

SCIENCE NEWS

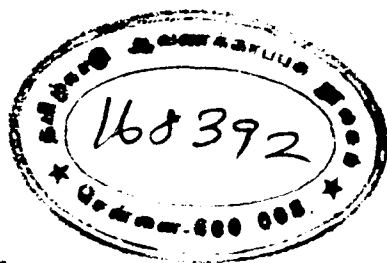
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CONTENTS

SOVIET EMBRYOLOGY	7
D. R. Newth	
DETECTING AND INTENSIFYING FAINT IMAGES	19
L. Mandel	
TEA: ITS PROCESSING AND CHEMISTRY	35
C. R. Harler	
NATURAL COLLOIDAL SILICATES	52
G. P. C. Chambers	
ACCLIMATIZATION IN INSECTS	71
K. Mellanby	
THE PART OF COAL THAT DOES NOT BURN	78
I. Berkovitch	
SHIP RESISTANCE	96
P. G. Morgan	
RESEARCH REPORT	113
A. W. Haslett	
SOME BOOKS RECEIVED	123
ABOUT OUR CONTRIBUTORS	127

12 illustrations are between pages 64 and 65

SOVIET EMBRYOLOGY

D. R. NEWTH

AN APOLOGY

LOCAL and national differences are a real, but increasingly irrelevant, feature of science. They spring from the contingencies of our work – the peculiarities of a local fauna, the accidents of geography and geology, the cultural history of a people, or the heritage of individual genius. Though these differences may add colour to the scientific scene they do not determine the path of advance, more particularly in the most active and rapidly developing branches of science. The only justification for this article lies, then, in a failure of communication, in the comparative ignorance of present-day biological work in the U.S.S.R. that prevails in the West, and in the misunderstandings that derive from it. When, as it must, knowledge of Soviet work becomes more widespread,* such articles will be unnecessary.

A FUNDAMENTAL BRANCH OF BIOLOGY

We, and most of our domestic animals, are viviparous. In other words the young emerge from the mother's body only after a more or less prolonged period of pregnancy during which they have lived parasitically at her expense. This means that the most dramatic and far-reaching of all the changes that we undergo on our journey from conception to the grave are hidden from casual observation and are largely inaccessible to experimental or clinical interference. Thus it is the creatures that shed their eggs precociously – worms, sea-urchins, newts, and birds – that have so far given us our deepest knowledge of the fantastic but

*The decision of the Academy of Sciences of the U.S.S.R. again to provide foreign language summaries at the end of all the papers published in twenty of their major journals is most welcome. It would be pleasant if this gesture could, in some measure, be reciprocated.

ordered turmoil that converts the fertilized egg into a complex, differentiated, embryo and so sets it on the path to adulthood.

Exotic though this may make embryology appear to be, it has many valid claims to our attention. One is that even adults have recourse to processes of growth, repair, and regeneration which are compounded of elements most clearly seen and most easily analysed in the embryo. But the modern embryologist defines his field of interest broadly. All the progressive changes in the life history of the individual, including post-embryonic ones, are his concern. Even the senescence which, although it does not kill us, ensures that we shall die, is accepted without sense of paradox. Now it is against the background of these changes that all physiological or biochemical processes occur, and it is through them that the inheritance of an organism is made manifest. Hence we may fairly say that embryology, genetics, physiology, and biochemistry are co-extensive in their material, and differ only in their approach to it. Each presents the others with information that limits and prescribes their independent growth and checks their tendencies to one-sided development. Each, in fact, is fundamental to the others and to all our knowledge of vital activity.

The opportunity to visit last autumn a number of the laboratories in the U.S.S.R. wholly or partly devoted to embryological research (for which I am indebted to the Academy of Sciences of the U.S.S.R.) was consequently welcome not only for the valuable professional and personal contacts that it made possible, but for the direct access it gave to work at the heart of animal biology from which ignorance of Russian would otherwise have barred me. It was also a pilgrimage to one of the major centres of classical embryology.

A RUSSIAN TRADITION

In 1834 the Imperial Academy of Sciences in St. Petersburg invited a young Estonian of German descent, K. E. von Baer, to join it. He had already done his greatest embryological work, but he remained intellectually active for decades afterwards and provided the inspiration for a school of Russian embryology

that flourished throughout the 19th century and continues its work today. Von Baer is now chiefly remembered as the discoverer of the mammalian egg and as the founder of comparative embryology. His observation that the embryos of different vertebrates might be so alike that to distinguish them from one another presented difficulties was used by Darwin, quite properly, as an argument for evolution.

Russian workers, notably Kowalewski and Metschnikoff, and their pupils, played an important part in the methodical survey of the major groups of invertebrate animals from the point of view of evolutionary embryology. Later Koltzoff, Sewertzoff and Schmalhausen were, with equal distinction, to represent in Russia the comparative approach to vertebrate development.

However, in the closing years of the last century a new kind of embryology came into prominence. Using experimental interference with the embryo as its tool, it sought to unravel the causal relations between the parts of the developing system, and between the environment and the whole animal. First in Germany, then in the U.S.A., France, Belgium, and Britain, experimental embryology became a major field of enquiry. In this Russia undoubtedly lagged behind, and it was not until the 1920s that she had any number of experimental embryologists. We may then first ask what the balance between the old tradition and the new is in the U.S.S.R. and what, at the present time, in general, is the scope of research interest there.

A CONFERENCE OF EMBRYOLOGISTS

My own visits were to laboratories in Leningrad, Moscow, Tbilisi, and Sukhumi. A fair sample in all probability, but for a better picture of the overall pattern of research it is perhaps wise to turn to the published abstracts of papers read at the first All-Union Conference of Embryology which was held in Leningrad in 1955. This was, so several of the participants informed me ruefully, rather too much of a good thing. Six days and 120 papers are enough to make the most hardened conference addict blench, and I gather that in future it is proposed to hold less ambitious meetings on limited topics. However, since a majority

of the most active workers in the country read papers there. I have an adequate survey of the Soviet embryological scene.

There is, I think, no need, even if there were space, to attempt a detailed analysis of the conference programme. The unsensational truth is that it showed an enormous area of common interest between embryology in the U.S.S.R. and elsewhere. The sections into which it was divided, and the number of papers read in each section are perhaps worth recording:

Gametes and Fertilization (11); Embryonal Histogenesis (26); Comparative Embryology (10); Embryology of Agricultural Animals (9); Immunity of Embryos (8); Regeneration and Asexual Reproduction (11); Early Stages of Embryogenesis (9); Influence of Conditions of Development upon Embryogenesis, etc. (11); Embryology of Plants (9); Development of Man (10); Physiology and Biochemistry of Development (6); Other (General) Problems (2).

While there is little in this list that permits one to distinguish the conference from a similar meeting anywhere else in the world, the papers themselves do show differences in the emphasis of Soviet research. It is true that perhaps the majority of them are on subjects of universal interest. It is, for instance, gratifying to see that L. N. Zhinkin has cleared up one of the minor scandals of comparative embryology by working out the developmental history of the aberrant worm *Priapulid*, hitherto unknown. On the other hand, more of the papers deal with the influence of environmental factors on the course of development than would be the case in most such conferences, and many fewer deal with problems of embryonic induction.

Embryonic induction is a process by which one part of an embryo persuades another, contiguous, part that is not committed to any definite fate, to become so committed. It is a process of fundamental significance in the formation of the vertebrate embryo and its analysis occupied a considerable body of workers in the years 1920-40. As Abercrombie pointed out some year ago in *Science News* 13, the failure to discover the actual nature of the influence passing from inductor to induced produced a reaction of disappointment in embryology and a tendency to move on to other things. None the less a considerable

amount of excellent work is being done, in many countries, on the nature of induction, and the lack of such work in the U.S.S.R. was a noticeable feature of this conference.

It is perhaps natural that Moscow and Leningrad should have dominant positions as scientific centres, but an analysis of the distribution of the papers read by town of origin shows that they do not have a monopoly. Moscow leads with 42, followed by Leningrad (35), Kiev, Sverdlovsk, Tbilisi (4), Kharkov, Lvov, Voronezh (3), and sixteen other places with one or two each.

STURGEON VERSUS AXOLOTL

I mentioned earlier that much classical embryological work had, almost of necessity, to be done on newts. It is for this reason that a humble Mexican amphibian, the axolotl (*Siredon*) has colonized the zoological laboratories of the world where it is maintained as a source of large and handsome eggs.* In the Soviet Union, too, axolotls abound, but they are animals whose future is challenged by the increasing popularity of sturgeons and sterlets (*Acipenser*) for embryological work.

The reason for this is, I think, twofold. In the first place sturgeons have nice eggs and make good experimental material. They are also animals whose natural conditions of life are open to study within the country and they are therefore particularly suited for work on the role of environmental factors on the course of development. But further, they present a practical problem to the fisheries industry which a knowledge of their developmental history may help to solve. Sturgeons (and of course their roe or caviar) are an important source of food that is now threatened by the development of hydro-electric schemes in South Russia. These interfere with the sturgeon's normal run down the rivers to the sea and their return upstream to breed. The devices that help salmon to overcome this problem are ineffective with sturgeon, and it is consequently important to try to persuade them to breed in the rivers without a run to the

*Thus embryological laboratories, like poultry farms, give reality to Samuel Butler's dictum: 'A hen is only an egg's way of producing another egg'.

sea. This problem is being tackled by the active school of Professor Gerbilski in Leningrad, in whose laboratory the forlorn axolotls certainly had their noses out of joint. His Institute of Ichthyology is primarily concerned with the endocrinology of sexual reproduction in fish, the histology of the reproductive organs, fertilization and early development, and the properties of species hybrids in sturgeons.

Work on sturgeon embryology is also being carried out in the Institute of Animal Morphology in Moscow. Here Professors Detlaff and Ginsberg, after distinguished careers in amphibian embryology, have turned to sturgeons. They have recently produced a valuable monograph on the development of these animals together with a brief survey of the ecology, systematics, and breeding behaviour of the Russian species. Their work is perhaps a little unusual by our standards in that while treating fully of the normal events of fertilization, embryogenesis, and post-embryonic life, and reviewing the results of experimental researches, it also deals with pathological development and the conditions of culture of the eggs and embryos that provoke it. It has, in fact, its eye on the applied scientist (here the fish-farmer) as well as upon the laboratory one.

I do not doubt that the Soviet scientist is normally more conscious of the practical consequences of his work and more interested in them than some of his Western colleagues, and that this does weigh with him in the choice of the problems he tackles. The final balance struck, in embryology at least, seems to me to differ only slightly between the two. If there is any moral at all to be drawn from this, it can only be flattering to the good sense of embryologists East and West.

SOME TEACHING AND RESEARCH LABORATORIES

Under the non-committal title of Sukhumi Biological Station the Academy of Medical Sciences runs what is really a monkey institute on a hill overlooking the Black Sea. It is the main source of monkeys for biological and medical research in the Union and maintains a stock of about 900 animals. Although these can be sent to scientists elsewhere, the station has facilities for any

guest worker who feels that he can resist the distractions of a Black Sea resort. The permanent staff is itself scientifically active and work is at the moment being done on the endocrinology of the menstrual cycle and upon the influence of the cycle on higher nervous activity. The station has long been interested in interspecific hybrids and some of the recent crosses of which Dr. Utkin told me have not, as far as I know, been recorded before. Two of them are:

Papio hamadryas ♂ × *Theropithecus gelada* ♀
(Sacred baboon) (Abyssinian gelada)
↓
'Piogela' ♀ × *T. gelada* ♂

At the time of my visit 'Piogela' was gravid.

Macaca nemestrina × *Macaca mulatta*
(Pig-tailed Macaque) (Rhesus Macaque)
↓
'Neptune' ♂ × *Papio hamadryas* ♀
↓
'Prima' ♀ & 'Markissa' ♀

So far 'Prima' and 'Markissa' have proved infertile.

Two of the other laboratories that I saw were the teaching departments in the Universities of Moscow and Leningrad. These universities are so large (too large, if an outsider may comment) that what we should normally call departments have become faculties with several thousand students, and what we should, at most, call a sub-department has become a full department. Thus it is that the zoologists at both places have a Department of Embryology within the larger administrative unit.

The department in Leningrad (under Professor B. P. Tokhine) is now fifty years old. It has workers investigating the development of parasitic Hymenoptera, and in Professor I. I. Sokolow a distinguished veteran of invertebrate embryology who is now studying the formation of gametes in ticks and scorpions. The laboratory is also much concerned with phenomena in embryos that parallel the immunity mechanism of phagocytosis in adults. Researches there deal not only with the outcome of

discussion of Michurinism widespread, but facilities for neo-Mendelian work are again available.*

Even the critics of Michurinism claim, however, that the controversies associated with it have been useful in prompting a re-examination of fundamental biological ideas, and that their own work has altered in consequence. The chief sign of this appears to be the greater concentration on study of the effect of the environment on the course of animal development that I noted earlier, and, perhaps, the emphasis on the value of tackling problems on animals of economic importance.

Embryology has its own controversial issues too, and the most widely known one is the claim of O. B. Lepeshinskaya to have demonstrated in a number of animal situations that cells can arise *de novo*, not, it is true, from inorganic or dead material, but from the non-cellular material that exists in animals or in extracts of them.

She sees this process as a logical outcome of the 'law' of biogenesis or recapitulation of Haeckel . . . a law that is now generally regarded as an unjustified extension of the more sober generalizations of von Baer. Her claims, if substantiated, would be of enormous consequence for biology, but they have been received with scepticism. Attempts in the U.S.S.R. to repeat some of her most critical experiments have yielded negative results, and her observations are on material that presents the greatest difficulties for decision. Most of the embryologists with whom I discussed this matter were content to treat her case as unproven and still open, though Professor Polezhaiev believes that he has found similar processes occurring in regenerating tissues of amphibia.

On the whole I found that wherever Soviet biologists had reported results that seemed to me of doubtful validity, my doubts were shared by many of their own colleagues.

*Professor N. P. Dubinin, one of the most distinguished of Soviet cytogeneticists, told me that he was returning to work on mutations induced by X-radiation in a new laboratory created for him, and Professor A. R. Zhebrak is working on amphidiploidy in plants.

KNOWLEDGE OF FOREIGN SCIENCE

This article began by suggesting, not unfairly I hope, that biologists in the West are inadequately informed about the work of their Soviet colleagues. In so far as this is true the reason lies almost entirely in the fewness of the biologists able to read Russian and in the fact that we have not, as yet, the translating and abstracting facilities that chemists and physicists have. But is the Soviet worker under an equivalent disadvantage?

It is, I think, only fair to say that a good deal of Soviet scientific literature, and especially pedagogical writing, has given little sign of appreciation of recent foreign work. This said, it remains true that such work does arouse interest and is readily available to the research worker, to the teacher, and to the student. Indeed most Soviet biologists are better informed of Western work than we are of theirs, and sometimes than some of us are of work in our own language. (I owe to G. V. Lopashov my knowledge of an important paper in the Proceedings of the National Academy of Sciences of the U.S.A. that had appeared two months before we met.) Soviet scientists are helped in this by the nature of their initial training. During the first two years of the five-year university course the student learns two foreign languages, and most Russian scientists can now at least read papers in two non-Russian languages. This tends to leave them with little sympathy for those of us who have shirked learning theirs.

Pride of place in this matter must, however, go to the newly established Institute of Scientific Information of the Academy of Sciences. This is now in its second year of work as the publisher of an abstracting journal covering the whole of natural science. The journal appears in six sections, each devoted to a different branch of science, and is now abstracting 1,000 Soviet and 7,000 foreign journals (these include 1,416 from the U.S.A., 844 from the United Kingdom, and 491 from France at the one extreme, and 27 from Portugal and 3 from Madagascar at the other). The biological section appears fortnightly and provides about 100,000 abstracts a year. The international importance of

his enterprise is very great, partly because it handles the Chinese and Japanese literature as well as journals publishing in European languages. It is quite possible that a knowledge of Russian will become the easiest way of access to an oriental literature that would otherwise be difficult to survey!

At the moment the Institute is able to issue abstracts about one year after the appearance of the original papers. It is hoped that this delay will soon be reduced to little more than half that time. The work of preparing the abstracts is done by senior scientists who are able to call upon a translating service when they are faced with papers in languages they cannot understand. This venture provides the Soviet scientist with one of the most important facilities he could wish for – and does it admirably.

I have to thank Mr R. Browning for his services as a translator.

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DETECTING AND INTENSIFYING FAINT IMAGES

L. MANDEL

NATURE, or a self-imposed limitation, sometimes compels us to carry out observations at very low intensities of light. The disadvantage of a faint image has then to be accepted, and it is natural to direct attention to the image detector. In recent years this has been the subject of much development and has led to the appearance of two distinct types of instrument. The devices in which a faint image at the input gives rise to a brighter image at the output are known as image intensifiers and are analogous in many respects to amplifiers. Output can be observed visually or photographed. Sometimes, however, the functions of detecting and recording are best combined in one instrument, which then becomes an integrating image storage device.

It is perhaps a little strange to find that, despite the obvious applications of these instruments and although the basic constructional principles have been well known for some time, the subject is a relatively new one. Although a few intensifier-tubes are now available commercially, it would be fair to say that the development of a really satisfactory device is still to come.

The fields in which these instruments are probably of greatest importance are astronomy and diagnostic X-ray fluoroscopy. During X-ray examinations, the radiation intensity has to be deliberately limited to avoid damaging the tissues. At this level, the image appearing on the fluorescent examination screen is very faint and so can often only be studied after prolonged dark adaptation of the radiographer's eyes. Hence the importance of image intensification.

The weakest light is undoubtedly encountered in astronomy,

where the sensitivity of the photographic plate generally imposes a limit on the faintest objects that can be investigated. Similar limitations also arise in spectroscopy.

Before discussing the principles of the various image devices, it will be useful to discuss briefly the gains to be expected from their introduction, when compared with detectors now in use. We shall find that the quantal nature of light leads to certain fundamental limitations.

IMAGE DETECTORS AND THEIR LIMITATIONS

The commonest image detectors are, of course, the eye and the photographic plate, each with distinctive merits and disadvantages. The outstanding characteristic of the eye is its high quantum sensitivity. At the peak of monochrome vision, around $5600\text{\AA}$, between one and four absorbed photons give a visual stimulus. Generally, of course, not every incident photon is absorbed by the retinal rods and, on the average, about 70 photons are required to produce a sensation of light. While the dark-adapted eye ranks among the most sensitive image detectors, it is unable to provide a permanent record. But perhaps its most serious limitation is its inability to integrate or store the incoming light for longer than about a tenth of a second. It behaves as though the retinal image were eradicated ten times a second. This explains the well-known experience that there is little to be gained (apart from dark adaptation) by watching a faintly visible object for a long time. In short, the eye is most effective as a detector of transient images.

The photographic emulsion, on the other hand, is distinguished by its ability to integrate incident light over long periods and so is more suited to the detection of very faint stationary images. Its quantum sensitivity is, however, much lower. A fast panchromatic emulsion requires of the order 1000 photons of wavelength between $3000\text{\AA}$ and $6000\text{\AA}$ to produce one developable grain.

Quite recently several devices known as storage-tubes have been developed; these combine the functions of image intensification and recording. They have high quantum sensitivities

and, in a sense, combine all the optimum operating conditions, but are still only in the experimental stage.

Let us for the moment revert to the photographic plate used as a recording detector and consider the improvement to be gained by interposing an image intensifier. One of the obvious advantages is a shorter exposure time. This is particularly important in astronomy, where image quality generally improves as the exposure time is reduced, because of image fluctuations caused by atmospheric turbulences. On the other hand, we might prefer to trade some of the extra light against a finer grain – and therefore slower – emulsion.

From the reciprocity law of photography we expect an n -fold light intensification to lead to an n -fold reduction in exposure, for the same grain density. The situation is, however, a little more complicated. In the first place, the reciprocity law breaks down at very low light levels and hardly any grains are then rendered developable. The introduction of an intensifier therefore enables us to record images that are otherwise outside the range of the photographic plate.

Secondly, there is an effective upper limit to useful intensification. All image tubes use a photo-electric surface as primary light detector. The most sensitive photo-emissive surface – antimony: caesium – has a quantum sensitivity of the order ten per cent for daylight, so that, whatever the overall light gain of the instrument, not more than about one incident photon in ten is detected. Now suppose that each detected photon gives rise to a thousand at the output. This corresponds to a total light gain of about a hundred. As we have seen that about a thousand photons are required, on the average, to render a silver halide grain developable, it is clear that there is little to be gained by increasing the light gain very much above a hundred. This conclusion is of course qualitative, and often it is preferable for a light point to produce a small cluster of developed grains.

Suppose now that images are to be observed visually *via* an intensifier. As the eye responds to about one incident photon in a hundred and the photo-electric surface to about one in ten, it might appear that there is little point in increasing the effective

gain much above ten. The position is, however, complicated by the peculiar physiological properties of the eye. The one per cent figure for the visual quantum sensitivity holds only for the dark adapted eye. Under normal light conditions the contrast sensitivity is considerably lower. Furthermore, the resolving power of the eye adjusts itself to suit the light level, so that more detail can, in principle, be seen in a bright picture than in a dark one. There is therefore a real advantage to be gained by increasing the effective light amplification at least one order of magnitude above ten.

Finally let us very briefly examine the special merits of the image storage tube. Here again use is made of the photo-electric effect to detect incident photons, but the photo-electrons form a representation of the image as a charge pattern on a storage plate. The charges grow as the time integral of the incident light and the image can, at any time, be 'read off' and displayed on a cathode ray tube. Like the photographic plate, the storage tube is therefore an integrating detector. From the respective quantum sensitivities we deduce that the light gain, when compared with the photographic emulsion, is about 100, though this figure is not always realizable, on account of the attendant problems of electric signal amplification. Unlike the emulsion, however, the storage tube is a linear device and does not suffer from reciprocity failure or saturation—at least over a very wide range. It can collect and store considerably more light than the photographic plate. It is this feature that makes the instrument particularly applicable to astronomy, where the differentiation of a faint star image against a brighter sky background is a well-known problem. Thus, with the 200-inch Hale telescope at Mount Palomar, a photographic emulsion becomes saturated if exposed for longer than about half an hour at the prime focus.

THE SIMPLE IMAGE INTENSIFIER AND ITS VARIATIONS

Let us now look at the construction of some typical image intensifiers. As there is considerable development still going on in this field at present, it is by no means clear yet which type of instrument is most likely to be generally adopted.

It has already been pointed out that all the devices developed so far use the high quantum sensitivity of the photo-electric effect to detect the primary optical image and convert it into the corresponding electron image. A simple intensifier tube is shown schematically in Figure 1. A is a transparent photo-emissive sur-

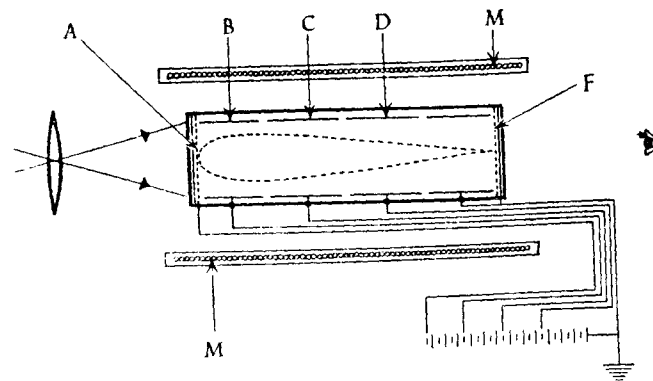


Fig. 1. The Basic Image Intensifier. A, Transparent Photo-emissive Surface; B, C, D, etc., Accelerating Electrodes; F, Fluorescent Screen; M, Solenoid.

face deposited on the inside of a sealed glass tube. The primary image is focused on this surface. Photo-electrons are emitted from it with very low velocities, but the electrodes B, C, D, etc., accelerate them to a high potential. The solenoid M, acting as a magnetic electron lens, focuses the electrons on a fluorescent screen F, where they give rise to a visible image. The screen F is usually given a very thin aluminium film backing to act as an optical reflector, and to prevent the luminescent light from reaching the photo-cathode A.

The choice of the photo-electric surface depends on the application of the device. The most sensitive surface (Sb:Ce), which has already been mentioned, has a peak quantum sensitivity in the blue of nearly 20 per cent. The final light output

depends largely on the accelerating voltage, although only a fraction of the kinetic electron energy is normally converted into luminescent light. For the blue emitting ZnS:Ag phosphor this fraction may be around 20 per cent. The light output can, in principle, be increased simply by increasing the accelerating potential, but, in practice, we are limited by the danger of electric breakdown in the tube. Typical accelerating voltages are in the region of 20,000 volts.

It is instructive to carry out a rough calculation of the expected light gain in such a tube. Suppose that, on the average, one photon in ten gives rise to a photo-electron which is then accelerated to 20 kV. Each photon of blue light emitted from the fluorescent screen has an energy of about 2.5 electron volts, so that each 20 kV electron could give rise to 8,000 photons. But, since the conversion efficiency has been assumed to be 20 per cent, only about 1,500 photons will be emitted per electron. With a quantum sensitivity of 10 per cent, the number of secondary photons per primary photon is around 150, so this figure is the light gain of the instrument.

While such a figure is attainable theoretically, it has not been approached in practice on account of many difficulties in construction. The gains so far reported are an order of magnitude lower. But even if the light gain is high our problems are by no means over, because we have still to get the luminescent image on to the detector, be it the eye or, more frequently, the photographic plate. It is clear that, on looking at the fluorescent screen, only a small fraction of the emitted light enters the eye and a similar small collection efficiency is met when an optical lens system is used. Even an $f/1$ lens used at a one to one magnification collects only about 2.5 per cent of the emitted light, so that our *effective* light gain quickly falls to a very small figure, say four.

Several suggestions have been made for overcoming this difficulty. Even an effective light gain of four could become significant if several intensifiers were used in cascade (e.g. $4^3 = 64$), so that the luminescent image of the first is focused on the photo-cathode of the second, and so on. While this method is

practicable with sufficiently high gain image tubes, it is rather inelegant, besides calling for a multiplicity of apparatus.

If the photographic plate could be placed immediately behind the fluorescent screen, all the light would reach the emulsion. But, since the image tube is evacuated, it is clear that there must be an appreciable thickness of glass between the screen and the plate, and this would lead to very poor definition. However, if the plate itself were maintained under vacuum, a thin glass membrane would suffice to support the fluorescent screen and the separation between the plate and screen could be reduced to about a thousandth of an inch.

Such an instrument needs a vacuum photographic plate-changer of the type used in electron microscopy; this in turn requires continuous pumping. This limitation of having to be permanently connected to a vacuum pump makes the device unwieldy for many applications.

A compromise between the last two methods has been suggested. It consists of a two-stage image tube as shown in Figure 2,

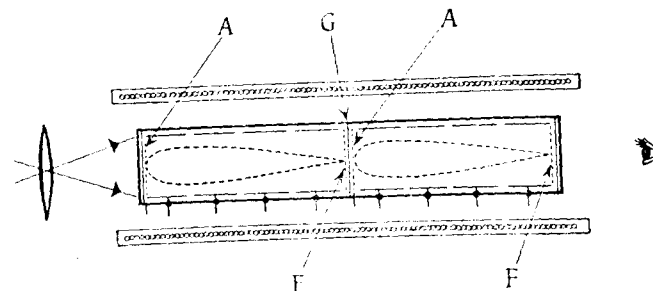


Fig. 2. Two-stage Image Intensifier. A, Transparent Photo-cathode; F, Fluorescent Screen; G, Thin Glass Membrane.

in which the first luminescent screen and the photo-cathode of the second stage are deposited on opposite sides of a thin glass membrane. As there is now little light loss in the transition from one stage to the other a high overall gain should be achievable.

The use of a lens system to focus the final luminescent image on the plate can now be entertained and the tube is detachable from the vacuum system after manufacture.

While such a device has been successfully constructed with an appreciable light gain, it did not prove to be an unqualified success. In the first place no appreciable potential difference could be applied to the thin glass membrane, so that the accelerating voltage of each section of the image tube was only half the maximum from end to end. Secondly, the resolving power of the complete tube was not very satisfactory. The resolution of the normal powdered fluorescent screen is limited by grain size and halations, and, when such screens are used in cascade, image quality quickly deteriorates. A method of chemically depositing transparent fluorescent screens with greatly improved resolution has been described recently by Cusano and Studer. It may well be that the application of this technique to a two-stage image intensifier will make it a more attractive proposition.

Finally it may be of interest to look at a commercially available one-stage image tube. This was developed by Philips for the visual examination of X-ray fluoroscopic images, and is shown in Figure 3. The tube is used with the photo-cathode in contact with the fluorescent screen on which the faint X-ray image

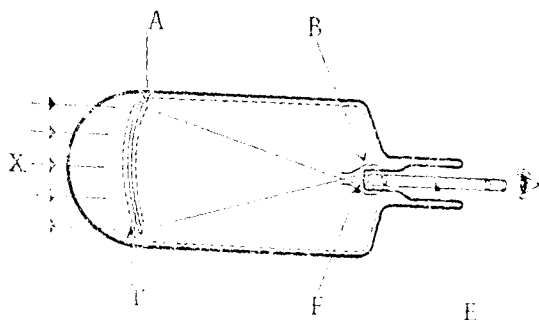


Fig. 3. Philips X-Ray Image Intensifier. X. Incident X-rays; F. Fluorescent Screen; A. Photo-cathode; B. Focusing Electrode; E. Eyepiece. (Redrawn from *Philips Technical Review*.)

appears. The arrangement is quite conventional, but the electrons are focused electrostatically by a system of electrodes within the tube. While electrostatic lenses are generally inferior to magnetic ones, in the sense that the images have a higher aberration, they do not require heavy coils, and stabilized current supplies. In the tube illustrated in Figure 3 the electron image is reduced approximately ten times and then observed through an eyepiece. This ensures that a large fraction of the light output reaches the pupil of the eye. While the actual light gain from photo-cathode to luminescent screen is only of the order ten, the decrease in size results in a further increase in photon density, and therefore brightness, of about 100. As a result the total effective gain is of the order 1,000, and the final image is comfortably visible without dark adaptation.

THE LALLEMAND METHOD AND ITS VARIATIONS

The difficulty of getting an appreciable fraction of the luminescent light from the screen of an intensifier on to the photographic plate led Lallemand to propose a basically different scheme. As early as 1936 he suggested that the electron image be received directly on a photographic emulsion, without a fluorescent intermediary. At first sight this appears to lead to a substantially simpler tube, having a photo-cathode at one end and a photographic plate at the other, with the usual system of accelerating and focusing electrodes or focusing coil.

Whereas only about one incident photon in a thousand falling on the emulsion normally gives rise to a developable grain, practically every electron of energy 10–20 kV renders at least one grain developable. If the quantum sensitivity of the photo-cathode is about 10 per cent we see that the effective increase in speed of the Lallemand image tube, as compared with an ordinary photographic plate, is about 100. Further, this figure is substantially independent of accelerating voltage.

Lallemand proceeded to develop an instrument along the above lines and he achieved an effective gain of the expected order. This image tube, however, leads to a serious practical difficulty. A photo-electric surface, such as Sb:Ce, requires a

high vacuum and quickly deteriorates in the presence of even very small amounts of active gas, such as oxygen. Now, not only does a photographic emulsion continuously evolve small quantities of gas, but the plate has somehow to be introduced into the vacuum system without ruining the photo-cathode.

Lallemand solved the latter problem by forming the photo-cell separately in a sealed envelope. Both the cell and the plate were then introduced into the image tube which was evacuated. Not until an adequately high vacuum was reached was the cell broken open to expose the photo-electric layer. Despite this complication the photo-sensitivity fell rapidly once the surface was exposed, so that the image tube became useless after about a quarter of an hour. In any case the photo-cell was destroyed after use, when the plate was removed for developments.

With admirable perseverance Lallemand proceeded to tackle this difficulty too. He built an electro-mechanical plate changer which could expose up to six plates in succession; he introduced 'getter' material to absorb the evolved gases; and he refrigerated the photo-cathode. By the beginning of 1955 he had produced an instrument whose sensitivity remained constant for several hours, even without continuous pumping.

This was not achieved without considerable complication in manufacture, as the diagram of the equipment shows (Figure 4).

After six exposures the device is opened and the plates are removed and developed. The tube is washed in distilled water, baked and repumped. The 'getters' are then fired, the next photo-cell is broken open and drawn into position magnetically.

These complications, coupled with the need for considerable skill in vacuum technique, have caused astronomers and other potential users of the instrument to fight shy of it. Although the principle of the Lallemand image tube is most attractive, we see that the practical difficulties involved are considerable. To overcome them a number of variants of the scheme have been proposed. Hiltner has suggested that the tube be sealed off by a very thin aluminium film and the photographic plate placed immediately behind it. The plate and photo-cathode would not then share the same vacuum and there should be no appreciable

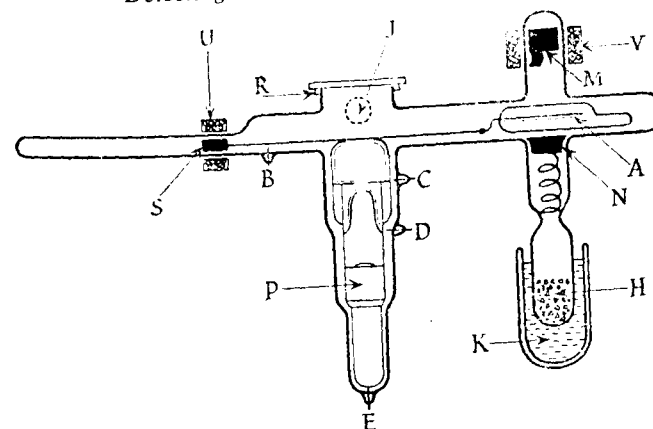


Fig. 4. Lallemand's Apparatus. A, Photo-cathode; B, C, D, E, Electrodes; P, Plate Charger; M, Hammer; N, Sprung Anvil; H, Activated Carbon; K, Liquid Air; S, Iron Slug; U, V, Solenoids; R, Rubber Gasket; J, Pumping Tube. (Redrawn from *Comptes Rendus de l'Académie des Sciences*, Vol. 218.)

deterioration insensitivity. The plates would have to be held in vacuum plate holder and changed as in electron microscopy. There are two difficulties with this arrangement. In the first place, the apparatus still requires continuous pumping. Secondly, it is very difficult to produce sufficiently thin aluminium films free from pinholes, for the electrons must be able to traverse the film without losing most of their energy. Baum has had some success in overcoming the latter problem by using two very thin films in contact, but the scheme is nevertheless still in the development stage.

INTEGRATING STORAGE TUBES

All the recording image devices so far considered have used photographic plates as the light integrating and recording medium. We have already discussed some of the limitations of the emulsion, and it is not surprising, therefore, that thought

off at any time, particularly while focusing and other adjustments are made. While the details of the scheme remain to be determined by experiment, there is little doubt that a successfully developed storage tube would be in great demand, particularly in astronomy.

THE ELECTRO-LUMINESCENT IMAGE INTENSIFIER

Finally, a particularly simple newcomer to the class of image intensifiers is of interest. It has been described by Cusano and Williams and, in its present form, functions only with incident ultra-violet light. The apparatus is shown in Figure 6. A con-

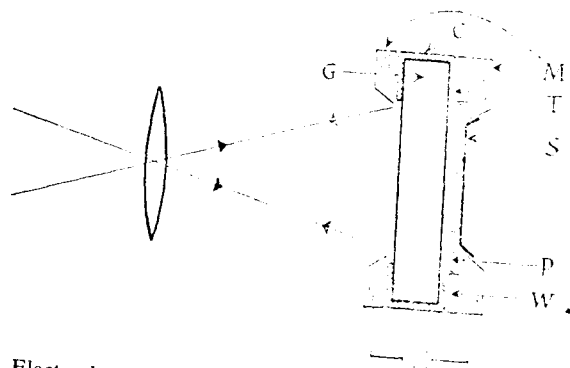


Fig. 6. Electro-luminescent Image Intensifier. G, Glass Base; C, Conducting Paste; T, Transparent Conducting Film; P, Evaporated ZnS Phosphor; W, Mica Spacer; S, Silver Film; M, Metal Electrodes. (Redrawn from *Journal of Applied Physics*, Vol. 26.)

ducting transparent film of titanium dioxide (TiO_2) is deposited on a glass plate and an electro-luminescent phosphor (manganese activated zinc sulphide) is evaporated on to it. A conducting silver film is formed on this phosphor, which is thereby sandwiched between two conducting layers to which a potential difference can be applied.

The ultra-violet image to be intensified is now focused on the

phosphor, which fluoresces faintly with a yellow light. The image brightness increases however with increasing voltage, until, with a polarizing potential of 100 volts, about ten times as many photons are emitted by the phosphor as fall on it.

The intensifier has therefore a particularly simple form and requires no electron optical equipment of any kind. Its behaviour is not yet completely understood, although F. E. Williams has recently interpreted it on the basis of a mechanism involving the creation of charge carriers in a region of high field strength. The device is in a very early stage of development and it remains to be seen whether it can ever be made to function with visible incident light.

SOME APPLICATIONS

We see then that the problems of detecting and recording faint images have led to many ideas and devices. A few applications of the instrument have already been mentioned, but new ones arise from time to time, occasionally in rather unexpected directions. For example, the use of an image intensifier tube as a very high speed camera shutter has recently been described by Saxe and Chippendale. The electron beam can be turned on and off by the application of suitable voltage pulses to one of the electrodes, thereby making possible exposures of the order of a hundredth micro-second.

It is however in the field of astronomy that the image tubes are likely to reap their richest rewards, because a device that increases the speed of the astronomer's recording medium (usually the photographic plate) by an appreciable factor, say a hundred, is effectively increasing the aperture of his telescope by a factor ten. Many modest 20-inch telescopes throughout the world would thereby acquire the present range of the giant 200-inch Hale telescope at Mount Palomar. It is true that the optical resolving power is not similarly increased. However, in practice, the image fluctuations due to atmospheric turbulences determine the resolution, which rarely approaches the optical limit.

It has already been mentioned that photographic exposures at

the prime focus of the 200-inch Hale telescope are limited to about half an hour. Thereafter the light from the sky background quickly causes saturation. The faintest objects that can just be detected on a plate so exposed have been estimated to be at a distance of about 1,000 megaparsecs, or 2×10^{22} miles. As it happens astronomical observations become particularly interesting just at, and beyond, this distance. Thus the current theory of the expansion of the universe, which is based on the linear increase with distance of the recession velocities of the nebulae, is really just beginning to be put to the test at this range. The highest measured recession velocity - of a star cluster in Hydra at a distance of about 400 megaparsecs - is about 40,000 miles per second, or about a fifth of the velocity of light. Clearly it is particularly important to increase the range of measurement beyond this figure. The introduction of photo-electronic image tubes should therefore help to throw light on some of the most fundamental questions of our time, by extending the range of the universe at present observable.

TEA: ITS PROCESSING AND CHEMISTRY

C. R. HARLER

THE crop harvested from the tea plant, *Camellia sinensis*, is the young leaf shoots consisting of two to five leaves and the unopened terminal leaf bud. These are rich in the alkaloid, caffeine, and certain tannin bodies spoken of as polyphenols. Any treatment whereby the plucked leaf is preserved so that the caffeine it contains can be made available when needed serves, in the broadest sense, as a method of preparation of tea.

A pound of good tea as made and infused in Great Britain gives 200 cups of the beverage. The caffeine content of the better grades of tea is about 3.5 per cent of the weight of the dry leaf, so that a pound of such tea contains perhaps 245 grains of the alkaloid. Of this total about 180 grains are easily extracted and a cup of tea from the first five-minute brew usually contains about 0.9 of a grain of the stimulant. The second brew yields only about 0.3 of a grain per cup, while further brews do not contain any caffeine. Poor tea, made from the coarser leaves, contains and yields less caffeine than the above quantities.

The annual *per capita* consumption of tea in Great Britain is at present 9.4 lb. This consumption works out at 5 cups per person daily, and represents not less than 4.5 grains caffeine if the tea is of good quality. The warmth of the beverage gives immediate comfort on drinking, but the effects of the caffeine are only realized some minutes later when it acts on the muscle, including cardiac muscle, the central nervous system, and the kidneys. The effect on the motor processes is quickly realized and is transient, whilst on the mental processes it comes more slowly but is more persistent. No secondary reactions have been observed from caffeine, not even after a 10-grain dose.

Pickled Tea Leaf

China is usually considered to be the home of tea, and it is generally assumed that tea, either as a medicine or a beverage, originated there. Yet it is possible that tribes living in the highlands of Further India, led by the instinct that prompts even primitive peoples to make use of alkaloid-yielding plants, may have taken tea in some form for at least as long as the Chinese.

The simplest method of preparation of tea leaf in use today is that followed by the tribes of the Shan States of Upper Burma, Upper Siam, and south Yun-nan, China. These people pickle the leaf and keep it in the wet state, eating it in due course as a salad mixed with oil, garlic, dried prawns, etc. At other times the Shans, when they have heavy work to do, drink an extract of the pickled leaf or chew the leaf itself. In Burma the pickled leaf is called *leppet* tea, in Siam, *miang*. The Shan habit of eating the leaf is a logical one in that it makes full use of the proteins and other foods in it.

In preparing *leppet* tea the fresh leaf is first put into a wooden container with a plaited bamboo base and placed over a vessel of boiling water. The steam softens and kills the leaf, which after five or ten minutes' treatment is thrown on to a bamboo mat and kneaded for a few minutes. It is then placed in a cement-lined pit and covered with planks weighed down by stones. More leaf is added daily, and finally the full pit is left for a period ranging from ten days to six months or more. Sometimes, when only small quantities of leaf have to be dealt with, the steamed and kneaded product is rammed into a bamboo for keeping.

The Preparation of Tea in China

In China, the origin of tea is lost in mythology. One legend relates how Dharuma, a Buddhist monk, during a prolonged meditation, found that he was becoming drowsy and, seizing his offending eyelids, cut them off and cast them from him. Where they fell a plant grew, the tea plant, from whose leaves can be prepared a drink that drives away sleep. The first authentic account of tea was written by Lo-yu in A.D. 780.

In China, tea preparation passed through several phases which may be roughly divided into three stages: the cake tea, which was boiled; the powdered tea, which was whipped; and the leaf tea, which was steeped. The early Chinese steamed the fresh leaf, then dried it over a fire and pressed it into cakes or crushed it into a powder. In Lo-yu's time it had become customary to roll the steamed leaf in the hands so that each leaf after drying was separate, resembling in this respect the tea commonly used today. The killing of the fresh leaf by heat stops chemical changes in it and as a result the so-called green tea is produced. This yields a liquor light yellow in colour and presents the caffeine in an easily extractable form.

The words *te*, *chia*, and *cha* denote tea in various Chinese dialects, and one or other of these forms is now in use to designate tea in other languages.

It was presumably noticed at some time in China that if the fresh leaf is first bruised or damaged before steaming, the liquors given by an infusion of the dried leaf are red in colour, and have more body and bite (strength) than a green tea infusion. It was also observed that if the fresh leaf is allowed to wilt or wither till it is flaccid it is more easily and thoroughly damaged in rolling than is the fresh, turgid leaf. Thus the preparation of the so-called black tea, miscalled fermented tea, was evolved.

The Chinese developed and still follow a complex process of black tea preparation, one open to endless variation and modification. The following account gives a general outline of the procedure. The tea industry in China is a village one, and the farmer may have only a few tea bushes or a quarter of an acre or so of tea. The leaf is plucked in the morning on a bright sunny day after the dew has gone. The leaves are first exposed to the sun and air till they have wilted sufficiently for the stalks of the shoots to be bent double without cracking. This exposure lasts for an hour or two. The leaves are then lightly turned by hand and manipulated till they become red and some juice is expressed. The bruised leaf is then put in a cool place for three hours or so, during which time the aroma is suitably developed. After this the leaf is thrown into a shallow iron pan which is

heated almost to dull redness over a wood fire. The leaves crackle and give off a vegetable odour which later subsides and gives way to the characteristic aroma of tea. The leaves have now been killed and are taken from the pan to be rolled on a table. Alternate panning and rolling continues till the leaves are too crisp for further manipulation. The final drying, called *poey*, is carried out with great care on small bamboo trays each placed in or on its own tubular, open-ended, waisted basket, called a *poey-long*. These baskets are between two and three feet high, and each stands over its small charcoal fire which is damped down with rice husks and ash as drying proceeds. This process is a slow one and may last several hours.

In addition to making black or fermented tea, and green or unfermented tea, the Chinese make *Oolong*, a semi-fermented tea. There are also scented teas treated with flowers, brick teas, tablet teas, and ceremonial teas, all of various pickings, districts, and grades. 'There are a thousand and ten thousand teas', wrote Lo-yu.

THE MANUFACTURE OF PLANTATION TEA

When the East India Company lost its monopoly of the tea trade in China in 1833, it set about growing tea itself instead of buying it at the port of Canton as it had done up to that time. This led to the establishment of the tea plantation industry in Assam, which got under way in 1839, and to its spread to Ceylon in 1875, to South India in 1895, to Indonesia about 1900, and some years later to Eastern Africa. In due course tea produced by the plantations practically ousted the teas of China from the world export markets.

In Assam the pioneer British planters brought in Chinese to show them how to grow tea and prepare the leaf, and in the early years the process described above was followed. But methods used in a village industry, where a farmer and his family deal with a few bushes, are not suited to a plantation of several hundred acres where a day's harvest may be 40,000 lb. leaf.

By the Chinese process as first followed in Assam there were no less than twelve operations lasting over three days, including

withering in the sun, four spells of hand rolling, two pannings, another sunning, two firings, and so on. Insets 1 and 2 show Indians at this period hand-manipulating the leaf and drying the tea in the waisted *poey-long*.

The first part of the Chinese process to be discarded was the short withering in the sun, because with large quantities of leaf this was impracticable. Instead the planter spread the day's harvest on bamboo trays and kept it in a shed overnight, ready to start rolling the next morning. This method of withering persists today in Assam, except that wire or hessian cloth racks are used. In later years, in the cooler, hill districts of Ceylon, South India, and Java, loft withering was developed, whereby warm air is sent by fans into enclosed lofts in which the leaf is spread on racks. Such controlled withering lasts about 18 hours, a period similar to that used in the open-air sheds in Assam. Inset 3 shows leaf spread on withering racks.

Next, the panning process and the *poey-long* or drying basket were abandoned. The withered leaf was simply hand-rolled, fermented on a cool cement floor and finally dried in a kind of chest-of-drawers over a charcoal fire. This dryer consisted of four or five movable wire trays. Fermented leaf was spread on the top tray which was moved through successive stages down towards the fire. In this way, as the leaf dried it met a hotter, drier air-flow from the fire. The process took about 45 minutes. These simplifications had been carried out in Assam by 1870, and from then on the tea house gradually became a tea factory.

Most of the labour in the Assam tea houses of this period was engaged in hand-rolling the leaf, for a man could only deal with 30 to 40 lb. withered leaf in an 8-hour day, and hundreds of men were required to perform this task, working in rows at long tables. The first rolling-machine was introduced in 1870, and by 1890 the principles still used in present-day rollers had been evolved. A modern tea-roller consists of a brass cylinder which revolves on three vertical cranks above a brass, battened table. The box may be 36 inches across, and is fitted at the top with an adjustable pressure-cap. A roller can take a charge of up to 500 lb. leaf, and in an 8-hour day one man can deal with

the rolling of up to 4,000 lb. withered leaf. The saving in labour that this invention brought about was great indeed, to say nothing of the improvement in hygiene. (Inset 4.)

No mechanization is needed in the fermentation process. The oxidation of the tannin bodies, the polyphenols, in the tea leaf begins as soon as the leaf cells are damaged, and much of the so-called fermentation takes place in the roller. After rolling, the leaf is spread about 1.5 inches thick on the fermenting space which may be a cement floor, or a sheet metal rack as shown in Inset 5. Foreign bacteria produce taints in tea, and the need for great cleanliness on the fermenting space is now fully realized. The reactions that constitute good fermentation take place at 80° F or rather less, and on this account fermenting and rolling rooms are, where necessary, air conditioned.

From 1870 onwards drying or firing machines for tea were invented and developed in Assam. The modern tea dryer consists of three parts, a tubular stove in which air is heated, a fan that blows the hot air into the bottom of the drying chamber – the third part of the machine. The fermented leaf is fed in at the top of the chamber, and, passing along six or eight 'endless' trays, makes its way down to the discharge, meeting, as it proceeds, hotter and drier air. (Inset 6.)

The two most notable names connected with tea machinery are William Jackson and S. C. Davidson, rival Assam planters, who from 1870 onwards invented rollers, dryers, sifters, and cutters, the principles of which still hold good today. Dozens of other machines have been invented by planters in India, Ceylon, and Indonesia, some with success, others predestined to failure because they ignored the science underlying tea manufacture.

Present-day procedure in plantation factories includes an 18 to 24-hour wither, during which 100 lb. fresh leaf dries to about 60 to 75 lb. Fresh leaf is about three-quarters water, so a wither to 75 lb. reduces the moisture content to about 66 per cent. Two half-hour rolls are given in Assam, but in the cooler districts of Ceylon, South India, and Java more rolls are needed, sometimes up to six. The fermentation period, including rolling, is about three hours. Firing may take place in one or two operations

taking 25 to 40 minutes. The initial temperature of the air-blast where it enters the dryer below the bottom tray is 180 to 200° F. By the time the air has passed upwards through the leaf on the successive trays it leaves the dryer at 120 to 130° F. A lower temperature than this does not kill the incoming leaf quickly enough, so that overfermentation may take place to produce a soft or flat tea, lacking strength and briskness. The leaf at discharge from the dryer contains one to three per cent moisture.

This procedure has been worked out over the years by a process of trial and error, with the essential guidance of the tea taster. Detailed records of conditions and times are kept daily in all tea factories, and every lot of tea is described and valued by several tasters, so that tea manufacture is in the nature of one continuous, recorded experiment.

The processes of manufacture that have just been described involve certain chemical changes in the leaf and produce the type of tea to which consumers are accustomed. Any marked departure from standard procedure brings about modified chemical changes, which result in a different liquor and lower prices at the tea sales.

THE STUDY OF THE CHEMISTRY OF TEA

The first work on the chemistry of tea was carried out in 1827 when an alkaloid was found in China tea and called theine. An alkaloid called caffeine had been found in coffee in 1820, and when it was later shown that caffeine and theine were the same substance the latter term was dropped. Caffeine also occurs in a South American plant, *Ilex paraguayensis*, an infusion of whose dried and roughly ground leaves furnish *yerba de maté*, the beverage of Paraguay and Brazil.

Between 1840 and 1860 various tannin bodies were found in tea. By 1890 analyses of fresh leaf gathered in Assam had been made, while in Japan it was shown that the main change in black tea manufacture involved a decrease in the water-soluble tannin in the leaf. During those years various analyses revealed the amount of fibre, protein, caffeine, ash, sugar, colouring matter, and the so-called tea-tannin in the leaf.

In 1879, a scientist writing in London on the chemical analysis of tea stated that the time was not far distant when the tea trade would buy wholly on analysis, but, while many more chemical data are available today than when this view was expressed, the time when the chemist will replace the taster is as far off as ever. A taster can describe and value a tea in less than a minute, and in so doing brings his knowledge of the particular estate, and market conditions, to bear upon his conclusion. A taster is not misled by a very good or a very bad sample; he relies greatly on his experience of what an estate can do. This is very necessary, for in evaluating a break of perhaps sixty chests (i.e., 6,500 lb. tea) all he has to work on is the infusion of three grams taken from a one-pound sample drawn from one chest. The possibilities of sampling errors will be appreciated.

In the early days frequent attacks were made on tea, as a beverage, by doctors and dieticians. These were usually based on the assumption that the tannin in tea acted like the *acidum tannicum* or digallic acid of the pharmacopoeia, which, by coagulating proteins and diminishing secretions in the stomach, produces constipation. It has also been suggested that tea tannin forms a kind of leather in the stomach, but tea is now so firmly established as an international beverage that such attacks carry little weight.

At the turn of the century, research on the changes that take place during tea manufacture were being carried out in India, Ceylon, and Java. The tea essential oil, responsible for the flavour of black tea, the chlorophyll group of compounds, and the red and yellow pigments, the anthocyanins and the flavones, were all studied in Java.

It was found that during withering the leaf continues to respire, evolving carbon dioxide, and as a result the total solids in withered leaf may decrease by as much as one-twentieth. After the leaf is plucked, certain building-up processes that take place in the growing leaf are apparently reversed, with the result that there is a small increase in sugars and amino acids at the expense of starches and proteins. Such changes take place with time, whether the leaf loses water, and withers physically,

or not. Slight though these changes are, they are perhaps connected with the development of quality in tea, a characteristic so far not defined chemically.

In 1901 it was shown that when fresh or withered leaf is damaged it absorbs oxygen from the air with the aid of an enzyme, an oxidase, occurring in the leaf cells. In Japan it was concluded that the preliminary heating of the leaf by steam or in a hot pan inactivated this enzyme, and that this accounted for the obvious difference between green and black tea. During the fermentation of black tea, the tannin is first oxidized, then condensed to give red products, which are desirable, and brown ones, which are not. The enzyme is inactivated at about 160° F.

The oxidation process in the manufacture of black tea was mis-named 'fermentation' by the early planters in Assam and the use of this term has persisted. Fermentation usually implies the decomposition of carbohydrates by yeasts to give alcohol and

TABLE 1: Composition of Tea Leaf and of Black Tea

Constituents	% in Fresh Leaf	% in Black Tea
<i>Insoluble in water</i>		
Cellulose and crude fibre, etc.	35.5	35.5
Protein	17.0	16.0
Chlorophyll and pigments	1.5	1.0
Starch	0.5	0.25
Tannin bodies, etc.	—	7.75
<i>Soluble in water</i>		
Tea tannin	25.0	13.0
Oxidized tannin	—	4.0
Caffeine	4.0	4.0
Amino-acids	8.0	9.0
Gummy matter and sugars	3.0	4.0
Minerals (ash)	4.0	4.0
Total ash	5.5	5.5
Tea essential oil	—	traces

gas, or acid and gas. Although various workers have suggested that true fermentation may take place when the leaf is rolled, because yeasts occur naturally on the leaf surface and the tea juices contain sugars, it is doubtful whether this is so.

Table I represented our knowledge of the chemistry of black tea manufacture at about 1930.

Polyphenols in Tea Leaf

Detailed knowledge of the tannin bodies in tea began with the isolation, in Japan, of (l)-epi catechin from tea leaf, soon followed by the separation of (l)-epi catechin gallate. In Java, gallic acid was separated from the tannin or polyphenol mixture in the tea leaf. Meanwhile the study of the chemistry of tea manufacture was started in India and Ceylon, and ultimately in London. By using the new technique of partition chromatography, whereby complex mixtures of closely related substances may be separated, the leaf was shown to contain a number of polyphenols in addition to those already mentioned.

The substances identified include: (a) simple catechins containing one catechol group per molecule; (b) gallocatechins containing one pyrogallol group per molecule; (c) galloyl esters of simple catechins containing one catechol and one pyrogallol group; and (d) galloyl esters of the gallocatechins containing two pyrogallol groups. These substances are flavanols of known structure. Another substance occurring in the polyphenol mixture has been shown to be a depside of gallic acid.

These identifiable polyphenols occur in practically the same proportion in leaf from different types of bush, and any slight variations are insufficient to explain the marked differences in the liquoring properties of manufactured teas. Traces of a number of other polyphenols have been detected in tea leaf, but in insufficient quantities to be of significance in determining liquoring properties. As shown in a later section, such differences are due to the proportions and concentrations of the condensed oxidized polyphenols.

The distribution of polyphenols in various parts of the leaf shoot has been studied and found to vary, and this difference

probably accounts for the varied character of the liquors made from different parts of the shoot. Thus, the depside of gallic acid decreases from the bud to the mature leaves, while the simple catechins increase.

As the leaf gets older, so the polyphenol content decreases. This is shown both by analysis and microscopic examination, and was fully realized many years ago because the older the leaf the poorer the liquoring qualities of the tea made from it. Most of the polyphenols are concentrated in the upper surface of the leaf, less in the lower surface, with few in between. The polyphenols vary inversely as the starch content of the leaf; the more the starch the less the polyphenols.

It is of interest to record the distribution of the polyphenols, the caffeine, and the amino-acid nitrogen, as a percentage of the total dry weight, in the various parts of the tea shoot as plucked in Assam. The high value of the amino-acid nitrogen in the upper stem should be noted; further reference to this figure, in connexion with theanine, will be made later. The Orange Pekoe grade of fine tea comes largely from the upper stem of the shoot.

TABLE II: *Analysis of Tea Shoots Plucked in Assam: expressed as percentage of total dry weight*

Part of shoot	Polyphenols	Caffeine	Amino-acid nitrogen
Bud	26.5	4.7	0.87
First leaf	25.9	4.2	0.68
Second leaf	20.7	3.5	0.57
Third leaf	17.1	2.9	0.51
Upper stem	11.5	2.5	1.03
Lower stem	5.3	1.4	0.69

The Chemistry of Tea Fermentation

With this recently won knowledge of the polyphenols in tea leaf now available it is desirable to consider their fate during fermentation. The enzyme that assists in the oxidation

of the polyphenols when the leaf is damaged and the juices exposed to the air, is an oxidase of the copper-protein type. It is located in the chloroplasts of the leaf cell, while the polyphenols are located in the vacuole. Its activity decreases slightly during withering, so that in freshly damaged leaf it is rather more active than in withered leaf. The activity of the enzyme decreases at temperatures above 80°F.

The cells of the tea leaf measure about one-thousandth of an inch across, and the enzyme and the polyphenols are kept apart by a semi-permeable membrane. When the withered leaf is rolled, few of the outer cell walls are damaged, yet 90 per cent or more of the polyphenols are oxidized during a three-hour fermentation; in due course they are all oxidized. It would thus appear that when leaf is rolled the enzyme and polyphenols are mixed without necessarily breaking the whole tissue. This is apparently brought about by the rupture of the membrane.

If tea leaf is placed in chloroform vapour, or heated to about 120°F, or frozen and then allowed to thaw, it turns brown owing to the oxidation of the polyphenols, although there has been no physical damage akin to rolling. It is likely that these treatments leave the cell walls unbroken but rupture the membrane.

When the tea polyphenols are first oxidized it is thought that ortho-quinones are the initial products. These substances are effective bactericides, and this accounts for the marked fall in the number of bacteria on the leaf surface that takes place when rolling starts and juices are expressed. Further oxidation probably takes place after this preliminary action.

The polyphenols are oxidized successively, and not simultaneously, and it often happens that the simple catechins are not appreciably oxidized by the time the fermenting leaf is taken to the dryer, about three hours after rolling was initiated. During fermentation a considerable amount of gallic acid is produced by the breakdown of the galloyl esters. The depside of gallic acid is not appreciably oxidized during fermentation.

After oxidation the polyphenols combine, or polymerize, to form complex compounds, and there is probably a whole range of these substances which give briskness, strength, colour, and

body to the tea liquors. Some of the lower polymers combine with caffeine probably to give the property known as briskness.

When a tea infusion cools, a precipitate or 'cream' settles; this is composed largely of lower polymers combined with caffeine. The higher polymers are considered to account successively for strength, then colour, then body, whilst the highest polymers have negative or harmful characteristics, and make for softness or flatness in the liquors.

Examples of polymerization or polycondensation are common in biochemistry, and the degree of condensation is affected by concentration and by temperature. It thus follows that the degree of the physical wither (which affects concentration) and the temperature of fermentation are important factors in tea manufacture.

As the condensation of the polyphenols increases, so does their ability to combine and form insoluble compounds with proteins; in other words their tanning properties increase. As condensation increases, solubility decreases, so that a high degree of condensation robs the tea infusion of solid matter on two counts, insolubility of the polymer, and precipitation by proteins.

It may be concluded that the changes that take place during the so-called tea fermentation consist largely of oxidation and subsequent condensation of polyphenols. During the early stages of the firing of tea, oxidation proceeds for a time till the enzyme is inactivated by heat, after which condensation goes on till the leaf reaches a certain degree of dryness. Much of the tea aroma and flavour is lost in firing, and the liquoring qualities of fired tea are inferior to those of fermented but unfired leaf.

Liquoring Qualities of a Tea Infusion

A tea taster wants briskness, strength, colour, and body in a liquor. He also wants 'quality', at present indefinable, with aroma and flavour. What then is the chemical make-up of a black tea infusion? When tea is treated with boiling water the substances extracted may be divided into four groups: (a) inorganic salts; (b) caffeine; (c) gummy matter; and (d) non-

nitrogenous substances, which are astringent and give a green or blue coloration with iron (ferric) salts. This last group of substances is composed of catechins, oxidized and non-oxidized, the former in various stages of condensation. Some of the catechins, or polyphenolic bodies, are extractable from an aqueous infusion by ethyl acetate, and in the discussion that follows they are called extractable catechins, and the others non-extractable catechins.

The composition of two liquors made from 100 grams tea, one a good tea and the other a poor one, is shown below. It will be seen that about 40 per cent of the weight of tea goes into solution on infusion.

TABLE III: Solid Matter in a Tea Infusion: expressed as weight in grams in 100 grams of tea infused

Constituents	Good tea	Poor tea
Extractable catechins	13.2	8.5
Non-extractable catechins	11.5	10.8
Caffeine	4.9	3.4
Gummy matter	9.2	11.9
Inorganic ash	3.8	3.4

Neither the inorganic ash nor the gummy matter contributes much to the taste or the colour of the infusion, and may be considered unimportant so far as liquoring qualities are concerned. The inorganic ash consists largely of potassium phosphate, together with the sulphates and chlorides of potassium, calcium, and magnesium. The gummy material contains many sugars, including glucose, fructose, sucrose, arabinose, and ribose. There are also amino-acids, including aspartic and glutamic acid, and a substance called theanine, an N-ethyl amide of glutamic acid, first found in Japan green tea and later in Assam tea. This may be a major component in the amino-acid fraction in tea leaf or made tea, amounting to as much as one or two per cent of the dry matter.

As far as taste is concerned caffeine is a minor component in tea, although it is important in that it forms part of the 'cream'

or precipitate that forms when an infusion cools. It is also thought to be connected with the briskness of a tea liquor.

It may thus be concluded that the catechins are the solids that contribute mainly to liquoring qualities. Moreover, as the non-extractable catechins are present to approximately the same extent in both the good and the poor tea under discussion, it seems that the catechin fraction extractable by ethyl acetate is the important one. These extractable catechins form an orange-coloured solution, and, like caffeine, are very astringent. The catechins not extractable with ethyl acetate form a weakly astringent dull brown solution with the taste of poor, weak tea.

The 'cream' or precipitate formed on cooling a good and a poor tea has the following composition.

TABLE IV: Composition of 'Cream' from Tea Liquors: expressed as weight in grams in 100 grams of tea infused

Constituents	Good tea	Poor tea
Extractable catechins plus caffeine	8.25	2.95
Non-extractable catechins	3.14	1.65
Inorganic ash	0.12	0.09

The 'cream' from the good tea was amber red in colour, while the other was muddy brown.

The poor tea gives about 65 per cent as much ethyl acetate extractable catechins as does the good one. When an infusion of the poor tea was made with half as much leaf again as was used with the good tea, it gave a liquor comparable in colour, strength, and pungency with that of the good tea. This agrees with the suggestion that liquoring qualities depend on the concentration of extractable catechins.

The Aroma of Black Tea

During the fermentation process in black tea manufacture, the so-called tea essential oil, responsible for the aroma of tea, is formed. All tea has an aroma, part of which, including the acrid portion, may already be present in leaf growing on the

bush. Some teas have marked special aromas in addition to the general one; these are highly valued and called flavours.

It may here be observed that taste, as distinct from aroma, is experienced mainly on the tongue or some other surface in the mouth. Briskness and strength are detected by the tongue. Astringency or pungency is a sensation, not a taste, and is realized largely on the gums. The thickness, body, or viscosity of the liquor is felt as the infusion is swilled round the mouth. 'Quality' is probably partly taste and partly aroma, the latter being detected by the organs of smell in the nose. Without the sense of smell it is practically impossible to tell the difference between one article of food and another because the main kinds of taste are similar on the tongue. The complex aroma that goes with all black tea, both good and poor, is peculiar to tea.

The subject of aromas and tastes is a complex one, while definition of the terms used by tea tasters to describe the good qualities and the blemishes of tea is a subject beyond the scope of this article. From time to time three volatile components have been reported in tea and considered to be responsible in part at least for aroma. These substances are phenyl-ethyl alcohol, citronellol, and hexenol. When these compounds have been added artificially to a tea infusion, tasters have reported a rawness akin to briskness, but no noticeable increase in aroma. The bulk of the volatile matter in tea consists of alcohols and aldehydes, but little definite information about them is yet available.

Many and varied aromas are associated with tea, including an acrid one resembling ginger root or the acrid part of the smell of hay. With flavoury teas there is a marked flower-like smell, as of roses, or geraniums. Some tasters can smell 'quality' on the growing leaf, a fact emphasizing the complexity of this characteristic, which is apparently partly taste, partly a sensation in the mouth, and partly a smell.

Micro-organisms on Tea Leaf

Growing tea leaf carries on its surface a large population of naturally occurring micro-organisms. During withering the numbers do not increase very much, unless the leaf is wet

superficially. When leaf is rolled, there is a rapid drop in the number of micro-organisms, due to the antiseptic properties of the oxidized polyphenols. Thereafter, foreign bacteria, which are omnipresent, may infect the leaf and produce taints hence the need for bacterial cleanliness in a tea factory. During the first fifteen minutes of firing, all the bacteria on the leaf are destroyed, but moulds have been known to persist even after thorough drying. Leaf sterilized with mercuric chloride still ferments, so it is now thought that neither bacteria, yeasts, nor fungi play any important part in the manufacture of tea.

CONCLUSIONS

From the account just given of the chemical changes that take place during the manufacture of black tea, it is apparent that there are still many gaps in our knowledge. Thus the full significance of the changes taking place during withering is still unknown; practically nothing is known about aroma and flavour and their formation during fermentation; and the exact nature of 'quality' needs much more study. Much has yet to be worked out regarding the physics and chemistry of the firing process.

Over the years a great mass of empirical knowledge has been accumulated as a result of close correlation between factory procedure and tasters' reports on the teas made. But, while the taster's description and evaluation of a tea are wholly satisfactory for trade purposes, to establish complete scientific control in tea manufacture it is essential to have more precise knowledge about the biochemistry of procedure and of the chemical characteristics that go to make a tea infusion. Work on this vast subject is proceeding in the research stations of the major tea areas, and in London, and results already obtained have done much to improve the general quality of the tea produced.

NATURAL COLLOIDAL SILICATES

ONE HUNDRED YEARS OF SCIENTIFIC PROGRESS

G. P. C. CHAMBERS

THE study of colloidal silicates goes back to the beginning of civilization. Man's interest in these materials is founded on their fundamental importance and widespread use in many branches of primitive craft as well as in modern industry. One has only to recall that ceramics had reached an advanced stage of development in China at a time when our own ancestors were still using very crude pottery utensils. The ceramic industry is still based on clays, in particular china clay, but the range of raw materials in use is now very extensive indeed. On the other hand the traditional use of clay materials for scouring wool, a use that gave rise to the term 'fuller's earth' for certain highly absorbent clays, has now largely given place to detergent scouring following the introduction of synthetic detergents and surfactants.

Today the study of colloidal silicates has progressed from a jumble of empirical recipes to a highly organized branch of science embracing colloid chemistry, soil science, agriculture, ceramics, and mineralogy. It plays an important part in the petroleum, food, foundry, pottery, and paper industries. An indication of the importance of the clay industry to the national economy may be realized from the fact that Cornish china clay is our third largest export to dollar markets.

While the use and study of clay goes back into the depths of time, a truly scientific study of it is barely one hundred years old. Indeed the earliest detailed account of clay minerals appeared in 1856. In that year M. Dufrenoy published his *Traité de Minéralogie*, five years before Thomas Graham in Great Britain used the term 'colloid' and defined its meaning. Between

that date and the second decade of this century the study of the colloidal clay minerals advanced but little, largely owing to lack of suitable experimental techniques. Since the introduction of X-ray analysis and electron microscope techniques the concept of clay materials as being composed of extremely small particles of crystalline minerals has been well established, and today it is generally recognized that the special attributes of clay minerals are in part the result of this very small size, and that in addition to size, the shape and surface properties of the particles give the essential characteristics to clay minerals.

CLASSIFICATION OF CLAY MINERALS

Today clays are generally classified on the basis of their crystalline structure, and of the behaviour that is a result of their structure. The following classification is based largely on that suggested by R. E. Grim in his book *Clay Mineralogy*.

There are two main groups: crystalline and amorphous. Of these the crystalline group is the more important and the amorphous group will not be further considered here. The crystalline group can be sub-divided into four groups based on the number of layers in the crystal structure:

Type A consists of those clays comprising two layers – one sheet of silica tetrahedra and one layer of alumina octahedra. This sub-division includes the important kaolinite mineral which occurs as china clay. Others are nacrite and halloysite – neither of commercial importance.

TABLE 1: Characteristics of Clay Minerals having a three layer structure

LATTICE TYPE	PARTICLE SHAPE	EXAMPLES
Expanding lattice	Equi-dimensional, i.e. platelets	Montmorillonite Vermiculite
	Elongate, i.e. needles or rods	Hectorite Nontronite
Non-expanding lattice	Indeterminate	Illite

Type B consists of those clays that have three layers in their structure – a layer of alumina octahedra between two layers of silica tetrahedra. This sub-division comprises a large number of clay minerals of varying composition and structure, and is best illustrated in Table I.

Type C consists of clays that comprise stacks of alternate layers of different types, i.e., alternate two-layer and three-layer structures stacked above each other. The group of micaceous clays called chlorites belongs to this sub-division.

Type D consists of clays whose layer structure consists of silica chains resembling the chains of hornblende linked together by alumina and magnesia octahedra. Representative of this type is the palygorskite group. This group is at present very incompletely investigated, but examples of it are finding increasing use in industry.

STRUCTURE OF THE COLLOIDAL SILICATES

X-ray crystallography has demonstrated that the structure of the silicate minerals is governed by the ability of silica to co-ordinate itself with four oxygen atoms arranged in space so as to occupy the corners of a tetrahedron.

Such a unit consisting of four oxygen atoms and one silicon atom carries four negative charges. These charges may be neutralized by further tetrahedrally co-ordinated silica atoms so that the whole structure repeats itself. If the repetition occurs but once we say that adjacent tetrahedra share a corner oxygen atom; if the repetition occurs twice the result is either a chain or a ring structure; and if it occurs three times a sheet structure is obtained. In the limit, if all four oxygens are shared by four more adjacent tetrahedra a solid, three-dimensional structure is obtained. It is not essential, of course, that the charges be neutralized by further silica tetrahedra, but while other cations may serve to neutralize the charges, choice is limited by consideration of size, valency, and co-ordination numbers. Charge and co-ordination number obey Pauling's Rule that charges must be balanced by immediate neighbours.

The colloid silicate minerals that are the subject of the above

classification, while differing from one another in certain structural aspects, all have distinct general features. They all have as part of their structure one or more sheets of silica tetrahedra and one or more sheets of alumina or magnesia octahedra. In the silica sheets all the silicon atoms lie on the same side of an hexagonal oxygen network and only three valencies of the silicon are contained in the sheet. The fourth is directed at right angles to the plane of the sheet and is satisfied by an oxygen atom which serves to link the first sheet to another sheet. In general this fourth oxygen forms part of another structural unit usually consisting of aluminium or magnesium atoms octahedrally co-ordinated with oxygen, i.e., each metal atom is associated with six oxygen atoms so disposed in space that they occupy the corners of an octahedron (Figure 1). We can now consider the structure of the clays classified above.

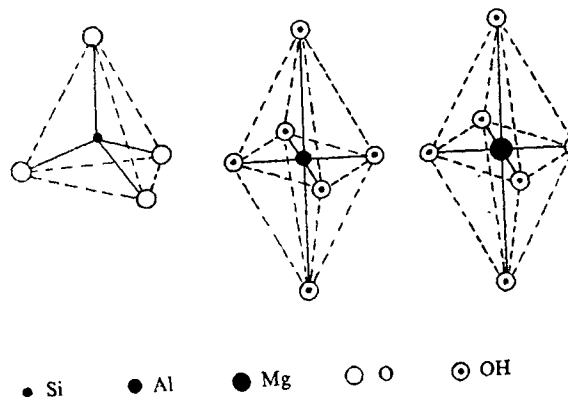


Fig. 1. Tetrahedral arrangement taken up by silicon atoms: octahedral arrangements of aluminium and magnesium atoms.

Kaolin Group (1:1 Lattice Type)

There are two layers in this type, one of silica and one of alumina. The ideal composition is $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. Kaolinite, dickite, nacrite, and meta-halloysite correspond to this ideal

formula, the structural differences being in the way in which the lattice units are stacked one above the other. It is thought that, whereas kaolinite appears to have triclinic crystal form, nacrite and dickite belong to the monoclinic system.

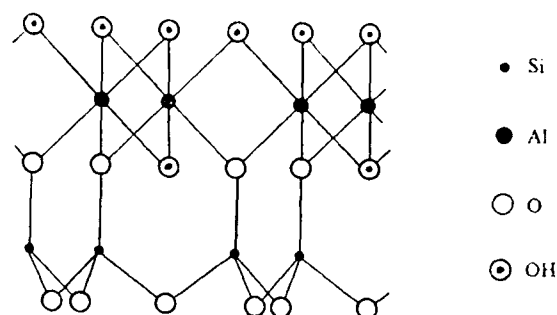


Fig. 2. Arrangement of atoms in Kaolinite (after E. A. Hauser).

The structure of kaolinite (Figure 2) comprises a single sheet of silica tetrahedra and a single sheet of alumina octahedra so linked in a unit that one oxygen layer is common to both sheets.

The charges within the structural unit are balanced and so the only basis for cation exchange capacity is from unbalanced charges occurring on the edges of sheets, hence cation exchange capacity is low. This explanation has been questioned recently, but remains, at present, the accepted one.

Montmorillonite Group (2:1 Layer Type)

This group comprises the clays possessing expanding lattices. According to modern thought montmorillonite is composed of units formed from two tetrahedral silica sheets sandwiching an octahedral alumina sheet. All the tips of the silica tetrahedra point inwards towards the octahedral alumina sheet, and the sheets are so linked that the tips of the tetrahedra and one of the hydroxyl layers of the octahedral layer are common. The ideal formula is $(\text{OH})_2\text{Si}_4\text{Al}_2\text{O}_{20}$.

The most striking property of the montmorillonite structure (Figure 3) is that water and certain other polar molecules can

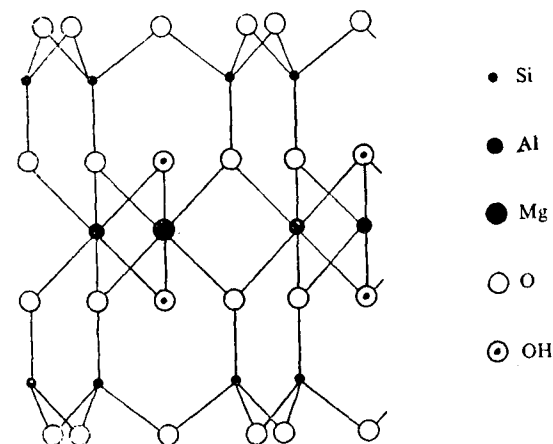


Fig. 3. Arrangement of atoms in Montmorillonite (after E. A. Hauser).

enter between the three-layer units causing the overall lattice to expand in the direction of stacking. The replacement of aluminium in the middle layer by magnesium gives rise to an overall excess negative charge on the lattice which is balanced by exchange cations (see below). These exchangeable cations occur between adjacent silicate sheets, and when the montmorillonite has been completely dehydrated the spacing between these sheets is governed to a certain extent by the size of the interlayer ion. Furthermore, on hydration the thickness of the layers of water between the units depends on the degree to which the cation hydrates at a given water-vapour pressure.

If montmorillonite is dried out at only moderate temperatures and then again immersed in water it will swell to many times its original volume, but if it is completely dehydrated it may lose this power, in part or completely, owing to lattice damage. The class of montmorillonite depends on the substitution in the lattice already mentioned above. The following table, after Ross and Hendricks (2), brings together the better known types and indicates the type of substitution occurring.

TABLE II: Formulae for some members of the Montmorillonite Group after C. S. Ross and S. B. Hendricks

MINERAL	COMPOSITION	SUBSTITUTION
Montmorillonite	$(\text{OH})_4\text{Si}_6(\text{Al}_{3.34}\text{Mg}_{0.66})\text{O}_{20}$	Al by Mg
Beidellite	$(\text{OH})_4(\text{Si}_{6.34}\text{Al}_{1.66})\text{Al}_{1.34}\text{O}_{20}$	Si by Al
Nontronite	$(\text{OH})_4(\text{Si}_{7.31}\text{Al}_{0.69})\text{Fe}_{1.34}^{3+}\text{O}_{20}$	Si by Al: Al by Fe
Hectorite	$(\text{OH})_4\text{Si}_6(\text{Mg}_{3.34}\text{Li}_{0.66})\text{O}_{20}$	Al by Mg: Mg by Li
Saponite	$(\text{OH})_4(\text{Si}_{7.34}\text{Al}_{0.66})\text{Mg}_2\text{O}_{20}$	Si by Al: Al by Mg

Illite Minerals (Non-Expanding Lattice Type)

The non-expanding members of the montmorillonite group, characterized by the illites, are closely allied to the micas. They share with the micas the distinction of having non-exchangeable potassium as a constituent of their lattices. The structural unit of the micas is similar to that of montmorillonite but with the difference that some of the silicons are always replaced by aluminium atoms and the resulting charge deficiency is balanced by potassium ions. The usual replacement ratio found in well crystallized micas is about one fourth of the silicons replaced by aluminium. Examples of micas are:

Muscovite $(\text{OH})_4\text{K}_2(\text{Si}_6\text{Al}_2)\text{Al}_4\text{O}_{20}$

Biotite $(\text{OH})_4\text{K}_2(\text{Si}_6\text{Al}_2)(\text{Mg.Fe})_6\text{O}_{20}$

Phlogopite $(\text{OH})_4\text{K}_2(\text{Si}_6\text{Al}_2)\text{Mg}_6\text{O}_{20}$

Different forms of biotite are known which vary in the manner in which the structural units are stacked and in the number of the layer units per unit cell of the crystal (Figure 4).

The illite clay minerals differ from the well crystallized micas in a number of ways. In general there is less substitution of Si^{+4} by Al^{+3} (about 1/6th for illites compared with 1/4th for micas). As a consequence the silica-to-alumina ratio of the illites is higher than in the micas. The nett-unbalanced-charge deficiency is reduced from 2 per unit cell to about 1.3 per unit cell, with a consequent decrease in cation exchange capacity (see below).

The structure of illite differs from that of montmorillonite in

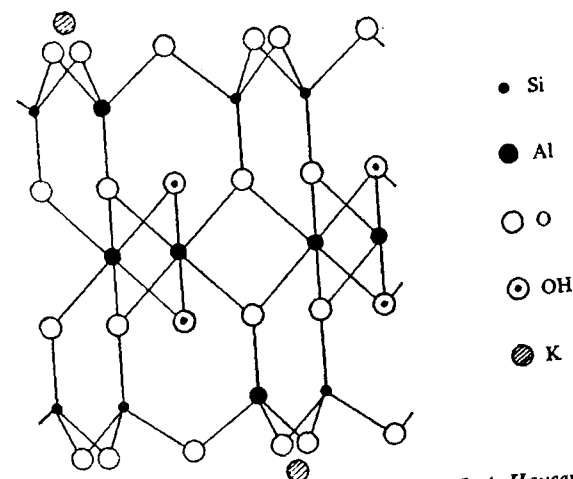


Fig. 4. Arrangement of atoms in Illite (after E. A. Hauser).

a number of ways. The seat of the charge deficiency, which is greater for illite than for montmorillonite, is largely in the silica sheet, whereas in montmorillonite it is chiefly in the octahedral sheet at the centre of the unit layer.

Chlorite Minerals

The structure of chlorite was first suggested by Pauling (3). All the true chlorites have a structural framework consisting of alternate mica-like and brucite-like layers. A typical composition of the brucite-like layer is $(\text{Mg.Al})_6(\text{OH})_{12}$, but various chlorites differ in the degree of substitution of aluminium or magnesium. Apart from Pauling's work very little has been published on the chlorite minerals and they have not been fully investigated.

Palygorskite Minerals Group

Until recently the only member of this group to be thoroughly investigated was the clay mineral attapulgite whose structure (Figure 5) was determined by Bradley in 1940 (4).

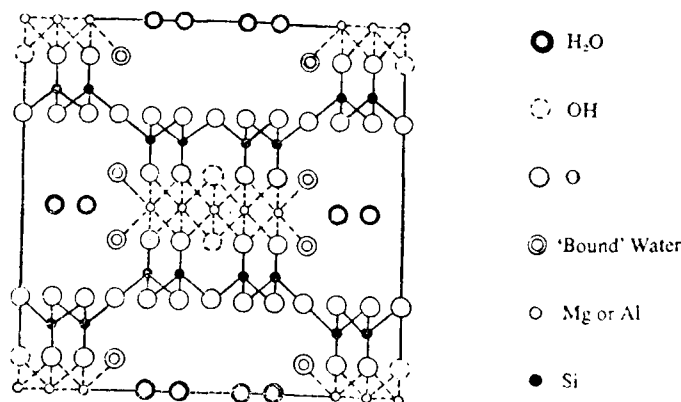


Fig. 5. Arrangement of atoms in Attapulgite (after W. F. Bradley).

According to Bradley, attapulgite comprises double silica chains (not plane sheets as in the other minerals) linked through oxygens at their longitudinal edges, in such a manner as to form ribbed sheets. This ribbing is brought about by the fact that the apices of the silica tetrahedra in each successive chain point away in opposite directions while the apices of successive sheets point in the same direction. The sheets are held together by aluminium or magnesium atoms octahedrally co-ordinated between successive sheets. Chains of water molecules are accommodated in the space between the silica chains. This space is caused by the fact that the octahedral layer, while being similar to that in the layer minerals, is continuous in one direction only. These cavities contain four molecules of water per unit cell. The structure is a balanced one, i.e. cation exchange capacity is low and the ideal composition is $(\text{H}_2\text{O})_4 \cdot (\text{OH})_2 \text{Mg}_3\text{Si}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$.

Recently a similar structure has been published for sepiolite, another member of the palygorskite group (Nagey and Bradley 1955) (5). These authors believe that sepiolite contains an entirely new form of silica chain similar to, but longer than, the chain found in attapulgite. They give an ideal composition as

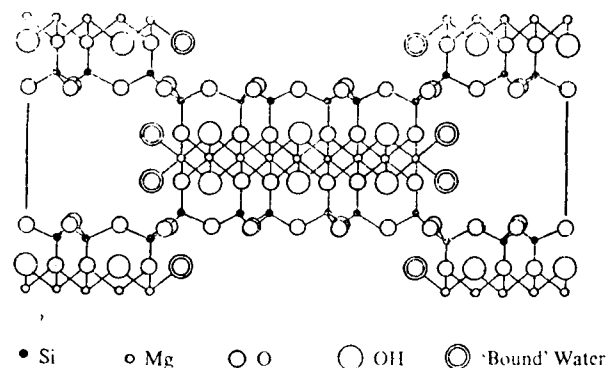


Fig. 6. Arrangement of atoms in Sepiolite (after B. Nagey and W. F. Bradley).

$\text{H}_4\text{Mg}_9\text{Si}_{12}\text{O}_{30}(\text{OH})_{10} \cdot 6\text{H}_2\text{O}$ and the schematic structure given in Figure 6.

COLLOIDAL PROPERTIES OF CLAYS

The colloidal properties of clays stem fundamentally from the very small size of the crystallites comprising the minerals. Indeed particle size is the yard-stick determining whether material is, or is not, colloidal. For practical purposes it may be considered that material of size no greater than two microns (1 micron = $1\mu = 0.001$ mm) is of colloidal size. Material in such a fine state of subdivision displays a very great surface area, and many of the colloidal properties of clays are due to behaviour attributable to this great surface area. Another property of the clays that has an important bearing upon their colloidal behaviour is that the particles normally carry negative electrical charges. These charges come from two possible main sources. They may be due to unsatisfied valency bonds at the broken edges of crystals, or to substitution of aluminium by an atom of lower valency (e.g. magnesium) bringing about a reduction of positive charges in the crystal lattice, thus giving rise to an excess of

negative charges.* These negative charges help the clay minerals to disperse in polar media such as water, because all the particles repel one another and so aggregation does not occur under conditions where the charges are not neutralized. In this state of stable dispersion the clay is said to be deflocculated or 'peptized'. The charges attract to themselves ions of opposite charge, so an electrical double layer is built up on the particles. The electrical potential across this double layer is called the *zeta potential*. This is the energy required to move unit charge from the surface of the particle to the outer edge of the 'atmosphere' formed by the layer of ions attracted to the surface. Any change in environment that tends to increase the zeta potential of the particles will tend to increase the degree of mutual repulsion and hence will aid the dispersion of the clay. For this reason alkalis, which increase the concentration of negatively charged hydroxyl ion in water, are good dispersing agents for clay minerals. Addition of too much alkali, however, leads to flocculation and precipitation due to formation of colloidal metal hydroxides which are oppositely charged and are attracted to the surface of the clay particles. As well as neutralizing the negative charges, this artificially increases the particle size and flocculation rapidly results.

Ion Exchange Properties

The property of adsorbing ions from a solution and exchanging these adsorbed ions for other ions in solution is possessed by all materials of great surface area and crystalline structure. In general this ability is very small and is due to stray unsatisfied valencies at broken edges of crystals, as is found in the two-layer kaolinite clays.

However, in the three-layer clays, as has been shown, considerable cation exchange ability arises from substitution of aluminium in the central layer by atoms of lower valency. Ion

*It is not possible here to go into the mechanism whereby positive and negative charges arise in crystals: interested readers will find the necessary information in textbooks on crystallography.

exchange ability is usually referred to as the cation exchange capacity (c.e.c.) of the clay and is expressed in milli-equivalents per 100 grams of clay. Some idea of the order of cation exchange capacities for various clays may be seen from Table III.

TABLE III: Cationic Exchange Capacity of Clay Minerals

MINERAL	CATION EXCHANGE CAPACITY (milli-equivalents per 100 grams clay)
Kaolinite	3 — 15
Montmorillonite	80 — 150
Illite	10 — 40
Chlorite	10 — 40
Attapulgit	20 — 30

The property of ion exchange is of very great importance in all the fields in which clay is used. Plant growth depends on ion exchange reactions taking place in the soil. The ions, which form the food of plants, are held in the soil and their availability to the plant is entirely dependent on this ability to release and exchange ions. The tilth of soil depends upon the nature of the exchange ion in the soil clays; a clay containing sodium ion renders the land unsuitable for agricultural purpose. This is largely the reason why land flooded by sea water becomes infertile, the sodium ions in the sea water exchanging with the calcium in the soil to form sodium clay. Treatment of the land with calcium salts will eventually render the land useful again.

The physical properties of clays are greatly influenced by the nature of the exchangeable cations carried by the clays. In general the plastic properties of a soil depend on whether the cation is sodium or calcium. In ceramics the plastic properties of clays can be altered and modified to meet the needs of the operator. Soda-ash is added to bulk clay to improve its plastic properties. Civil engineers can alter the property of soils to suit their requirements, but may accidentally cause an ion exchange reaction which will cause a change in soil properties that they have not allowed for.

Bentonite, a variety of montmorillonite, is widely used for a variety of purposes – two important operations, oil well drilling and plugging of canals and dams, depend upon the clay being a sodium montmorillonite. Calcium montmorillonites can be made suitable for such purpose by causing them to undergo ion exchange in which calcium ions are replaced by sodium ions.

In clays whose cation exchange capacity is small (kaolin, illite, chlorite, etc.) the sites at which the ions are probably adsorbed are on the edges of broken crystallites. In clays that have a high cation exchange capacity as a result of replacement in the crystal lattice (montmorillonites, vermiculites, etc.), the ions are believed to be sited largely between the three-layer units or packets of the crystallites, on the silica surfaces. It is believed that when sufficient water is present (more than required for development of plasticity) the ions are removed some distance from the surfaces and separated from them by water molecules.

Another group of minerals, closely related to the clay minerals, which show very considerable cation exchange capacities, are the zeolites. Some of these find application in water-softening plant. The investigation of exchange mechanisms has been proceeding very rapidly in recent years, using synthetic ion exchange resins, the attainment of equilibrium between the exchanging material and the solution containing the ions being faster with resins than with clay minerals.

Dispersion, Swelling, and Flocculation

It is natural to suppose that one factor governing dispersion would be the bond holding the individual units of the crystallites together. In clays whose lattice contains no replacements, such as kaolinite and the ideal montmorillonite structure (pyrophyllite), the sheets are bound together by van der Waal forces between the oxygen-hydroxyl and oxygen-oxygen sheets of the layer systems. As the oxygen-hydroxyl bond in kaolinite is a hydrogen bond, which is stronger than the oxygen-oxygen bond found in montmorillonite, this may explain why montmorillonite disperses more easily than kaolinite. It has already been mentioned that colloidal suspensions depend for their stability

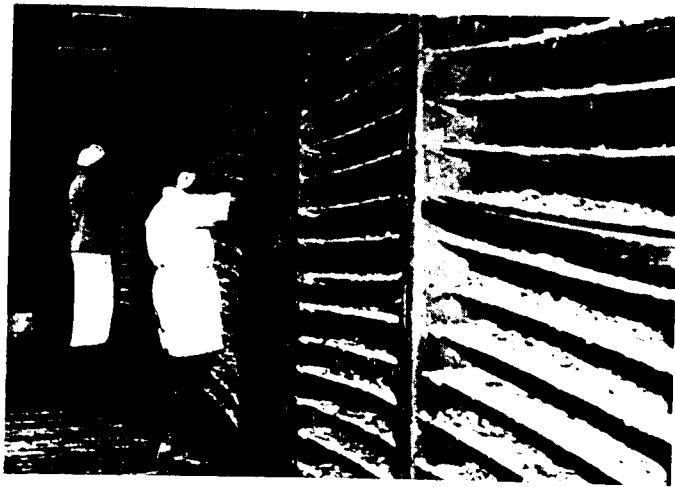
THE CHEMISTRY OF TEA



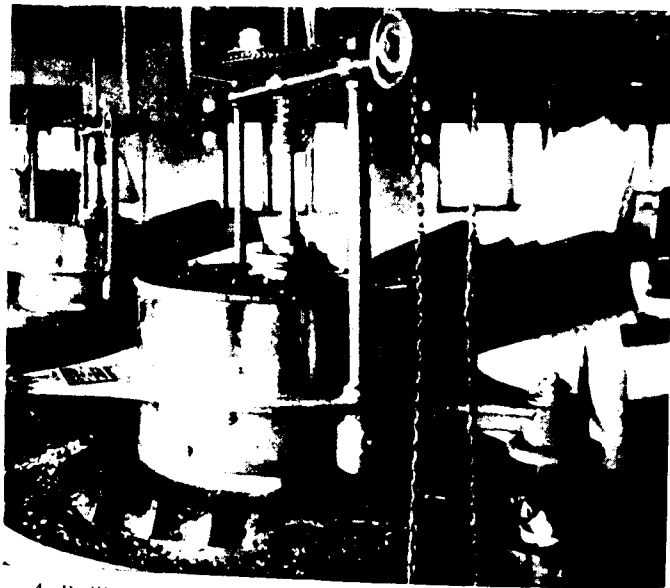
1. Old method of rolling leaf by manipulation with the hands and feet. (By courtesy of Davidson and Co. Ltd, Belfast.)



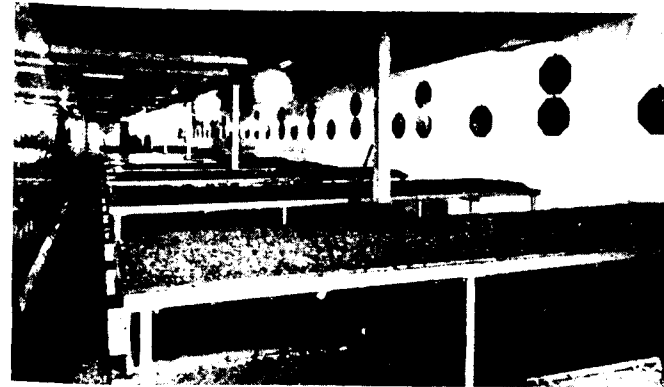
2. Old method of drying leaf on bamboo trays on the top of the waisted poey-long, which has a small charcoal fire at the foot. (By courtesy of Davidson and Co. Ltd, Belfast.)



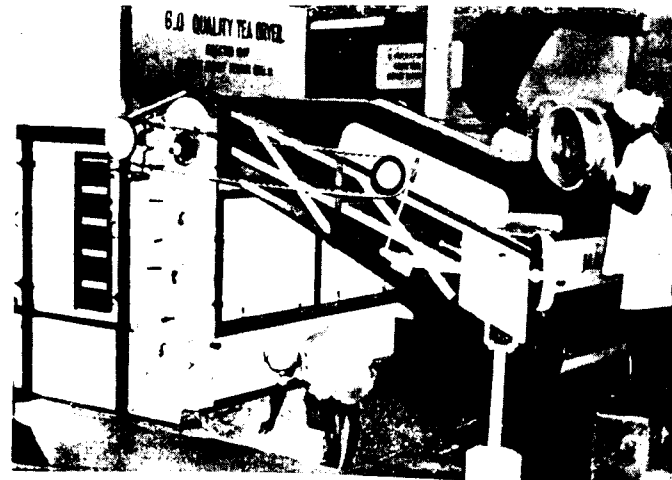
3. Withering leaf in Ceylon.



4. Rolling machine capable of handling 4,000 lb. of tea in a day.



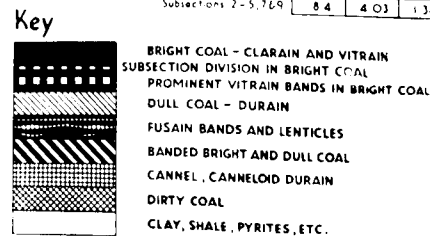
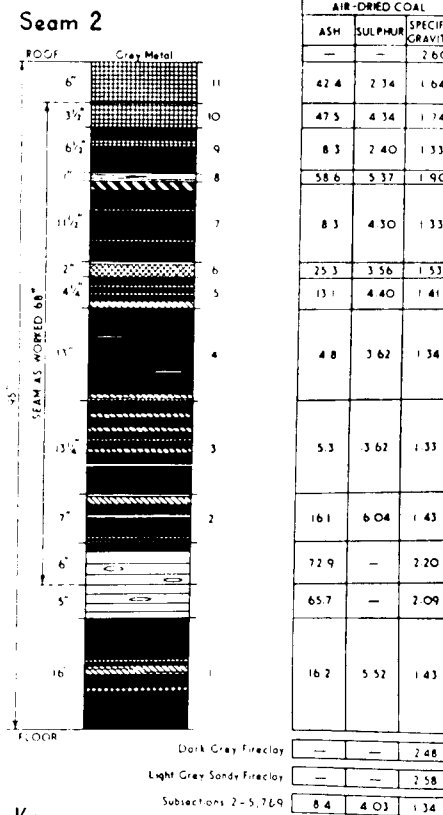
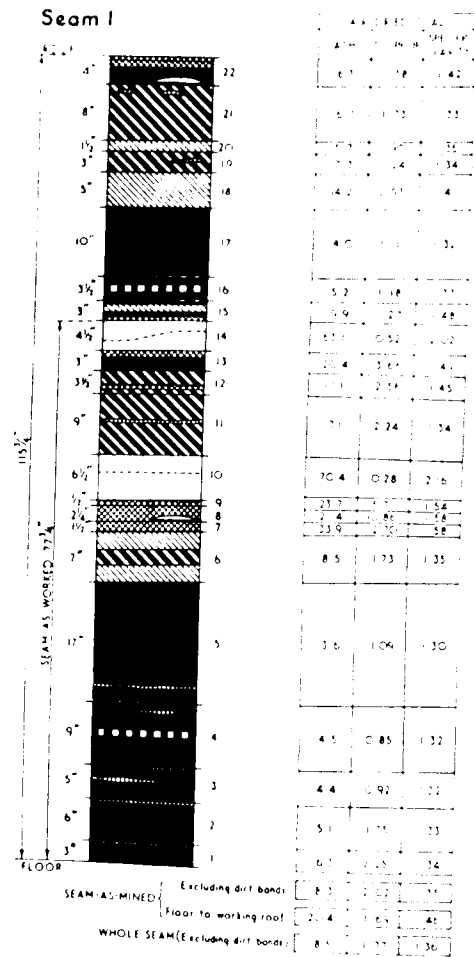
5. Fermenting space in an Indonesian tea factory.



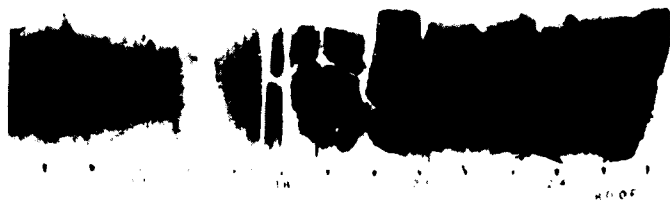
6. Tea dryer into which the fermented leaf is fed.

3-6. Modern practice.

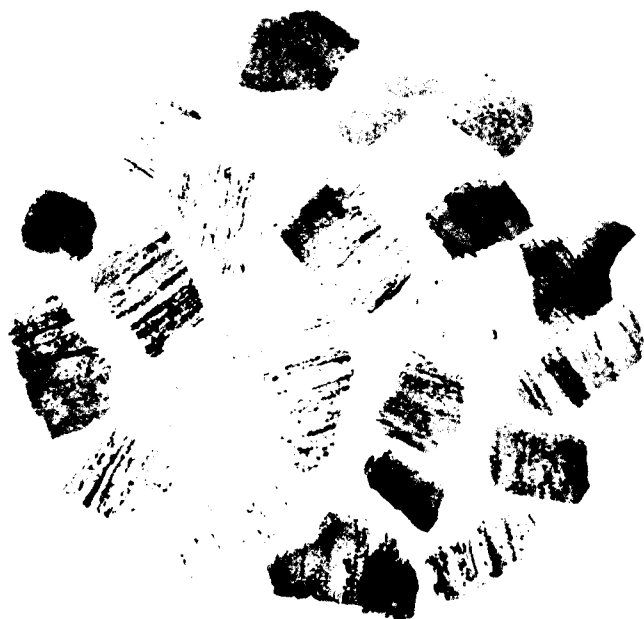
THE PART OF COAL THAT DOES NOT BURN



7 and 8. Sections of two typical coal seams illustrating the wide diversity of material found in them. They include bright and dull coal, bands of shale and clay, and show the varied ash-content of even apparently similar coals.



9. X-ray photograph of the top 14 inches of a seam in a Yorkshire coalfield, showing distribution of mineral matter in an apparently uniform thickness of coal. Root of seam is at right hand side.



10. X-ray photograph of thin sections of coal showing concentration of mineral matter, revealed as dark layers in the photograph. For laboratory examination it is possible to cut out these layers with a dentist's drill. (From J. B. Nelson, 'Assessment of the Mineral Species Associated with Coal', *B.C. U.R.A. Monthly Bulletin*, 1953, 17, 46.)



11. Photomicrograph of a 0.25 inch piece of Durham coal show that initially extraneous mineral matter has become part of the pl material of which the coal is composed. (Insets 7, 8, 9, and 11 from A. Grounds and A. M. Wandless, 'The Mineral Matter Coal etc.' in Institute of Fuel, *A Special Study of Ash and Clin in Industry*, 1952.)

SHIP RESISTANCE



12. General view of the Ship Tank at The National Physical Laboratory, Teddington, showing the towing carriage with a model under test. (By courtesy the Director, National Physical Laboratory.)

on the formation of a diffuse electrical double layer and that swelling and dispersion of clays is made much easier by any agent that increases the zeta potential of the clays. It has also been mentioned that in water clay particles acquire negative charges. In kaolins this entails the preferential adsorption of anions, because the particles themselves have no means of giving rise to such charges. These anions are usually hydroxyl ions, hence, as already mentioned, addition of alkalis or salts that have an alkaline reaction are good dispersants. For this reason such materials as sodium hydroxide, carbonate, silicate, phosphate, and tannate, all of which are alkaline, are used in dispersing clays.

The particles of montmorillonitic clays can become spontaneously charged by simple ionization of their exchange cations. In such instances the ability to swell and to disperse in water is closely related to the cation exchange capacity of the clay. A clay with high cation exchange capacity is obviously a clay whose lattice has a high negative charge owing to replacements in the lattice. This again may explain why montmorillonitic clays disperse more readily than kaolinitic ones. The exchange ions, especially if they are sodium ions, become hydrated and during this process they increase greatly in radius. This increase prisms the tiny particles apart and allows more water to penetrate, thus swelling the clay, an operation that is essential for complete dispersion. Clays carrying calcium ions as exchange ions do not swell to the same extent, but if a sodium salt of an anion capable of giving an insoluble calcium salt, e.g., sodium carbonate, is added to the dispersion phase, then replacement of calcium by sodium takes place and swelling occurs. It is of interest to note that the exchange reaction can be brought about in the 'dry' state by milling clay and sodium carbonate together, the water usually adsorbed on an apparently dry clay powder (which can amount to as much as 15% by weight of the clay) being apparently sufficient to promote the exchange reaction. However, a sodium clay prepared from a calcium clay or even from a hydrogen clay has never yet equalled the performance of a naturally occurring sodium clay,

although some come fairly close to doing so. This is probably due to particle size considerations.

Dispersions of clays in water, whether spontaneous or brought about by deflocculating agents such as those mentioned above, are very sensitive to the addition of electrolytes, and to changes of pH. Alteration of pH of the suspension towards neutrality, or the addition of small quantities of neutral salts, results in rapid flocculation and settling of the suspension. The quantity of neutral salt required to flocculate a given clay suspension decreases with increasing valency of the cation, in accordance with the rule of Schulze and Hardy. This rule states that an ion carrying a charge of opposite sign to that of a colloidal particle will bring about coagulation, and that the power to coagulate increases rapidly with the magnitude of the charge, e.g., $K^+ < Mg^{++} < Al^{+++}$. An added complication however is that the exchange cations also influence the coagulation mechanism. Clays having divalent exchange ions are more easily coagulated than those with monovalent exchange ions. This is because the zeta potential, arising from hydration of the ions, is already lower in divalent ions.

Rheological Properties

The rheological properties of clay dispersions are of particular importance in the ceramic and petroleum industries. Very dilute suspensions of clay obey Poiseuille's Law, but even moderately concentrated suspensions do not. Great influence is exerted on the properties of these suspensions by the state of aggregation of the clay, i.e. whether it is flocculated or peptized. For this reason deflocculants are added in ceramic practice to give fluid suspensions containing high concentrations of solid matter, thus ensuring that a minimum of water has to be removed. Certain clays suspended in solutions of alkali chloride of molar strength or greater will give gels that are thixotropic, i.e. gels that become fluid when stirred or agitated but set again when stirring is discontinued. This property is utilized when drilling through strata containing brine, when the clay mineral attapulgite is added to a drilling mud which would otherwise

be precipitated and rendered ineffective by the salt content of the brine.

INDUSTRIAL APPLICATIONS OF COLLOIDAL SILICATES

Clay minerals find very wide application in industry: perhaps the widest field of use is that of ceramics which utilizes a number of the different types, both two-layer and three-layer clays, in considerable quantities. The story of the use of clays in ceramics is a book in itself and the interested reader must look elsewhere for appropriate accounts.

The second largest application of the clay minerals is probably in oil refining. Clays are used in the refining of both mineral and edible oils, occasionally as crude clay of high adsorptive capacity, but much more frequently in the form of an 'activated' earth. Activated earths are prepared from three-layer clays, usually of the montmorillonite family, by heating them with acid. The length of heating and strength of acids varies according to the intended application of the activated earth, but it is generally about twelve hours in about 5N acid; the weight ratio of acid to clay is to some extent critical and depends on the nature of the clay. The effect of the acid is to dissolve out a proportion, about one third, of the central aluminium layer, thus making the clay crystallite porous and greatly increasing its surface. This increase in surface increases the ability of the clay to adsorb minor quantities of coloured impurities in oils and fats, thereby improving colour and, with edible oils, reducing the tendency to develop rancidity. For refining shale oils, attapulgite, activated by simple heating to drive off adsorbed water, has been mainly used in recent years.

Another important application of clays is in well-drilling fluids, commonly described as drilling muds. The usual method of drilling bore holes for oil and gas wells is by a rotary drill attached to the bottom of a drill pipe. The drilling mud is pumped down the drill pipe and up again through the space between the pipe and the wall of the borehole. The main function of this mud is to carry the debris formed by the drill up and out

of the borehole. If drilling is temporarily stopped, however, as it must be to attach further lengths of drill pipe, the mud must be capable of suspending the fragments until boring starts again. To support the debris the mud must be thixotropic, i.e., as explained above, it should form a viscous gel under static conditions but break down to a fluid of relatively low viscosity under the application of suitable shearing forces, in this example the rotation of the drill and drill pipe. A clay suitable for this purpose also possesses wall-building properties. These wall-building properties are evinced by the formation of an impervious filter cake on the wall of the borehole which prevents loss of mud into the formation being bored. This filter cake also strengthens the wall and reduces the incidence of *caving*, *heaving*, and *sloughing*. The best clays for use as drilling muds are the swelling types exemplified by Wyoming bentonites.

A further wide application of clays is as a bonding material in metal founding. Metals are usually cast in sand, and in order that the sand may retain the shape of the mould it is bonded by incorporating a small amount of clay which coats the grains of sand and bonds them together. This bonded mixture has sufficient plasticity to conform to a pattern and retain its shape after the pattern is removed. Clay-bearing, naturally occurring, sands, usually termed 'natural sands', have been used for centuries for casting metals, but they have a number of grave disadvantages that are eliminated by using pure silica sand and adding the necessary amount of clay. Chief among these disadvantages is the short 'life' of a natural sand, the clay burning out rapidly. This can be avoided by choosing a clay and sand that do not contain impurities of low refractoriness. Furthermore the plastic behaviour of the added clay can be altered and controlled at will – a very great technical improvement on the hit-and-miss control of natural sands. Clay of all types, swelling and non-swelling montmorillonitic, and kaolinitic clays are used in modern foundry practice. The foregoing three applications account for the major proportion of clays employed in industry.

Minor quantities of clay are used in the soap and cosmetic industries. Clay is also used for coating and 'filling' paper; it has

also been used to treat the effluent from paper manufacture. Thixotropic bentonite suspensions are used in the manufacture of adhesives and in rubber processing. Bentonite clays are also used as stabilizing agents in the manufacture of bituminous emulsions for road surfacing and roofing purposes.

A very recent application of clays has arisen from the observation that clays of high cation exchange capacity react with organic amine salts, and that the products have properties very different from the reactants. These clay-amine complexes actually shed water rather than disperse in it, and disperse in organic liquids to form clear firm gels. The degree to which they disperse in organic liquids is governed in a complicated manner by the chain length of the amine and the polarity of the organic dispersion phase. The most important application of these new clay compounds is their use to 'body' lubricating oils to form greases that have temperature-liquefaction properties superior to the usual greases prepared from metal soaps and oils. Another important application of these novel materials is in 'bodying' paint vehicles to give the paint improved thixotropy and spreading abilities. The new compounds are also being used in printer's ink.

It is certain that all the possible applications of these materials have not been fully investigated and a very wide future appears open for these clay-amine complexes.

CONCLUSION

We have seen that the colloidal silicate minerals, which are collected under the umbrella term clay, can be grouped broadly into four general classes, and that each class contains a number of related species. We have further seen that a basic structural unit of all these materials is a sheet of silica tetrahedra linked to other sheet structures comprising aluminium or magnesium atoms, or both, in octahedral co-ordination with oxygen atoms and hydroxyl groups. Amongst members of each series some of the atoms, e.g. silicon and aluminium, are interchangeable in the silica layer, and the octahedral atoms are replaceable by other atoms capable of octahedral co-ordination and possessing ionic

radii comparable to the atom being replaced. A major result of these replacements is an excess negative charge on the crystal lattice of these minerals which is balanced by external cations which are, themselves, interchangeable and so endow the mineral with a cation exchange capacity, and also to some extent govern the overall behaviour of the various mineral types. It has also been shown that the principal physical properties of these minerals are largely governed by the extremely small size of the crystallites and by their shapes.

The industrial applications of clays are very wide indeed and are largely decided by the utilization of the unique colloidal properties possessed by clay minerals.

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ACCLIMATIZATION IN INSECTS

KENNETH MELLANBY

COLD-BLOODED animals, and this includes all forms of animal life except birds and mammals, have body temperatures that fluctuate with the temperature of the environment. Their temperatures are often said to be the same as that of the air or water in which they live, but that is not the case, for a poikilotherm, as a so-called cold-blooded animal is called, is seldom if ever exactly as warm or as cold as its surroundings. Even an aquatic *Amoeba*, which is only a thousandth of an inch in length, produces some heat of metabolism, and is perhaps a millionth of a degree warmer than the water in which it swims. A terrestrial reptile exposed to the rays of the sun may have a body temperature many degrees above that of the air. Many cold-blooded animals living under dry conditions evaporate water from their bodies and are thus cooled considerably below the temperature of their surroundings. Nevertheless under ordinary circumstances most poikilothermous animals have body temperatures that fall when the environment becomes cooler, and rise when it becomes warmer, and, particularly in aquatic forms, the difference between body and environmental temperature is seldom more than a fraction of a degree. The smaller the animal the less is this difference; as insects are mostly small they therefore have internal body temperatures very near to those of air or water in which they live.

When we talk about the conditions to which an animal, particularly a small animal, is exposed, we must be careful to measure the correct conditions. In the past many workers have been content to take the ordinary meteorological data, giving the temperature and humidity of the air as recorded in the standard Stevenson Screen, and have assumed that these results represent conditions over a wide area. In fact they do not: within

a few square yards widely different conditions of temperature and humidity may exist, and by moving a short distance an animal may experience changes comparable to those shown by ordinary meteorological data for different continents. Thus among vegetation it is usually cooler and moister than over bare ground, and there is quite a steep gradient in the inch or so above a growing leaf. Even when the air outside is very dry, saturated conditions usually exist in shallow burrows in the soil. The upper surface of stones exposed to sunlight may be many degrees warmer than the shade temperatures measured in the Stevenson Screen, while the damp under-surface may be many degrees cooler. It is to these 'microclimates'* that insects are exposed; and these conditions affect their metabolism.

Even warm-blooded animals are affected by temperature changes, but the whole life of cold-blooded forms is controlled by the temperature of the environment. Their range of activity is restricted above and below by temperatures that produce first coma and finally death. It is roughly true to say that animals found in cold climates can tolerate colder conditions than those from the tropics, and, to a lesser extent, vice versa, but, as will be shown below, this is by no means always true. The narrowness of the temperature zone where life is possible is striking. Except for some resting stages whose physiology is imperfectly understood, insects are almost all killed when their tissues are subjected for only a few minutes to temperatures of 50°C (122°F); and in most cases a much lower temperature, say 40°C (104°F), cannot be tolerated for very long. Even a tropical insect like the tsetse fly, *Glossina palpalis*, cannot continue its

*Biologists frequently use the word 'microclimate' differently from meteorologists. They use it to refer to any situation where temperature and humidity are distinct, and will differentiate between such environments as a rat's burrow or the surface of a growing leaf. In the past meteorologists have tended to apply the term to much larger units, for instance the lower ten thousand feet of the atmosphere or the bottom of an alpine valley, but there is now a welcome tendency for them to devote more attention to the much smaller units of interest to biologists and to insects.

life indefinitely even at 30°C (86°F), because its reproductive cycle is upset by these conditions, and mayfly nymphs from cool moorland streams soon die when the temperature rises to only 20°C (68°F).

The position at the lower end of the temperature scale is more complicated. Heat coma occurs and is reversible only if the temperature is dropped rapidly within a few minutes. At moderately low temperatures (about 2°C (35°F) in the case of the cockroach, *Blatta orientalis*) insects may survive in chill coma for many weeks, and this is the normal way in which many arctic forms pass the winter. The majority of insects are killed when their tissues are frozen, though some species are not harmed by freezing. Most insects which in nature survive exposure to temperatures below freezing point do not freeze but, instead, their body fluid is supercooled, and can remain in this state for long periods. It should be remembered, moreover, that even in the Arctic the protective layer of snow prevents most insects from being exposed to anything like the low temperature of the outside air. Many species, particularly of tropical insects, are killed quite quickly by cold at temperatures that may still be some degrees above freezing point.

Chill coma is induced by temperatures that may be much higher than those that cause cold death. It is usually (as mentioned above) a reversible process. Although a period in chill coma may not harm an insect, it is clear that a species cannot survive unless the temperature rises for substantial periods above the point at which activity is prevented, so it seems probable that the position of the chill coma temperature is the most important single factor in determining geographical distribution.

It was previously believed that for each species of insect the position of the different temperatures at which, for instance, cold death, chill coma, or heat death occurred were as fixed and definite as the morphological characters used by the systematist. More recently it has been recognized that in insects, as in fishes and some other animals, these points are by no means fixed, but depend to a lesser extent on the conditions under which the

reaction' controlling the process; they have not been successful. We must admit that, though we may be able to foretell how a change of temperature will affect the behaviour and metabolism of an insect, we have little idea how the change is effected.

It has been shown that by acclimatization we may alter heat and cold death points, but here again the cause of death is not understood. We think that freezing in some instances causes death by damaging the cells, but we do not understand how death from cold without freezing is caused. We are equally ignorant of the cause of death from exposure to high temperatures. It is often suggested that the cause is coagulation of some protein, but there is no evidence to support this, for most forms of life are killed at 40°C (104°F), which is much below the coagulation temperature of the proteins concerned; in species accustomed to cool water which die at 20°C (68°F) there clearly must be some other reason for death.

It seems probable that in the types of acclimatization so far discussed a similar mechanism comes into play in the reactions to heat and to cold. There is, however, another mechanism about which we are a little better informed which is concerned with the prevention of death from actual freezing.

It has been stated above that many insects that die when their tissues freeze may survive severe and prolonged cooling below freezing point by being supercooled. This condition may continue for many weeks without damage. Considerable differences in the ability of individuals of the same species to withstand low temperatures by supercooling have been observed. At one time this was explained by saying that much of the water in resistant individuals was 'bound' by the proteins of the tissues, while the less resistant individuals had a higher proportion of easily frozen or 'free' water. This was supported by measurements of the freezing point of the insects, and by the fact that cold-resistant insects often contain a lower proportion of water in their bodies than cold-susceptible individuals. The difference would now appear to be more simply explained. If the cuticle of an insect exposed to temperatures much below freezing point is dry, supercooling usually occurs. If a spot of water is placed on

the cuticle, this freezes easily and seems to 'inoculate' the insect's body so that freezing of the tissues takes place. An insect that is somewhat desiccated, and has no fluid in its intestine, is thus less likely to be 'inoculated' and to freeze. Cold resistance may thus be achieved by keeping the cuticle dry.

The main conclusion that emerges from work on acclimatization is that insects, and most other cold-blooded animals, are even more dependent on environmental conditions than was previously realized. Instead of always reacting in the same way to the same climatic conditions, reaction differs according to the previous history of the individual insect. As its climatic history depends on the microclimatic conditions around it, it will be seen that this subject, and its practical implications, are such that much further work is still required before simple solutions of practical problems are likely to be discovered.

FURTHER READING

The best summary of work relating to this problem will be found in: Wigglesworth, V. B.: *Principles of Insect Physiology*. (Fifth edition with addenda) London, Methuen, 1955.

THE PART OF COAL THAT DOES NOT BURN

ISRAEL BERKOVITCH

In all coal there is an incombustible part, even if the proportion that does not burn is exaggerated by indignant users. This incombustible part is of some importance, usually because it produces undesirable effects, but occasionally because it is useful as a source of raw materials or has some particularly desirable properties.

WHY BOTHER ABOUT COAL?

To those who have not studied the figures, the announcement of the expansion of the British atomic energy programme may have given the impression that coal is declining in importance. But this is only relatively true. Although the proportion of the fuel-load taken by coal is decreasing, the absolute amount of coal required annually is likely to go on increasing for a further generation at least.

Probably the most impressive recent study of energy requirements in Britain is that by Dr. Daniel of the Ministry of Fuel and Power.¹ Dr. Daniel assumes a rate of growth of the national income of 3 per cent a year compound, and that for every 1 per cent increase in national output there will be an increase in fuel consumption of 0.7 per cent. This leads to an estimate that, after allowing for other contributory sources of energy, the demand for coal will rise from 230 million tons in 1954 to a peak of about 40 million tons in 1970. Only subsequently will the demand for coal be eased by 'the massive injection of nuclear power'. Although these figures are reckoned as a high estimate, they were used by Dr Daniel 'in order to be on the safe side', and the author follows the same course throughout this article.

On the basis of the above figures the total energy demand may

The Part of Coal that does not Burn

79

rise from 269 million tons of coal-equivalent in 1954, to 329 million tons equivalent in 1955, 397 in 1975, and 479 in 1985. By 1975 it is hoped that the current nuclear power programme will contribute the equivalent of 40 million tons of coal a year and that it will continue to expand. The other major energy contributor is oil which in 1954 supplied the equivalent of 38 million tons of coal. In future further small contributions may be made by expanded hydro-electric generating capacity and possibly by the underground gasification of coal.

These estimates of coal equivalents are based on the assumption that in most industries a ton of fuel oil will do the work of between 1.5 and 3 tons of coal. Taking into account the pattern of utilization, one ton of oil products is regarded as equal to, overall, 1.7 tons of coal. Electricity is expressed in tons of coal, on the basis that in 1954 a ton of coal yielded 1,650 units of electricity and that in thirty years' time this yield will increase to 2,300 units.

But in addition to its use as fuel, coal is also a chemical raw material yielding both organic products, and rare metals. Since we are constantly hearing alarming forecasts of the early depletion of our mineral resources it is well to give attention to a source of raw materials that has a couple of hundred years' reserve, at present rates of use, even if, as an ore it is only considered to be low-grade.

Thus research on coal retains its importance, and an increased effort is being devoted to it in order to discover more about the basic properties of coal, and to find what useful products can best be made from it. One facet of this research, which will probably grow in importance, is that on the mineral matter in the raw coal.

WHY BOTHER ABOUT THE PART THAT DOES NOT BURN?

The most important present-day use of coal is as a source of energy, so the most important property of coal is its combustibility. Yet the part that does not burn is by no means unimportant.

Let us start by examining the ash and dirt content of British

coal seams. Below I shall refer to the distinction between ash and mineral matter, but here it will be sufficient to consider ash and free dirt together as estimates of that part of the coal that does not burn.

In 1952 an authoritative paper on ash and clinker was presented at an Institute of Fuel symposium by Arthur Grounds and A. M. Wandless of the National Coal Board. In considering the following figures one must remember that, within a bed that is geologically recognized as a coal seam, there are many subdivisions including dirt bands. The ash figures given refer to the coal in the seam after the dirt bands have been removed by hand from a pillar sample of the seam. Grounds and Wandless reported that in 1950 about 85 per cent of the coal produced came from seams containing less than 7.5 per cent of ash. They pointed out that, as compared with other major coal-producing countries, Britain is probably favoured by having mainly clean coal. However, the proportions both of the free dirt in the seams and of the ash content of the clean coal within the seams is increasing. In 1938 about 56 per cent of the output came from seams containing no dirt bands, but in 1950 this figure fell to 42.5 per cent. Correspondingly the proportion coming from seams containing over 10 per cent of free dirt rose from 15 per cent in 1938 to 30 per cent in 1950, so that the average dirt content of the seams worked increased from 4.8 to 5.5 per cent.

This decline in the quality of the coal seams is likely to continue because the old coal-owners worked the better seams first. In addition, due to increased mechanization, more of the dirt will be loaded out, a trend that can only partially be offset by improved and extended coal-cleaning techniques.

This incombustible matter is mainly a bane although it has its assets: but, first, let us consider the bill of indictment.

MINERAL MATTER

The Bane

If you live in a town you cannot avoid inhaling some of the half-million tons of ash particles that are discharged into the air every year with the smoke produced by the incomplete

combustion of the coal substance itself. Thus the principal charge against mineral matter is that it is an offender against public health, and that it is the source of the material that pollutes buildings and fabrics. In addition, in the domestic grate it creates the ash that has to be cleared away by the householder. In industry the ash problem is particularly important. For example, every year the British Electricity Authority has to dispose of over five million tons of ash products. The mere magnitude of this task constitutes a design and planning problem, and furthermore, within any combustion plant design has to be modified to cope with increased ash. This involves what one boiler maker described as requiring 'an overall liberality of design to meet the efficiency and availability criteria with an elaboration of ancillary equipment'.

The first and obvious effect of ash on the direct performance of any combustion equipment is that it acts as a diluent so that for a given heat requirement a greater weight of the coal has to be fired than would be the case with a lower ash coal. This involves greater freight and handling charges per heat unit. There are, however, important secondary effects, both direct and indirect, which tend to cause reductions in efficiency. Direct effects arise from the trapping of unburnt carbon and carrying away of heat in the ash. Indirect effects include clinker formation, boiler deposits, and corrosion, all of which not only affect the thermal efficiency of the plant but also the availability of the heat and thus the operating and maintenance costs. The indictment can be further broken down by specifically mentioning particular harmful properties but it is not appropriate to develop this theme here though one important example may be cited.

A joint committee of the Central Electricity Authority and other interested bodies, known as the Boiler Availability Committee, has carried out a series of investigations on the fouling of water tube boilers by external deposits.² The commonest cause of this fouling is the bonding of fly ash that has been entrained in the gas stream and then trapped in a matrix of inorganic salts, volatilized from the coal, which forms a pasty surface on the tubes. There is a correlation between the severity of this trouble

and the chlorine content of the coals burned, and it has been found possible to use chlorine content as an indication of the easily volatilized sodium and potassium present. This criterion is so effective that blending coals to produce a mixed fuel of low chlorine content results in a great improvement in boiler availability. High ash content can also cause a reduction in efficiency of shell boilers of from 0.1 to 1.0 per cent for every 1 per cent of ash present.³ Similarly, workers on gas producers of the types used in the manufacture of town gas have found that development of new types of plant with increased output is hindered by difficulties associated with clinker formation. In the development of the coal-fired gas-turbine it has also been stated that the main difficulties to be overcome are those associated with the presence of ash so that, despite intensive development work, no coal-burning plant is yet in commercial operation. Ash in coke for blast furnaces is also a diluent and requires an addition of lime to flux it and form a slag. Above a moderate concentration, say 10 per cent, it causes such a marked increase in costs that to use it is quite uneconomic.

These harmful effects of ash are recognized by the National Coal Board in their technical price structure for industrial coals, where they permit a deduction from the price depending upon the ash-content to compensate for its effect on the combined thermal and economic efficiency of a coal. The Board also acknowledge this effect in their programme of expansion of coal preparation plant.

On the other hand the Board's Steam Generation and Combustion Engineer, Mr. Karthaus, is a strong advocate of facing the unpleasant fact that there will be increasing quantities of fines of high ash and moisture content. He advocates designing plant that can use high ash coals efficiently. At the conference of the Institute of Fuel referred to above he made a number of detailed design proposals for coping with this problem. Given sufficient engineering effort he considers that the use of high inert fuels will become economical for such users as collieries, electricity generation, and industry generally, a situation that augurs well for the future.

The asset

There is a small credit to be entered into the account. Fly-ash produced in boilers fired by pulverized fuel can be used in making building materials. In 1955 the Central Electricity Authority held a display of bricks, concrete, and lightweight aggregates made from this material. This ash even has some advantages over other sources of shales since the unburnt carbon in it contributes heat during the firing and results in a certain fuel economy. At stoker-fired power stations a large part of the coarse ash and clinker can be sold for ballast, road-making, or making breeze blocks. In addition the Coal Board is the largest brickmaker in Britain, using as raw material the shales associated with coal seams.

Finally, the metal germanium is now being produced on an appreciable scale from some flue dusts. No massive source of this element is known and in Britain flue dust from gas-works represents the major source. In these dusts it may be present in concentrations of up to 1 per cent by weight. Its main application is in the production of rectifiers and of triodes (transistors) which are used in compact robust electronic equipment. In the form of magnesium germanate it is being increasingly used for fluorescent tube coatings in which it gives an improved deep red colour.

The analytical complication

A knowledge of the mineral matter in coal is needed for accurate analysis of the organic part since until recently the two could not be separated.

Coal analyses may be worked out on a number of bases because the moisture content changes continually from the time the coal is cut. But apart from the complication introduced by variable moisture content, the interpretation of analyses is bedevilled by the problem of allowing for mineral matter. Unless allowance is made, it becomes impossible to assess trends or to interpret the properties of the organic matter of the coal. For example, an apparent shift in carbon content within one seam

between one point and another may not be due to a change in the coal substance but to local changes in mineral content. Thus fundamental studies on the coal substance cannot be made on the analytical figures reported on the basis of air-dried coal, which is the state in which the coal is normally analysed. The figures must be converted by the following formula :

$$\begin{array}{lcl} \text{Property} & = & \text{Property} \times \text{Factor} \\ \text{(coal substance basis)} & & \text{(air dried coal basis)} \\ \\ \text{Factor} & = & \frac{100}{100 - \text{moisture} - \text{mineral matter}} \\ & & \text{(air dried coal basis) (air dried coal basis)} \end{array}$$

In determining calorific value there is a further complication, because any pyrites in the coal is oxidized during determination of calorific value and contributes heat. So an allowance has to be made for it in the numerator of this fraction when calculating the calorific value of the true coal substance.

The formula, of course, begs one important question, which is that of determining the quantity of mineral matter. To this point I shall return later.

An allied field is that of permitting coals to be accurately classified. This is no mere academic exercise since classification of coal is closely linked with the selection of suitable coals for particular uses. The most important specific needs so far are for carbonization and gasification, but another field calling for a precise selection is for combustion in closed stoves.

In classifying coal the so-called 'volatile matter' content is an essential datum. This is an easily determined property derived from measuring the loss of weight of a sample of coal heated under standard conditions. It was formerly thought to be a purely empirical figure which was helpful when deciding how to use the coal. Recently, however, it has been found to be related by equations of fair accuracy to fundamental properties of the coal, such as the carbon, hydrogen, and oxygen content. However, in determining this property, and before applying the above formula for converting the figure to the basis of pure

coal substance, allowance must be made for the gas evolved from the mineral matter.

How did it get there?

It is useful to start considering how the mineral matter got into coal by looking at some examples of coal seams. Insets 7 and 8 show section diagrams of coal seams. The great diversity of material is evident. The seam may include layers of coal of any 'ash content', the coal itself may be bright, dull and hard, or dull and friable; there may be clay or shale bands, or 'intergrown' carbonaceous shale. White streaks, golden streaks, or lenticles may also occur.

An X-radiograph can usefully supplement what can be seen by the unaided eye. Mineral matter has a higher absorbing power than coal, therefore X-rays reveal the distribution of the dispersed mineral matter within the coal. Inset 9 is the result of work along these lines in the Leeds Coal Survey Laboratory.⁴ It shows how it is possible to sub-divide an apparently uniform thickness of coal into sub-sections of differing mineral matter content. The method may also prove practicable using γ -rays from a radioactive source. Now how did these 'impurities' get there?

Coal is the converted remains of plants that grew in tropical swamp forests roughly between 210 and 285 million years ago. The forest swamp condition persisted for many centuries, and as the trees and giant ferns died, they formed a thick sludge of decaying vegetable matter. There were places where the land sank, with the result that the forests were overwhelmed with water, and rivers poured layers of sand and mud over the area. From time to time sinking ceased, the water became shallow, new swamp forests grew up, and the cycle was repeated many times over. These vegetable residues were subjected to temperature and pressure and were converted, first by bacteria and then probably by purely chemical action through various stages into our present-day coal seams. This gives a clue to the various sources of non-organic matter in coal. They are as follows:

- a. All plants contain a small amount of mineral constituents:

most of this is likely to have remained in the coal although a little may have leached out.

b. While it was still exposed, or was just beginning to be covered, silt was doubtless blown and washed into the decaying organic matter.

c. The waters of the swamps, or those that later poured on to the overlain decaying matter, had dissolved salts in them, some of which may have remained and ultimately been incorporated into the coal.

d. At all subsequent stages, up to the time of exposure in the seam, waters almost certainly trickled through from overlying strata and may have contributed both dissolved and suspended matter.

Attempts have been made to distinguish between so-called 'inherent' mineral matter, which is chemically combined with the organic part of the coal, and 'extraneous' or 'adventitious' mineral matter, which is the physically admixed remainder. However, the remarkable photomicrograph shown in Inset 11 indicates the difficulty of making this kind of distinction since minerals that started as extraneous to the plant material can become intimately interwoven and may partly have entered into the structure of the plant. And even the purely physically admixed material can occur in particles down to 2μ in diameter, so that for most purposes it is inseparable from the coal.

Many properties of coal vary so regularly over the area of a seam that they can be mapped. This is true, for example, of the caking properties or the volatile matter, corrected to a coal substance basis. But the mineral matter usually varies so irregularly that such mapping is impossible. Correspondingly, extracted coal varies so much with regard to mineral content that a whole series of investigations has had to be made to provide a basis for getting to the laboratory a fair and honest sample of any bulk quantity before determining its 'ash content'.

How has it been investigated and what has been found?

The simple way in which most of us discover the existence of incombustible matter in coal is by seeing free dirt in the coal

delivered to our homes, or grey, white, or golden streaks inter-banded within the coal. But even if all of this material is carefully separated coal after burning leaves a residue. This ash is the end product of a number of chemical reactions within the finely disseminated and combined mineral matter. Many attempts have been made to relate it to the starting material. Usually this has been based on chemical analysis of the residue plus chemical analysis of the mineral matter in the original coal.

This indirect approach was necessary on account of the difficulties of physical or chemical separation. The above discussion and illustrations have shown how finely the organic and non-organic matter is interspersed making complete physical separation of the ash-forming constituents virtually impossible. There is also no way of dissolving out the organic coal substance to leave unaffected mineral matter. Nevertheless, attempts at separation have been made by acid attack of the chlorides, carbonates, or sulphides, by cautious low temperature (380°C) oxidation of the organic coal substance, by float and sink methods, by froth flotation, and by magnetic or electrostatic methods. One rather attractive technique tried in the B.C.U.R.A. laboratories is to make an X-radiograph of a thin section and magnify the print.⁹ An example is shown in Inset 10. The mineral matter clearly shows up as the darker parts of the picture. Guided by it, the operator can cut out the mineral matter from the matrix of coal by the careful use of a dentist's drill. None of these methods is wholly successful except perhaps the last one which is, however, time-consuming.

A promising laboratory technique for separation of most of the physically mixed mineral matter is to ball mill coal with paraffin and water using case-hardened steel balls in a stainless steel pot.⁶ The method was based on the expectation that, after the coal has been ground to a size where it can separate into its mineral and organic constituents, the former would tend to disperse into the water and the latter into the paraffin. This was indeed so and from coals of ash-content ranging from 2.4 to 9.8 per cent, coal-substance-fractions of ash-content from 1 to 3 per cent, and mineral-matter-fractions containing about 0.5

to 5 per cent of organic carbon can be obtained. Using the latter fractions the most soundly based determinations that have yet been reported of the combined water in finely disseminated shales have been made.

In addition, last year, a German scientist, Dr. Radmacher, proposed a direct method of determining the quantity of mineral matter in coal which appears to be giving results very similar to those from more elaborate chemical methods.⁷ In this direct method, carbonates and chlorides are removed with hydrochloric acid, and the silicates by hydrofluoric acid. Thus, after allowing for pyrites, the residue which is not attacked by either of these reagents, and any other residual ash material, enables an estimate of the mineral matter removed to be made directly. The main possibilities of error are that from time to time other minerals may occur which are not attacked by these reagents, and certain coals may be attacked. The scope of this method is therefore being very closely checked at present and we must await result before reaching a final decision.

The method most widely used in Britain for determining mineral matter is based on the usual chemical composition of the major constituents and their normal behaviour in ashing. The usual minerals in coal are as follows:

- a. The larger part of the mineral matter is complex aluminosilicate material, belonging either to the shale group of minerals or the kaolin group. Examples of the former are muscovite, illite, and montmorillonite, while a characteristic example of the latter is kaolinite.
- b. Next come minerals of the sulphide group usually known as pyrites, FeS_2 , but also including the orthorhombic form, marcasite. They account for about half the sulphur in coal, most of the remainder being organically combined.
- c. In still smaller concentration there is the carbonate group, consisting of carbonates of calcium, iron, magnesium, and manganese, generally known as calcite, ankerite, and siderite.
- d. There are probably also chloride minerals including the potassium and sodium compounds, sylvine and halite; the presence of these particular minerals is however only inferred, and

recent work has lead to the conclusion that a fresh approach is now necessary to the problem of chlorine in coal.

e. In addition there are large numbers of other minerals usually present in much smaller concentration. Noteworthy among these is quartz, whose presence may have an important bearing on lung disease in miners.

In general, ultimate chemical analysis for all the constituents of the mineral matter would be a lengthy process, and even when completed might be difficult to interpret. For example, an ultimate analysis will not distinguish between a clay consisting of half kaolinite and half quartz, and another consisting entirely of montmorillonite. Furthermore, in most cases identification of the individual minerals is not needed, but only the total concentration. Hence the so-called 'rational analysis' method is widely used, in which a limited number of distinctive constituents or chemical groups are determined, and the results multiplied by factors to give the proportion of the mineral group present. Using this approach, and taking into account the mineral species in coal and their chemical reactions during ashing, it is possible to derive a formula, with considerable chemical justification which permits a determination of the concentration of mineral matter in coal from six chemical determinations. As proposed in 1936 by members of the Fuel Research Station,⁸ the formula is as follows:

$$m = 1.09A + 0.5S_{\text{pyr}} + 0.8\text{CO}_2 - 1.1\text{SO}_3(\text{ash}) + \text{SO}_3(\text{coal}) + 0.5\text{Cl}$$

where m = mineral matter, A = ash, S_{pyr} = pyritic sulphur.

For some parts of the country, slight variants of this formula are required. In it the largest term is that derived from the ash so the coefficient applied to the ash is of key importance. This coefficient is intended to compensate for the loss of chemically combined water in the shales and clays of the mineral matter known as the water of constitution. Following the work on separation referred to above, a survey of the values of water of constitution for shales associated with coals covering the full range of rank in all coalfields of Great Britain has been carried out.⁶ These results show that the factor applied to the ash should

be a little higher, and 1.13 has been suggested to allow for evolution of water of constitution during ashing.

An interesting development of this work has been the discovery by workers at the B.C.U.R.A. laboratories that an adequate estimate can be made by using a simpler formula based only on the concentration in the coal of ash, total S, and CO₂. Tested on 1,413 coals, this simpler formula gave results showing an average difference from the full formula of only 0.002, and 95 per cent of the difference figures were within 0.5.*

The minerals as such have also been investigated by techniques of optical microscopy, X-ray diffraction, differential thermal analysis, infra-red spectroscopy, ion exchange and so on, but the results are too detailed for discussion here. Trace elements are being actively investigated and are dealt with below.

One other line of work may, however, be mentioned. Pure substances, on heating, melt sharply at well-defined temperatures, which are characteristic for the substance. Mixed substances often have a softening range between a state that is recognizably solid and that when it is clearly liquid. Most ashes are in this latter category. Softening properties are involved in liability to clinker, but they are becoming of greater significance now that more plant is being designed in which ash is removed in the molten state. The two main types of furnace using this method are the slag-tap furnace, and the cyclone burner. The main physical properties involved are the temperature of softening, the rate of decrease of viscosity with temperature, and the freezing temperature. Naturally, work is in progress to try to relate some of these properties with chemical composition. A number of equations and graphs have now been proposed to enable workers to assess from the chemical composition of the ash whether a coal will be suitable for use in one or other of these slagging furnaces.

Getting Rid of It

In industry, incombustible matter in coal is removed mainly by washing, a process based on separation by differential flotation. Pure coal has a specific gravity of about 1.3, although this

varies with a number of other properties of the coal. Shale minerals have specific gravities exceeding 2; pyrites is much denser with a specific gravity around 5. It is evident that, in principle, a liquid of specific gravity between 1.3 and 2, or a water column operated to give a similar effect, should allow the clear separation of the coal from the rest. In practice the complex seam structure illustrated in Inset 8 does not necessarily break down cleanly into coal and dirt, so that particles of all specific gravities from less than 1.30 to greater than 1.80 are encountered. This is illustrated in the table below (after Grounds and Wandless).

Specific-Gravity Fractionation of Run-of-Mine Coal

Sp. gr.	Run-of-mine coal at Colliery X			
	Seam A		Seam B	
	Yield, per cent	Ash, per cent	Yield, per cent	Ash, per cent
<1.30	86.2	1.5	6.7	3.0
1.30-1.35	4.1	6.5	31.1	7.2
1.35-1.50	2.6	13.8	22.1	16.8
1.50-1.60	0.7	24.9	3.9	35.5
1.60-1.80	3.0	51.9	11.4	47.2
>1.80	3.4	73.3	24.8	70.8
	100.0	6.1	100.0	30.5

Consequently, there are often 'middlings' in a coal-washing process, but if these 'middlings' are crushed to a smaller particle size the new smaller particles tend to be more clearly differentiated in their specific gravities so that a sharper separation is possible.

Separation is also affected by the dispersibility of the clays and shales in water. Here again there is a wide range of characteristics, some shales showing scarcely any tendency to break down, while others form a complete slime. When shales do break down they can cause great difficulties in the operation of a plant so that attempts are being made to develop tests to assess

the liability of shales to break down in water. Other tests are being designed to assess ease of filtration of the resultant suspension, with and without the use of flocculating agents, for those plants in which water is precious and has to be recirculated. One objective of this work is to develop economical means of controlling liability to breakdown.

The Ore

It was mentioned above that there has been increasing interest in recent years in the germanium in coal. However, an almost unique range of trace elements commonly exists in coal and consequently the mineral is being examined for various elements of interest. In some cases extraction processes have been developed. The Chemical Research Laboratory at Teddington played a major part in the early stages of the germanium extraction process; they have also devised a process for extracting gallium. Gallium melts below 30°C, so in warmer climates it is a liquid. In addition it has marked electrical anisotropy with a conductivity that is seven times as great along one axis as along another axis at right angles to it. Along with other low melting metals it has been considered by the U.S. Atomic Energy Commission as a possible medium for transferring heat from nuclear reactors.

In discussing the elements that have been considered at various times and places to occur in sufficient concentration to be of interest, it is difficult to avoid giving the appearance of a catalogue. For example, L. Horton and K. V. Aubrey of the Fuel Research Station published in 1950 concentrations of the following elements in vitrains from the Barnsley Seam.¹⁰ The elements sought were as follows: antimony, beryllium, boron, chromium, cobalt, copper, gallium, germanium, lead, manganese, molybdenum, nickel, phosphorus, tin, titanium, vanadium, zinc, zirconium.

By separating the coal into fractions of different specific gravity they showed that the majority of these eighteen elements were associated predominantly with the organic matter. The relative abundance differed in some respect, however, from

those of modern living plants, and the authors suggested that the differences arose from modifications that took place later than the life of the vegetation that was transformed into the coal. The proportions of the elements in the original coal were all of the order of a few parts per million or per hundred thousand, although in the ash this was increased up to hundredths or tenths of one per cent.

A similar survey was carried out for the West Virginia Geological Survey covering 38 elements from 16 coal seams representative of the major coal-producing area in West Virginia. Its authors studied variation of concentration throughout the height of the seam to see if there was any evidence of enrichment in any particular portion of the seam. In Britain this has been found in the case of germanium, which tends to be found near the roof and floor of seams.

At the present time the National Coal Board is initiating surveys of the minor elements in coal employing the following general strategy. It is taken as self-evident that in order to gain useful knowledge of coal mineral matter it is necessary to know the distribution of the constituents that occur in concentrations between 0.5 and 50 per cent in ash, calculated as oxide. In this category are almost always silicon, aluminium, iron, calcium, magnesium, the alkali metals, and probably titanium. Occasionally, zinc, vanadium, chromium, and nickel are also present, but except for vanadium it is not very likely that any of these elements would be considered for extraction from this source, although a knowledge of their distribution is necessary as fundamental information.

In addition there are many elements of special interest because of their value, toxicity, corrosive or other special properties. Examples include fluorine, a non-metal that corrodes both metals and siliceous material like firebrick; mercury in coal has caused corrosion in gas-making plants; boron almost certainly plays a role in the formation of boiler deposits; zirconium is an element of growing importance for producing alloys with special high-grade properties. One must also mention phosphorus whose presence has long been determined in routine

analysis, particularly in laboratories dealing with coking coals; this non-metal, largely contributed by the mineral fluorapatite, causes embrittlement of iron and so is an undesirable constituent in coke. Consequently, in coals intended for making metallurgical coke for the manufacture of pig-iron to be converted into steel by the acid process, it is usually specified that the phosphorus content should not exceed a figure of the order of 0.01 per cent.

In addition to some 24 such elements modern spectrographic analysis makes it economically possible to add a further 14 elements that occur in detectable amounts in coal. This programme is in its very early stages but it is reasonable to expect that within a couple of years results of an extensive survey of the distribution of all these elements in British coal seams will be available. This should prove a great addition to our knowledge of the seams and may well prove of major industrial importance.

It has to be recognized, however, that enrichment of a particular element can occur in various ways during the use of the coal for some other purpose. Ash is richer in most metals than is the original coal: mercury in exceptional cases has been found in elemental form in the main gas offtake at gasworks.

The significance of trace elements may be far removed from the initial concentration in the seam. For example, when there is suspicion that drainage from dumps of ash is poisoning pastures or rivers it may be necessary to consider first the chemical changes in the production of the ash, and then the by-products of second stage action such as leaching by rainwater or surface waters. Thus a survey of the elements in a coal seam may only be the beginning of the story.

CONCLUSION

Increasing attention to technical efficiency in the use of coal means that more of its properties have to be taken into account when selecting coal for a particular application than was formerly so. This trend will continue even when the coal is used only as fuel, and the longer term perspective of using the coal for chemical processing will further accentuate the tendency.

It will be evident that the full utilization of Britain's most

valuable mineral deposit demands careful attention to the part of the coal that does not burn as well as to the more obvious claims of the combustible part.

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SHIP RESISTANCE

P. G. MORGAN

THE use of models to find the resistance to motion of a ship probably owes its origin to the experimental work of Newton, Euler, and Bernoulli, all of whom investigated the fluid resistance of flat and curved plates and of geometric bodies. The first experiments with ship models were carried out by Beaufoy between 1793 and 1798 in the Greenland Dock at Deptford, and he was also the first to experiment with flat plates with the specific intention of measuring frictional resistance. His results, and those of succeeding experimenters, were of little value, however, as they all failed to predict the true ship resistance from model tests.

About the middle of the nineteenth century the general lack of scientific knowledge in naval architecture, particularly in the fields of the strength, stability, and propulsion of ships, led to the setting up of a committee to report on existing knowledge of these subjects. The report of this committee, published in 1869, recommended the performance of experiments on ships to determine their resistance and rolling characteristics, emphasizing that these were aspects of ship design concerning which reliable information was most urgently needed. One member of this committee, William Froude, while agreeing with the desirability of trials on full-scale ships, considered that reliable information could be obtained from model tests. He had been led to this view by the results of his own tests, carried out in the river Dart, on geometrically similar models. The results were imperfect in some respects but were considered by Froude to confirm the law of comparison, a law that now bears his name. Briefly, the resistance of a ship is determined from that of its model in proportion to the cube of the linear dimensions at the corresponding speed. The latter is proportional to the square root of

Ship Resistance

97

the linear dimensions. This law of comparison laid the foundation for a scientific basis of ship design.

From a dimensional analysis of the factors involved in the resistance of a body moving in a fluid with a free surface,

$$R = \rho L^2 V^2 \phi \left\{ \frac{gL}{V^2}, \frac{\rho VL}{\mu} \right\}$$

where R = Resistance to motion.

ρ = Density of the fluid.

L = Length of the body.

V = Speed of the body.

g = Acceleration due to gravity.

μ = Viscosity of the fluid.

ϕ indicates that the resistance to motion is some unknown function of gL/V^2 and $\rho VL/\mu$. These two variables are the Froude number gL/V^2 , which governs the wave-making resistance, and the Reynolds number $\rho VL/\mu$ associated with the shearing stresses in the laminae of fluid surrounding the body, i.e., the frictional resistance.

The equation shows that for complete dynamic similarity between model and ship,

$$\left(\frac{V^2}{Lg} \right)_{\text{model}} = \left(\frac{V^2}{Lg} \right)_{\text{ship}}$$

and simultaneously

$$\left(\frac{\rho VL}{\mu} \right)_{\text{model}} = \left(\frac{\rho VL}{\mu} \right)_{\text{ship}}$$

It is impossible to satisfy these two conditions simultaneously, and failure to appreciate this division of the resistance components was the reason for the lack of success of the earlier experimenters.

If we restrict our discussion to a ship at sea, the total resistance is made up of (a) skin friction resistance; (b) wave-making resistance; (c) eddy-making resistance; (d) air resistance; (e) rough weather resistance. Each of these components depends

upon physical conditions that differ from those of the other components.

Rough weather resistance is of course of considerable interest: it is bound up with the problem of ship motion, but it is customary to concentrate, at least in the early stages of design, on the resistance of the hull form in calm water.

Air resistance is a very variable quantity and cannot easily be estimated. Experiments indicate that it seldom amounts to more than 3 per cent of the total resistance, and it is usually neglected in the analysis. An allowance is usually made for it later.

For a well designed hull, eddy-making resistance is small and it is usual to combine it with the wave-making resistance to form the residuary resistance, so that our analysis deals with the two components, skin friction resistance and residuary resistance.

If it is now assumed that, with the data available for the frictional resistance of flat plates, the frictional resistance of the hull can be accurately estimated, it only remains for the residuary resistance to be measured. Unfortunately, there is no way of measuring residuary resistance independently of frictional resistance, but, if the total model resistance can be measured,

Total model resistance = Frictional resistance +

Residuary resistance, and the frictional resistance calculated, the remainder can be attributed to residuary resistance. The residuary resistance of the ship at the speed corresponding to that of the model test is then directly proportional to the residuary resistance of the model in the ratio of the displacements: thus the frictional resistance of the ship's hull can be calculated and the total resistance of the ship obtained. The principle is illustrated by the scheme given in Figure 1.

The aim of the early experimenters was to find some simple law by which the total model-resistance could be scaled directly to the total ship-resistance, but any law founded on this basis was, of course, foredoomed to failure, and it did in fact occasionally produce some expensive mistakes. It must be remembered that at that time little was known of the physical laws governing

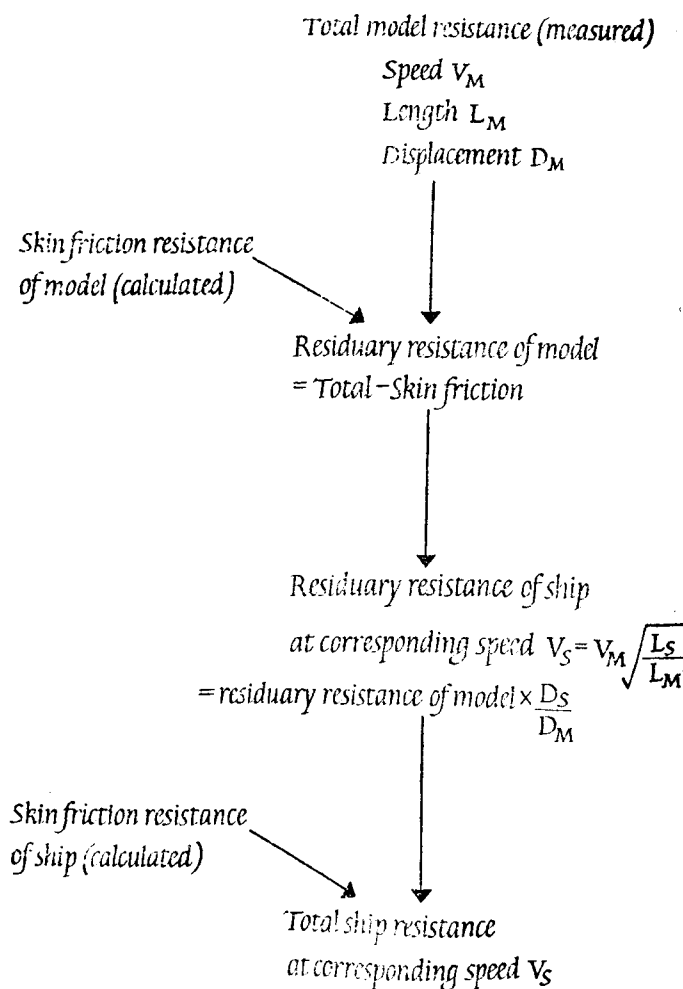


Fig. 1. Estimation of ship resistance.

frictional or wave-making resistance, and it is not surprising therefore that Froude's investigations and analysis differed from that described above. He found by experiment that the wave patterns were identical as far as could be measured at corresponding speeds, i.e., speeds $\propto (\text{length})^{1/2}$. From his measurements, Froude found that curves of Resistance Displacement to a base of $V/L^{1/2}$ had similar characteristics and, since the wave patterns and shapes of the resistance curves agreed so closely, the failure of the curves to be identical must be due to some other contributory factor; this could only be because frictional resistance did not follow the law of comparison. He thus formulated the basis on which the whole field of model experiment and prediction of ship performance is based.

THE EXPERIMENTAL TANK

Initially, Froude's proposals met with sharp criticism, but the Admiralty decided to support his idea and in 1872 an experimental tank was completed at Torquay under Froude's direction and in accordance with his plans. The original Torquay establishment was of a temporary nature and after 14 years it was replaced by a tank on the present site at the Admiralty Experiment Works, Haslar, i.e., in 1887. Ship model research is still carried out in this tank. The importance of model tests was rapidly established and today there are at least fifty such tanks in existence throughout the world. They range from the comparatively small laboratory channel to the modern long high-speed tank. The increase in size has culminated in the tank at Carderock, U.S.A., of length 2,775 ft, breadth 51 ft, and depth 22 ft, in which models up to 32 ft. in length and 5 tons in weight can be tested at speeds up to 60 knots.

The chief feature of an experimental tank is a long covered waterway in which models are towed and their resistance measured. The waterway is spanned by a travelling carriage equipped with a precision dynamometer for measuring model resistance over a range of speeds; it is essential for the carriage and model to have a uniform speed and in most large tanks this can be maintained to within a tolerance of 0.25 per cent. The

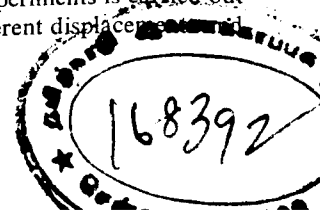
ends of the tank are sloped to form beaches which break up the waves created by the model, and wave traps are sometimes fitted to reduce reflection of the waves from the sides of the tank. In addition, most modern tanks are fitted at one end with a wave-generating device to allow experiments to be carried out on the resistance of the model in waves. A ship tank at the National Physical Laboratory, Teddington, with a model being towed by the travelling carriage, is illustrated in Inset 12.

The models used in the tank are generally between 12 ft and 20 ft in length, the actual size being governed by the speed, the limitations of the dynamometer, and the strength of the model. It is normal practice to use the largest practicable model because one wants to obtain as high a Reynolds number as possible, since at low Reynolds numbers the flow around the model is part laminar and part turbulent, making it difficult to get consistent results under these conditions. Models are usually made of paraffin wax to which a hardening constituent has been added; they take the form of shells, upwards of an inch thick when finished, and are accurately shaped to guidance grooves cut in the wax by special machines. Wax models have the advantage that they can easily be modified as experiment indicates to be necessary, but models are sometimes made of wood either for strength purposes, e.g., in seaworthiness tests, or to avoid trouble from distortion when the temperature is high.

In small tanks it is not possible, nor is it necessary, to use an elaborate travelling carriage. The model is towed by a wire tensioned by a hanging weight; it is thus towed by a constant force and the resulting speed measured, in contrast to the constant speed used along with the measurement of force in large tanks.

In a normal test the model is fitted with the necessary arrangements for connecting it to the dynamometer. It is then weighed and ballasted to the correct displacement and trim, i.e., fore and aft inclination. A full programme of experiments is carried out over a specified range of speeds, at different displacements and trims.

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SKIN FRICTION

Froude's classic experiments on the frictional resistance of flat plates were carried out on planks, both smooth and coated, up to 50 ft in length and towed at speeds up to 650 ft/min. Curves were plotted of resistance R to a base of speed V from which Froude deduced that the curves followed a law of the form

$$R = FSV^n$$

where S is the wetted surface area, and F and n depend upon the nature and length of the surface. The work was continued by his son, R. E. Froude, who re-analysed the previous results and incorporated his own to show that $n = 1.825$; he tabulated values of F which have since been standardized. If Froude's formula is converted into non-dimensional form, $R = FSV^{1.825}$ becomes

$$\frac{R}{\frac{1}{2}\rho SV^2} = 2FV^{-0.175} = 2F \left(\frac{\rho VL}{\mu} \right)^{-0.175} \therefore \left(\frac{\mu}{\rho L} \right)^{-0.175}$$

so that the resistance coefficient is not a simple function of Reynolds number but has a separate curve for each length. Some of these curves are shown in Figure 2 from which it is seen that the resistance coefficient increases with increase in length. Froude's formula permits of the prediction of ship skin friction resistance without any correction being necessary for surface roughness, suitable allowance for roughness being included in the F values. These F values are based on results obtained from towing tests carried out by Froude on H.M.S. *Greyhound* in 1874.

Froude's results have been criticized on the grounds that the extrapolation of the resistance coefficients of relatively short planks to values applicable to ship lengths is unsound; moreover, the increase of the resistance coefficient with length, which can be regarded as a roughness allowance, appears to be opposite to that obtained from modern experiments, which suggest that the roughness allowance decreases with length.

In recent years the basic skin friction data have received much attention and it is now generally agreed that a skin friction formulation more in line with modern boundary layer theory is

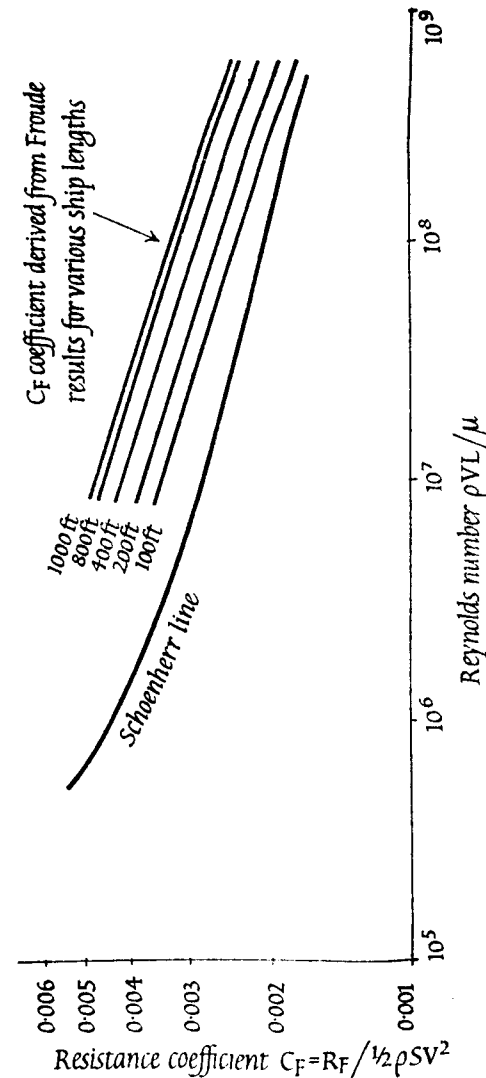


Fig. 2. Curves of skin friction resistance.

essential. Schoenherr proposed a general skin friction line deduced from previous plank experiments and wind tunnel work which was in effect a mean line through all the values previously obtained. The Schoenherr formula is

$$\frac{0.242}{\sqrt{C_F}} = \log_{10} (\text{Reynolds No.} \times C_F)$$

$$\text{where } C_F = \frac{R}{\frac{1}{2} \rho S V^2}$$

This has a theoretical basis in the laws of Prandtl and Schlichting. It gives for the first time a theoretical basis for the extrapolation of the results of models to full scale. Difficulties in applying the method are considerable, however. The resistance is known to vary considerably with surface roughness, and in order to allow for this in the skin friction resistance assessment, Schoenherr's curve has been proposed as the basis with a constant addition to the resistance coefficient to allow for surface roughness.

We thus have the two alternatives: the empirical Froude procedure, in which confidence has been established by long and successful experience, and the Schoenherr method with a theoretical basis but requiring a correction for surface roughness. Recently, the British Shipbuilding Research Association carried out full-scale trials on a small ship, the *Lucy Ashton*. Propulsion was by four jet engines whose thrust could be accurately measured, thereby establishing the ship resistance within fine limits. This method overcame the difficulties previously encountered on full-scale resistance tests of measuring a tow-line pull and at the same time avoiding interference from the wake of the towing vessel. The main purpose of the trials was to check the predictions from a series of different sized models of the ship: the evidence obtained so far endorses the Froude procedure in principle, and at higher speeds very largely in magnitude also, though not completely at all speeds.

It has long been recognized that resistance depends upon the condition of the hull surface, and the *Lucy Ashton* trials confirmed this. The skin friction resistance with exposed plate edges

and butts, as in a riveted ship, was found to be 5 per cent greater than with the edges faired to simulate to some extent a welded ship. Moreover, when the ship was coated with a very smooth aluminium paint in lieu of red oxide paint, resistance was reduced by a further 5 per cent. This advantage of a smooth hull is also brought home by evidence being accumulated from the results of trials of modern ships of welded construction. It has also been suggested that a further advance is possible if the hull surface could be well bonded with plastic, but the problem is much more complex than the production of a smooth surface. For example, precautions must be taken to avoid corrosion of the steel hull due to chemical and galvanic action which in sea water can be severe. Moreover, the hull soon becomes coated with marine growth. The nature of this growth depends upon the conditions of service of the ship, but as a general average it has been said that skin friction resistance due to fouling increases at the rate of approximately one-eighth per cent per diem. This is large, since it means, for example, that friction resistance will be increased by about 50 per cent when the ship is one year out of dock.

Tests on models at low Reynolds numbers show an erratic tendency, and this may be traced to the persistence of laminar flow over part of the model. The flow past the model is thus part laminar and part turbulent, while the flow around the ship is almost completely turbulent. The flow in model tests is to some extent unstable, and this accounts for the difficulty in obtaining consistent results when repeating model experiments. Much thought has been given to methods of avoiding transitional flow on models: the immediate solution would appear to be testing at sufficiently high Reynolds numbers for the flow around the model to be completely turbulent, though this is not always possible on tests of small models. Other methods of inducing turbulence may be divided into (a) methods in which turbulence is produced in the water ahead of the model, and (b) methods in which the laminar boundary layer close to the bow of the model is broken up by roughening the surface or by fitting a turbulence stimulator. The second method is probably the better approach,

and the most favoured method is to use a trip wire close to the wax surface at the forward end of the model.

WAVE-MAKING RESISTANCE

Model experiments indicate that skin friction accounts for as much as 80 per cent of the total resistance of many merchant ships and about 50 per cent in fast warships and liners. If a ship is long and narrow skin friction resistance increases owing to the greater wetted surface of the hull, and the residuary resistance is comparatively small. On the other hand, if the ship is short, and full, the wetted area, and therefore the skin friction resistance, is reduced, but, at higher speeds, at which wave-making is important, the residuary resistance will be large. A broad ship may well have less resistance than a narrow one, and this early discovery from ship model research led to an increase in safety of ships.

Optimum proportions and shape can be clarified by model experiments but, in deciding on the shape of a specific design compromise must frequently be accepted. To quote one example, a warship must be propelled economically at cruising speed in the interests of greater endurance, but it must also be possible to obtain the highest attainable speed, and the requirements of hull shape for cruising and full speed are often conflicting.

The wave system accompanying a moving pressure point may be examined mathematically and shown to be made up of two systems, a transverse and a diverging set of waves. As a first approximation a ship form may be regarded as equivalent to two pressure points, one near the bow and the other near the stern; we would expect the wave system pattern around the ship to consist of two sets of transverse waves and two sets of divergent waves. This conclusion has been completely justified by observations on both models and ships, as is illustrated in Figure 3.

The work absorbed by the wave-making resistance is equal to the energy contained in the wave system left behind the ship, and we shall now consider the characteristics of the wave systems for a ship moving forward at uniform speed.

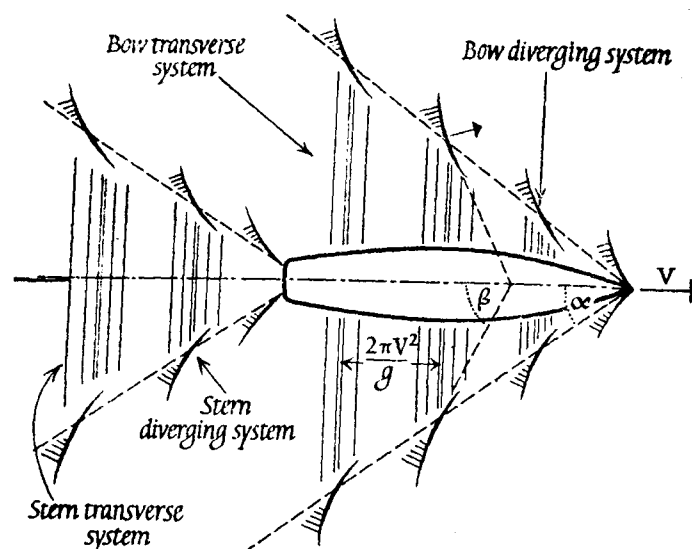


Fig. 3. Diagram of the wave system round a ship.

The bow diverging system consists of two groups of waves, one to port and one to starboard trailing away diagonally *en echelon*, with the line of maximum height of crests making a constant angle α with the middle line. The wave crests subtend an angle $\beta = 2\alpha$ with the middle line, with each wave advancing perpendicular to the crest line. The waves have substantially the same properties as trochoidal waves in deep water, but the whole of the energy in the diverging wave system is lost; the hull form must therefore be selected to give the least possible diverging wave system. The diverging wave system from the stern is similar to the bow system but is not so pronounced.

For the transverse systems, the bow transverse system is made up of a series of waves contained within the bow diverging system with crest lines perpendicular to the middle line and of wave length $2\pi V^2/g$. The wave height diminishes progressively

aft, since the energy contained in the wave is constant and its breadth increases as the diverging waves spread.

A similar system is associated with the stern of the ship. If there is a great length of parallel middle body separating the bow and the stern, the transverse waves from the bow will have practically disappeared before reaching the stern, and the stern system can be observed. With normal ship forms at working speeds the separation of the bow and stern is insufficient and the two transverse wave systems interact with one another. If a trough of the bow system coincides with a crest of the stern system they tend to cancel each other out and reduce the disturbance left behind the ship, thus reducing the resistance. On the other hand, if two crests coincide the wave system is accentuated and the resistance increased. From Figure 4 it is seen that the bow system starts with a crest and the stern system with a trough, so that the interference between the two systems varies with the speed of the ship or the $V/L^{1/2}$ value. The relation is governed by the approximate formula $V/L^{1/2} = 1.8/n$ where n is an integer, odd for a hump in the resistance curve and even for a hollow. For speeds below $V/L^{1/2} = 1$ the humps and hollows are very close to one another and are almost indistinguishable. The most marked hump is for $n = 1$, and at speeds greater than this no further interference between bow and stern systems can occur; such speeds are generally so high that abnormally powerful and compact machinery would be needed for a large ship to bridge the hump speed of, say, about 70 knots.

Over the years considerable research has been devoted to the determination of a methodical series of model hulls systematically varied in proportions and shape. The results of the first series of such tests were published by Froude as long ago as 1878, and the methodical series have since covered a very wide range, with variations of length, beam, draught, displacement, and details of the shape of the waterlines and hull sections each receiving attention. The basic information obtained is invaluable to the designer in deciding the shape of a hull, but, even so, to obtain the utmost efficiency, it is necessary to arrange for tests on the model of the specific ship. Attention must also be paid to

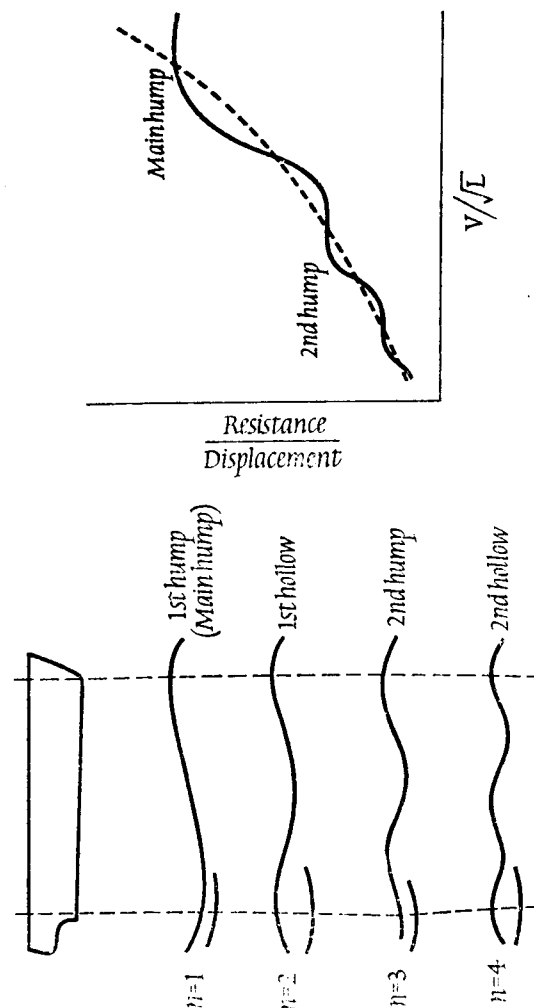


Fig. 4. Interference of wave systems and typical resistance curves.

hull appendages, bilge-keels, rudders, supports to propeller shafts, etc., all of which are sources of resistance which must be minimized.

So far most of our knowledge of wave-making resistance has been gained from tank experiments, but considerable progress has recently been made with methods of calculating wave resistance, by representing the ship by a series of pressure points, or hydrodynamical sources and sinks.

FUTURE DEVELOPMENTS

Whatever future developments in propulsion may occur, the resistance to motion of a ship on the surface of the water will be caused by skin friction and wave-making, and it is in the reduction of either or both of these that progress will be made.

Smoother hulls can be expected with an attractive reduction in skin friction resistance, although progress will largely be determined by shipyard practice and economics. The possibility of the hull surface being made so smooth that the flow regime becomes laminar instead of turbulent should not be overlooked. In either case the skin friction resistance will then be very small, but it will be necessary to devise means of avoiding imperfections due to marine growth or corrosion. All service openings would have to be arranged aft, otherwise turbulence would be stimulated. If these idealistic requirements are realized, economy of propulsion at cruising speeds should be revolutionized. The maximum speed of a submerged submarine, whose resistance depends entirely on skin friction, would be greatly increased, but the increase in speed of a surface ship would be more limited on account of the rapid growth of a wave-making resistance (Figure 5).

At very high speeds the resistance curve shows that when a ship of appropriate design reaches a speed past the main hump the ship rises in the water and the resistance decreases. This action is amplified in the planing hull or hydrofoil, but the principle has so far only been applied to comparatively small craft with correspondingly low main hump speeds. It is in this direction that progress must be expected.

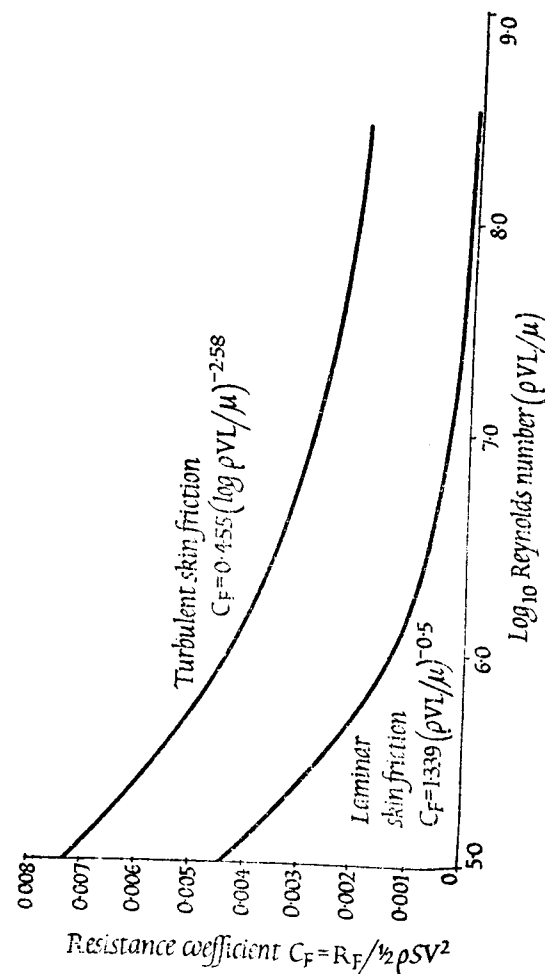


Fig. 5. Skin friction: resistance for laminar and turbulent flow.

In experimental tank work, emphasis is now being placed on the development of the best hull shape for seagoing conditions rather than as previously for calm water.

Summing up, it would appear that future progress is more likely to be on the lines of more economical propulsion, i.e., less power for a given speed, rather than in a great increase in ship speed. Any development, however, must be bound up with the production of more powerful and compact propelling machinery and advances in propulsive efficiency.

RESEARCH REPORT

A. W. HASLETT

HONEYBEES AND PRAWNS

IN worker honeybees the development of the ovaries is inhibited. So also is it in prawns, though not accompanied by the specialized compulsion of life in a colony. In prawns there is first a continuing inhibition – up to the reversal of sex from male to female, which is part of their life cycle – and later, a seasonal regression of the ovaries. Different as are the conditions, inhibition of the development of the ovary in these species has lately been related through the combined researches of C. G. Butler, Head of the Bee Department, Rothamsted Experimental Station, Harpenden, and D. B. Carlisle, of the Marine Biological Laboratory, Plymouth. Together, they have shown that the inhibitory substances which affect worker bees and prawns are chemically similar so far as knowledge of them goes, and that each can act on the other species. And Butler, from his own work, has shown that the inhibitory substance of honeybees inhibits also the development of ovaries in worker ants under experimental conditions. Butler and Carlisle suggest, therefore, that 'these two substances are the same or related compounds, possibly steroids, and that they occur in a number of arthropods'.

The indications from Butler's earlier experiments were that a substance, 'queen substance', is produced by queen honeybees; that a relatively small number of worker bees, the 'household bees', obtain 'queen substance' directly by licking the body of the queen; and that it is then shared round the colony in the same way that sugary liquids collected by bees have been shown in 'tracer' experiments to be shared. The published evidence up to this point is illustrated by an experiment on the rearing of

queenless bees. They were given a protein-rich diet, to which were added the contents of the honey-stomachs of worker bees. For one group of queenless bees, workers were used which had lately licked the bodies of their queens; for a second group of queenless bees, workers were used who had not been near their queens for several days. The ovaries of queenless bees in the first group were significantly less developed than those of the second group, which had received less 'queen substance'.

Sex-reversal in prawns has been known since 1912. The following summary of what happens is from a paper by Carlisle - interpretation (so far as it comes in) being based on his own recent researches:

The young are born chiefly in the spring. Testicular development has an early start, and, by next January, when the animal is 9 months old, the testis is fully formed and the animal is a functional male about 25 millimetres long. For the next twelve months it remains as such and gradually grows larger, the ovarian inhibiting hormone functioning all the time. Towards mid-winter, while the testis is still fully functional, the ovary begins to develop from the mere rudiment that it has been up to now - the ovarian inhibiting hormone has ceased its action. In about April, when the animal is about 40 millimetres long, the critical moult takes place at which the animal reverses sex [the moult at which it sheds the male external characters and assumes the female aspect]. By June or July, the ovary is fully developed, and the prawn may lay eggs. About August, the ovarian inhibitor comes into play again, and the ovary undergoes involution. The testis all this time has hardly diminished at all, and from now on it decreases slowly in activity and size during the next twelve months - animals after this have no trace of testis. During autumn the ovary is gradually decreasing in size under the influence of the ovarian inhibitor, but about mid-winter there is a cessation of its production and the ovary begins to grow again. . . . The next year is a repeat of this, ending most probably in the animal's death at the end of its fifth year of life at a length of about 64 millimetres.

Sex reversal in the prawn thus begins as a change in its physiology and internal anatomy, and, when this has gone far enough, the external and functional changes which complete the transformation follow at the next opportunity. Only one sexual

inhibitory hormone need therefore be postulated. Such a hormone is found in the eyestalks of prawns; it is stored in their sinus glands. Removal of the eyestalks from young prawns whose ovaries have not yet developed increases both the rate of growth of the ovaries and the rate of sex-reversal; conversely, injection of eyestalk extracts into prawns whose eyestalks have been removed restores the inhibitory effect.

A complication is that there are also present in the eyestalk two further hormones which produce different effects; one of them inhibits moulting, and the other accelerates it. There seem to be good arguments for thinking that the ovary-inhibiting hormone is independent of both. On any basis, the hormone which accelerates moulting could not contribute to the inhibition of sex reversal; for it is on moulting that the external change is completed. In the case of the hormone which inhibits moulting, there is a discrepancy in time of action, to which Carlisle has called attention; when the ovary is growing most quickly (in January), moulting is least. The ovary-inhibiting hormone, he concludes, is most likely a distinct substance.

The sequence of earlier research was complicated, and involved a number of workers. Among them were J. B. Panouse, in France, who first suggested that there is an ovary-inhibiting hormone in the eyestalks, and P. F. R. Dohrn, working at the Naples Zoological Station, where Carlisle, too, has done most of his work. It was Dohrn who pointed out that, as sex reversal did not take place at any particular size, age, or moult, it was probably controlled in part by a hormone.

The most recent discovery, made jointly by Butler and Carlisle, is that the 'queen substance' of honeybees inhibits the development of ovaries in prawns; and, the other way about, that ovary-inhibiting hormone taken from the sinus glands of prawns is inhibitory also in bees. For experiments of the first kind, 'queen substance' from a single mated queen was extracted with alcohol; and 36 female prawns, at a time of year when their ovaries are regressed, were divided into three groups. Those in the first group were given no treatment, and the weight of their

ovaries after a week averaged 4.90 milligrammes. Prawns in the second group had their eyestalks severed, and were given injections of a control emulsion which did not contain 'queen substance'; the average weight of their ovaries after the same interval was 17.67 milligrammes. This represented the usual release of growth after removal of the prawn inhibitor. Prawns in the third group had also had their eyestalks severed, but had been given injections containing 'queen substance'. The weight of their ovaries averaged 6.56 milligrammes; in these prawns the bee inhibitor was almost, but not quite, as effective at the dosage used as prawn inhibitor.

In the reciprocal experiment, ovary-inhibiting hormone was extracted from its store in the sinus glands of female prawns, and was then dispersed in syrup and given to newly emerged bees in a pollen-candy mixture. A control group, also of newly emerged bees, was given the same treatment but without the inhibitory hormone. Nineteen days later, the ovaries of seven out of every eight bees in the control group had developed; the ovaries of those that had received the inhibitor were about equally divided – half developed, and half not; in the presence of a queen none would have developed. Between honeybee and prawn, there is thus a marked, but not necessarily a perfect, reciprocity; the hormone of either works in the other.

Chemical evidence is slight so far, but concordant: both substances are 'stable to heat and to acids, but less so to alkalis, and are soluble in acetone and alcohol'. The conclusion that they are 'the same or related compounds' is thus based mainly on their effects in the two animals; that they are 'possibly steroids' is an inference from other sex hormones, the chemistry of which is known.

Butler, C. G. *Report of the Rothamsted Experimental Station for 1954*, p. 133, and abstract of Publication No. 173 (p. 232). Harpenden, 1955.

Carlisle, D. B. *Pubblicazioni della Stazione Zoologica di Napoli*, 1953, **24**, 355.

Carlisle, D. B., and Butler, C. G. *Nature*, 1956, **177**, 277.

SOLAR FLARE

A solar flare began at about 3.30 a.m. (G.M.T.) on 23 February and produced effects on the earth which were unusual in several respects. The visual flare was seen at Kodaikanal Observatory India, and in Tokyo. It was close to the limb of the sun. The position of a flare, as seen from the earth, is relevant to many of the effects which it produces. As well as the visual flare, and a simultaneous outburst of ultra-violet radiation and also of radio waves, there are often delayed effects caused by the arrival of high-speed particles from the sun; and on a very few occasions – only five so far, including the February flare – there has been an increase in the arrival on the earth of particles of very much higher energy, those of cosmic radiation. Since in each case most of the particles in question are protons, there may be no hard-and-fast division between one effect and the other. Particles recognized as cosmic radiation are observed as such because of their exceptionally great energy*; those which produce the 'delayed effects' after a flare are brought to notice because of the great numbers in which they must reach the earth. It is possible, therefore, that there may also be particles of intermediate energy which do not qualify, in either respect, to attract attention.

The particles which produce 'delayed effects' reach the earth after an interval from the time of the flare which, on the average, is about 26 hours. Because of the magnetic field of the earth, and because the particles are electrically charged, they are concentrated predominantly in polar regions. Their arrival in the ionosphere causes magnetic disturbances, displays of aurora, and interruptions of radio communications on routes crossing the Arctic and Antarctic. Evidence that the particles in this group are protons comes from observations on aurora. As a rule, these delayed effects are produced only when the flare is within about 45° from the centre of the sun's disc – that is, when the flare is roughly directed at the earth. The February flare,

*See, for example, the article by Dr E. P. George in *Science News* 27 (1953).

though near the edge of the sun's disc, was followed none the less by delayed effects. One result was an unnecessary period of anxiety for the safety of the British submarine *Acheron*, which at the time was between Greenland and Iceland. *Acheron*, when attempting to make a 'check' radio call to her base in Scotland at 10 a.m. on the day following the flare, was unable to make contact.

The second unusual feature about the flare was the increase in cosmic radiation which followed it within minutes. This increase was markedly bigger than the biggest previously recorded – on 19 November 1947 – although it seems unlikely that any entirely direct comparison will be possible. At the University of Chicago, where routine counts of cosmic radiation are made, there was an increase of 20-fold in the number of neutrons at ground level; the neutron component of cosmic radiation is the result of disintegrations produced in the atoms of the air by the impact of the primary protons. At the high-altitude observatory at Climax, Colorado, the increase was greater; and records obtained during high-altitude balloon ascents showed an increase of several hundred-fold. So large an increase is of interest not only as an isolated occurrence. The greater the maximum increase, the more surprising on general grounds is the absence of much more numerous occasions when a comparatively small increase is observed. The discrepancy has suggested to T. Gold, of the Royal Greenwich Observatory, Herstmonceux, the existence of some form of threshold for the emission of cosmic radiation particles from the sun – or, more probably, as he thinks, for their escape from its near neighbourhood. On this view, there must be enough particles to produce sufficient modification in the magnetic field of the sun to permit their own escape; otherwise there will be no contribution from the sun to the number of cosmic-radiation particles reaching the earth.

CHINESE CLOCKWORK

A mechanical 'missing link' between the water-clocks of Babylonia and Greece, whose time-keeping depended on the rate of flow of water, and the European clock with its movement con-

trolled by an escapement has been brought to light through the study of Chinese texts, of which a preliminary account has been given by J. Needham, Wang Ling, and D. J. Price, working together in Cambridge. The use of astronomical time-keeping devices by the Chinese has been known from literary references and a few fragmentary remains. What has now been discovered is that they combined the principle of the water-clock with a form of escapement based on the weighbridge. The key text is an account written by Su Sung in A.D. 1090; and in the light of this a tradition of design based on these two principles has been traced back at least to A.D. 725. Earlier devices, built at dates between A.D. 130 and A.D. 590, are thought also to have included an escapement. But this is not certain.

The astronomical clock described in Su Sung's 'New Design for a (Mechanized) Armillary (Sphere) and (Celestial) Globe' was large and complicated. He gave enough detail for working drawings of it to be prepared. The driving force was supplied by the flow of water or mercury into a series of containers or scoops attached to a wheel, which was thus rotated (the scoop wheel). On this, a system of mechanical control of movement was superimposed. It included a weighbridge which prevented the fall of each scoop until full, a check on the rotation of the wheel at another point, and a device which prevented recoil. The driving system included gearwheels, shafts, and, in later models, chain drives. Among other problems, that of securing rotation about an axis inclined to the driving shaft had been solved. The fluid-flow system included three reservoirs, at successively lower heights, and the water or mercury for twenty-four years' running was raised by mechanical means to the top reservoir.

In sum, the interval between the falling of one scoop and the next was controlled by the rate of flow of the water or mercury, and the course of movement between falls by the check and anti-recoil arrangements. It is in this sense that the design was a 'missing link'. It included the idea and the realization of an escapement, but this did not provide the main control of time-keeping. For the rest, the arrangements for the control of water flow had been carefully thought out; the escapement was nearer

to the European anchor escapement of the late seventeenth century than to the European fourteenth-century type and the design as a whole shows that Chinese astronomical clocks, planetary models, rotating star maps, and the like, though meant rather for demonstration than for accurate time-keeping, were 'the earliest complex scientific machines'.

Needham, J., Ling, W., and Price, D. J. *Nature*, 1956, 177, 600.

AFRICAN RECORD OF LAVA FLOW

A note on a geologically recent lava flow in East Africa, published lately by the Geological Survey, Tanganyika, has a claim to more general interest from the way in which evidence of the date of the flow has been obtained. The principal source is 'a local historian, one Andulile Kajigiri, a headman from Lusanje Village, on the north side of Kiejo'. His account, based on information passed down through three generations, is as follows:

The eruption was predicted a year before it happened by a prophet, Kipenya Nkunguruka, who said it would commence at about 7 o'clock in the morning. The first sign of activity was a long plume of whitish smoke seen at 10 o'clock in the morning. By about noon this had reached cloud-like proportions and blotted out the sun. The people were much afraid and began to pray to their gods. Rumbling and thunder-like sounds also began at noon and went on until about 8 o'clock at night. When night came they saw fire and red-hot ash coming out of Sarabwe and Fiteko. They waited until midnight and, as nothing had happened by then, went to bed for the night. Shortly afterwards, at about 1-2 a.m., the lava came down the valley, engulfing villages whose people were still asleep. Those on the higher ground saw the red glow of the lava spreading below them and smoke rising from it. When morning came the lava was still smoking and was quite soft. It kept moving for two days, slowing up and finally stopping on the third day. Smoke, fire, and cinders continued to be emitted from the cones - Sarabwe was active for the first day only, but Fiteko continued for three days - with waning activity. People would not cross over the lava flow for about 16 months afterwards.

Sarabwe and Fiteko are two cones, about half a mile apart, in the group of which Rungwe is the major central volcano.

D. A. Harkin, the author of the report, had concluded from geological evidence that the flow from these cones represents the most recent activity in the district. Whereas other rocks in the district are covered with pumice tufts from the more recent Rungwe eruption, those of the Sarabwe-Fiteko flow are not. An approximate dating of the flow was made possible by the fact that Andulile Kajigiri had sufficient record of his ancestry, and of the tradition embodied in his account, for it to be asserted that the original narrator was one Mwambapa, that the flow took place when he was a young man of about 25, and that this must have been about A.D. 1800. As Mr Harkin points out, Mwambapa's account 'might well apply to a present-day eruption'. For those familiar with African customs, it should perhaps be added that the times given have been translated from African usage to European.

Harkin, D. A. *The Sarabwe Lava Flow, Kiejo, Rungwe District*. Geological Survey, Dodoma, Tanganyika.

STRUCTURE OF BIOLOGICALLY ACTIVE MOLECULES

I am indebted to a correspondent for the following note: 'The work of C. H. Li and his colleagues of the University of California on the structure of ACTH, the adrenocorticotrophic hormone (mentioned in 'Research Report' in *Science News* 38) while it was the first determination of the structure of the hormone from sheep, followed the earlier determination of the structure of pig ACTH by workers of the American Cyanamid Company. Its chief interest is that it allows comparison of the same hormone from two different species. The Californian formula* differs from that of the Cyanamid workers† only in having two amino-acid residues in place of two others; a minute but distinct difference in the polypeptide chain of 39 amino-acid residues. The difference is that there are alanine and serine residues at loci 31 and 32 in place of leucine and alanine in pig ACTH. There is still some disagreement on one other part of the

*Li et al.: *Nature*, 1955, 176, 687.

†Bell: *Journal of the American Chemical Society*, 1954, 76, 5565.

chain; on its central portion no successful results were published before Bell's note in 1954. The structures of large portions near the end of the chain had previously been discovered at the Armour Laboratories, Chicago (for pig ACTH) and at the University of California (for sheep ACTH). Workers in these laboratories have now studied the whole molecule and their most recent formulae differ both from each other and from a correction recently made by the Cyanamid workers to their original formula. Since more than one form of ACTH can be extracted from the pituitaries of one species, comparisons between the structural formulae suggested by different groups of workers may be complicated by more than the species differences.

Part of the interest of the work of Sanger and his colleagues at Cambridge (mentioned in the same 'Research Report') was that it allowed comparison of the structures of hormones with the same biological activity which, however, came from different mammalian species. The insulins of pig, sheep, and ox are so similar in their physico-chemical properties that, once mixed, they cannot at present be separated. This is not surprising in view of the very small difference in the complex molecule made up of 51 amino-acid residues, with its system of cross-linking between chains which is common to all three species. The only portion of the sequence where a difference has now been found is:

threonine-serine-isoleucine	(pig)
alanine-serine-valine	(ox)
alanine-glycine-valine	(sheep)

The only other case where such a comparison was possible before was that of the hormones of the posterior lobe of the pituitary gland: oxytocin (milk-ejection hormone) and vasopressin (anti-diuretic hormone). These substances, whose structures have been confirmed by synthesis by V. du Vigneaud and his colleagues at New York, are peptides each made up of 9 amino-acid residues. They have the same structure apart from two of the amino-acids; and, while oxytocins from pig and ox are the same, vasopressin from pig and ox contains lysine and arginine respectively at the same place on the chain.

SOME BOOKS RECEIVED

ATOM HARVEST by Leonard Bertin (London: Secker and Warburg, 1955), pp. 253, 20s.

For the past four years Leonard Bertin has been the science correspondent of the *Daily Telegraph*. Based on what are described as facilities never before enjoyed by anyone outside a government department he has produced a book that is a rare mixture of the authoritative and the human.

Much of it is a carefully documented history of our own time: the perplexities that faced the atomic scientists (they weren't so-called in the thirties); the realization of Lise Meitner and Otto Frisch that nuclear fission was a reality; the setting up of the 'Directorate of Tube Alloys'; the far from smooth course of our collaboration with the Americans during the war; and, with the horrors of Hiroshima and Nagasaki fresh in our minds, the slamming of the door to peacetime collaboration with the passing of the McMahon Act.

Then follows the fantastic story of Britain's post-war nuclear energy development, dotted with names that will be as nostalgic to future generations as are those of Watt and Stephenson, the Rocket and Rainhill, to ours.

And tucked away everywhere are engaging human details: asparagus in the Cockcrofts' garden; Hinton as the antique collector; Penny paying £450 excess luggage for the collection of scientific 'junk' collected from the Japanese atomic explosions and brought back to Britain by Clipper.

But enough has been said to indicate that *Atom Harvest* is a valuable documentary of our time.

THE NUMBERS OF MAN AND OF ANIMALS edited by J. B. Cragg and N. W. Pirie (Edinburgh and London: Oliver and Boyd, for the Institute of Biology, 1955), pp. 152, 15s.

The proceedings of a symposium held in the autumn of 1954 by the Institute of Biology. The aim of the meeting was to bring together specialists in many different subjects who, however, had a common

interest in the numbers of men and of animals. Papers range from competition between beetles to the effects of mutations on fertility. Each paper is followed by a short discussion in which many of Britain's leading experts took part. Much of it is thought-provoking, dealing, as it does, with the relation between scientific and medical ethics and the inevitable increase in population that faces the world today.

GENETICS IN THE ATOMIC AGE by Charlotte Auerbach (London and Edinburgh: Oliver and Boyd, 1955), pp. 106, 8s 6d.

Dr Charlotte Auerbach is a distinguished geneticist who works at the Institute of Animal Genetics in the University of Edinburgh. In this small volume she attempts to describe the essentials of genetics without recourse to the usual technical language and mathematical symbolism that often makes genetics so formidable to the uninitiated — and she does so with a large measure of success.

Roughly the first two-thirds of the book are straightforward genetics, while only the latter third is devoted to radiation-induced mutations. There is a useful short appendix of genetic terms which will prove useful to readers who wish to extend their study of the subject. Of this little volume one of America's leading geneticists, H. J. Muller, has said: 'This charmingly written account of heredity and mutation by one of the world's foremost pioneers in these fields will make clear to the reader why the use of atomic energy requires the most scrupulous protective measures if future generations are not to pay the cost.'

NUCLEAR MAGNETIC RESONANCE by E. R. Andrew (Cambridge: at the University Press, 1955), pp. 265, 35s.

Successful experiments on nuclear magnetic resonance only date from the end of the war and this is the first book devoted to a comprehensive review of the subject. It is not intended for the general reader, but workers in many diverse fields of science will find it of value. Nuclear magnetic resonance is of interest to all physicists, and it is also of increasing importance to chemists, metallurgists, and electrical engineers. In the industrial field it has been used already by the oil industry and it also has applications in industries connected with magnet construction, isotope extraction, plastics, and rubber.

THE CYTOLOGY AND LIFE-HISTORY OF BACTERIA by K. A. Bissett (Edinburgh and London: E. and S. Livingstone, 1955), pp. 164, 25s.

Dr Bissett has produced a second edition of his book which originally appeared six years ago. In introducing it then he pointed out that bacteria, as living creatures, had been little studied, and that it was in the main their pathological activities that had received all the attention. In this new edition he adds to our knowledge of bacteria as organisms worthy of study in their own right. While all scientists may not agree with what the author has to say about the structure and behaviour of bacteria, even the general reader will derive great pleasure from the large number of remarkable electron micrographs with which the volume is illustrated.

ATOMS AND THE UNIVERSE by G. O. Jones, J. Rotblat, and G. J. Whitrow (London: Eyre and Spottiswoode, 1956), pp. 254, 25s.

When there is much talk of the fragmentation of science it is refreshing to find three scientists of very different interests coming together to produce a joint work. The authors of *Atoms and the Universe* are all primarily physicists but their particular studies range from the very small (the atom and its structure) to the very great (the problems of the universe). Atoms are much older than atomic bombs and in the first two chapters readers will find useful background information which helps towards a proper understanding of present developments in the field of nuclear energy.

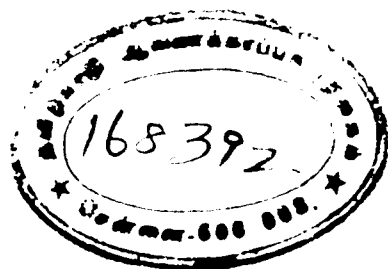
Atom smashing and atomic energy are adequately treated but not to the exclusion of less glamorous, but none the less important, topics such as the properties of matter in the mass. A short chapter takes us from classical to modern physics and the latter third of the volume treats of the structure, size, and age of the universe.

While obviously such a vast field has to be treated in outline only, it is useful to find in one book a simple introduction to the researches of classical physicists, nuclear physicists, and astrophysicists in such diverse fields as the structure of matter and the structure of the universe. The thirty-odd plates include some particularly fine astronomical photographs from the Mount Wilson and Palomar Observatories.

and King's College, Cambridge. Has held many important appointments including Director, Sorby Research Institute, 1941, first principal University College, Ibadan, Nigeria, 1947-53, Reader in Medical Entomology, University of London. Is now Head of the Department of Entomology, Rothamsted Experimental Station. Author of many papers on Insect Physiology, Ecology, and Medical Entomology. Likes walking, travelling, good food and wine.

P. G. MORGAN graduated from London University as an external student in 1949 and joined the Royal Corps of Naval Constructors as a Constructor-Lieutenant. After four years he was appointed an Assistant Constructor at the Admiralty. He is now a lecturer in mechanical engineering in the University of Manchester.

D. R. NEWTH is a lecturer in Zoology at University College, London, whose interests lie mainly in the early embryonic development of vertebrate animals and in the capacity of older ones to regenerate lost parts. Made an extensive tour of the U.S.S.R. in the autumn of 1955 as the guest of the Soviet Academy of Sciences.



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