; manganese, 0·04; boron, 0·02; zinc, 4; distilled water to one litre and *ph* 5·0.

The total riboflavin synthesized at the end of a ten-day incubation period was determined fluorimetrically[6], All experiments involving the determination of the vitamin were carried out in subdued light. The results of experiments carried out with this organism using γ-3,4-(ureylenecyclohexyl)-butyric acid and biotin sulphone as the antibiotin compounds are represented in Tables 1 and 2.

TABLE 1 — INFLUENCE OF γ-3, 4-(UREYLENE-CYCLOHEXYL)-BUTYRIC ACID ON RIBOFLAVIN SYNTHESIS IN *ASPERGILLUS ORYZAE*

INHIBITOR mg./25 cc.	WEIGHT OF MAT mg.	RIBOFLAVIN μg./g.
0·0	203·0	84·7
0·5	228·4	60·1
1·0	214·4	62·0
1·5	221·6	52·8
2·0	219·0	53·2
2·0*	212·8	77·5

*Biotin added = 25 μg.

TABLE 2 — INFLUENCE OF BIOTIN SULPHONE ON RIBOFLAVIN SYNTHESIS IN *ASPERGILLUS ORYZAE*

INHIBITOR μg./25 ml.	WEIGHT OF MAT mg.	RIBOFLAVIN μg./gm.
0·0	214·0	82·6
1·0	210·2	71·4
2·0	206·0	66·0
3·0	203·8	59·3
5·0	201·2	56·9
5·0*	204·5	79·2

*Biotin added = 10 μg.

From the results it may be observed that biotin is able to overcome the inhibitory effects of the two compounds. The results also indicate that growth of the fungus is not appreciably affected and that there is a comparatively greater inhibition of the synthesis of riboflavin. Although biotin has a pronounced influence on the utilization of glucose and in carbohydrate metabolism[1,7-9], it appears as though the synthesis of riboflavin is affected to a major extent rather than the utilization of carbohydrate. It has been established that inositol occurs as an intermediate in the cyclization of glucose to polyphenols[10] and that inositol alone is primarily concerned with the biosynthesis of riboflavin in *Eremothecium ashbyii*[11]. In view of the fact that biotin is concerned with the biosynthesis of inositol[12] (RADHAKRISHNAMURTY, R. and SARMA, P.S., unpublished data), it is very likely that the inhibitory effects of the anti-biotin compounds are more towards the metabolism of inositol, which is primarily responsible for riboflavin formation, rather than a direct function of biotin in the synthesis. Further work is in progress as to the mechanism of action of biotin in the synthesis of riboflavin and will be published elsewhere.

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A NOTE ON ERROR IN GRAPHICAL INTEGRATION BY WEIGHING THE PAPER

FOR EVALUATION OF CERTAIN RESULTS, IT is necessary to measure the area bound by the experimental curve plotted on graph paper. Overall transmission of light through a coloured and transparent medium, for instance, can be calculated from the area under the spectrophotometric transmission curve, showing the percentage of transmission at different wavelengths. The conventional procedure of counting the number of squares falling within the area bound by experimental line is, however, somewhat tedious and inaccurate, especially for an irregular shape. The alternative method is to cut out the portion of the graph paper and weigh. Knowing the weight per unit area of the paper, the area of the given portion can be easily calculated from its weight.

Although the method is quick and fairly simple, the weight per unit area of the paper cannot be the same throughout the sheet and hence some error is invariably introduced in the results due to such nonuniformity. In the present note an attempt has been made to check the reliability of this method by estimating statistically the amount of error introduced in the result when a certain quality of graph paper was used to find out the overall transmission from transmission curves for coloured glasses[1].

Five samples (6 × 13 cm.) were carefully cut out from different sheets of the graph paper and each of them was further subdivided into six equal " strips " (1×13 cm.). Due care was taken in cutting the paper so that no appreciable amount of error was introduced. All the thirty " strips " were weighed individually and a certain amount of variation in the weights was observed (Table 1). To estimate the error introduced in the integrated result due to nonuniformity of the paper, these values were subjected to "analysis of variance"[2]. Using this well-known statistical technique it was possible to estimate the variance within the five samples and between the five samples. The variance within the samples gave an estimate of the variation in the weight of individual " strips " cut out from the same sample, while the variance between the samples was an estimate of the degree of nonuniformity among the five different samples.

Arithmetical operations carried out on the experimental data for estimation of the variances are described in Tables 1 and 2, and the results are given in Table 3. It

TABLE 1 — WEIGHTS OF THE INDIVIDUAL STRIPS FROM DIFFERENT SAMPLES

	Sample No.				
	1	2	3	4	5
$x = (W - \cdot 0900) \times 10^4$ where W = wt. of an individual strip (1 × 13 cm.)	109	91	39	61	67
	100	91	73	74	94
	100	115	62	78	65
	95	105	72	73	65
	99	95	59	46	71
	105	81	76	61	71
Sum Σx	608	578	381	393	433
	Grand total $X = 2393$				
Mean $\bar{x} = \Sigma \frac{x}{6}$	101·3	96·3	63·5	65·5	72·1
	Grand mean $\bar{X} = \frac{X}{30} = 79 \cdot 77$				

TABLE 2 — ARITHMETICAL COMPUTATIONS FROM THE DATA OF TABLE 1

Crude total sum of squares	$\Sigma x^2 = 109^2 + 100^2 + \ldots 71^2 + 71^2 = 201569$
Crude sum of squares between the samples	$(\Sigma x)^2/6 = \frac{608^2 + 578^2 + 381^2 + 393^2 + 433^2}{6}$ $= \frac{1190847}{6} = 198474$
Correction factor due to mean	$\frac{X^2}{N} = \frac{2393^2}{30} = 190881 \cdot 6$
Total sum of squares	(1) − (3) = 10687
Sum of squares between the samples	(2) − (3) = 7593
Total degree of freedom	Total No. of observations − 1 = 30 − 1 = 29
Degrees of freedom between the samples	No. of samples − 1 = 5 − 1 = 4

TABLE 3 — ANALYSIS OF VARIANCE

(*Based on Table* 1)

Source of variation	Sum of squares	Degree of freedom	Variance
Between samples	7593	4	1898
Within samples	3094	25	124
Total	10687	29	

can be seen that the variance within the samples was much smaller than that between them, or in other words, the uniformity within a certain sample was significantly more than that between the samples, taken from different sheets of the graph paper. Now the error in finding out an unknown area, say of an individual " strip " of paper from the weight of another " strip " taken from the same sample, can be calculated from the variance within the sample. The error can be conveniently expressed in terms of probable error[3], which means that the chances for the error in an individual measurement being more or less than this standard amount are equal.

Probable error " E " is related to the variance V by the following equation:

$$\begin{aligned} E &= \sqrt{V} \times 0{\cdot}6745 \\ &= \sqrt{124} \times 0{\cdot}6745 \\ &= 7{\cdot}5 \text{ or } 0{\cdot}00075 \text{ g.} \end{aligned}$$

Average weight of a strip = 0·09798 g.

The probable error was, therefore, less than 1 per cent of the weight of an individual strip.

From the analysis of variance it was concluded that:

(1) the variation in weights between the " samples " was significantly greater than that within a " sample ", and

(2) the probable error in the estimation of the area of an individual " strip " from the weight of another one from the same " sample " was found to be less than 1 per cent.

Accuracy of the present method is illustrated by different examples placed below.

Types of Measurement		*By weighing*	*By conventional method*
Overall visible transmission through a coloured glass in arbitrary units	(a)	36·50	—
		37·00	—
	(b)	17·78	17·80
Mean thickness of a step lens, in.		0·28	0·28
Internal surface area of an ampoule in sq. dm. (calculated from the projected area)		64·40	65·10

The author is thankful to Dr. Atma Ram, Director, Central Glass & Ceramic Research Institute, for his kind permission to publish the note.

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27 *April* 1954

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Supplement

LITERATURE REVIEW ON FATS & OILS

1952

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The main task of preparing this review was taken up by Mr. M. N. Krishnamurthi, Technical Assistant, who deserves praise for his assiduous efforts in compiling this review. The Committee's thanks are also due to Mr. M. V. Lakshminarayana Rao, Dr. M. R. Sahasrabudhe and (Major) N. V. R. Iyengar for reading through the manuscript and making a number of valuable suggestions and to (late) Dr. G. T. Kale, Head of the Information and Statistics Division, Central Food Technological Research Institute, Mysore, for the supervision of the work.

CONTENTS

EDIBLE OILS & FATS
INCLUDING HYDROGENATED PRODUCTS

THE present review covers a number of new findings published on the technology of oils and fats during the year 1952. While by no means a complete survey of all the work done during the year, this review contains representative findings which are likely to be of special interest to Indian industries and research workers.

In accordance with the procedure approved by the Committee, the review is confined to edible oils and fats. Those which are classified as non-edibles are also of economic importance, and many factories in the country handle the " edible " as well as " non-edible " oils and fats, depending on the available facilities and demand. Moreover, certain oils and fats are classed as " non-edible " chiefly because of some objectionable flavour and taste. These can, however, be consumed without any ill-effect and, in restricted areas where they are plentifully available, they are actually being used for human consumption. As instances of this, we may cite linseed and *mahua* oils. There are other oils and fats which, after processing, could be converted into edible products. In view of this, it is considered desirable to add, in future reviews, a section devoted to " Non-edible Oils and Fats ". Some of these oils which are being increasingly used for edible purposes will then be transferred to the other group and treated along with edible oils and fats.

STATISTICAL SURVEY OF FATS, OILS & OILSEEDS

In the Annual Literature Survey on Oils and Fats for 1951, the trends in the production and supplies of principal edible fats, oils and oilseeds in India and other important world centres during the pre-war years as well as in 1949-50 and 1950-51 were reviewed. The present review covers the position during the year 1951-52.

World situation

The world production of fats and oils in 1952 was estimated at 24·3 million tons which shows an increase of 0·92 million tons over the year 1951. The total exports from principal producing countries in 1952 recorded were 5·74 million tons or 0·123 million tons more than in 1951 (*Comm. Ann. Rev.*, **85**, 257).

In 1951-52 the acreage under groundnuts in French West Africa was smaller than in the previous year due to sharp fall in groundnut prices. In India there was a decline in the production of groundnuts due to drought conditions. The production of coconuts and copra in the Philippines and Indonesia showed a decline due to typhoons, but the world palm oil production showed a rise (*F.A.O. Ser.— The State of Food & Agric. Rev. & Outlook, No. Cl* 16/2, 1952; *Paint Oil Col. J.*, **123**, 105).

In recent years sunflower is receiving increasing recognition in many countries as an oil-bearing plant. The production figures for 1952 are not available, but those for 1951 show a record level. This increase was mainly due to expansion in cultivation in many countries, particularly the U.S.S.R., Argentina and Uruguay. The chief countries having exportable surplus of this commodity are Turkey, Rumania, Bulgaria, Hungary, Yugoslavia, and East and South African countries (*Paint Oil Col. J.*, **122**, 705).

Table 1 shows world production and export figures of major oilseeds during 1951-52 (*F.A.O. Ser. — Year Book of Food & Agric. Statist.*, **6**, Part 2, 1952; *Monthly Bull. agric. Econ. Statist.*, **1**, No. 6, 1952; **2**, No. 4, 1953; *Commodity Ser. Bull. No.* 24, Feb. 1953; *Comm. Ann. Rev.*, **85**, 257). In cases where figures for 1951-52 are not available, the previous year's figures are incorporated in Table 1.

During the year 1952 oils and oilseeds showed a steeper fall in prices than in the previous year. The prices of fats, oils and oilseeds declined in international markets in April 1951 and continued through April 1952. By the middle of 1952 many oils were priced lower than in the pre-Korean War days and in some cases by 50 per cent and even more. As a result of this bearish tendency there was a widespread desire in 1951-52 to reduce the relatively large stocks built up in the previous year (*F.A.O. Ser.—The State of Food & Agric. Rev. & Outlook, No. Cl* 16/2, 1952; *Paint Oil Col. J.*, **123**, 105, 1953).

Reviewing the marketing possibilities and import difficulties in world markets in oils and oilseeds, Catlein (*Paint Oil Col. J.*, **122**, 408) summed up that there were good export possibilities in 58 markets in 1952 as compared with 71 in 1951 and 55 in 1950 and that the export trade in most markets, with the exception of Russia and her allies, Greece, Argentina, Egypt and Persia, had strengthened considerably. Apart from occasional offers of groundnuts, India did not participate as an exporter during the year under review. So far as the United Kingdom was concerned, the bumper crop from Nigeria provided most of her requirements. China came forward as a seller in the last few months of 1952, but on most occasions her prices did not prove attractive to buyers (*Paint Oil Col. J.*, **123**, 105).

TABLE 1 — WORLD PRODUCTION AND EXPORT OF PRINCIPAL OILSEEDS IN 1952

(*Thousand metric tons*)

COMMODITY	PRODUCTION	EXPORT
Groundnut (excluding U.S.S.R.)	9600	640
Sesamum (excluding U.S.S.R.)	1830†	80†
Cottonseed* (excluding U.S.S.R.)	12600	340†
Soyabean (excluding U.S.S.R.)	17600	1300†
Rapeseed	5400†	130†
Sunflower seed	1750†	65†
Copra	2420†	1780†

*The production of cottonseed is calculated from lint by applying the factor 1·75.

†1950-51 figures repeated.

TABLE 2 — MARGARINE PRODUCTION

(*Thousand tons*)

YEAR	U.S.A.	CANADA	UNITED KINGDOM	NETHERLANDS	WESTERN GERMANY
1938	172	—	208	70	—
1950	418	42	374	176	385
1951	463	47	446	172	465

Butter and margarine — The production and consumption of margarine in almost all the main consuming countries were at record levels in 1951. During the period, total world production of margarine was about 2 million tons. Margarine production and *per capita* consumption of butter and margarine in selected countries during 1938, 1950 and 1951 are recorded in Tables 2 and 3; figures for 1952 were not available (*Commonw. Econ. Committ., London, Dairy Produce*, 1952).

In 1951, the estimated butter production in major producing areas was 2·8 million metric tons which was slightly less than that in 1950 and about 11 per cent lecs than in the pre-war years. The countries which regained their pre-war levels and showed rising trends in the production of butter were the Union of South Africa, Belgium, Finland, Sweden, Italy, France and New Zealand while Denmark, Greece, Ireland, Netherlands, Norway, United Kingdom, Canada, U.S.A. and Australia recorded downward trends. In Austria, Western Germany and Switzerland, however, the production was approaching the pre-war level (*F.A.O. Ser. — Commodity Ser. Bull. No.* 24, Feb. 1953; *Commonw. Econ. Committ., London, Dairy Produce*, 1952).

The price relationship of margarine and butter was found to vary greatly from country to country. For example, in Austria, Belgium, Western Germany, Norway and Switzerland, the price of margarine was only about one-third and in the United Kingdom and the U.S.A. about half of that of butter (*F.A.O. Ser.—Commodity Ser. Bull. No.* 24, Feb. 1953; *Commonw. Econ. Committ., London, Dairy Produce*, 1952).

TABLE 3 — ESTIMATED *PER CAPITA* CONSUMPTION OF BUTTER AND MARGARINE

(*Pounds per year*)

YEAR	U.S.A.		CANADA		UNITED KINGDOM		NETHERLANDS		WESTERN GERMANY	
	Butter	Margarine	Butter	Margarine	Butter	Margarine	Butter	Margarine	Butter	Margarine
1938	16·4	2·9	31·9	—	24·1	10·0	12·3	15·7	19·4	13·4
1950	10·7	6·1	23·5	6·8	16·8	16·7	6·0	37·5	13·2	16·3
1951	9·7	6·5	22·6	7·4	14·6	18·3	6·2	37·7	13·5	17·2

International trade in margarine was about 1 per cent of the amount produced. The trade is mainly conducted by special arrangements and not through normal trade channels. Before the war Netherlands accounted for nearly two-thirds of the world's exports, but during the war and early post-war years substantial shipments were made from the United Kingdom, Netherlands, Austria, France and the U.S.A. (*F.A.O. Ser.— Commodity Ser. Bull. No.* 24, Feb. 1953; *Commonw. Econ. Committ., London, Dairy Produce,* 1952).

Butter exports in 1951 were 0·44 million tons, which is 10 per cent less than in 1950 and 27 per cent below the pre-war volume. The leading exporters in butter were Australia, New Zealand, Denmark, Netherlands and Sweden, while the United Kingdom and Germany were the main importers (*F.A.O. Ser.— Commodity Ser. Bull. No.* 24, Feb. 1953; *Commonw. Econ. Committ., London, Dairy Produce,* 1952).

India's position

India is one of the principal oilseeds producing countries of the world and, until recently, contributed a substantial share to the world trade in vegetable oils and oilseeds. Details of acreage and production of the principal edible oilseeds are given in Table 4 (Directorate of Econ. & Statist., Ministry of Food & Agric., Govt. of India, *Agric. Situation, India,* **8**, Nos. 1 and 3, 1953).

In India the production of groundnut is concentrated mainly in the southern and western parts of the country, Madras, Bombay and Hyderabad accounting for 80 per cent of the production. Uttar Pradesh accounts for 65 per cent of the total production of rape and mustard. Details of State-wise acreage and production of groundnut, sesamum, rape and mustard during the year 1952-53 are given in Table **5** (Directorate of Econ. & Statist., Ministry of Food & Agric., Govt. of India, *Agric. Situation, India,* **8**, Nos. 1, 3 and 5, 1953).

TABLE 4 — PRODUCTION OF PRINCIPAL EDIBLE OILSEEDS

(*In thousands*)

CROPS	AREA (acres)		PRODUCTION (tons)	
	1950-51	1951-52	1950-51	1951-52
Groundnut	11130	11798	3437*	3045*
Sesamum	5629	5731	453	441
Rape and mustard	5097	5707	748	900
Cottonseed	14556	16213	910†	959†

*In terms of nuts-in-shell.
†Estimated from lint production by applying the factor 1·75.

Exact figures of production of oils in the country are not available. According to certain marketing surveys undertaken a few years ago, the quantity available for crushing in the country was estimated at 76 per cent for groundnuts, 79 per cent for sesamum and 89 per cent for rape and mustard [MOHINDRA SINGH, Directorate of Econ. & Statist., Ministry of Food & Agric., Govt. of India, *Agric. Situation, India,* **7** (1952), 333]. The estimated production of vegetable oils from the principal oilseeds during 1951-52 based on the above figures is given in Table 6.

Recently, the Indian Central Coconut Committee estimated that India needs at least one lakh tons more of coconut oil per annum. Since it is difficult to obtain additional supplies from abroad, the Indian Central Coconut Committee has on hand measures to augment internal production. The Committee is now investigating the feasibility of growing coconuts in the Western Ghats, on the embankments of irrigation canals and along the channels in the Godavari, Krishna and Cauvery deltas, on either side of the railway lines in Mysore and Travancore-Cochin, along irrigation canals in Madras, on the borders of ricefields in Mysore, Travancore-Cochin, Madras and West Bengal and on the banks of rivers in these States. Besides, the Committee has recently sanctioned schemes to extend the cultivation of coconuts in West Bengal and in the Andaman Islands [GOPALAN, *Indian Fmg.,* **2** (1952), 10-13].

India was one of the leading exporters of oilseeds during the pre-war period. During the post-war period, however, oilseed exports dwindled to very low levels, but was partly compensated by the exports of oils. This change in the export policy of the Government of India was intended to promote industrialization of the country and to retain the valuable oil cake for the benefit of the people. In the operation of export control, the Government of India had ensured proper export regulation so as to prevent any sudden or large rise in internal prices and to provide the importing country

TABLE 5 — ALL-INDIA ESTIMATES OF PRINCIPAL EDIBLE OILSEEDS — 1952-53

(*In thousands*)

	GROUNDNUTS (IN SHELL)		SESAMUM		RAPE AND MUSTARD	
	Acreage	Production (tons)	Acreage	Production (tons)	Acreage	Production (tons)
Assam	—	—	—	—	262	41
Bihar (excluding merged territories)	—	—	57	5	292	44
Bombay	2404	337	337	26	63	11
Madhya Pradesh	513	91	498	34	175	28
Madras	4348	1613	721	78	4	*
Orissa	55	18	237	22	106	16
Punjab	90	30	61	6	329	46
Uttar Pradesh	265	117	1248	94	3174	533
West Bengal	—	—	13	3	226	44
Hyderabad	2216	422	741	46	6	*
Madhya Bharat	407	40	350	29	123	17
Mysore	263	47	52	4	6	1
PEPSU	31	5	5	1	107	14
Rajasthan	77	15	774	63	188	26
Saurashtra	1157	143	281	8	—	—
Travancore-Cochin	25	13	2	—	—	—
Ajmer	—	—	19	—	1	1
Bhopal	3	—	50	4	2	*
Bilaspur	—	—	1	1	—	—
Himachal Pradesh	—	—	1	1	9	1
Kutch	7	2	16	1	—	—
Tripura	—	—	10	1	9	2
Vindhya Pradesh	1	1	277	26	36	3
TOTAL	11862	2894	5751	451	5155	828

*Less than 500 tons.

TABLE 6 — PRODUCTION OF PRINCIPAL EDIBLE OILS*

(*In tons*)

OILS	1951-52
Groundnut	687000
Sesamum	104000
Rape and mustard	280000

*Factors used for converting seeds and nuts to oil equivalent are: groundnuts in shell 30 per cent; sesamum 30 per cent; and rape and mustard 35 per cent.

with adequate supplies of oils. Though this policy seemed sound, the result was not very satisfactory, since to that extent the foreign exchange earnings fell down. This could have been avoided (*Commerce*, **85**, 257) if the Government were prompt in announcing export quotas. The foreign exchange earned by exports of oils and oilseeds in 1951-52 was nearly 3 per cent of the total earnings from exports. The countries to which oils and oilseeds were exported during the year were Netherlands, the United Kingdom, Italy, West Germany, Belgium, Canada, Burma and a few others (*Accounts relating to the Foreign Sea & Airborne Trade & Navigation of India for April* 1952 *& April* 1953). Details of net export trade in oils and oilseeds during 1950-51 and 1951-52 are given in Table 7 (*Accounts relating to the Foreign Sea & Airborne Trade & Navigation of India for April* 1952 *& April* 1953).

As regards imports, India obtained coconuts, copra and coconut oil chiefly from Ceylon, Singapore, Federated States of Malaya and a few other countries. In 1951-52, the quantity of copra or coconut kernels and coconut oil imported was 11,536 and 31,096 tons respectively as compared to 8,627 and 18,230 tons in the preceding year.

In 1952 prices of oils and oilseeds experienced steeper fall in India as in the other parts of the world. The reasons for the downward trend of the Indian market were chiefly: (1) increased world supplies of oils and fats, (2) absence of indications of the

TABLE 7 — EXPORT TRADE IN PRINCIPAL OILS & OILSEEDS

(*In tons*)

COMMODITY	EXPORT	
	1950-51	1951-52
Groundnut kernels	38345	19744
Sesamum	926	2268
Rape and mustard	185	429
Niger	3307	4489
Groundnut oil	83149	20218
Rape and mustard oil	118	147
Coconut oil	91	—
Vanaspati	—	3062

U.S. Government's willingness to buy oilseeds for stockpiling purposes, (3) tight money conditions and (4) staggering export quotas. The downward trend which commenced in the latter half of 1951 gathered momentum during the first quarter of 1952, and prices crashed to new low levels never reached during the past five years. In view of the serious situation, the Bombay oilseeds market was declared closed early in March 1952 by the Bombay Oilseeds Exchange. The Government of India, in order to help the producers and traders, abolished export duties on groundnut oil, *kardi* and niger seeds, liberalized export quotas and relaxed control on vanaspati. At the end of August 1952, the price of groundnut oil was a little lower than in 1947-48. At the end of the year again the market tended to look down (*Commerce*, **85**, 257).

Vanaspati or hydrogenated oils — The general position of the industry improved materially. The Government control on the price of vanaspati was removed in June 1952. In view of the improvement in the transport position and favourable attitude of the Government of India with regard to the nutritive value of vanaspati, the production of vanaspati in 1952 improved over that in 1951. The total production of vanaspati from 49 registered factories in 1952 was recorded as 1·9 lakh tons, an increase of 18,600 tons over the year 1951. The installed capacity of the 49 factories is 3,39,000 tons per annum and at present the vanaspati industry is the second largest food processing industry coming next to the sugar industry (Ministry of Comm. & Industry, *Monthly Statist. Prod. Select. Industr. India*, **5**, No. 5, 1953).

CROP CULTIVATION & STORAGE OF OILSEEDS

Chlorella culture — While pursuing a research project on the world's food needs, Spoehr and Milner (*Plant Physiol.*, **24**, 120; *J. biol. Chem.*, **176**, 813; *Carnegie Institution of Washington Year Book No.* 47, 100) found that by supplying iron and other mineral salts to *Chlorella pyrenoidosa*, a fresh-water alga, they could obtain yields of 1,350 lb. of fat or 1,000 lb. of pure protein per acre per year in contrast to an average dry land yield of 360 lb. of peanut oil per acre per year. In subsequent experiments *Chlorella* grown in 12 in. deep fresh-water ponds and manured with iron sulphates, manganese, ammonium phosphates and carbon dioxide yielded up to 100 tons of dry growth with a fat content of 85 per cent per acre per year. According to an estimate made by Dr. Berk, Director of the Cytho Chemistry Unit at the U.S. National Institute of Health in Bethesda, Maryland, an area of the order of 50 sq. miles properly engineered for algal and related farming will meet the calorific requirement of the entire population of the U.S.A. Assuming that the *per capita* requirement of 65 g. of protein per day was to be obtained from the algal source, the total area required would be less than a million acres for the present world population. This relatively is such a small area that the introduction of algal culture need not displace the existing agricultural crops. Such a cultivation would rather mean utilizing land not suited for agriculture. The use of increasing areas of such land for algal culture would be a means of keeping the food supply in balance with a steadily growing world population.

The first attempt made in the U.S.A. to translate the biological requirements of algal culture for a large-scale culture plant was at the Stanford Research Institute in 1948-50. At the same time, this problem was tackled in Germany. During 1951 a further advance was made through the construction and operation of a pilot plant for *Chlorella* culture at the Carnegie Institution by Arthur D. Little Inc. Although the pilot plant showed the possibility of continuous culture of *Chlorella*, the economic feasibility of the project is yet to be established [*Algal Culture*, Carnegie Inst. (Washington) Pub. 600].

Coconut palm cultivation — In view of the urgent necessity for stepping up the production of coconut oil in India, research on improved strains and on the incidence of root disease of coconut palms is of paramount importance. The Ceylon Coconut Research Institute has undertaken a long-range research programme on artificial pollination of coconut palms to produce high grade seed nuts. Until such time that any results emerging from these experiments are put into practical application, the most reliable and expeditious means of rehabilitating and planting up new areas would be by using selected " block nuts " (*Ceylon Cocon. Quart.*, **3,** 73). Mennon *et al.* (*Indian Cocon. J.*, **5,** 71) have carried out investigations to find out to what extent water logging of the soil is responsible for the incidence of root disease. If weeds and plant debris are incorporated in the soil instead of their ash, the texture and moisture-holding capacity of the soil are found to improve greatly; however, the growth of weeds needs to be controlled (MAHADEVAN, *Ceylon Cocon. Quart.*, **3,** 33). Rockwood (*Ceylon Cocon. Quart.*, **3,** 27), recording the results of his experiments on a coconut estate, observed that the triangular method of planting gave 15 per cent more trees per acre as compared with the square method. Exposure of the soil to direct sun's rays is minimized, thus reducing escape of moisture from the soil. Nirula *et al.* (*Indian Cocon. J.*, **5,** 57) and Gopalan (*Indian Fmg.*, **2,** No. 7, 20) reviewed some of the problems of improving yield by checking pests and diseases in coconut plantations. Peiris (*Ceylon Cocon. Quart.*, **3,** 75) has observed that systematic soil cultivation according to the requirements of a particular soil or palm will secure high yields. Application of phosphoric acid and potash yields better results. The pests and diseases in coconut groves accounted for a loss of over 15 per cent of the crop. Other information on coconuts refers to the flourishing production of coconut groves in Tanganyika on the shores of Lake Victoria. A novel feature of these plantations is that some palms thrive with their roots permanently under water (*Nyasald. agric. quart. J.*, **8,** 76-79).

Groundnut cultivation — Studies were carried out with different varieties of groundnuts, and with respect to spacing and insect pests. Gambia and Spanish bunch were observed to be capable of giving high yields. Experiments on spacing showed that the closer the planting the higher the yield (*Nyasald. agric. quart. J.*, **10,** 101). Poos *et al.* (*Bur. Ento. Plant Quarant.*, E-820, **16,** 1951) found that benzene hexachloride controlled effectively the insect pests of peanuts.

An important publication on the economic importance of groundnuts is by Venkatanarayana (*Madras Agric. J.*, **39,** 317). The paper reviews the origin and history, acreage and production, varieties, germination and growth, cultivation, pests and diseases, genetics and breeding of groundnut. The effects of climate and soil on the yield, quality and oil content of improved strains of groundnuts have been discussed. In conclusion it has been shown that by the application of scientific methods it would be possible to obtain 60 per cent increase in the existing production of groundnuts in Madras without encroaching on the areas under other food crops.

McGregar and Hay (*Sci. Agric.*, **32,** 204) have reviewed the Canadian experiment on safflower cultivation. Greater yields have been reported on irrigated than on dry lands, although the incidence of disease was greater and maturity was retarded over a week on the irrigated lands.

Some of the papers of interest to Indian farmers are: Hints to the Farmer for the Cultivation of Oilseeds (*Indian Fmg.*, **2,** 8); A Discussion of the Farmer's Problems of Production and Prices in Growing Peanut and Other Cash Crops (*Peanut J. & N. World*, **38,** 36); Peanut Growing in Queensland (KARR *et al.*, *Qd. agric. J.*, **72,** 63); and Land Development and Large Scale Food Production in East Africa (*Econ. Bot.*, **6,** 55).

Oilseeds storage — A special research scheme on the storage problems of groundnuts was worked out in Madras (VENKATANARAYANA, *Madras Agric. J.*, **39,** 364) and the investigations have yielded useful results of importance to trade. These are: (1) groundnuts are better stored as pods (nuts-in-shell) than as kernels; (2) if it is necessary to store groundnuts as kernels for long periods, they should be thoroughly dried to bring the moisture content to below 5 per cent; (3) kernels intended for long storage should be properly decorticated so that the percentage of " splits " and "brokens" is minimum; (4) only kernels from winter crop (rain-fed) should be stored for long periods. Produce from summer crops (irrigated), which has a poor keeping quality and 3 per cent higher oil content, should be utilized for immediate crushing; (5) kernels should be stored in clean, well-ventilated godowns; and (6) kernels should be stacked only on soft bedding materials like sand. The bags should not be stacked to more than ten units lest the bottom-most bags get caked up.

Patents issued to Altschul *et al.* (*U.S. Pat.* 2,571,095; 2,584,972) on preventing deterioration of oil in stored cottonseed pertain to spraying the seed with a solution of propylene glycol dipropionate and with 1, 3-dimethyl-4, 6-bis-(chloromethyl)-benzene or solutions of liquid halohydrin such as ethylene chlorohydrin, propylene chlorohydrin and related compounds. Autoclaving and drying of rice bran stabilized the bran against the possible deterioration of its oil during storage (LOEB and MAYNE, *Cereal Chem.*, **29**, 163).

PROCESSING OF OILSEEDS

Preliminary treatment methods — In extracting oil from oilseeds, preliminary treatment methods constitute an important step. Robert Boby (*Overseas Engr.*, **26**, 8) has designed a new groundnut decorticator, which combines the functions of cleaning, decorticating, separating and grading in one single self-contained unit. This machine reduces the percentage of damaged kernels, thus minimizing the tendency to turn rancid when the kernels are stored in bulk. In a new method for the removal of skins from groundnut kernels, the kernels are treated with water, dried at 120°-50°F. to 4·5 per cent moisture content and blanched in a standard split-nut blancher. The meal and protein obtained from kernels prepared by this method were suitable for utilization as foodstuffs and were equal to those produced by the caustic soda method developed by Pominski *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 48-51). In the preliminary treatment of soyabean, Singer and Deobald (*U.S. Pat.* 2,609,299) cracked soyabeans and separated the hulls. The larger grits were again cracked and the moisture content so adjusted as to obtain a tough flake. For the treatment of cottonseed, feasibility of separating meal, hulls and linters after solvent extraction of whole comminuted cottonseeds was tried by Clark and Wamble (*Tex. exp. Stat. Bull.*, **125**, 77). It was found that this process was practicable only after the removal of first-cut linters. In another patent (*U.S. Pat.* 2,618,103) delinting of cottonseed is effected speedily by pre-wetting the seed with an aqueous solution of a water-soluble dye, preferably a sulphonic acid salt. Williamson (*U.S. Pat.* 2,595,825) found that when a mixture of hydrocarbon and alcohol solvents pre-wet the flakes, they swell, thus permitting further reduction in flake thickness, resulting in easier extraction. Luedtke and Wamble (*Tex. Engng. exp. Stat. Res. Rep.*, **39**, 1-7) studied the variations of residual oil in meal, free gossypol content of rolled meats and refining loss with respect to flake thickness and moisture content. Variations in flake thickness and moisture content did not significantly affect the colour of the refined oil.

Oil extraction — Most of the literature on vegetable oil extraction pertains to solvent systems. In the working of a vegetable oil extraction plant in India, Parekh (*Chem. Age, India*, **6**, 139) reported that the process is economical under Indian conditions. Chatterji (*Chem. Age, India*, **6**, 148-50) has laid stress on the economical aspects of solvent extraction process as applied to Indian conditions. Raghunatha Rao (*J. sci. industr. Res., India*, **11A**, 414) has described a solvent extraction process for oil cakes using ethyl alcohol or petrol-alcohol mixtures preheated to 50°-76°C. The recovery of oil was 90-95 per cent leaving 1 per cent residual oil in the extracted meal. Kyokaishi (*J. Oil Chem. Soc., Japan*, **1**, 1952, 111-14), has described various types of continuous solvent extraction plants such as Bollmann, Hildebrandt, Crawn, Allis-Chalmer, Kennedy, Desmett and Chiyoda. A series of articles on various types of solvent extraction plants, in which the special claims of manufacturers of the equipment are set forth, is being published. The first is a study on the Lurgi continuous solvent extraction plant under working conditions (*Manderstam. Tech. Dig.*, **5**). Recently, a number of solvent extraction systems have been developed, but details are not available [KOYAMA, *Jap. Pat.* 857 (1950); UMI *et al.*, *Jap. Pat.* 856 (1950); KOYANAGI, *Jap. Pat.* 1,310 (1950); TATARA, *Jap. Pat*, 1,538 (1950); TAKEMOTO and IGARASHI, *Jap. Pat.* 3,738 (1950); BREGMAN, *Brit. Pat.* 667,262; JOJAT, *Fr. Pat.* 963,658].

A number of patented inventions related to the engineering aspects of solvent extraction systems. One U.S. patent (*U.S. Pat.* 2,585,473) described the mechanical improvements in the Kennedy extractor. Iguchi obtained a patent [*Jap. Pat.* 172,096 (1946)] for grinding the charge with the solvent in the extraction system invented by him. Another Japanese patent [KAMIBAYASHI, *Jap. Pat.* 1,175 (1950)] relates to the use of high frequency sound waves during extraction. The new improvements in the Bonotto system comprise devices for flaking cottonseed meats, reintroducing the hulls to aid percolation of solvent, auxiliary settling tank for collecting fine-free miscella and separation of dust-free solvent vapours by heating with superheated solvent vapours and later with steam (*U.S. Pat.* 2,567,179; 2,594,117; 2,582,675; 2,594,117). In another patent (*U.S. Pat.* 2,608,565) Bonotto has dealt with the problem of fines in a novel way. In this, the smaller particles are mechanically pressed into bigger ones and used as a filtering medium. Among the other notable engineering improvements may be mentioned a patent (*U.S. Pat.* 2,609,186) issued to Anderson for vapour scrubbers for separating the solvent from the vapours leaving the meal dryers, the patent (*U.S. Pat.* 2,585,638) to Drew for an absorption tower for recovering waste gases issuing from oil extractors and the patent (*Brit. Pat.* 670,958) to Manning for mechanical solvent circulating devices during extraction.

Ingebo (*Iowa St. Coll. J. Sci.*, **25**, 258-59) studied the efficiencies of various packing materials in stripping columns. Stripping of solvent in a column packed with metallic cloth was far more efficient as compared with Raschig rings. Arnold and Ingebo (*J. Amer. Oil Chem. Soc.*, **29**, 23-28) reported that stripping in columns packed with spaced spiral weave metallic cloth decreased steam consumption and increased column capacity. Smith and Weigel obtained a patent (*U.S. Pat.* 2,567,450) for settling the fines and flakes in miscella by reducing the flow rate in special channels after leaving the extractors. An investigation into the practicability of the spray desolventization of soyabean oil which has been extracted by means of trichloroethane was carried out by Barr (*Iowa St. Coll. J. Sci.*, **25**, 153-54). The quality of oil obtained by this method was found to be superior.

In the extraction of cottonseed with different solvents, although the commercial hexane, benzene, ether, acetone or butanone gave the same yield of oil, the commercial hexane was preferred due to superior quality of the oil obtained (EAVES *et al.*, *J. Amer. Oil Chem. Soc.*, **29**, 88). Amongst the many solvents tested, butanone with 10 per cent water is found to be more effective in the removal of toxic gossypol as compared with other solvents (DECHARY *et al.*, *J. Amer. Oil Chem. Soc.*, **29**, 339). With respect to rate of extraction Mayalle (*Bull. mens. ITERG*, **6**, 96) placed the solvents in the following order of decreasing efficiency: trichloroethylene, carbon disulphide, hexane and methyl-ethyl ketone. A further investigation showed that alcohol is suitable for the extraction of peanut oil, but when applied to rapeseed, yielded an oil with bad odour. In the extraction of cottonseed oil with isopropanol, Harris and Howard (*Bull. agric. Mech. Coll. Texas*, **6**) found that alcohol is more efficient than hexane. Beckel obtained a patent (*U.S. Pat.* 2,584,108) for the continuous extraction with alcohol. According to one patent (CRAWFORD, *U.S. Pat.* 2,596,010) the C_6 iso-paraffin solvents were better with regard to yield and quality of oil and meal as compared with n-hexane. Mixtures of chlorinated hydrocarbons are used as extraction solvents according to another patent (WEIZMANN, *Austrian Pat.* 164,021). In patents (*U.S. Pat.* 2,605,271; 2,605,272) issued to Hum *et al.*, vegetable material is first melted with a polar organic solvent and subsequently extracted with a non-polar solvent. The polar solvent being immiscible with the miscella forms a separate layer containing both the fines and the solid particles. Freeman obtained a patent (*U.S. Pat.* 2,573,898) for using naphtha as a reflux in fractionation of soyabean, linseed or cottonseed oils. The oils gave higher iodine values, lower free fatty acid contents, contained lesser proportion of impurities and had brighter appearance. According to Ayers and Scott (*J. Amer. Oil Chem. Soc.*, **29**, 213) hexane containing 5 per cent lower alcohol proved a better extractant than n-hexane alone.

Studies on extraction rates, viscosities, flake thickness, temperature and related problems have received attention. Clark and Wamble (*J. Amer. Oil Chem. Soc.*, **29**, 56) modified the laboratory apparatus to suit many varieties of seeds for determining the rate of extraction of oil. The relation of extraction rates and other factors to thickness of soyabean flakes has been graphically presented by Schoenemann and Voeste (*Fette u. Seif*, **54**, 385). Pilot-plant data are presented on the variation of oil yield for wheat germ, milk weed seed, sorghum, flaked groundnuts, waste waxed paper, safflower seed and cottonseed with extraction time and in some cases with flake thickness (RUSSEL, *Iowa St. Coll. J. Sci.*, **25**, 348-49). Smith (*J. Amer. Oil Chem. Soc.*, **29**, 421-25) established that the extraction rate varied directly with the diffusivity and viscosity of oil and solvent, and inversely with the square of the thickness of the material and temperature. In a graphic chart presented by Decosses *et al.* (*U.S. Dept. of Agric. Bur. agric. industr. Chem.*, **292**, **304**) composition relationships with density, temperature and viscosity for hexane miscella of cottonseed and peanut oils have been recorded. For estimating fines in miscella, Graci (Jr.) *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 71) have developed a rapid control method, based on centrifuging the sample and measuring the volume of the sediment. Antonioli and Turriziani (*Ann. Chim. Rome*, **41**, 255-63) found the values obtained for the energy of activation for the diffusion of oil into solvent not in agreement with the values deduced from viscosity measurement on oil-light petroleum mixtures.

Information relating to mechanical processes of extraction is rather limited as compared with solvent methods. In the extraction of coconut oil, Coconut Process Inc., Manila, have developed a new enzymatic process for the extraction of oil from fresh coconut meat. According to the inventors this new process yields good quality oil, and dispenses with the subsequent refining process (*Food Engng.*, **24**, 143). In one unconventional process, Sodergreen (*U.S. Pat.* 2,583,022) extracted coconut oil by steaming the material, the object being to sterilize as well as to loosen the meats from the shell, drying and grinding the meats with 5 parts of water into a slurry and separating the oil by filtration. In the working of the " Super Duo " oil expellers, Dunning and Keahey (*J. Amer. Oil Chem. Soc.*, **29**, 627-28) obtained increased capacity by increasing the cooking volume and speed of the barrel shaft. A novel system of extraction of oils and fats by a cold process from animal, marine and vegetable material was recently demonstrated at the factory of British Glues & Chemicals Ltd. (*Chem. Engng. News*, **30**, 5266; *Chem. & Process Engng.*, **33**, 659; *Chem. Processing*, **16**, No. 1, 38; *Chem. Week*, **71**, No. 25, 42; *Food Manuf.*, **27**, 487; *Nature*, **170**, 881; *Times Rev. Ind.*, **6**, 35). The process is based on the principle of impulse rendering. The material is treated with about 7 times its weight of water. The impulses rendered through the water blast the fat from the bone cells in a matter of seconds. The inventors claimed that this new extraction system gives higher yield and increases the vitamin content of the oil twofold.

Meal treatment methods — A number of communications were concerned with the effect of processing on the quality of the oil cake and meal. In the technique of solventization of meal for edible purposes, Leslie obtained a patent (*U.S. Pat.* 2,571,143) for the use of superheated solvent vapours for heating the meal before steaming. Graci *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 41) designed a special four-stage continuous dryer for treating the extremely fine meal obtained by the fractional method of processing. Rice (*U.S. Pat.* 2,615,808) has described the production of cottonseed meal of very low toxicity, high nutritive value and attractive colour. Dunning *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 153) carried out experiments to determine pre-cooking conditions for producing high quality edible cottonseed meal. In a similar work Belter and Smith (*J. Amer. Oil Chem. Soc.*, **29**, 170) denatured the protein in the final meal by subjecting it to a process of deodorization, toasting and desolventization. Dangoumau *et al.* (*Bull. mens. ITERG*, **5**, 306) showed that the damage to protein in soyabean and rapeseed is greater through moist heating than with dry heating. Burnet (Jr.) and Arnold (*J. Amer. Oil Chem. Soc.*, **29**, 619), while processing oil cake for the livestock, found that moist treatment produced a superior protein meal. Amanullah Khan (*J. Sci. Soc. Harcourt Butler Tech. Inst. & Indian Inst. Sug. Tech., Kanpur*, 1952, 24-30) reviewed the work carried out on toxic principles in common oil cakes and their removal. Pominski *et al.* [*Industr. Engng. Chem.* (*Industr.*), **44**, 925-28] obtained a peanut protein by successive peptization and also by grinding the meal before each peptization. Bolley and McCormack (*J. Amer. Oil Chem. Soc.*, **29**, 470) studied the separation of phytin from oilseed protein flours.

Articles of general interest published during the year are: Modernization Plans of Edible Fat and Oil Industry in Poland (SCHMIDTGAL, *Food*, **21**, 245, 78-79); Ghani versus Mill Controversy in India (GOPAL

GUPTA, *Oils & Oilseeds J.*, **4,** 14); Production Method in Rice Bran Oil in the Houston Plant of Wonder Rice Oil Co., U.S.A. (*Chem. Engng.*, **59,** 222); A Continuous Solvent Extraction Plant for " Ardil " Fibre Meal at the British Extracting Co. Ltd., Broomborough, Cheshire (*Industr. Chem.*, **28,** 113, 119); New Whale Processing Factory on Board the Ship *Jeran Peron* (*Overseas Eng.*, **25,** 220).

PROCESSING OF OILS & FATS

Butter fat — A new patent (*Brit. Pat.* 659,406) describes a process for continuous production of butter of the desired consistency from concentrated cream. The process consists in cooling the cream with a high fat content below 14°C., causing a phase inversion of oil-in-water to water-in-oil type and reheating it to 18°-30°C. before finally cooling to a storage temperature of 10°C. King (*Meddelande,* No. 30) has discussed the influence of structural changes of alpha butter on butter consistency. In order to obtain higher fat extraction, Surkov *et al.* (*Chem. Tech. Inst. Meat Ind., Moscow, Mol. Prom.*, **12,** 16-18) recommended the process of separating the butter from a mixture of whole milk and cream instead of treating them separately. Evenhuis (*N. Off. Org. K. Ned. Zuivelb*, **44,** 56-57), while discussing the manufacture of butter with diacetyl aroma, has stressed that the butter must contain suitable strains of bacteria and citric (or pyruvic) acid to raise the redox-potential in the churning process, a condition necessary for producing diacetyl in butter. A weak reducing starter containing citric acid with a less thorough wash of the butter has also been shown to raise the redox-potential. Thompsen (*Canad. Dairy Ice Cr. J.*, **30,** 36) has discussed the skimming of whey and cream in the manufacture of butter. He found that the whey butter is poorer in keeping quality than natural butter. Piskarev (*Molochnaya Prom.*, **13,** 32-36) found that the substances which reduce elastic and viscous properties of the adsorption layers of fat globules are responsible for the acceleration of the churning process and butter formation. Muller (*Aust. J. Dairy Tech.*, **7,** 44) developed a method for counting the moisture droplets in butter, and correlated the results obtained to certain aspects of its manufacture and keeping quality. Miller and Tracy (*J. Dairy Sci.*, **35,** 292) found that the copper contamination in milk products is associated with the non-fat portion and not the fat phase. The lowest content of copper was found in butter obtained by the continuous process, and was less than the amount in original cream and much less than that in the butter obtained through batch systems. Petersen (*Fette u. Seif,* **54,** 280) has pointed out the superiority of natural butter both with regard to its flavour and nutritive value. It was further found that the souring properties in unsalted butter of *p*H less than 5 is due to the acetic acid bacteria (*Fette u. Seif,* **54,** 471). Sommer (*Milk Dealer,* **41,** 58-74) has discussed fat emulsion in milk from a chemical standpoint. In two recent communications on preparation of butter oil, Patton and Stine (*U.S. Pat.* 2,617,731; *J. Dairy Sci.*, **35,** 655) reported the use of de-emulsifying agents such as Tergitol-7 to break the emulsion. The butter oil prepared by de-emulsification methods was believed to be stable at room temperature for a long time and may be used in preparing butter, sweet butter, icecream mixes and in reconstituting non-fat dry milk to whole milk. In another paper, Patton (*J. Dairy Sci.*, **35,** 324) reported the use of an aqueous reagent containing n-butylamine and n-butanol as a de-emulsifying agent for milk, cream and a number of other fluid dairy products.

Information on engineering feature has shown that the process of continuous butter making in Fritz machine is unsuitable for Canadian market due to the difficulty of controlling moisture in the butter below their legal requirement of 16 per cent and also due to the unsuitability of the equipment to produce salted butter (PEARCE *et al.*, *Canad. J. Tech.*, **30,** 167). Patents issued to Ahlborn (*Germ. Pat.* 816,170) and North *et al.* (*U.S. Pat.* 2,564,715) describe continuous and semi-continuous butter making machines. The continuous machine consists of a cylinder with two oppositely rotating disc bearing agitators. The Alvan Blanch Development Co. developed a new system called the Blanch-Electrix Air Flow Butter Maker. This machine has no moving parts and the butter is made entirely by air agitation. It is claimed that the butter produced in this machine has a better flavour and keeping quality. Thorstensson and Rydberg obtained a patent (*U.S. Pat.*

2,617,732) for a batch churn. This comprises of a rotating tilting container equipped with a jacket for heating or cooling. Shorland · (*Fette u. Seif,* **54,** 521-30) reviewed the subject of fat research in New Zealand with particular emphasis on the work of the Institute for Fat Research.

Fish and body fats — Suzaji [*Japan* 37 (1951)] and Shimizu and Yamada (*Bull. Res. Inst. Food Sci. Kyoto Univ.*, No. 5, 29) treated fresh fish liver with alkali for preservation during transit and storage. It is believed that this treatment helps in freeing the oil during the subsequent digestion. In a similar work, Rübenberg (*Pharm. Zentralhalle,* **91,** 111) found that when fresh livers are frozen in containers filled with carbon dioxide at −15° to −18°C. prior to extracting the oil, they produce a better quality vitamin oil. Koike patented [*Jap. Pat.* 1,117 (1951)] a simple method for obtaining oil fractions rich in vitamin A from comminuted liver by heating with high frequency electric current. Lebermann (*Brit. Pat.* 653,676) exposed animal, vegetable or fish oil or fat (or a concentrate thereof) containing pro-vitamin A to the action of alpha rays in presence of a catalyst such as di-iodinated castor oil to produce vitamins.

Other information on rendering comprises treating general slaughter house waste with ammonia and ammonium-diacid-phosphate under pressure for peptonization and separation into aqueous and fat phases in order to produce edible fat and proteins (HANESCHKA and HELINGER, *Austrian Pat.* 159,739). Fladmark (*U.S. Pat.* 2,565,173; 2,590,303) effected improvements in oil separation and in steam economy while drying the protein meal in a continuous rendering equipment. Davis (*U.S. Pat.* 2,614,110) using suitable centrifuges separated the comminuted cooked material in stages. In the first stage, the cooked material was separated into dry solids and liquids and in the second stage the liquid was separated into oily and aqueous portions. A review published during the year deals with expellers, vibratory screens, vacuum dryers, coagulating chambers, tube dryers and solvent extractors on a new whale factory ship (Anon., *Intl. Chem Engng.*, **33,** 28).

Vegetable oil refining — Commercial oil refining consists of degumming, neutralizing, bleaching and deodorizing processes.

Degumming methods — Rider and Gershon obtained a patent (*U.S. Pat.* 2,544,725) for the removal of gums, phospho-proteins and other non-fatty components from edible fats by treatment with water containing 3 to 5 per cent oil-soluble emulsifier such as mono or diglycerides, partial fatty acid ester of a polyhydric alcohol, or a polyoxyethylene derivative of propylene glycol glucoside. An important feature of another patent (*Brit. Pat.* 655,948) is the process of recovering the oil from the sludge obtained after centrifuging by emulsifying it with water. In such emulsification excess water was found necessary for increasing the oil recovery. Degumming of soyabean oil with 10 per cent alkali phosphate before neutralizing with alkali reduced the refining loss (Lever Bros. & Unilever Ltd., *Brit. Pat.* 661,703). Maltikow (*U.S. Pat.* 2,576,957) found that crude solvent-extracted oils can be partially degummed in the presence of 25 per cent solvent at an optimum temperature of 30°-60°F. Piskosh *et al.* (*Curr. Sci.*, **20,** 16-17) devised a method for the purification of mustard oil contaminated with argemone oil up to 5 per cent. The process consists in agitating with 20 per cent aqueous ferric chloride for 20 min. followed by heating the emulsion for 30 min., settling and filtering. A further treatment with about 0·5 per cent fullers' earth improved the colour and removed the traces of ferric chloride.

Alkali refining — Free acid neutralization with sodium carbonate is interesting from the point of using a cheaper raw material, but the evolution of carbon dioxide in the neutralizer has so far precluded its use on a commercial scale. Clayton (*U.S. Pat.* 2,607,788), using the sodium carbonate as a neutralizing agent, recommended treatment under pressure. Kulikov (*Rybnoe Khoz,* **27,** No. 5, 45) regenerated the oil used for frying by refining with a mixed solution of sodium carbonate and caustic soda. Kroonen and Feuge (*J. Amer. Oil Chem. Soc.,* **29,** 65) evaluated the effect of caustic lye strength, time, speed of agitation and temperature in the re-refining of cottonseed oil. For removing gossypol-like pigments, they found that the " high sheer vigorous " agitation is most effective. A new patent (*Brit. Pat.* 684,035) described a two-stage oil refining process. In the first stage a strong caustic lye is used to neutralize all the free acids and the soap stock formed is separated in a centrifuge. This partially refined oil is again treated with some more lye and stirred vigorously at a higher temperature, the soap stock being separated by a special arrangement provided in the equipment.

Some of the special oil-refining apparatus developed during the current year refer to automatic metering of oil and alkali and a system of mixing, heating and centrifuging by continuous process (KELLY, *Paint Oil Col. J.*, **121**, 1421; *Brit. Pat.* 673,632).

In a study of oil losses during alkali refining, Soccart (*Oléagineux*, **7**, 65) reported a mathematical relation between the loss coefficient, alkali, reaction rates and phase separation; Pinto [*Bol. tech. inst. agron. norte.* (*Belem, Brazil*), No. 21, 3] correlated the refining cost with the acidity of oils.

In the alkali refining process, the use of solvents has been the subject of investigation by many research workers. Nojima [*Jap. Pat.* 1,819 (1950)] refined the rice bran oil by first dissolving it in benzene and then treating with alkali and alcohol. The soap stock separates out into the alcoholic aqueous layer. In a process developed by Pueschal (*Ital. Pat.* 461,372) alcohol reduces the emulsion and improves the centrifugal separation of soap stock. Munakata *et al.* [*Jap. Pat.* 2,888 (1950)] recommended the use of 70 per cent methyl or ethyl alcohol in alkali refining of rice bran oil by continuous method. In a similar study Sagava [*Jap. Pat.* 179,842 (1949)] favoured the use of 85 per cent ethyl alcohol. Jaky (*Mezögazdaság és Ipar*, **3**, No. 11/12, 8), while treating sunflower seed oil of high acid value, found 90 per cent ethyl alcohol to be more effective than 96 per cent alcohol. A new patent (*Brit. Pat.* 652,376) described a phase separation in the process of refining, when propane is added to the oil and the temperature raised above the critical temperature. The upper phase contains decolourized oil and the lower phase the coloured bodies. These could further be fractionated into triglycerides, phosphatides and vitamin concentrates.

Some of the deacidification steps were confined to distillation methods. Obara and Oka (*J. Japan Soc. Food Nutr.*, **3**, 138) separated the different fractions of free fatty acids in highly acid rice bran oil by molecular distillation. A similar method was found unsuitable with coconut oil (BROOKER and HARTMANN, *N.Z.J. Sci. Tech.*, **33B**, 488). Mares patented (*U.S. Pat.* 2,594,953) a method by combining free fatty acid distillation with adsorbent bleaching and deodorization.

Other communications on deacidifying refer to one method for esterifying the free fatty acids to form glycerides (SANTELLI, *Oléagineux*, **6**, 699) and an attempt by Venkatasubramaniyan and De (*Sci. & Cult.*, **17**, 180) to deacidify oils by adsorbing the acids on resins. According to a British patent (Establishments J. J. Carnanel and Forges de Basse-Indre, *Brit. Pat.* 585,566) emulsification purifies the oil separating the fatty acids and impurities.

Of the other publications that appeared in the current year one refers to a patent (*U.S. Pat.* 2,579,946) issued to McClaim for using water-soluble organic salts as filter aids, which could be recovered in hot water. Unchuld Henry (*U.S. Pat.* 2,516,733) described a soyabean oil refining process which consists in heating between 100° and 520°F. at atmospheric pressures by passing electric current through spaced electrodes immersed in the oil. Lecithin, phosphatides and fatty acids are separated in less than one minute when worked at 100-700 milliamperes, 500-2,000 V. and a frequency of 500-4,000 cycles.

Bleaching — Various improvements were proposed for bleaching oils. Bailey (*U.S. Pat.* 2,618,644) reduced production cost by first bleaching the oils with partially spent bleaching adsorbent at elevated temperatures before treating the oils with fresh adsorbent. According to several communications, treatment of crude oils with acids before bleaching with adsorbent is more efficient and practical [YAMAKITA, *Bull. Inst. Chem. Res. Kyoto Univ.*, **24**, 24; TSUCHIYA, *Japan* 37 (1950); NAKAJIMA and KOSUGE, *J. Nippon Oil Tech. Soc.*, **4**, 23]. Christenson and Harpet (*U.S. Pat.* 2,569,124) described the method of bleaching oils in presence of steam. For bleaching solvent-extracted oils Mormor and Moyer (*U.S. Pat.* 2,608,566) found that a prior treatment with adsorbent before evaporating the solvent was more efficacious. Gee (*U.S. Pat.* 2,577,079) developed a method for separating the oil from the bleaching adsorbents by using organic solvents such as petroleum naphtha, low boiling hydrocarbons, chlorinated hydrocarbons and ketones. He found that 0·25-5·0 parts of solvent were required for one part of clay. Andrea Paleni (*Olearia*, **6,** 19-25) has reviewed the subject of decolourization of oils with fullers' earth.

In several countries the bleaching properties of local earths have been investigated. Joshi obtained encouraging results with Indian earths on treatment with acids and activation at 300°-350°C. Others (*Ion*, **11,** 135; RAMOS and VEGA, *Anales. real. soc. espon. fiz. y. quim.*, **48B,** 247; JAKAYASU, *J. Jap. Soc. Food Nutr.*, **3,** 133) described the technical aspects of improving the clays for bleaching oils. Kimomura (*J. Oil Chem. Soc. Japan*, **1,** 81) found some Japanese commercial clays superior to American clays. According to a patent issued to Heinemann (*U.S. Pat.* 2,563,650) bauxite calcined with silica gel was a good decolourizer.

Some of the processes developed refer to bleaching oils and fats with oxidizing agents. Glorifet and Constelle [*Fr. Pat.* 965,495; TSUCHIYA *et al.*, *Jap. Pat.* 861 (1950)] used persulphuric acid; Kawai [*Jap. Pat.* 2,388 (1950)] and Nojima and Ishikawa [*Jap. Pat.* 3,633 (1950)] recommended hydrogen peroxide; Woodward obtained a patent (*U.S. Pat.* 2,592,226; WOODWARD and FENRICH, *Chem. Engng.*, **59,** 174) for the use of chlorine dioxide; and Uchida *et al.* [*Jap. Pat.* 173,487 (1946)] found manganese trioxide and air as suitable oxidizing agents; Yoshitaka Mochurda [*Jap. Pat.* 3,317 (1951)] decolourized rice bran oil with suitable dilution of sulphuric acid.

A recent communication describes the use of the Solexol process for fractionating and decolourizing vegetable and animal oils to edible products and vitamin concentrates (*Industr. Chem.*, **28,** 324).

Of the two communications on the utilization of oil refinery, the one by Verma (*Indian Soap J.*, **18,** 55-57) discusses the feasibility of extracting tocopherols from the wastes and byproducts of the fatty oil industry, while the other is a general review by Desikachar *et al.* (*Indian Soap J.*, **17,** 289-93).

Deodorization — New information available on the subject of deodorization is rather limited. Thurman obtained patents (*U.S. Pat.* 2,621,196; 2,621,197) for deodorizing oils, primarily soyabean oils, to produce edible oils stable to reversion and rancidity, and for obtaining concentrates of vitamins A and D, tocopherol, stigmasterol and silosterol. As compared with batch methods, the continuous deodorization processes were shown to yield valuable byproducts with non-reverting oils such as corn, cottonseed, peanut, sesame and sunflower seed.

Some of the other publications of interest are: Ghosh and Chakravarti (*Trans. Indian Inst. Chem. Engng.*, **3,** 21) described methods used in Indian factories, and the others a semi-continuous laboratory deodorizer (ALLEN *et al.*, *J. Amer. Oil Chem. Soc.*, **29,** 380), a thin film distillation apparatus (THOMPSON, *U.S. Pat.* 2,611,741) and a technique of deodorization (BATAILLE, *Bull. mens. ITERG*, **6,** 361). Two American patents (*U.S. Pat.* 2,559,129; 2,615,833) refer to stripping and deodorization of edible oils. Boyle (*Food*, **21,** 372) described the deodorization of edible oils with particular emphasis on the Foster Weeler Dowtherm system. Bataille (*Industr. Perfum.*, **6,** 369-71) devised a method for vacuum deodorization by the injection of superheated steam.

Hydrogenated fats (vanaspati, margarine and other shortenings) — Some of the fundamental work carried out on hydrogenation relates to selectivity in fat hardening. Belekar *et al.* (*J. sci. industr. Res., India*, **11B,** 140) examined the fatty acid composition and properties of various oils and their hydrogenated products, and found that most of the hardened products contained considerable amounts of iso-oleic acid while the linoleic acid content was low, which indicated a highly selective hydrogenation. Miyake obtained a patent (*Brit. Pat.* 670,906) for selective hydrogenation of oils. The fats or oils containing both mono and poly-unsaturated acids are treated with hydrogen at 100°-230°C. and 1-20 atm. or at 100°-200°C. and 20-80 atm. in the presence of a copper catalyst. This treatment results in the conversion of poly-unsaturated acids to mono-unsaturated acids. According to Ueno (*Fette u. Seif*, **54,** 467) the double bonds of the carbon atoms of partially hydrogenated methyl linoleate at 15-16 positions are the easiest to hydrogenate and those at 9-10 position coming next, and carbon atoms at 12-13 position are the most difficult to saturate. Lie and Spillum (*J. Amer. Oil Chem. Soc.*, **29,** 601) advanced the theory that temperature influences selectivity of hydrogenation through the conjugation of the double bond. Sims (*J. Amer. Oil Chem. Soc.*, **29,** 347) reported that at high pressures the selectivity of hydrogenation varied directly with the amount of agitation and inversely with the catalyst concentration. Earlier workers, however, reported the reverse effect for moderate pressures. Janssen (*Chem. Weekbl.*, **47**, 490-94) has derived a mathematical expression for hydrogenation of oils, representing the diffusion of glycerides, activated adsorption, hydrogenation and desorption as constants. These constants were found to vary with the influence of temperature, pressure and poisoning of the catalyst, in the selectivity of hydrogenation process. Norris *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 28) found that solvent residues of over 0·003 per cent in the oil extracted by using trichloroethylene retarded the hydrogenation without influencing the selectivity. Refining methods generally overcome this difficulty.

Among the new inventions in the technique of hydrogenation, the application of supersonic waves is an interesting contribution [OHJYO, *Jap. Pat.* 862 (1950)]. Mockel (*Chem. Engng. Tech.*, **24**, 153-54) found it possible to conduct hydrogenation in open vessels employing supersonic waves as these waves created the necessary internal pressure at the gas and liquid interface. Some of the engineering developments refer to a combination of hydrogenation and deodorization in a single unit (Armour & Co., *Brit. Pat.* 673,273), a new hydrogenation equipment in which hydrogen is obtained from ammonia cracking [JACOB (Jr.) and VANDE EIVEN, *U.S. Pat.* 2,602,806] and a continuous hydrogenation system (Proctor & Gamble Co., *Brit. Pat.* 654,692; 658,188; 658,189).

Developments of catalysts form the subject of some communications on hydrogenation. A method for the recovery of nickel and fat from spent nickel catalyst has been worked out by Bhasin *et al.* (*J. sci. industr. Res., India*, **11B**, 248). The recovered nickel can be re-used in the form of precipitated carbonate or formate for the hydrogenation of oils. Iron usually present as an impurity in the spent catalyst does not affect the activity of the nickel catalyst, and can be removed from the nickel solution as hydroxide or with the aid of precipitated chalk. Ramaswamy (*Indian Soap J.*, **18**, 20-24) has discussed the conversion of spent nickel into active nickel for re-use in hydrogenation process. Faulkner obtained a patent (*U.S. Pat.* 2,609,346) for preparing a nickel catalyst. In this process the catalyst is dispersed in a molten glyceride fat containing some filter-aid. A new nickel-copper catalyst which is resistant to poisoning when used either in the form of pellets or as powder has been developed (Empresa Nacional "Calvo Sotelo" de Combustibles liquidos Y. Lubricants, *Span. Pat.* 192,979). A mixed catalyst composed of carbonates of nickel, copper, calcium and cobalt has been reported by Ueno [*Jap. Pat.* 1,118 (1951)]. A few communications reported some of the practical ways of hardening fatty oils with similar unreduced catalysts (UENO *et al.*, *J. chem. Soc. Jap.*; *Industr. Chem. Sect.*, **53**, 43, 140, 218, 252). According to one Japanese communication, a mixture of nickel dioxide and kieselguhr, when used as a catalyst, resulted in a very stable fatty oil (ENDO and KAWAKANI, *Jap. Pat.* 181,347). Morris and Khym (*U.S. Pat.* 2,602,807) advocated filtering through acidified bleaching clay after hydrogenation for the efficient removal of the catalyst. Belekar *et al.* (*J. sci. industr. Res., India*, **11B**, 28), in a study on the recovery of nickel from spent nickel catalyst, obtained maximum recovery of nickel with a suitable mixture of sulphuric and nitric acids. Some of the reviews published on the subject of hydrogenation are: Hydrogenation Catalyst, by Bailey (*Industr. Engng. Chem.*, **44**, 990); Hydrogenation of Oils, by Muscari-Tourajoli (*Olii minerali grassi e saponi colori e. vernici*, **29**, 57-63 and 74-79); and Sulphur Dioxide as a Fat Hardening Catalyst (*Food*, **20**, 236).

Developments on margarine, shortening and other compound cooking fats are reviewed here. According to a continuous method of manufacture, margarine, after pre-cooling and emulsification, is passed through screens before it is completely set. The setting to final consistency is effected under conditions where shearing does not take place (ROURKE and Dow, *U.S. Pat.* 2,611,707). Soft palatable margarine is made from fats from which high melting glycerides are removed by crystallization (WILSON *et al.*, *U.S. Pat.* 2,592,224). In a method of margarine manufacture the temperature of fatty and aqueous portions is so adjusted that, after mixing, the temperature of the finished product is lower than the solidification point of the fat component (ZACHARIASSEN and BORCK, *U.S. Pat.* 2,605,185). A patent on a margarine churn taken out by Turgasen is described in detail by Slater (*Food Engng.*, **24**, 111-14). It is claimed that the final product resembles butter both in appearance and texture. Storrs and Froedge (*U.S. Pat.* 2,609,300), while using fatty acid as an emulsifier in place of protein, obtained a margarine resembling butter in spreading and other characteristics. Barnhart and Hassinem (*U.S. Pat.* 2,611,706) patented the method of manufacture of an infant food, the fat component of which was made up of 50 per cent unsaturated acids, 5 per cent C_{12}-C_{14} saturated fatty acids and the remainder above C_{14} saturated acids.

For colouring margarine, Schuchardt (*Fette u. Seif*, **53**, 689) recommended two parts of lactoflavin for one part of carotene in place of synthetic dyes. Adler *et al.* (*U.S. Pat.* 2,600,381) prepared a dye tablet containing yellow synthetic dyes, compressed with starch. Other patents on colouring of margarine include those issued to Brown (*U.S. Pat.* 2,607,697) and Henzgen (*U.S. Pat.* 2,610,917; 2,617,733).

SPOILAGE IN FATS

Stability of fats — Some of the new techniques to prevent spoilage in fats are reviewed here. Antilla *et al.* (*Acta agric. Scand.*, **2**, 210-14) investigated the stability of vitamin A and carotene in butter by different techniques. They found a marked increase in acid and peroxide values and a 6 per cent loss of vitamin A content by the use of ordinary butter salt. Makerin (*Molochnaya Prom.*, **13**, 24-27) improved the stability of butter by the addition of buffer salts. Bettman (*U.S. Pat.* 2,612,454) invented a process to protect butter from rancidity over relatively long periods of time without refrigeration. According to his method butter is heated to boiling with 0·25 per cent sodium chloride. The modified butter separates on cooling which is then heated with hot aqueous solution of high grade gelatine resulting in a butter of good keeping and spreading qualities. Thomé (*Svenska Mejeritidn*, **42**, 195, 207) suggested the use of salt containing some sodium carbonate and sodium acid phosphate near a *p*H range of 6 and 7. Tollenaar (*Ned. melk-en Zuiveltijdschr*, **5**, 46-50) prevented the oxidative defects in cold-stored butter by treating with tetra-alkyl thiuram disulphides. It was found that the antioxidant effect of tetra-alkyl thiuram disulphide was less in unsalted than in salted butter.

Sjorstrom and Larsson (*U.S. Pat.* 2,609,297) removed the unpleasant taste and odour in margarine and dairy products by heating them to 80°C. with reducing sugars and increasing the *p*H to 9 by means of an alkali. Diatchenko (*Lait*, **31**, 308, 505-10) investigated the influence of albumins on the stability of butter. He attributed the various off-flavours to decomposition in the serum, rather than to fat, and found that the off-flavour increased with the amino nitrogen content. Holm *et al.* (*Medd. Mejerifor. Malmo*, **37**, 14) observed that the oily flavour development in butter is a direct result of the formation of α-β unsaturated carbonyl compounds. Wagenaar (*J. Dairy Sci.*, **35**, 403) reported that the incidence of surface taints in butter could be markedly lowered by adopting necessary sanitary measures in the dairy plant. As a step in this direction, he recommended inactivating the bacteria by chlorination. Negratti [*Mondo d. latte*, **1** (1952), 10] observed that butter from milk treated with hydrogen peroxide had very much lower coliform titres and bacterial counts and better keeping qualities. Hillig (*Ass. off. agric. Chem.*, **35**, 844) has shown that when cream is stored at 4°C., no deterioration took place, but when removed from storage at 4°C. and with subsequent keeping at 25°C., deterioration was rapid resulting in a cream unfit for the manufacture of butter. Arfeva and Golovkin (*Molochnaya Prom.*, **13**, 23-26) expressed the loss in weight of butter during refrigeration and prolonged storage life by means of a mathematical formula. Gelpi (Jr.) *et al.* (*J. Dairy Sci.*, **35**, 93) found that ethyl caffeate, when used as an antioxidant in the presence of copper, was more efficient than hitherto known butylated hydroxyanisole in frozen stored summer cream. Thomé *et al.* (*Medd. Mejerifor. Malmo*, **32**, 21) extracted antioxidant from whey for the use of cream and butter.

Hannan and Shephard (*Nature*, **170**, 1021) showed that the peroxide formation in butter fats after irradiation with high energy electrons is greater at higher temperatures. The accelerated oxidation after treatment is reported to be maximum in fats in the region of —20°C.

Mack *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 14) have investigated the relationship between tocopherol content, fatty acid composition and stability of commercially refined, bleached and winterized cottonseed oils. They observed that the changes in fatty acid composition and tocopherol content tend to counter-balance one another leading to the same final stability in each product. Inglett (*Diss. Abstr.*, **12**, 565) has carried out free radical and infra-red studies of some tocopherols and other 6-hydroxychroman antioxidants.

Thurman (*U.S. Pat.* 2,621,191) obtained an edible non-reverting hydrogenated glyceride oil by pretreating soyabean oil with steam at reduced pressure; the tocopherol content in the oil was brought down to less than 0·03 per cent by this treatment. The oil was hydrogenated and deodorized with steam. For corn or cottonseed oil milder pretreatment conditions are recommended. Matil obtained a patent (*U.S. Pat.* 2,613,215) for improving the flavour and stability of glyceride oil by hydrogenation, whereby the iodine value is decreased from 4 to 20 and by removing the unsaponifiable portion completely through solvent extraction. Ueno and Shigeno (*J. chem. Soc., Jap., Industr. Chem. Sect.*, **53**, 228) attributed the different susceptibilities to oxidation in the case of hydrogenated oils as due to varying quantities of highly unsaturated fatty acids remaining in the products.

Bentz *et al.* (*Food Tech.*, **6**, 302) have shown that the stability of 12 fatty foods studied by them could be increased from 43 to 3,200 per cent using antioxidants. Petrovskii (*Myasnaya Ind. U.S.S.R.*, **23**, No. 3, 30) attributed the differences in the stabilities of individual animal fats to the natural antioxidants present. Gemmill (*Food Engng.*, **24**, No. 5, 102) assessed the commonly approved antioxidants for stabilizing steam-rendered lard. In a study on the stabilization of lard and cottonseed oil by means of antioxidants, Moore and Bickford (*J. Amer. Oil Chem. Soc.*, **29**, 1) gave the following order of increasing effectiveness at the 1 per cent level: cottonseed oil — di-tert-butyl-*p*-cresol, sesamol, nordihydroguaiaretic acid, norconidendrin, hydroquinone and propyl gallate; lard — lecithin, gum guaiac, α-tocopherol, γ-tocopherol, butylated hydroxyanisole, di-tert-butyl-*p*-cresol, sesamol, norconidendrin, hydroquinone, nordihydroguaiaretic acid and propyl gallate. Mack and Bickford (*J. Amer. Oil Chem. Soc.*, **29**, 428) reported that α and β conidendrols are efficient antioxidants for vegetable oils and lard, and even superior to butylated hydroxyanisole, di-tert-butyl-*p*-cresol, hydroquinone and phenyl-β-naphthylamine in some respects. Nair *et al.* (*Sci. & Cult.*, **17**, 295) observed that lime juice affords protection against development of rancidity. Dalmau (*Afinidad*, **28**, 205) has reported the anti-rancid properties of nordihydroguaiaretic acid in lards and baked products containing the protected lards. Citric acid, when used as a synergist, improved antioxidant properties considerably. Tests on antioxidant properties of nordihydroguaiaretic acid and hydroquinone showed a fall in efficiency in the *p*H range 5 to 9·2, and at *p*H 9·2 the efficiency was practically nil (SPETSIG, *Svensk. kem. Tidskr.*, **64**, 191). Alkyl esters of gallic acid are valuable antioxidants for lard (RUTKOWSKI, *Roczn. Zakl. Hig. Warsz.*, **3**, 71).

Osler (*Food Engng.*, **24**, 140) reported that the vitamin A in fat is not only susceptible to oxidation but also subject to destructive action by enzymes like carotenases, and lipoxidases, and by ferric iron and heat. Hence he suggested heating the oils under vacuum or in an inert atmosphere, and use of antioxidants to retain vitamin A. Bickoff *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 445) found hydroxy and amino substituted diphenyl amines, *p*-substituted phenylenediamines, and derivatives of 2, 2, 4-trimethyl-1, 2-dihydroquinoline antioxidants the most effective among 89 antioxidants in preventing oxidation of carotene. The same author, in another study, found that pyrogallol derivatives as antioxidant for carotene showed remarkable activity in some systems while they are of little value in others. Thus all the derivatives which are more effective than pyrogallol in protecting carotene in mineral oil are very much less effective than pyrogallol in lard and, with two exceptions, are also less effective in coconut oil (BICKOFF *et al.*, *J. Amer. Oil Chem. Soc.*, **29**, 51).

Bertram and Wynia (*J. Amer. Oil Chem. Soc.*, **29**, 629) studied the effectiveness of sulphur compounds for improving the keeping quality of fats and oils. Heating lard with 0·05 per cent sulphur for 4 hr. at 180°C. combined with a subsequent addition of 0·02 per cent gallate antioxidant improves the keeping quality. Alkylmercapto ketones are equally effective as antioxidants for lard (THOMPSON *et al.*, *Industr. Engng. Chem.*, **44,** 1659). The other antioxidants that are found effective for lard include certain spices and condiments (CHIPAULT *et al.*, *Food Res.*, **17,** 46). Sethi and Agarwal (*J. sci. industr. Res., India,* **11B,** 468) found that heating the oil or fat with spices and condiments to high temperatures to check the development of rancidity was not an economical process when applied on an industrial scale. However, their studies indicated that antioxidant principles present in spices and condiments could be easily extracted by hot oil and are not destroyed at the temperatures usually employed for frying.

In a study on the pro-oxidant effects of certain metals in groundnut oil, Hasaini and Saletore (*Indian Soap J.*, **18,** 192) reported the following order of effectiveness: lead, zinc, copper, aluminium, silver and stainless steel. They further observed that the oxides of these metals were more pro-oxidant than the metals.

The following antioxidants, in addition to those already mentioned, were patented during the year: aromatic substituted ethanol amines (*U.S. Pat.* 2,576,458); a mixture of tocopherol and palmitoyl ascorbate (*U.S. Pat.* 2,582,395); *p*-toluene sulphonic acid (*U.S. Pat.* 2,583,602); gallic acid esters of C_8-C_{12} aliphatic alcohols (*U.S. Pat.* 2,586,274); iminodisuccinic acid (*U.S. Pat.* 2,594,294); substituted coumarins (*U.S. Pat.* 2,599,810); acetondicarboxylic acid (*U.S. Pat.* 2,605,186); a mixture of propylene glycol with an alkylated hydroxyphenyl ether with or without alkyl gallic acid ester (*U.S. Pat.* 2,607,745-6); phytic acid (*U.S. Pat.* 2,610,973); and azo dye yellow OB or yellow AB [*Jap. Pat.* 686 (1951)].

Toxicity — Some of the toxic effects of antioxidants are reviewed here. Takata *et al.* (*Vitamins*, **5,** 126, 203, 206) found that the new antioxidant 3, 4-bis-(*m, p*-dihydroxyphenyl)-n-hexane is more toxic than nordihydroguaiaretic acid. Another antioxidant, 2, 6-bis-(4-hydroxy-2-methyl-5-isopropyl benzoyl)-*p*-cresol, is found to be less toxic than the antioxidants now used in margarines. Itaconic acid, when used at 2 per cent level as an antioxidant, does not show any toxicity (BOOTH *et al.*, *J. biol. Chem.*, **195,** 697).

Flavour reversion — Evans *et al.* (*J. Amer. Oil Chem. Soc.*, **29,** 61) studied the effects of processing on the metal contamination in soyabean oil. They found that copper and iron present in the oil were capable of promoting flavour reversion. Although refining removes 95-98 per cent of the metals from the oil, deodorization increases the iron content forty-fold in many cases. Therefore, the deodorization process is the most critical and sometimes a very undesirable process for the stability and quality of soyabean oils. Lips *et al.* (*Canad. J. Tech.*, **30,** 1) studied the effect of different refining processes on stability. Treatment of soyabean oil with activated magnesia or with hydrochloric acid after alkali refining is detrimental to flavour stability. Rapeseed oil also showed flavour reversion after deodorization (DELOBEZ and MESTREIT, *Bull. Inf. cent. tech. Ind. Fond,* **5,** 468). Lange and Folzenlogen (*U.S. Pat.* 2,589,097) checked flavour reversion in hydrogenated oils by heating the oils before hydrogenation with activated alumina, bauxite and aluminium silicate.

Goldman and Rayman (*Food Res.*, **17,** 326) developed methods for studying the bacterial hydrolysis of fats. *Pseudomonas fluorescens* completely hydrolysed fats containing less than 10 g. per 100 cc. of the emulsion; while in fat at 20 g. per 100 cc. of emulsions, 90-95 per cent hydrolysis occurs. The lypolytic power of different strains of *Pseudomonas* varies widely in both the rate and the extent of hydrolysis.

Mechanism of autoxidation — Autoxidation of fats with 1, 3 and 1, 4-spaced unsaturated fatty acids leads to peroxide formation, while with oleic acid, hydro-peroxides are formed with the double bond migrating through the molecule (TREIBES and ROTHE, *Chem. Ber.*, **84,** 370). Feuell and Skellon (*J. chem. Soc.*, 1952, 59) observed that peroxide formation decreased from ethyl, propyl to butyl oleates. It was further observed that oleic (*cis*) esters react more rapidly than elaidic (*trans*) esters. Glimm *et al.* (*Fette u. Seif*, **54,** 462) studied the changes in the characteristics and the development of hydrogen peroxide in the autoxidation of fat. At maximum peroxide value, the acid and saponification values increase while the iodine value and the thiocyanogen values decrease. Under anhydrous conditions, water is split off which helps the progress of the reaction. On standing for 5-6 weeks, hydrogen peroxide is formed leading to increase in acid value and decrease in saponification value. In a polarographic study of autoxidation of various fats, Nagami *et al.* (*J. pharm. Soc. Jap.*, **71**, 813, 818) observed a reduction wave due to the double bond of oleic acid, besides two distinct waves and a maximum wave due to unstable peroxides that form in the initial stage of autoxidation. These unstable peroxides turn to stable peroxides which can be determined by chemical methods but not by polarography. Kawahara and Dutton (*J. Amer. Oil Chem. Soc.*, **29**, 372) identified acetaldehyde, propionaldehyde, α-pentanol and hexanol in the volatile cleavage products of autoxidized soyabean oil. Evidence has also been presented for the presence of croton aldehyde. A kinetic study of the reaction between tocopherol and the peroxides of ethyl oleate and also between tocopherol and ethyl oleate in the process of oxidation has been carried out. The results showed that tocopherol reacts with the initial unstable form of peroxides rather than with the final more stable form (DUBOULOZ *et al.*, *Oléagineux*, **7**, 265).

Methods of testing — There are many methods of testing the resistance of fat to atmospheric oxidation. Some of them are: A.O.M. or Swift stability test, Schaal or oven test, Kreiss test, Schiff test and peroxide test. The peroxide test is useful in evaluating the extent of oxidation of fats, while the Kreiss test determines advanced deterioration or incipient rancidity based upon the presence of aldehydes. Schiff test is a qualitative test for aldehydes. The following review refers to improvements to existing methods of measuring deterioration in fats. Drozdov and Materanskaya (*Myasnaya Ind. S.S.S.R.*, **23**, No. 3, 73) reported a new method based on the determination of carbonyl groups by means of reaction with hydroxylamine for estimating spoilage in fats. This result, however, needs correction for the amount of acidity in the original sample. In the estimation of peroxide in fat by iodometric methods, Hartmann and White (*Anal. Chem.*, **24**, 527) recommended a 10 per cent solution of citric acid in a mixture of tert-butyl alcohol and carbon tetrachloride in place of widely used acetic acid-carbon tetrachloride mixture. This eliminates the necessity for a blank titration. The same workers (HARTMANN and WHITE, *J. Sci. Fd. & Agric.*, **3**, 112) reported high peroxide values by the dichlorophenol-indophenol method of estimation. Kartha (*J. sci. industr. Res., India*, **11B**, 263) studied the induction periods of mixtures of oils and fats with fully saturated glycerides freed from antioxidants. The results showed that the absolute concentration of the inhibitor has no influence on the induction period, and that the nature and amounts of the antioxidant present in the oil determine the induction periods which are in agreement with the requirements of Christiansen's hypothesis. Smith (*J. Sci. Fd. Agric.*, **3**, 26) proposed a modification in the photometric ferric thiocyanate method of peroxide estimation. The fat is extracted with benzene and treated with methanol to make it miscible with aqueous reagents. Ammonium thiocyanate mixed with ferric chloride is then added to the test solutions. Lea (*J. Sci. Fd. Agric.*, **3**, 586) found that the iodometric, the 2,6-dichlorophenol-indophenol and the ferric thiocyanate methods of peroxide estimation are all affected by atmospheric oxygen, but the last method gave the best reproducibility. Alcala and Quijano (*Anal. Soc. esp. Fis. Quim.*, **48B**, 255) recommended the addition of sodium carbonate to the reaction mixture employed in the Wheeler peroxide method to inhibit the adverse effect of air by the evolution of carbon dioxide. In the assessment of the keeping properties of butter, a rapid " Oven Sorting Out " test was found satisfactory for detecting incipient oxidation (BARNICOAT, *N.Z. J. Sci. Tech.*, **33**, 37-43).

Handwerk (*Iowa St. Coll. J. Sci.*, **26**, 212) has studied the reaction effects of reagents upon the analytical results of the products of fat deterioration. The different rates of reaction of the Emerie and Engel reagent with different tocopherols were used as a basis for determining the presence of tocopherols other than α-tocopherols. For the assay of non-oxidized tocopherol in oxidized milk fat, Handwerk recommended the Kjolhede method, which is a modification of the Emerie and Engel method. Schmalfuss (*Fette u. Seif*, **53**, 689) suggested that spoilage characteristics of fats should be reported in standard measurements: for example, peroxide in lea value, acidity in milligrams potassium hydroxide required for neutralization, ketones in micrograms of methylnonyl ketone, aldehyde in micrograms of heptaldehyde, and epihydrinaldehyde also in micrograms, all the values being based on one gram of fat.

Glavind and Hartmann (*Acta chem. Scand.*, **5**, 975) measured spectrophotometrically the colour developed in fats and pure compounds in the thio-barbituric test, the Kreiss test and the Hartmann-Glavind test for fat spoilage. The colour developing in the first two tests is due to various complex compounds, whereas on the H.G. test it is a specific reaction for peroxides. Kahan (*J. Ass. off. agric. Chem.*, **35**, 186) reported that the ferrous reagent method of determining the amount of antioxidant (propyl gallate) in fats showed about 90 per cent recovery and that the nordihydroguaiaretic acid and tocopherols do not interfere while gallic and tannic acids do.

Reviews on the subject include: Rancidification of Fatty Oils (CAROLA, *Olii. min.*, **29**, 3); Mechanisms of Oxidation of Fats (ISHII, *J. Oil Chem. Soc. Japan*, **1**, 85); Chemical and Physical Agents Causing Alteration in Fats (VALVERDE and GUILLENTA, *Act. congr. peruano quim.*, **2**, 603); Fat Studies and Antioxidants in the U.S.A. (MARCUSE, *Fette u. Seif*, **54**, 530); Flavour Deterioration of Fats (LIPS, *Food in Canada*, **12**, No. 6, 9); Application of Antioxidants (RAEITHEL, *Z. Lebensm-Untersuch*, **95**, 246); Selection and Application of Antioxidants to a Variety of Foods (BENTZ *et al.*, *Food Tech.*, **6**, 302); Use of Propyl Gallate as an Antioxidant (MOLINARI, *Olii. min.*, **25**, 70); Pharmacological Evaluation of Antioxidants (LEHMANN *et al.*, *Advanc. Food Res.*, **3**, 197); Chemicals in Food (LEA, *Chem. & Ind.*, 1952, 178); Protection of Fats against Rancidity (PIERRE DUBONLOZ, *Oléagineux*, **7**, 1952, 465-71); Nitrogen guards Food Quality (*McGraw-Hill Dig.*, **7**, 1952, 36); Causes and Effect of Rancidity (*Milling*, **118**, 610); and Spoilage of Fats and Fat-containing Baked Products (*Getre.*, **2**, 103-6).

CHARACTERISTICS & COMPOSITION OF FATS

A number of procedures for determining the characteristics and composition of fats have been reported during the year.

Physical characteristics — Some of the physical characteristics such as surface tension, interfacial tension against water, viscosity and refractive index at 75°C. for saturated even-numbered fatty acids of C_2 to C_{18} carbon chain, as well as for their corresponding methyl and ethyl esters, were presented by means of a chart by Gros and Feuge (*J. Amer. Oil Chem. Soc.*, **29**, 313). The temperature effect on myristic acid is also included. Sedgwick *et al.* (*J. Org. Chem.*, **17**, 327) determined the solubilities of the C_{10}-C_{18} saturated even-carbon fatty acids and their methyl esters in benzene, cyclohexane, carbon tetrachloride, chloroform, ethyl acetate, butyl acetate, methanol, 95 per cent ethanol, n-butanol, acetone and acetonitrile solvents. Paquot (*Bull. Inf. Cent. tech. Ind. Fond.*, **6**, 174; *J. Rech., Paris*, **3**, 138), in two separate communications, represented by means of a graphical chart the titres of binary and tertiary mixtures of the most common fatty acids and stearic and palmitic acids and their methyl esters. Craig *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 128) recorded the coefficient of expansion of the solid and liquid states of triglycerides. Kartha (*J. sci. industr. Res., India*, **11A**, 354) gave a new method for calculating the amount of saturated triglycerides in a fat. This was based on the observation of the melting points of glycerides that happened to be 4°C. higher than the mixed fatty acids. The same author, in another communication, pointed out that the alterations produced by inter-esterification in the melting points and micropenetration values of various animal tallows could be explained on the basis of the glyceride type composition as assigned by him. This explanation is contrary to the one given by Hilditch and his collaborators (*J. Amer. Oil Chem. Soc.*, **29**, 109). Schlenker (*J. Amer. Oil Chem. Soc.*, **29**, 94) showed how oleic acid in mixtures of palmitic and stearic acids influenced their melting points and solubility in methanol solution. Vaeck (*Int. Choc. Rev.*, **6**, 350) determined the melting and solidification points of the three polymorphic forms of cacao butter. Application of the Bloom Consistometer to shortening, butter, margarine and other plastic products is described in a paper by Clardy *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 591).

Chemical characteristics and composition — Some of the investigations were concerned with the methods of determining moisture, fat, free fatty acids, saponification value, unsaponifiable matter, Reichert-Meissl value, Polenske value, iodine value and thiocyanogen value.

Francois and Juillard (*Bull. Inf. Cent. tech. Fond.*, **6**, 427) have prepared a chart for the moisture in rapeseed wherein the effects of time of contact of moisture and intensity of crushing are also indicated. In the determination of moisture in oilseeds and oil cakes by the dielectric method, Massoni and Desnuelle (*Bull. Inf. Cent. tech. Fond.*, **6**, 39) obtained more accurate results, if the moisture in the sample was above 6 per cent. Pasquier and Francois (*Bull. Inf. Cent. tech. Fond.*, **6**, 280) described new infra-red ray equipment for rapid determination of moisture in oilseeds and compared their values. Fauve and Lacoste (*Bull. Inf. Cent. tech. Fond.*, **6**, 70) reported that with samples having 8-13 per cent moisture, infra-red ray method of drying was more effective than the oven drying method. Janvry and Francois (*Bull. Inf. Cent. tech. Fond.*, **6**, 117) recommended the Carl Fischer method for determining moisture in oilseeds where the oven method is not obligatory.

Work on the determination of fat pertained to developing rapid methods or to improvements in the accuracy of existing methods. Chopra *et al.* (*Indian J. agric. Sci.*, **22**, 183) have developed a rapid and economical procedure for oil determination in small seeds and cakes. Lips (*J. Amer. Oil Chem. Soc.*, **29**, 300) has developed an apparatus for extracting fats from various raw materials for studying characteristics and composition. In the estimation of fat in foods, Stoldt (*Fette u. Seif*, **54**, 206) determined the ideal conditions for heating and extraction to obtain the highest results. Hadorn and Jung Kunz (*Mitt. Lebensm Hyg. Bern.*, **43**, 197) found that among the many methods of fat estimation in pastry, the acid digestion method was the best and most reliable. For the determination of oil in soyabeans, Hunt *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 258) developed a new dielectric equipment. Venkatasubramaniyan (*J. sci. industr. Res., India*, **11B**, 132) examined and reported component fatty acids in soyabean oil. Some of the laboratory tests with crude soyabean oil were based on such determinations as acetone insolubles, HCl heat break and centrifugal foots that closely simulate wash-kettle practice in neutral oil losses (FREYER and SHELBURNE, *J. Amer. Oil Chem. Soc.*, **29**, 403, 408). A series of papers published on grade specifications and trade standards emphasize on fatty acid composition, particularly linoleic acid content [*Chem. & Ind.*, (1951), 846; *J. Sci. Fd. & Agric.*, **2**, 543; *J. Oil Col. Chem. Ass.*, **34**, 354].

Hartmann *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 177) reported that the Wesson method of determining the refining loss is the best method of quantitatively finding the degree of refining. For estimating the neutral fractions in oils of extreme acidity, Accinelli (*Olii min.*, **28**, 76) recommended neutralizing the oil with caustic potash, separating out the soap stock after treatment with a mixture of water, alcohol and salt and subsequently extracting with ether. Anders (*Dtsch. Farben. Z.*, **6**, 133) discussed the methods for determining acid and saponification values, suitable indicators and extraction solvents. Shermon and Dillistone [*Chem. & Ind.*, (1952), 130] designed a new continuous method of extraction of unsaponifiables for use in analytical work as they consider the existing British standard method inaccurate. Williamson [*Chem. & Ind.*, (1952), 379] contradicts this statement and maintains that the British standard method gives precise and accurate results and does not register high values. Flaschka and Lackner (*Fette u. Seif*, **54**, 141) evolved a new apparatus for the micro-determination of acid values. Sandermann and Klein (*Fette u. Sief*, **54**, 269) found that saponification in glass apparatus introduced errors on account of the action of potassium hydroxide on glass. Rhodium-plated copper flasks were recommended for accurate work. Marine (*Olii min.*, **28**, 105) proposed treatment of crude oils with ligrine and then with ether for determining non-oil constituents. Other literature on saponification value refers to the development of a micro-procedure by Van Etten (*Anal. Chem.*, **23**, 1697) and a method of analysing fatty sulphonyl chlorides (WEBER, *Fette u. Seif*, **54**, 201).

Various procedures for determining the iodine values of fats were dealt with in detail by Alonso [*Pr. Montevideo*, **1** (2), 39]. Basu (*Indian Soap J.*, **17**, 216) developed a procedure for determining the iodine value of commercial fats using hypochlorous acid. Mukherjee (*J. Amer. Oil Chem. Soc.*, **29**, 97) modified the hypochlorous acid procedure for application to biological lipids and Grunbaum and Kirk (*Mikrochem. vir Mikrochim. Acta*, **39**, 268) adapted the Hanus procedure to small amounts of biological samples. In the case of oils with conjugated double bonds, Dupin (*Bull. Inf. Cent. tech. Ind. Fond.*, **5**, 469) showed that the Rosenmund Kuhnhenn method, when catalysed with mercuric acetate, gave higher iodine values as compared with the Hanus method. Duke and Maselli (*J. Amer. Oil Chem. Soc.*, **29**, 126) reported that titrations in amperometric apparatus improved the accuracy of iodine value determinations with the Hanus, Benham-Klee and Wijs's reagents. Gengrinovich and Yudovich [*Aptecchnoe Delo.*, **5** (1952), 17-22] determined iodine value satisfactorily for a number of fats in aqueous medium. A new apparatus for the determination of iodine value (PACK *et al.*, *J. Amer. Oil Chem. Soc.*, **29**, 227; SAVACCOL and ULLYOT, *Anal. Chem.*, **24**, 715) and some improvements in the precision of semimicro analytical methods (VANDENHEUVEL, *Anal. Chem.*, **24**, 847) were reported in three separate communications. Lindner (Jr.) (*Mag. Chem. Foly.*, **56**, 441) described a less expensive modification of the Winkler method for rapid determination of iodine values of fats. Bonilauri (*Olii min.*, **28**, 89) has explained the Woburn method of obtaining iodine number, partial iodine number and the diene values of fats. Tsuchuiya *et al.* (*J. Nippon Oil Tech. Soc.*, **4**, 30) employed pyridine bromide as a reagent in the determination of iodine values of fats having conjugated double bonds. A modification of the bromine vapour gravimetric method was discussed by Atmore and Hawke (*J. Afr. Chem. Inst. N.S.*, **3**, 23). Meara [*Chem. & Ind.*, (1952), **667**] explained the higher iodine value and poly-unsaturated acids content of almond oil produced in England as due to the cooler climate. Stansbury and Hoffpauir (*J. Amer. Oil Chem. Soc.*, **29**, 53) expressed mathematically the composition of cottonseed oil as a function of iodine value and percentage of unsaponifiables. This was based on the characteristic increase in iodine value in cottonseed oil with increase in linoleic acid and decrease in oleic and saturated acids. Tamayo and Estada (*An. esp. fis. Quim.*, **47B**, 815) found that *p*-benzoquinone reagent gave higher diene value as compared with maleic anhydride. Substituting n-heptane solvents in place of petroleum ether, White and Brown (*J. Amer. Oil Chem. Soc.*, **29**, 292) obtained higher values in the estimation of di-unsaturated acids and linoleic acid. In the determination of chemical characteristics, the saponification and hydroxyl values are reported in mg. KOH/g. and iodine and thiocyanogen values in percentage of iodine. Hence Meier (*Farbe u. Lack*, **57**, 483) has recommended standardization of all values to an equivalent system so that results could be easily compared. Further, values in equivalents could be converted into molecular equivalents, thus giving an insight into the composition of the oil.

Hansen and Shorland (*Biochem. J.*, **50**, 207) isolated from butter fat two isomeric C_{17} branched long chain fatty acids formerly unidentified in natural glycerides. These are iso acid of m.p. 54·4°C. and ante-iso acid of m.p. 39·8°C. Analytical results for aged and fresh cream by the Rose-Gottliebe gravimetric and Gerber volumetric methods showed considerable differences (LEHMANN, *Schweizg. Milchztg*, **78**, 122). Methods for standardizing the Babcock test for analysing fat in milk were discussed by Herreid *et al.* (*J. Ass. off. agric. Chem.*, **35**, 202). Rexach and Tracy [*Ice Cr. Fd.*, **58** (5), 60] gave two methods of analysis — one for samples of low fat content and another for samples of high fat content. In preparing milk fat, Patton (*J. Dairy Sci.*, **35**, 324) studied the use of some organic compounds as de-emulsifiers. He found that an aqueous reagent containing n-butylamine and n-butanol de-emulsified milk cream and other fluid dairy products. Advantages of the method employing this reagent are that it is rapid, reasonably quantitative, involves no tedious extraction procedure and does not require a rigorous digestion of the sample. Schain (*Proc. Ann. Mtg. Milk Ind. Foundation, Lab. Sect.*, 1950, 46) employed a mixture of tetra-decyl desoxypolyethylene glycol diacetyl sodium phosphate, oil Red O dye and methanol as de-emulsifier in a single solution detergent method for determining butter fat in milk. It was claimed that this method is far simpler and more accurate than either the Babcock or Gerber or any of the other known methods. Tucker and Bird (*J. Dairy Sci.*, **34**, 1170) reported a method for determining free fatty acids in milk fat, which is a modification of the one by Breazeale and Bird. In this method, they substituted a Skelly solve B n-propanol mixture for petroleum ether and absolute methanolic potassium hydroxide for absolute ethanolic potassium hydroxide for titration. Hillog (*J. Ass. off. Agric. Chem.*, **35**, 748) proposed the estimation of water-insoluble acids for sorting out samples of cream from which butter is to be made. Shorland and Jhonnesson (*Nature*, **168**, 75) recorded the amounts of mono-, di-, tri-, tetra- and pentaene C_{20} and C_{22} acids in samples of butter fat. Hansen and Shorland (*Biochem. J.*, **50**, 358) isolated from butter fat a C_{20} saturated acid fraction containing at least three or possibly four methyl groups.

Pathak and Agarwal (*Biochem. J.*, **51**, 264) studied fatty acid composition of some Indian fresh-water fishes. The component acids of body, viscera and liver fats from *bhakur* (*Catla buchanani*) show significant differences in their proportion and degree of unsaturation; Patakoot *et al.* have analysed the oils from 12 fishes of Indian waters (*J. Univ. Bombay*, **19B**, Pt. 3, No. 28, 18). A Japanese communication reports the separation of the solid fat in the liver oil of *Spheroides stictonotus*. This solid fat comprised chiefly palmitic and stearic acids in the ratio of 2:1 (KANEKO *et al.*, *J. Jap. Chem.*, **3**, 23).

As a result of widespread use of spectrophotometric method for determining vitamin A in fish liver oils and concentrates the spectroscopic properties of vitamin A have assumed special significance. These studies are concerned with the calibration of the spectrophotometer and spectroscopic properties of all *trans*-vitamin A in fish liver oils (CAMA *et al.*, *Biochem. J.*, **50**, 48). In a new method for determining vitamin A in margarine, a mixture of alcohol, petroleum ether and ethyl ether was used for spectroscopic measurements (JAMPOLER, *Roczn. Zakl. Hig. Warsz.*, **2**, 190). Melnick *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 104, 121), in standardizing procedures for estimating the potency of vitamin A concentrates in fortifying margarine, compared the usefulness of the biological, colorimetric ($SbCl_3$) and spectrophotometric assay methods for routine analysis. The colorimetric method was found useful as a screening test for market samples. In the examination of beef fat through infra-red spectrophotometric methods, Swern *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 44) found 5-10 per cent of *trans* acids. Sinclair *et al.* (*J. Amer. chem. Soc.*, **74**, 2570, 2575, 2578) presented data on infra-red absorption spectra of many saturated and unsaturated fatty acids, their methyl esters and the brominated derivatives of the unsaturated acids, while Freeman (*J. Amer. chem. Soc.*, **74**, 2523) has provided data on 27 branched, long chain fatty acids. The application of this data in analytical work has been discussed. Batishcheva *et al.* (*Bull. Acad. Sci., U.S.S.R., Phy. Ser.*, **14**, 458) discussed results of analysis of sunflower seed oil and hydrogenated and non-hydrogenated cottonseed oils. O'Connor *et al.* (*J. Amer. Oil Chem. Soc.*, **29**, 461) pointed out that the A.O.C.S. spectrophotometric method gave 2·4 per cent higher results for linoleic acid in cottonseed oil than those calculated from iodine and thiocyanogen values. A new analytical procedure for the determination of sesamol, sesamolin and sesamin in sesamin concentrates and oil is based on solvent separation of free and bound sesamol and use of either spectrophotometric or photocolorimetric methods to determine each component (SUAREZ *et al.*, *Anal. Chem.*, **24**, 668).

Dalvi and Morton (*Biochem. J.*, **50**, 43) have devised an analytical procedure for determining neovitamin A esters and neoretinene in fish liver oil, based on chromatographic and ultraviolet absorption studies. Brown's method (*Biochem. J.*, **51**, 237) of determining α, β and γ-tocopherols in oils was based on separation by paper chromatography. Tous and Pizarro (*An. esp. fis. Quim.*, **46B**, 375) demonstrated the separation of binary mixtures of saturated and unsaturated acids by chromatographic techniques. Other reports refer to the method of separation of mixtures of stearic and oleic acids (YAMAKITA and AIDS, *Bull. Inst. Chem. Res., Kyoto Univ.*, **27**, 72), segregation of a mixture of methyl esters of stearic, oleic, linoleic and linolenic acids (KURTZ, *J. Amer. chem. Soc.*, **74**, 1902) and separation of mixtures of C_2 to C_{12} normal fatty acids (VANDENHEUVEL and HAYES, *Anal. Chem.*, **24**, 960). Hamilton and Holman (*Arch. Biochem.*, **36**, 456) employed a chromatographic displacement technique for the isolation of cholesterol, ergosterol and other steroids. This technique is similar to the one previously used for isolation of fatty acids. Sen Gupta and Basu

(*J. Indian chem. Soc., Industr. Edn.*, **15**, 39) described a chromatographic process by which groundnut oil could be separated into two parts, one containing mainly the glycerides free from free fatty acids, the oxidized bodies and most of the unsaponifiable matter present in the oil, and the other containing most of the non-glyceride constituents. Kaufmann *et al.* (*Fette u. Seif*, **54**, 7, 10, 73, 348) employed fluorescent dyes as indicators for separating and identifying linoleic, oleic, elaidic, erucic, stearic, caproic, caprylic, heptanoic, decanoic, octanoic and undecylenic acids and for detecting conjugated unsaturated acids and polymerized oils by paper chromatography. Reid and Lederer (*Biochem. J.*, **50**, 60) used ammonium salts of the fatty acids and n-butanol-aqueous ammonia solution for separation and estimation of lower fatty acids. Paper chromatography has been found useful in the analysis of solutions of hydroxamic acid derivatives of the fatty acids, potassium permanganate decomposition of certain acids, and analysis of oxidation products, ozonides (INOUE *et al.*, *J. agric. Chem. Soc. Japan*, **23**, 368; **24**, 291-95; **25**, 161, 491, 496). The technique could also be applied to many normal acids, their diacid oxidation products, butter and coconut, linseed, rapeseed, soyabean, olive and herring oils.

A mixture of fatty acids of peanut oil and ricinoleic acid was analysed by an ester-fractionation method. The method involved separation of the saturated acids by lead salt precipitation of the unsaturated acids as urea complex, separation of these from hydroxy acids and distilling off the saturated and unsaturated components. The composition is calculated from the weight, iodine value and saponification equivalent of the fractions (ACHAYYA and SALETORE, *Analyst*, **77**, 375). Swern *et al.* (*J. Amer. chem. Soc.*, **74**, 1655) showed how the character of urea complex formed determined the configuration of certain acids.

Detection of adulterants — The problem of ghee adulteration in India bears a close analogy to the adulteration of butter with margarine in Europe. Subrahmanyan *et al.* (*J. sci. industr. Res., India*, **11A**, 277) reviewed the problem of checking adulteration of ghee with hydrogenated oil and colourization of vanaspati in the light of work done in various parts of the country. They advocated a compulsory addition of sesame oil and fortification with fat-soluble vitamins to vanaspati in order to render it more nutritious. Ambrosetti [*Boll. Lab. Chim. Prov. Bologna*, **2** (1/2), 9] recommended the iso-oleic acid test for detection of adulteration of butter with hydrogenated oil. Phatak *et al.* (*Curr. Sci.*, **21**, 162) gave a method for identification of iso-oleic acid in hydrogenated fats through paper chromatography. Bhide and Kane (*Indian J. Dairy Sci.*, **5**, 183) pointed out that distinct critical temperature ranges of dissolution of ghee, butter and vanaspati could form a basis for detecting and estimating vanaspati in ghee. Ultraviolet spectrophotometric method for detecting margarine and cottonseed oil in butter fats and olive oils was the subject of a recent communication (MORRIS *et al.*, *Anal. Chem.*, **24**, 1396).

Anselmi and Cesari (*Ann. Chim. Rome*, **41**, 573) investigated possible effects of the hydrochloric acid, acid furfural, tin chloride colorimetric tests on other oils and dyes in the identity of sesame oil. The acid furfural colour reaction seemed most specific for the identity of sesame oil. Pavolini and Isidoro (*Olii min.*, **28**, 137-40; **29**, 33) undertook a series of studies on the chromatic reactions of sesame oil, pure sesamol and sesamin. Roy (*J. Indian chem. Soc., Industr. Edn.*, **15**, 171) studied the colour reaction and antioxidant value of sesame oil towards carotene in vanaspati. It was pointed out that the basic principle responsible for giving increased stability to the carotene used and intense colour in the Baudouin test was the presence of sesamol in the unsaponifiable portion of sesame oil. The Pavolini test could detect 5 per cent sesame oil when added to hydrogenated fats according to one source [RENKO, *Mondo d. latte*, **2** (1952), 715]. The Baudouin test for the detection of sesame oil, according to Bhatnagar and Dutt (*Indian Soap J.*, **18**, 196), was only a qualitative test and is sensitive only under certain well-defined conditions. Other new communications on detection of sesame oil pertained to description of the acid furfural colorimetric test (ISIDORO and PAVOLINI, *An. Ass. Quim. Brazil*, **9**, 95) and the concentrated hydrochloric acid reaction (HALIN, *Ciencia Mex.*, **11**, 80).

Some of the methods of detecting peanut oil in other oils are based on the Bellir index determination and on isolation and microscopic examination of arachidic and lignoceric acids [Mitra, *Curr. Sci.*, **20**, 158; Isidaro, *Boll. Lab. Chim. Prov. Bologna*, **1** (1), 18; Musso, *Act. y trabajos Congr. Peruano Quim. 3rd Congr.*, **2**, 525; Amato and Almiedo, *Engenh. e Quim.*, **4** (3, 7); Allavena, *Olii min.*, **28**, 57].

An improved method of determining Reichert-Meissl and Polenske values permitted detection of lauric acid containing oils in butter. Further, the C_{10} and lower acids are determined more easily by this method in a 5 g. sample than by the conventional methods (Vizern and Guillot, *Oléagineux*, **6**, 409). Mitra *et al.* (*Sci. & Cult.*, **17**, 522) described a method of estimation of argemone oil in mustard oil by the bromide-bromate test. The critical separation temperature of fats from aniline was used to identify several food fats. In applying this phenomenon for determining the purity of cacao in nut chocolate confection, Van Voorst (*Chem. Weekbl.*, **47**, 595) pointed out the tendency of oil exuding from nuts and interfering with the analytical results.

Some of the other reports published on the subject during the year were on the modifications effected in several analytical procedures issued by the Uniform Methods Committee of the American Oil Chemists' Society (Andrews, *J. Amer. Oil Chem. Soc.*, **29**, 47); the revised analytical methods of the German Society for Fat Science (Kaufmann and Baltes, *Fette u. Seif*, **54**, 257, 402, 445) and Progress in the Methods of Fat Analysis [Tetsu taro Hashimoto, *J. Oil Chem. Soc., Jap.*, **1** (1952), 142].

NUTRITION

In this section are described the more important findings on dietary fats, oil cakes and meal which influence growth, digestion and absorption.

Fatty acids and growth — Pyridoxine has been found to facilitate the formation of tissue essential fatty acids from dietary fatty acids (*Dairy Council Dig.*, **23**, **24**, 1952). Rats on a low fat diet deficient in pyridoxine failed to deposit fat in the body (Carter and Phizackerley, *Biochem. J.*, **49**, 227). Diets deficient in essential fatty acids markedly affected reproduction in rats (Kummerow *et al.*, *J. Nutr.*, **46**, 489). Bacon *et al.* (*J. Nutr.*, **47**, 383) observed that the development of symptoms of essential fatty acid deficiency with low fat diets was accelerated considerably by the inclusion of over 5 per cent mineral oil in the diet. In essential fatty acid deficiency the administration of pyridoxine along with a linoleate elicited higher rates of growth and fat synthesis, but did not relieve dermal symptoms any more rapidly (Witten and Holman, *Arch. Biochem.*, **41**, 266). Greenberg and Ershoff (*Proc. Soc. expt. Biol. Med. N.Y.*, **78**, 552) reported marked reduction in prostate and seminal vesicle weight in addition to symptoms of essential fatty acid deficiency. An interesting observation has been made by Witten and Holman (*Arch. Biochem.*, **37**, 90) on the toxicity of pro-oxidants. When a pro-oxidant was fed with essential fatty acids, the toxic effects of the pro-oxidants were nullified and the combination promoted greater gain in total body fat. The pro-oxidant in combination with linoleate is reported to be converted into hexaenate. Data on the requirements of fatty acids for rats, their distribution in foods containing fats and the extent to which these essential acids could prevent the deficiency symptoms have been published. When pure essential fatty acids were compared with natural oils, the latter were superior in curing essential fatty acid deficiency (Greenberg *et al.*, *J. Nutr.*, **45**, 521, 535).

The inclusion of rancid lard in a diet low in vitamin A accentuated vitamin A deficiency symptoms which were prevented completely by the addition of vitamin A palmitate or a " lard factor " (Stoerk *et al.*, *Arch. Path.*, **53**, 15). In the presence of adequate amounts of vitamin A rancid lard is not harmful. Based on this and similar observations with other dietary factors, Kaunitz *et al.* (*J. Nutr.*, **46**, 151) suggested that rancid fats destroy some vitamins and other factors, whereas normal fats provide substitutes for these factors or stimulate their production by the intestinal flora. Balakrishnan and De (*Indian J. Physiol.*, **6**, 1) reported that a high fat diet increased intestinal synthesis of vitamin B_1 in rats. In the preparation of sweets with ghee, Bhatia (*Bull. cent. Food tech. Res. Inst. India*, **2**, 72) reported that frying for long periods destroyed the vitamin A in it. Willich *et al.* (*Food Tech.*, **6**, 199) studied the effect of roasting and blanching on the thiamine content of peanut butter.

Cheng *et al.* (*J. Nutr.*, **48**, 161) noted that rats subjected to sub-lethal doses of X-ray irradiation at weekly intervals showed better resistance and longer survival when fat was incorporated in their diets. Immature rats fed on sucrose-casein diet to which thyroid has been added showed retardation of growth. Methyl linoleate and cottonseed oil administration was found to protect against this growth retardation (GREENBERG, *J. Nutr.*, **47**, 31). Rats reared on diets containing peanut oil had a longer life than those fed on carbohydrate alone, but a mixture of peanut oil and carbohydrate was definitely superior to either of these (VENKATASUBRAHMANYAN and DE, *Indian J. Physiol.*, **6**, 24, 115). Other fats did not appreciably influence the life span of the animals. In a comparative study of the nutritive value of butter fats and vegetable oils, cow and buffalo butter fats showed higher growth promoting values (NARAYANA RAO, *Bull. cent. Food tech. Res. Inst., India*, **2**, 54).

Fat digestion and absorption — Several fats (whale, shark, sardine and rice bran and their hydrogenated products), when fed at 40 g. level per day to human subjects, were utilized to the same extent, the coefficient of digestibility being 92-95 per cent (MATSUMURA, *J. Jap. biochem. Soc.*, **23**, 26). Phatak and Patwardhan (*J. sci. industr. Res., India*, **11B**, 533) found that partially hydrogenated oils (vanaspati) manufactured in India contained about 25-35 per cent iso-oleic acids. Rats were found capable of digesting about 91 per cent iso-oleic acids and 93-95 per cent oleic acids. Of the absorbed iso-oleic acids about 94 per cent was metabolized by the rat. The relation of emulsification to fat absorption has been a subject of much interest in recent years. Morales *et al.* (*Pediatrics*, **6**, 86, 644) showed how emulsification led to enhanced fat and vitamin A absorption in infants. Ely (*U.S. Pat.* 2,604,402) and Ely and Schott (*World's Poult. Sci. J.*, **8**, 133) found growth acceleration in chicks, and Huff *et al.* (*J. Dairy Sci.*, **34**, 1056) noted improvements in growth and health of calves when glycerol monostearate was used as an emulsifier in the synthetic milks administered to calves. Contrary to these findings, no improvement in fat absorption by exogenous emulsifiers was reported in some recent investigations (TIDWELL and NAGLER, *Proc. Soc. expt. Biol. Med. N.Y.*, **81**, 12; DASHER, *Science*, **116**, 660). Annegers (*Proc. Soc. expt. Biol. Med. N.Y.*, **81**, 277) found that when bile is absent, the addition of " Tween 80 " did not improve fat absorption. Bernhard *et al.* reported that in the absence of bile, only 50-80 per cent of the dietary fats were absorbed (*Helv. physiol. Acta*, **10**, 68).

An important contribution by Reiser *et al.* (*J. biol. Chem.*, **194**, 131) provided new quantitative data on the mechanism of absorption of dietary fats in the intestine. These workers have studied the intestinal absorption of triglycerides by using synthetic triglycerides in which the glycerol moiety has been labelled with C^{14} and the fatty acids with conjugated double bonds. Approximately 25-45 per cent of the injested glycerides were completely hydrolysed during absorption. The remaining 55-75 per cent were hydrolysed to the monoglyceride stage. Half of the lymph phospholipin formed from injested fat utilized the hydrolysed fatty acids and endogenous glycerol. Another interesting contribution from the Weimhouse School (*J. biol. Chem.*, **195**, 493) reports the oxidation of endogenous fatty acids by rat tissues *in vitro*. All tissues were found to oxidize the labelled fatty acids. Further evidence for the direct utilization of fatty acids by skeletal muscle has been provided by Wertheimer and Bentor (*Biochem. J.*, **50**, 573) and by Hansen and Rutter (*J. biol. Chem.*, **195**, 121) and it may now be taken as fairly certain that such a direct utilization does occur in the animal body.

In the study of lipids under diseased conditions, Chung *et al.* (*Pediatrics*, **7**, 491) found that fat absorption was proportional to fat intake in idiopathic celiac disease and cystic fibrosis of the pancreas. In assessing fat absorption in normal subjects and in sprue patients, Asenjo (*Amer. J. trop. Med. Hyg.*, **1**, 344) found that the daily faecal fat excretion of sprue patients averaged 12·5 g. as compared with 4 g. for normal individuals.

Nutritive value of oil cakes and meals — The relative merits of mechanically pressed oil cakes and solvent-extracted oil cakes showed that the latter increased the total butter fat content of the milk when used as a cattle feed. This effect was attributed to high concentration of digestible nitrogen and to the biological value of the proteins (LETARD *et al.*, *Oléagineux*, **7**, 495). Lal (*Indian J.*

med. Res., **40**, 471) determined the value of pressed groundnut cake flour as supplement to rice diet and found that both skimmed milk and pressed groundnut cake flour promoted growth. Allen and Dow (*Sci. Agric.*, **32**, 403) assessed the biological value of rapeseed oil meal as a component in the diet of young chicks. It was found that rapeseed oil meal can be effectively utilized in the ration for growing chicks both as a protein supplement and as a fattening agent. Similar response could be expected when fed to livestock. Van Horn and Benkitt (*Montana Wool Grower*, **26**, 4) found that cottonseed meals obtained by solvent extraction process and by the hydraulic presses were equal in nutritive value when tested on ewe lambs as a supplementary hay diet. It was found that cottonseed and groundnut oil cakes are valuable sources of lysine both for commercial manufacture and in the feeding of dairy cattle. Exceptionally high proportion of amino acid was found in the seed cake of *Holopelea integrifolia* (GOVINDARAJAN and RAMACHANDRAN, *J. sci. industr. Res., India*, **11B**, 477).

Some of the published reviews during the year were: Fat Metabolism (FRAZER, *Ann. Rev. Biochem.*, **21**, 245); Fat Soluble Vitamins (KEMMERER, *Ann. Rev. Biochem.*, **21**, 333); The Essential Fatty Acids (KAUFMANN, *Fette u. Seif*, **54**, 69); Value of Synthetic Fats in Nutrition (SCHEUNERT, *Pharmazie*, **6**, 652); Fat Soluble Vitamins and Refined Oils (FRANCIS, *Bull. Inf. Cent. tech. Ind.*, **6**, 436); Toxic Principles in Common Oil Cakes and Their Removal (KHAN, *Oils & Oilseeds J.*, **4**, 10); and The Value of Coconut as a Human Foodstuff (*Ceylon Cocon. Quart.*, **3**, 20).

APPENDIX

BOOK REVIEWS

INVESTIGATIONS ON THE COMPOSITION AND NUTRITIVE VALUE OF VANASPATI (Council of Scientific & Industrial Research, New Delhi), 1952, pp. 234

This book contains the results of investigations on the composition and nutritive value of vanaspati conducted under the joint auspices of the Ministry of Food & Agriculture and the Council of Scientific & Industrial Research, New Delhi. The investigations were undertaken in a number of laboratories according to a plan laid down by an expert committee consisting of Drs. V. Subrahmanyan, B. C. Guha and D. V. Karmarkar.

The book is to be welcomed especially in view of the several conflicting opinions so far expressed on the nutritive value of vanaspati. It is divided into two parts. The first part contains an account of the animal experiments, human metabolism studies and other feeding trials, together with the statistical analysis of the data collected. Comparative studies indicated the relative nutritive values of fats to be in the following descending order: (i) ghee, (ii) raw groundnut oil, vanaspati, m.p. 37°C., and refined groundnut oil which can be grouped together, and (iii) vanaspati, m.p. 41°C.

The second part of the book deals with studies on the nutritive value of blended vanaspati, antioxidant activity of sesame oil in hydrogenated fats, toxicity of nickel, and nutritive value of iso-oleic acids, and stability of raw, refined and hydrogenated groundnut oils. The composition and properties of various kinds of vanaspati and their corresponding crudes, investigated in detail for the first time, have been reported. The tocopherol content of Indian edible oils and fats and vanaspati and the manner in which it affects the stability of the oil is also discussed.

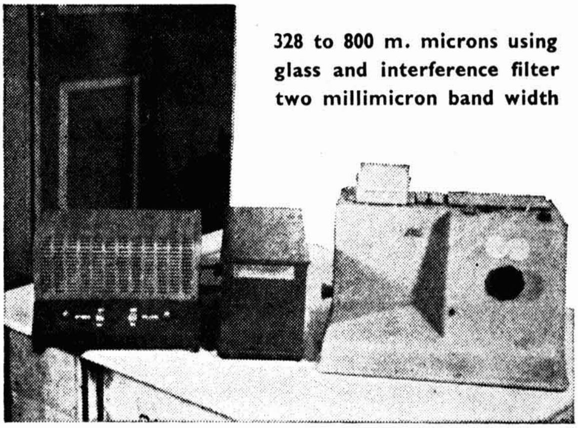
The book is an elegant record of current work carried out in India on the nutritive value of vanaspati and will be of value to those interested in having authoritative information on the subject.

PROGRESS IN THE CHEMISTRY OF FATS AND OTHER LIPIDS, edited by R. T. Holman, W. O. Lundberg & T. Malkin (Academic Press Inc., New York), 1952, pp. 186. Price $ 7.00

The material contained in this volume was originally intended for a new edition in English of the Hefter-Schoenfeld *Chemie and Technologie der Fette and Fett-producte*, but owing to the death of Dr. H. Schoenfeld, the articles have been published as the first volume of an Annual Progress Series. The subjects dealt with are as follows: The Molecular Structure and Polymerization of Fatty Acids and Their Derivatives; Sterols; Structure and Properties of Phosphatides;

Chromatography of Fatty Acids and Related Substances and Derivatives of the Fatty Acids.

The book describes the role of lipids in many important industrial applications such as in the manufacture of detergents, surface coatings, antiseptics, and in many biological processes. The section on chromatography is particularly welcome since it presents a rapid evaluation of the utility of this relatively new technique. This review in a fairly general way covers the work of many years, providing useful information to workers both in industry and research.



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