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HEINZ CORTE MEMORIAL LECTURE

# THE DEVELOPMENT OF MATERIALS SCIENCE WITH REFERENCE TO THE SPECIAL ROLE OF PAPER

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## ABSTRACT

The development of materials science over the last forty years has proceeded at a rapid rate and some of the early experiments and industrial needs which have helped to stimulate the development are discussed. Paper as a material poses many problems which are being tackled in terms of technology, science, and mathematical modelling, and modern methods of analysis will ensure that progress in both the understanding and the technological development of the structure of paper and its mechanical properties continues. It is pointed out that one of the strengths of Dr. Corte's many achievements in paper science and technology was to initiate and carry out experiments using relatively simple equipment but to interpret the results using substantial mathematical methods and with a clarity of thought about the physical, chemical and rheological implications. Some analogies between the properties of paper and other materials are drawn.

## HISTORICAL INTRODUCTION

Materials science as an integrated subject is essentially a discipline which has been developed since the last war, during which many new materials and new versions of old materials came into specialist and, in some cases, general use. The roots of the discipline go back somewhat further in that by the 1920's and 30's the X-ray crystallographers had made it possible to be fairly certain about the atomic and to some extent the molecular arrangements in crystalline materials. Wagner and Schottky (1) in Germany were pioneers in applying thermodynamics to the problem of disorder in crystals and the consequent changes in physical and chemical properties which result from this. The elastic properties of crystals were reasonably well understood and the phenomenon of plastic deformation had begun to be seriously studied and such features as slip bands investigated. Schmidt's critical resolved shear stress law summarised the results of the early systematic work and this together with Frenkel's calculation of the critical shear stress of an ideal crystal (2) paved the way for our appreciation of the necessity to invoke the so-called dislocations as the means for enabling plastic deformation in real materials to occur at applied stresses far below the values expected on the basis of the Frenkel calculation. In 1934, Taylor (3) and others published details of the atomic arrangements which could be expected in the region of a dislocation and another atomic arrangement, the screw dislocation, was proposed by Burgers (4) in 1938. The presence of dislocations was certain but their nature could only be inferred from measured properties and it was not to be until 1953 that their existence as postulated by Taylor, Orowan and Polanyi would be confirmed by two series of definitive experiments.

The use of metals and alloys had been developed over some thousands of years and much of the technology of metallurgy had been devised as a sophisticated craft rather than as a science and a tremendous storehouse of information was available in the 1920's and 30's. Nevertheless, it was realised that the properties of the few metallic single crystals that had been grown by such pioneers as Andrade were vastly different in their properties from polycrystalline samples of the same materials. Such differences were well known in the properties of iron and steel, but were found to be examples of a more general result.

Similarly, ceramic materials, usually based on oxides, had a long history being well known in the form of pottery, including flower pots and fine porcelain and these last usually being covered with a glaze, made use of another material, namely glass which has a history that can be traced over a period of some 6000 years. It was only in the 1920's and 30's that glass began to be studied by X-ray diffraction and that Zachariasen (5) could begin to give rules for the chemical and crystallographical requirements for materials to act as glass formers. Most of the early glasses were based on silicates, were good insulators and only showed significant electrical conduction at high temperatures and high electric fields as a result of the motion of charged ions, e.g. $Na^+$ ions in ordinary window glass. Some thirty years ago, it was discovered that certain transition metal phosphate glasses were electronic semiconductors of a rather special kind and this discovery helped to initiate a whole new series of oxide glasses which could be of importance in electronics in particular, as parts of active rather than passive electronic devices.

The group of materials known as semiconductors was one of the categories of solid whose study led to the major post-war studies of well characterised materials and whose subsequent development has transformed the electronics industry and indeed, from many points of view, our way of life. Semiconductors in the form of natural minerals were studied by Seebeck in his early work on thermoelectric generators and by Faraday who pioneered work on electrical conduction. Their basic physical properties were not really understood until the development of quantum mechanics in the 1920's and 30's leading to the beautiful work on the energy band theory of semiconductors published by Wilson in 1931 (6). Wilson's theory explained how certain impurities could act as donors (giving rise to free conduction electrons over and above the concentration expected in a pure material) and others could act as acceptors (giving rise to free positive holes over and above those expected in pure material). He and Wagner also accounted for the fact that the stoichiometric excess of a compound could act as an impurity and give rise to extra free electrons or holes. At this time, very few materials could be prepared beyond the normal limits of spectroscopic analysis (1 part in some $10^4$ or $10^5$) and the Wilson model suggested that impurity concentrations much less than this could have a profound effect on free charge carrier density and thus on electrical conductivity in other properties. In 1938, although silicon was being used as a detector of microwaves, it was not certain that the material was a semiconductor since it was difficult, if indeed possible, to reduce the impurities inevitably present after preparation, to below a level of about $10^{16}$ $cm^{-3}$, there being of the order of $10^{22}$ - $10^{23}$ atoms per $cm^3$ in most solid materials. Thus, at that time a few parts per million of impurities was the approximate limit of net purification. The material would probably have been less pure than suggested by these figures as the measuring techniques may well have yielded the difference between donor and acceptor impurities if electrical measurements were used, rather than the total impurity content.

In the immediate pre-war years, X-ray diffraction was well established as an analytical tool, electron diffraction was a new technique, techniques of optical absorption in the ultra-violet and visible regions of the spectrum were well established but infra-red absorption spectroscopy was limited to specialist laboratories, and electrical measurements on high resistivity materials presented difficulties since very low currents were measured using very special electrometer valves or high resistances by a CR time-constant technique. Alternating current properties could be studied over a reasonable range of frequencies, but the atomic and molecular processes, giving rise to a particular frequency dependence of electrical conductivity, had not been fully established.

Many other materials had come into use in the pre-war years, including polymers, thin films deposited by vacuum evaporation and the beginnings of a class known as composite materials. Synthetic textiles based originally on cellulose acetate and afterwards on high polymers were available but one material in its various forms and which had been in existence for many years, indeed millenia, was paper and the craft of making fine paper had been well established and of course we all know of samples of paper made centuries ago which have kept their attractive appearance, shape and size.

In the general consideration of materials concepts, the ideas of uniformity of composition and of perfection were well established particularly in relation to weak points or regions, to coagulation or flocculation in some materials, and the role of impurities which could be undesirable as in the case of insufficiently purified semi-conductors or insulators, or desirable as is exemplified in everyday life by the addition of carbon to iron to form the stronger steel which is a major constructional material of great reliability. In this context, paper is not only a random network composed of fibres which are themselves composite materials, but is also filled, so that it is in no sense "perfect" although on a macro-scale it may appear uniform.

As mentioned above, Wagner and Schottky had begun to employ atomistic and thermodynamic analyses to the problem of defects in materials and to their consequences for physical and chemical properties. At the same time around 1930, Sommerfeld and indeed A.H. Wilson were developing energy band theory to account for many of the properties of solid materials which depend on the states of electrons within them and the mathematical techniques employed were based on an averaging of the appropriate functions throughout the volume of the sample rather than looking at localized regions or following a process atom by atom. In subsequent developments of the subject, the two approaches have been found to be complementary and very often the choice of analytical technique is based on the convenience or ready applicability to a particular problem.

For years, there has been a controversy among paper scientists concerning whether paper should be treated as a continuum and the appropriate continuum mechanics applied to problems of strength and so on, or whether an atomistic approach based on local bonding is more fundamentally correct. I would suggest by analogy with the way that solid-state theory has settled down, that both approaches may be valid and appropriate for a particular problem. As we shall see, modern analytical techniques have enabled us to examine structures with an extremely high resolution and as a consequence, the validity or appropriateness of the two theories may be tested.

## MATERIALS SCIENCE SINCE 1945

The wartime efforts on electronics, polymer development, jet engines and controlled nuclear fission processes all led to major materials research efforts in academic, industrial and government organisations. One such research programme was at the Bell Telephone Laboratories where the basic war-time work on germanium as a possible replacement for silicon to be used in microwave detectors for radar equipment was extended under the direction of Shockley. Bardeen and Brattain were studying the properties of germanium and testing some ideas about its surface characteristics when they noted a phenomenon of power amplification and had in fact invented the point-contact transistor. In helping to explain how the device was understood to operate, Shockley proposed the junction transistor and these discoveries not only formed the base of the modern semiconductor electronics and information technology industries and also gained for its inventors the Nobel Prize for Physics, but it pointed to the need for germanium and silicon crystals of extremely high purity and perfection which could then be doped in a very controllable manner as would be required for the manufacture of semiconductor devices. By 1950 good single crystals of germanium were available and within a few years, silicon crystals of high perfection could be produced, although the higher melting point of silicon and its chemical reactivity when molten meant that many problems had to be solved. One of the techniques used to purify silicon, that of floating-zone refining, was subsequently applied to the preparation of refractory metals in highly purified form and it was found that their properties, e.g. mechanical strength were very different from the properties measured on samples prepared by traditional methods. Not only were semiconductors needed for active electrical devices, they were needed as optical materials in the form of filters, lenses and prisms for the infra-red region, as thermoelectric elements and for magnetic field devices. In all of these applications, the level of impurity and its characterisation, the perfection, the uniformity and its stability with time needed to be carefully ensured. The principles were applied not just to semiconductors but to a wider variety of materials such as metals, alloys, polymers, ceramics and so on.

Even if the material were a polycrystalline aggregate such as a ferrite, a fine grained alloy such as a die-cast metal intended for use as a door handle, or a polymer sheet or rod, the same principles began to be applied, i.e. controlled composition and degree of perfection, uniformity of composition and defects, and a stability of properties with time. Time-varying physical properties, e.g. the gradual extension of a solid material under constant stress or the gradual increase of electric current through a material at constant applied voltage, are examples of the phenomenon of creep which is of course found in paper and is associated with defects in the structure which move or adjust their positions over an extended period.

In 1960 the laser was invented and a variety of laser host crystals has been developed over this period, starting with substantial ruby crystals (aluminium oxide doped with chromium), and since these have to provide extended optical cavities they need to be large and of high perfection. From 1962 semiconductor lasers based on gallium arsenide have become available and these from the point of view of the optical specialist are more like microelectronic components, but again have to be essentially perfect and stable. In this case the material preparation involves not only introducing the correct impurities in the appropriate concentrations but maintaining also the relatively correct concentrations of gallium and arsenic in the compound. Some of these devices tend to become warm during operation and therefore studies of annealing effects are of importance.

In 1956 two important experiments were carried out (8) and the results established the nature of edge dislocations beyond doubt. One experiment involved the study of a simple tilt boundary in an otherwise single crystal of germanium by an etching procedure and also by a study of X-ray line broadening. From the correspondence between the two results the nature of an edge dislocation was established and at the same period the development of electron microscopy had enabled Menter (9) to photograph a sample of copper phthalocyanine in which the expected features of an edge dislocation were clearly visible. Thus several new conclusions were drawn. For example a characteristic feature of an edge dislocation is that there are unsatisfied valency bonds in the dislocation and these will have unpaired electrons on them. Thus edge dislocations will not only be of importance in controlling the plastic deformation in solid materials but may affect the electrical properties. In a similar way the colour of a crystal may be used to infer its probable electrical properties. Thus we see that even though materials may be held together by metallic, ionic, covalent, molecular or by mixed bonds, many of the above considerations concerning the inter-relations of physical and chemical properties will still apply and thus the whole subject of solid materials begins to acquire a unity.

As examples of this, metallic alloys such as brass have been known for millenia but recent materials technology has shown us how to make thermoelectric materials by adding substantial quantities of bismuth selenide to crystals of bismuth telluride or to make the crystals for semiconductor light-emitting diodes and lasers by growing mixed crystals of gallium arsenide and gallium phosphide.

Further developments have been in the field of composite materials of which examples such as carbon fibres embedded in a synthetic resin for making strong but lightweight turbine blades, polymers produced with metallic inclusions either for decorative purposes or to have electrical conduction to a desired degree, or paper strengthened by the inclusion of polymeric material during its manufacture, may be taken.

## THE INDUSTRIAL ROLE OF MATERIALS SCIENCE DEVELOPMENT

Much of the advance of the science of materials has come from fundamental laboratories in academic or government institutions but tremendous contributions including some at the very base of the subject, such as the photographing of an edge dislocation by Menter, were carried out in industry. Many of the large paper mills and paper companies support research laboratories and during the 25 years that Heinz Corte worked in England he was located in the Central Research Laboratory of Wiggins Teape and while there made numerous investigations of the basic science of paper. He was a trained chemist but had the flexibility of outlook and a wide ability which included a facility in physics and in mathematics. I had the honour of being associated with him, in particular in guiding the fortunes of some young men at the post-graduate stage and I can testify not only to the disciplined approach which he demanded but also to his concern that young scientists should work hard and succeed. To that extent he succeeded since some of the young men concerned are present at this Conference.

I should like to spend a moment considering one or two examples of telling but simple work with which Dr. Corte was associated. One concerns simply the uniformity of fibres and bonds in paper which could be studied by projecting a light spot which was scanned across the surface, the transmitted beam being recorded and showing in particular the thin spots. He was then capable of applying a full statistical analysis to the results and thereby gaining basic structural information which could be fed back to the pulp makers and the role of fines for example could be assessed. Dr. Corte then found that it was much more appropriate to study his paper samples by beta-radiography which had become well-established as a technique and he derived structural information from this work.

He was particularly involved with Dr. Dodson's experiment in which very fine tissue paper samples were gradually stressed and torn along a line and the clicks which were heard when bonds ruptured were amplified, recorded and could in due course be played back. From the results, knowing the speed of propagation of the point of rupture, the distribution of fibre bonds in a particular direction of the sample could be determined with precision. The main requirement for the latter experiment was a quiet background and the experiments were conducted in the old gazebo in the grounds of Butler's Court which had the solidity and sound insulation associated with Victorian architecture. The moral of the two examples which I have cited is that provided the research worker has a good analytical mind, there is still room for relatively simple experiments which, if properly chosen and the results correctly interpreted, can yield basic information which may assist in future pulp preparation or in the development of quality assurance procedures.

## MODERN ANALYTICAL TECHNIQUES

Since 1949 these have developed to an incredible level of precision and reliability. Chemical techniques include radioactivation analysis, solvent extraction, vastly improved mass spectroscopy and secondary ion mass spectrometry, and paper and gas-liquid chromatographic techniques. Physical techniques include X-ray and electron diffraction and the associated electron probe microanalyser which can detect local densities of a given element in a sample and which can be related locally to the electron micrograph and diffraction pattern. The electron microscope particularly the scanning electron microscope developed in the early 1950's has played an important role but the more recent techniques including electron spectroscopy for chemical analysis, X-ray photo electron spectroscopy, and extended X-ray absorption fine structure, have all made possible a speed and an accuracy of analysis which would have been unthinkable some 30 years ago. The use of digital systems and microcomputers has helped tremendously in these endeavours and such devices have also transformed optical spectroscopy, particularly in the infra-red region, where the advances in materials science, particularly in the field of semi-conductors, have given us improved light sources in the form of lasers and detectors in the form of photoconductive and related cells. A sophisticated technique known as nuclear magnetic resonance has been applied in recent years to the analysis of paper and its constituents.

Many of these techniques have been applied to paper and to pulps and the accuracy which may now be obtained, when it is required to determine the detailed nature and even the date of manufacture of paper, is very high indeed.

## DIAGNOSTICS OF PAPER

Although many complex analytical tools are widely employed in paper laboratories, diagnostic and forensic examinations are often needed and may involve simpler tests, particularly when portability of equipment is a consideration. The standard testing methods for pulps which may involve test samples of hand made paper are well-known, but seen from the standpoint of materials science the properties of paper are found to be very sensitive to the conditions of preparation, temperature of testing and to the relative humidity. Munday (10) has described the modern testing and quality control methods as used in the mill and has indicated that at present it is not possible to make a paper machine completely automatically controlled. Some sophisticated feedback and control based on an assessment of grammage can be achieved but for other quality parameters compared for example with the automatic growth of silicon crystals, the systems are fairly primitive and their improvement provides a continuous challenge. The two main manufacturers of industrial computer control equipment have between them over 2000 installations on paper machines in spite of the shortcomings and complex control theory, such as the use of Z transforms is being applied.

Clearly, as with other materials, a uniform product, free from flocculation and properly bonded, of well-characterised shape and size is required and this can be achieved although with the increased speed of modern paper-making machines, problems of uniformity have been found. It must be borne in mind that the origins of paper are essentially organic and to this extent paper is an unusual material.

Apart from regular testing and basic work on paper in the laboratory, the nature of a particular paper sample may need to be determined for other reasons, e.g. to detect forged documents or bank-notes or to establish the falsity of watermarks. Such forensic examination has now become a very precise art and as such, uses many of the analytical tools referred to earlier. In view of the necessity on occasion to preserve the supposed integrity of a document, only a microsample of paper may be available for analysis. We may place the questions to be asked in three categories.

i) What is the origin or source of the paper?
ii) When was the paper made?
iii) Are two samples of paper identical or not?

We must also keep in mind that printing, folding and other modifications to sheets of paper can have quite profound effects on their basic characteristics because of chemical changes or mechanical deformation.

In the same way that in assessing the detailed nature of a glass sample, a multiplicity of measurements needs to be made, so with the identification of paper it is important to note that several measurements may prove necessary. Having given the paper a visible and possibly microscopic inspection, some of the subsequent tests will be destructive so that small samples for testing may be all that is available. The thickness, grammage, mechanical strength and possible mode of formation may be readily studied and optical measurements such as colour, reflectivity, opacity, uniformity of composition, and possible fluorescence are well established, but much of the subsequent measurement may be made after re-pulping or chemical treatment and involve an analysis of the fibres and of their treatment and of the various fillers and coatings. The plastic coatings now used on some papers for protection from the environment can make some chemical analysis rather difficult. It may also be found that because of lack of precision in machine control, there may be substantial variations in some characteristics of paper samples from different parts of the roll. Traditionally wiremarks can be seen by wetting the paper with water or dilute sodium hydroxide and using a microscope fitted with an eyepiece micrometer. Such techniques are analogous to the measurement of the density of dislocations in a silicon crystal by etching the crystal and subsequently counting the etch pits. In the same way that crystal stacking faults and other directional defects are introduced into metals that have been processed through a rolling mill, so the bonding in paper is different in the direction of travel of the paper in the machine compared with the transverse direction. As with metal sheets therefore the mechanical properties will be anisotropic even in the plane of the paper. Hand-made papers tend to have isotropic elastic propeties except perhaps near the edges of the sample where the shrinkage and resultant stress may be greater, a phenomenon analogous to the general properties of solid materials whereby the unsatisfied bonds at a crystal surface give rise to additional electron energy levels, and the physical properties at the surface region are different from the bulk properties.

Indentation marks in paper, even after transmission of pressure through several sheets may be identified by an electrostatic imaging process and forged signatures on cheques may be identified with an electronic pattern recognition system which responds to changes in the identation pattern between a true signature and a forgery.

The most useful optical properties are spectral reflectance and the infra-red absorption spectrum and some information may be obtained from measurements of fluorescence.

Many of the other methods for identifying papers and old documents are chemical and destructive in nature but do enable careful inspection of fibres to be made and the detailed analysis of the fillers and sizing materials to be achieved. For example a hot water extract of a paper may be concentrated and chromatographed on a specially prepared Whatman filter paper. A recent technique uses inverse paper chromatography and is based on using the paper as a chromatographic sorbent medium on which a known mixture of dyestuffs is separated under standard conditions. This method for characterising papers is simple, inexpensive and more or less non-destructive. Only a small sample is needed and a permanent record for evidence or report is retained. Other routine methods of chemical analysis are used and the nature and structure of the fibres can be studied in detail by using the scanning electron microscope which can also give information on the relative concentrations of particular elements present when used in conjunction with the electron-probe micro-analyser.

Tracing the origin of a particular kind of paper involves a great deal of investigative work and a considerable degree of experience.

## MECHANICAL PROPERTIES OF PAPER

This subject has probably been subjected to as thorough a treatment as any other branch of paper science, particularly when the properties are related to the known or assumed structure (11). In some ways paper is similar to a metallic foil and has indeed been analysed in similar terms. However, the strong anisotropy in bonding with direction on the roll and the tendency to irreversible effects causing damage, means that parallels with other forms of solid foil do not help to any marked extent in using analogies for the analysis of elastic and related properties. If we consider the normal paper manufacturing process, then the filtration during manufacture leads to a layer-like structure rather than a quasi-woven texture and the drying process can give a shrinkage of up to 20%. Thus local stresses are built in to the paper and since on a micro-scale paper can be inhomogeneous to a marked degree, even though averaged over a larger area the paper may seem to be homogeneous, a close analogue could only be a highly disordered solid. In non-metallic solids we are used to layer compounds such as mica, molybdenum disulphide and indeed most metallic dichalcogenides, in which the bonding forces are weak along the Z-axis but strong parallel to the cleavage planes. Current work in the University of Cambridge is aimed at understanding the effects of inserting impurity atoms between the cleavage planes, a process known as intercalation. It may be that some of the filler material in paper could be regarded as an intercalated impurity between the fibre layers but difficulties with this analogy may arise since in a crystalline solid the intercalated impurities may either destroy bonds in the Z-direction or even improve the bonding. However with paper the filler invariably reduces the strength of the network. Generally in paper the greater the degree of inhomogeneity, the greater is the reduction in mechanical strength.

One of the great disadvantages of paper viewed through the eyes of a materials scientist is the reduction of mechanical strength as moisture is absorbed. It has been established for some twenty years that the water content needs to be some 5-7% before there is a rapid decrease in mechanical strength and this fact has been explained in terms of the known binding energies of cellulose to cellulose, cellulose to water and water to water. An analogy may be found here with many of the properties of a disordered materials such as a glass. One or two per cent of added impurity may make very little difference to the structure or physical properties of the glass but beyond, say 5%, the glass network is altered and the properties, including mechanical strength, may change markedly.

Network models of paper, even with the detailed micrographic and other data currently obtainable to build up the details of the model, and accompanied by sophisticated statistical analyses, can only be used with confidence in mathematical terms to reflect the behaviour of real paper and cannot be applied beyond the region of small strains, since a great deal of energy is lost irreversibly in any real sample even at moderate strains. In the literature the theoretical approaches to small strain behaviour use the concepts of molecular, network and statistical foils and two main approaches to fracture are found, normal crack theory as originally derived for crystalline materials and a different model which involves a rate of energy dissipation proportional to the stored strain energy.

The model of paper as a random bonded fibrous network may be compared with oxide glass as a random ionic network. The traditional approach to crystal physics is to assume a crystal potential characteristic of the material and to use this as a uniform constant quanitity when analysing the band structure; indeed this quantity is crucial when such calculations are undertaken. Glasses and other solid materials in which the short-range order is preserved and the long-range ordering is destroyed by comparison with the regular ordering both long-range and short-range, of the same material in crystalline form, have been treated in recent years as if they were heavily disordered crystals and the regular crystal potential is replaced by a pseudopotential which can be inferred from measurements of X-ray and neutron diffraction. The understanding of such random structures, even if the samples are of accurately uniform composition, has increased as a result of this approach and Sir Nevill Mott and Professor P.W. Anderson shared a Nobel Prize for Physics for their important fundamental contributions to this subject. It may be that the statistical approach used by Dr. Corte and of course others, could take a similar form and paper could be treated as a perturbation of a regular fibrous network. Indeed, the established fact that only one per cent or so of the hydrogen bonds in the paper are actually involved in holding the fibres together suggests that percolation theory which has been successful in studying transport phenomena in amorphous materials may have a place in studying the propagation of local stresses and also cracks in paper. The analogy between paper and a highly disordered solid may be further developed when we condier the marked decrease in elastic modulus which Salmen and Back (12) found at 200°C and which resembled the glass transition process found in some polymers.

The plastic deformation of crystals arises from the motion of dislocations and enables the material to deform at applied stresses well below the value predicted theoretically for an ideal material. The points at which plastic deformation in paper and subsequently its fracture are initiated and associated with regions of low areal density and some elegant work on this subject was reported by Corte and Herdman (13) who showed that if paper were dried under uniform stress then the heavier regions grew at the expense of the lighter regions. One problem in modelling the bonds between fibres is the fact that the fibres are of finite width and this means that their stress fields are extended and this complicates the mathematical modelling. The traditional network analysis has been developed for many years and the recent developments have been concerned with refinement and with the finite-element approach which is appropriate to paper. When the network breaks down locally or fractures, one surprising result is that the process of fracture is non-localised. Only a small energy per unit area is needed to create a new surface by fracture whereas the energy per unit area needed to create a nominally new surface is vastly greater. This arises because when paper is stressed to tearing or fracture point, many bonds throughout the paper break, but only the line of broken bonds at the tear expose a new surface. Thus much of the work done is expended in generally weakening the paper. By studying these phenomena it has proved possible to define a specific surface energy for paper which does not depend significantly on the mode of fracture. Corte, Schaschek and Broens (14) had measured the extent and energy of the hydrogen bonding introduced in the paper-making process and they found that the tensile rupture energy of strip samples increases in proportion to the specimen length and has a positive intercept. Then the extrapolation of the rupture energy curve to zero specimen length can be used as a measure of work done in the failure zone. The analysis of these phenomena enabled the underlying molecular processes to be modelled and indeed a calculation based on the energy density of hydrogen bonding gave a value for the rupture energy at zero length which was of the correct order of magnitude.

Apart from the various mechanical and optical tests which are carried out in examining the structure of paper samples, modern analytical techniques which can be used with advantage in order to detect local chemical composition and its variations are the electron probe microanalyser and electron spectroscopy for chemical analysis. As stated earlier, these techniques need to be employed in association with simpler and more traditional techniques. These considerations apply to crystal and amorphous or glassy materials and these are relatively simple materials to characterise. It is therefore clear that a complex material such as paper needs an even greater battery of techniques for its characterisation and understanding.

## CONCLUSIONS AND GENERAL THOUGHTS

Paper is a random bonded fibrous network carrying filler material. The great advances in electronics over the period covered by the recent histroy discussed above have been associated with the replacement of natural materials by simpler well-characterised man-made products. For example radio-frequency capacitors are now built with polymers such as polyethylene as the dielectric instead of oil-impregnated paper. Resistors are now built of oxides, man-made ceramics or specially deposited thin dielectric films rather than cracked carbon. Virtually the whole of signal translating devices such as transistors and diodes and of course silicon integrated circuits (or chips) are built up from silicon monocrystals of very high purity and perfection rather than from traditional thermionic vacuum tubes. Equally, natural fibres have given way to rayon, nylon and other man-made materials for woven textiles. Is it feasible to replace the wood or rag fibres by man-made fibres and to produce paper based on such a product? Is there some special feature of wood fibres which could not be reproduced by such a material? What would its properites be? Would it assume a more regular structure?

Some success has been achieved in making a paper web from rayon fibres which can have a sufficiently ridged structure to sustain hydrogen bonding, but in general polymers do not readily form a paper web. They are or course used for fillers and coatings on some papers. Possibilities are considerable but perhaps the established helical sub-structure of the inner secondary concentric wall of a wood fibre is necessary to give paper its mechanical strength and elastic properties.

It is my impression that the enormous number of results of measurements of many properties have already given an insight into the structure of paper and its influence on those properties. Nevertheless compared with many solid materials, particularly those prepared in crystalline and monocrystalline form, and for which most of the observed physical properties may be related to the known structure, many problems of paper remain unsolved. The use of substantial statistical and variational methods has helped in reaching our present state of understanding but it may be that the problems associated with a network based on natural materials, even though their local structures may be directly observed with the scanning electron microscope and their local chemical constitution verified with the elctron microprobe analyser, are ultimately not capable of exact solution. However many of our advances in science generally have come from a series of successively more precise approximations, and perhaps the new techniques of analysis and the application of increasingly fertile minds to these problems will lead to a closer approximation and to an even more exact understanding of paper.

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