OPTICAL, THERMAL AND ELECTRICAL PROPERTIES OF CARBONS OBTAINED FROM THE COCONUT-SHELLS AVAILABLE IN BANGLADESH

BY

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CERTIFICATE

This is to certify that this thesis which I have presented for an M.Phil degree embodies the results of my course of further study and research and that this work has not been submitted elsewhere for the award of any degree or diploma.

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CERTIFICATION OF THESIS WORK

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has been accepted as satisfactory in partial fulfilment for the degree of Master of Philosophy in physics and certify that the student demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on 27 August, 1991.

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ABSTRACT

The thermal, optical and electrical properties of carbons obtained from coconut-shell collected from different parts of Bangladesh have been carried out.

Differential Thermal Analysis (DTA) traces of the raw and partially carbonised coconut-shell samples ascertains that coconut-shell on pyrolysis gives rise to carbons of non-graphitic in character.

Again, when observed with cross-polars, the polarized-light photo-micrographs of the carbons obtained by pyrolysis of coconut-shell within the mesophase temperature region also depicts an isotropic and hence non-graphitic behaviour. The physically appearing carbons from coconut-shell having high microporosity and relatively low density also shows the non-graphitizing nature.

The average activation energy obtained from the conductivity measurements of the different carbon samples comes out to be 11.1 Kcal/mole, which also support the DTA and optical findings that the samples under investigation are non-graphitizing in character.

CONTENTS

CHAPTER 1

INTRODUCTION

Carbon is an extremely versatile element. Its usefulness to mankind is reflected in its wide uses. Its importance and applications are growing each year. The use of carbon is apparent only when we single out the many phases of our everyday living where this adaptable element is essential in the black pigment of the ink of our books, magazines, newspapers, in carbon paper, in pencils, as the black colour in many paints, automobile finishes, and shoe blackening, as a strengthening and toughening constituent of rubber tyres, tubes, and other rubber goods, and as an essential element in the construction of a very large amount of electrical equipment from the household vaccum cleaner to the largest dynamos. The carbon arc is used in the production of visible and ultraviolet radiations for use in an increasingly large number of industrial processes dependent on photochemical reactions. The irradiation of milk to produce a higher vitamin D potency is one example of this use. Carbon and graphite products as structural materials are finding new and increasingly extensive application to chemical and metallurgical industries. Graphite is used both as moderator and as structural material in nuclear reactors due to its low atomic mass and low neutron absorption. Electrodes made of carbon and graphite are very important industrial equipment; indeed, electrodes represent the largest single outlet for a carbon product. Most of the diamonds found are not the gem quality but are used in industries for cutting and polishing metals or stones.

During the heat-treatment of carbon containing materials to high temperatures, the removal of noncarbon atoms, usually oxygen, hydrogen, nitrogen or sulphur, as well as some carbon constitutes the process what is known as 'carbonisation'. The process follows a rearrangement of atomic order within the remaining carbon atoms giving a greater degree of order within the carbon produced which may develop a three-dimensional order. Simply this development of a three-dimensional order which produces a structure very close to the well-defined structure of pure graphite is termed as 'graphitization'.

Very little is known in the open literature as to the properties of carbons obtained from coconut shell, although it is well known that the percentage of carbon obtained by the pyrolysis of coconut is very high. As carbon have manifold uses and its allotropic forms: graphite and diamond are valuable elements, the objective of this investigation is to find the nature of carbons obtained on pyrolysis of coconut shell.

The Differential Thermal Analysis (DTA), the polarized light technique and resistivity measurement have been applied to investigate the graphitic or nongraphitic nature of carbons obtained by heat-treatment of powdered coconut shell. To date the plastic or liquid state mesophase formation of optical anisotropy as a prerequisite to graphitization is a well-known phenomena[1,2,3,4]. In this phase, the pyrolysed sample in the temperature interval 350-600°C exhibits formation of spherules and its growth by coalescence with increasing temperature and ultimately the formation of mosaic texture. This mesophase can be observed by polarizing microscope with cross polars putting the gypsum plate (red-1 plate) at 45° with one of the polars (sensitive Tint Technique).

The DTA of the sample with few exceptions shows an endothermic peak in the initial stage provided it is graphitizable[5,6,7]. The exothermic peak indicates generally the non-graphitizability of the sample. The exothermic reaction gives rise to cross-linking between a pair of layer planes in the sample for which it becomes non-graphitizable. On the other hand, endothermic reactions allows the formation of planer distribution of the molecules in the sample thereby producing oriented aromatic rings which is one of the criteria of a graphitizable organic compound.

The resistivity measurement of the sample with increasing temperature gives an insight about its conducting or semiconducting nature[8,9]. We know that all graphites have semi-conducting nature but all organic semi-conductors are not graphitic in nature. So resistivity measurements of the carbons obtained from coconut shell with increasing temperature gives an idea as to whether it is semiconducting or not. In the process of heat treatment the random variation of resistivity in the initial stage of carbonisation is expected to occur due to the evolution of various hydrocarbon gases, CO_2 etc. present in the specimen and due to the rearrangements of the molecules within the samples. In a graphitizing sample the rearrangement of the molecules lead to a stable graphitic state where an energy gap is created and hence the valence electrons need more energy to be transferred from valence band to unfilled conduction band. This is manifested in the resistivity increase with the rise of temperature at the mesophase stage. This is an expected unavoidable character of all graphitizable organic semiconductors.

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CHAPTER 2

CARBON AND ITS DIFFERENT FORMS

2.1 Introduction

Carbon, the sixth element in the periodic table, has an atomic weight of 12.011 on the chemical scale. The electron configuration of carbon is $1S^2 2S^2 2P^2$. Out of the six electrons in a neutral carbon atom, the outer four electrons in the L-shell ($2S^2 2P^2$), are always available for chemical bonding by the oxidation of one s - electron into a p-state, followed by orbital mixing.

In the elementary form, carbon occurs naturally in 'amorphous' forms such as charcoal, lignites, gilsonite and in more limited quantities in its two allotropic crystalline forms as natural graphite and diamond.

The arrangement of the electrons in the outermost level of carbon when carbon is covalently bonded is not the same as when carbon is in the atomic state. The electron configuration of carbon in the atomic state is $1S^2 2S^2 2P^1 2P^1$. From this configuration, it would be expected that carbon would form bonds by combining or overlapping of the two partially filled P orbitals with S or P atomic orbitals of other atoms.

Carbon uses SP^3 hybridized orbitals when it forms bonds with four other atoms. However, organic compounds do not contain carbons with SP^3 hybridized orbital only. In addition, carbons with SP^2 and SP hybridized orbitals are possible.

The combination of one S orbital and two P orbitals forms three SP^2 hybrid orbitals. The hybridization process results in the following change in the electron configuration:

$$\underset{\text{Atomic state of carbon}}{1S^2 2S^2 2P^1 2P^1 2P^0} \xrightarrow{\text{hybridization}} \underset{SP^2\text{ hybridized state of carbon}}{1S^2 2[(SP^2)^1 (SP^2)^1 (SP^2)^1] 2P^1}$$

The three SP^2 orbitals are coplanar, and the angles between them are 120^0. Each orbital contains one electron. The remaining P orbital contains one electron and lies perpendicular to the plane of the SP^2 orbitals. The SP^2 orbitals with the lobes of the P orbital above and below the plane are shown in Fig. 2.1.

Carbon uses SP^2 hybrid orbitals when it is bonded to three other atoms. The combination of one S orbital and one P orbital produces two SP hybrid orbitals. The hybridization process results in the following change in the electron configuration:

$$\underset{\text{Atomic state of carbon}}{1S^2 2S^2 2P^1 2P^1 2P^0} \xrightarrow{\text{hybridization}} \underset{SP\text{ hybridized state of carbon}}{1S^2 2[(SP)^1 (SP)^1] 2P^1\ 2P^1}$$

The two SP orbitals are 180^0 apart and lie along the same line. Each orbital contains one electron. The remaining two P orbitals each contain an electron and are perpendicular to one another. The SP orbitals with the lobes of one P orbital above and below the plane of the line joining the two SP orbitals and the other P orbital in front of and behind the line joining the two SP orbitals are depicted in Fig. 2.2. In summary, carbon uses SP^3 hybrid orbitals when it forms bonds with four other atoms, as in methane; SP^2 hybrid orbitals when it forms with three other atoms, as in ethane; and SP hybrid orbitals when it is attached two other atoms, as in acetylene.

2.2 Different forms of carbon

Nonfabricated industrial carbon is represented by lamp-black, carbon black, activated carbon, graphite, and industrial diamonds. The first three are examples of amorphous carbon. In general, carbon is chemically inert and is infusible at atmospheric pressure. There are only two allotropic crystalline forms of carbon: (i) graphite and (ii) diamond. Graphite and diamond resist oxidation even at fairly high temperatures. Both the graphite and diamond are found in nature or can be produced artificially from many carbon containing materials. The difference in properties between these two allotropic forms is determined by the forces lying within and between crystallites.

Graphite is a laminar structure and is the anisotropic allotropic form of carbon. Each layer consists of a very large number of carbon atoms co-valently linked to form what may be considered to be a huge polynuclear aromatic macromolecule. Each layer is planer, or very nearly so. The accepted ideal crystal structure which was first established by Bernal[1](1924) is illustrated in fig. 2.3. Graphitizing carbon are generally relatively soft and are of high apparent density. It is a stable hexagonal lattice where the basal planes or layer planes consist of open hexagons with inter atomic C-C distance 1.415 A^0 for strongly linked ones and these planes are stacked in an alternating sequence, the inter planer distance being 3.354A^0 for weak bonding ones.

Diamond is a face-centered cubic material with each carbon atom bonded covalently to fours in the form of a tetrahedron, the inter atomic distance being 1.54A^0. It is the hardest known naturally occurring substance due to the rigidness of the tetrahedral covalent bond lattice of the single macromolecule that forms the perfect crystal. Diamond is metastable to graphite. It has great industrial importance in cutting, shaping and polishing hard substances. Diamond is a pure crystalline form of carbon and also the hardest available substance.

The graphite is converted into diamond by the assistance of crystals as well as high temperatures and pressures. Though the structure of diamond (fig. 2.8) is not the hexagonal, but Ergon and Leroy[2] have shown that a hexagonal structure for diamond is possible. Again diamond changes spontaneously at ordinary pressure to graphite[3] above 1500^{0}C. Thermodynamically, graphite at atmospheric preeeure is the more stable form of carbon.

Crystallographically perfect graphite has a density of 2.266 gm/cm^3, while for diamond the density is 3.53 gm/cm^3. It is believed that they are formed deep in the earth under great pressure and temperature. 30% of the diamond used industrially are now produced synthetically. In the graphite structure only three of the four valence electrons of carbon form regular co-valent bonds with adjacent carbon atoms. The fourth electron is free and it resonates between the valence bond structures. The weak Van der Waals forces exist between planes, while the strong chemical bonding forces exist in the basal planes. The bonding energy between planes is only about 2% of that within the planes[4,5].

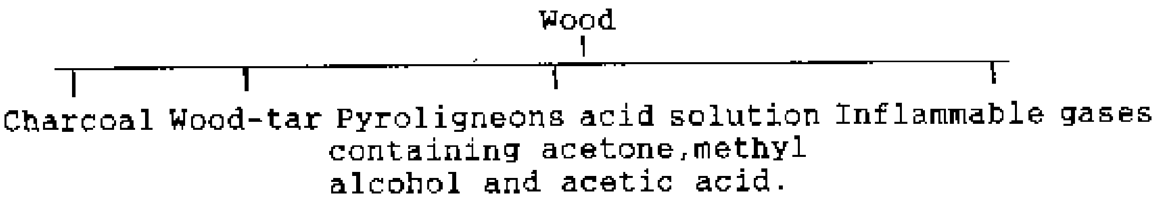
In the case of hexagonal graphite structure, AB AB is the stacking sequence of the planes as shown in fig. 2.3. So that the atoms in alternate planes are congruent. A rhombohedral structure has been found to exist in many graphites where the stacking sequence is ABC ABC as shown in fig. 2.4. Lipson and Stokes[6] (1942) were able to show this rhombohedral lattice which was originally proposed by Debye and Scherrer[7] (1917) to account for the extra X-ray lines found in some powder photographs of graphites. The proportion of the rhombohedral phase may be increased in graphites by grinding[8] the sample. This indicates that the change arises from the movements of the layers of carbon networks with respect to one another.

A third allotropic form of carbon which is known as 'amorphous carbon', apart from diamond and graphite is available in nature,. Coal, Carbon black, charcoal, and similar products are primarily amorphous carbon. They lack the crystalline structure of diamond and graphite and usually contain impurities.

All amorphous carbons possess a short range of order, although literally it means a structureless form of carbon. The first application of x-ray diffraction method to amorphous carbons, however, led to the concept that they were also graphitic with their apparently amorphous character which arises from the very minute size of the crystallites. These amorphous carbons can be prepared by the combustion of hydrocarbons in an incomplete supply of air. Carbon blacks, charcoal and lamp-blacks belongs to these forms.

Charcoal:

Charcoal is obtained by the destructive distillation of wood, bone, blood or sugar. The products obtained by the destructive distillation of wood are as follows;



There are several varieties of charcoal of which the following are important.

(i) Wood charcoal:

Wood charcoal is prepared in the modern process by the destructive distillation of wood in closed retorts. In a crude way, wood charcoal is prepared by burning a pile of wood in a charcoal pit or kiln and covering it with sods and earth so as to allow only a limited supply of air. The charcoal so obtained is called 'pit charcoal'.

(ii) Animal charcoal:

a. Bone charcoal.

Raw bones are first boiled with water and then treated with CS_2 which dissolves out grease and fatty matters. Degreased bones are then strongly heated, out of contact with air, in iron retort untill 'bone black' or animal charcoal containing a mixture of calcium phosphate and carbon is obtained and watery liquid containing ammonia, pyridine, bone oil etc. is given off.

The bone black is treated with hot HCl to dissolve out the calcium phosphate. The residue which is a pure form of carbon is carefully washed, dried, powdered and sieved when it goes by the name 'ivory black'.

b. Blood charcoal:

It is obtained by the destructive distillation of blood which may be obtained from slaughter houses.

(iii) Sugar charcoal or (Pure charcoal):

Sugar charcoal is prepared by the action of strong sulphuric acid upon a concentrated solution of cane sugar in water. Sulphuric acid abstracts the elements of water from sugar and the carbon particles that are set free, are then washed with water to remove the soluble matters, filtered, dried and ultimately heated in a current of chlorine to remove hydrogen, if any.

(iv) Lamp-black or Soot:

It is prepared by burning substances rich in carbon, such as petroleum, turpentine, tar, kerosene oil, acetylene, etc. in the presence of a limited (i.e. insufficient) supply of air and passing the smoke into chambers where the soot is collected by deposition. This lampblack contains hydrocarbons as impurities which can be removed by heating to redness in an atmosphere of chlorine gas when the pure soot is obtained. A still finer variety called 'carbon black' is prepared by allowing the flame of natural gas to impinge on a moving metallic surface.

(v) Gas carbon:

During the manufacture of coal gas by the destructive distillation of coal, the gas carbon is obtained as a deposit inside the upper part of the distilling retort. It is very pure carbon and is hard.

(vi) Coke:

Coke is the residue obtained when soft coal is subjected to destructive distillation. It contains all the nonvolatile substance present in coal.

2.3 Structure of carbon as determined by x-ray.

There are two distinct and well-defined types of carbon - graphitizing and non-graphitizing, soft and hard.

Graphitizing carbons may be defined as those which begin to develop three-dimensional order on heating to a temperature near 1700°C. Such carbons are formed by two main processes: (a) the deposition from the vapour phase and (b) the solidification from the liquid or plastic state to form cokes. Substances which produce graphitizing carbon from the liquid or plastic state include vitrinites of medium volatile coking coal, high temperature coaltar pitch, petroleum bitumen, polymers such as PVC and polynuclear aromatic compounds. The carbons normally obtained by heating these substances are coke-like in appearance and they show complex patterns of optical anisotropy under the polarizing microscope.

'Non graphitizing carbons' are those types of carbons where the graphite-like layers lie in parallel groups but are not oriented like the crystalline structure of graphite, the three dimensional structure of crystalline graphite is absent in these types of carbons. On heating certain non-graphite carbons to sufficiently high temperatures between 1700°C and 3000°C, the graphite-like layers shows a tendency to change from a 'random layer structure' towards an ordered structure of crystalline graphite. The intermediate type of structure in which the three-dimensional graphite structure is partly developed are called "graphitic carbons". Such formation have been observed by Franklin[9]. Also there are carbons which on heating to temperatures between 1700°C and 3000°C showed a continuous change from a non-graphitic to a graphitic structure were called 'graphitizing carbons' and those which on heating to 3000°C still don't exhibit three dimensional ordering were called 'non-graphitizing carbons'. These two types can be distinguished in terms of the relation between crystal height and crystal diameter on heat-treatment which are shown in fig. 2.5 where L is the average layer distance and M is the mean value of the number of parallel layers per crystallite.

Graphitizing carbons are generally relatively soft and are of high apparent density. Such types of carbons possess little microporosity and are relatively rich in hydrogen or low in oxygen, sulphur and nitrogen. They were termed as' soft carbons' by Mrozowski[10], During the early stages of the carbonisation process Franklin[11] considered that the crystallites in the graphitizing carbons were fairly mobile and that in the temperature region of 1000°C, a high proportion of the crystallites lay nearly parallel to each other. Weak cross-linking was supposed to exist between the crystallites. A model (reproduced in fig. 2.6) was put forward by Franklin for the structure of a graphitizing carbon. X-ray data also suggested the movable nature of the whole layers or groups of layers with the increase of the heat-treatment temperature. But the most significant factor was that the neighbouring crystallites had to be nearly parallel. The layer planes were linked together for the crystallite growth.

Non-graphitizing carbons are generally hard carbons and are of low apparent density. Such type of carbons have a high microporosity and are relatively rich in oxygen, sulphur and nitrogen or low in hydrogen. They were correspondingly called hard carbons by Mrozowski[10]. Again Franklin[11] put forward a model which is shown in fig. 2.7. to account for their formation. In this model the parallel layer groups were oriented at all angles and were joined together at their extremities, thus accounting for the microporosity. With the increase of heat-treatment temperature there was some growth in the basal plane direction by incorporation of disordered carbon atoms at the edges of the crystallites. Other carbon atoms acted as linkages between crystallites.

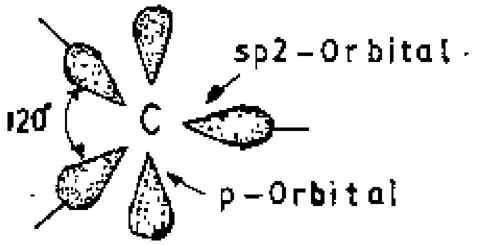


FIG. 2.1. AN SP^2 HYBRID ORBITAL. THE P-ORBITAL LIES PERPENDICULAR TO THE PLANE OF THE SP^2 ORBITAL.

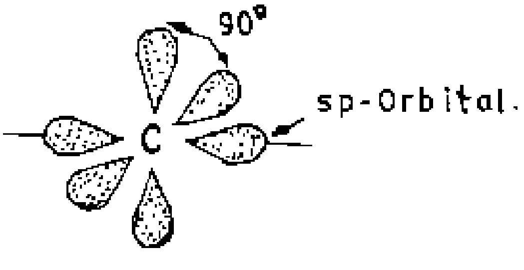


FIG. 2.2. AN SP HYBRID ORBITAL. THE ANGLE BETWEEN THE TWO P-ORBITAL IS 90°.

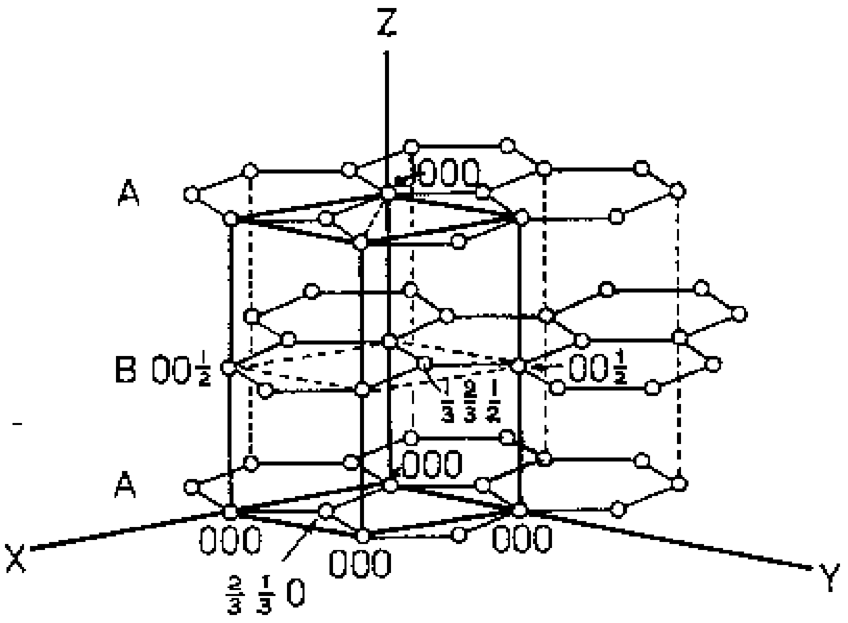


Fig. 2.3. The ideal graphite crystal structure with the hexagonal unit cell with crystal axes and lattice co-ordinates.

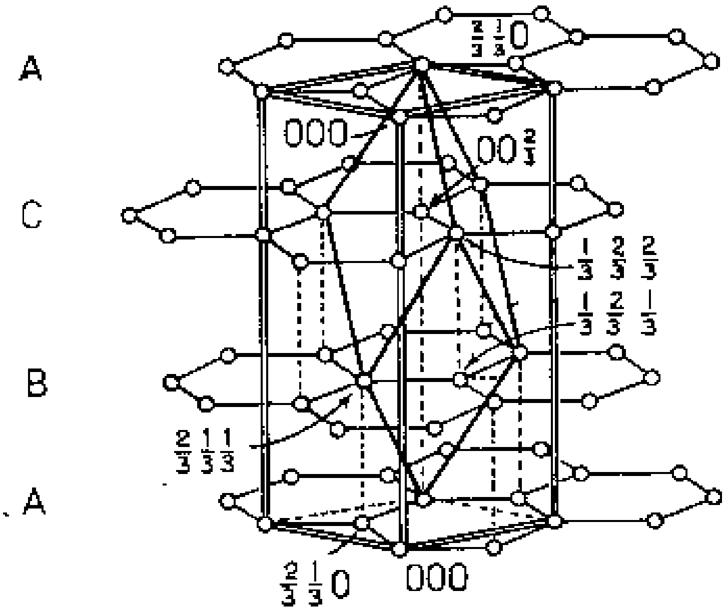
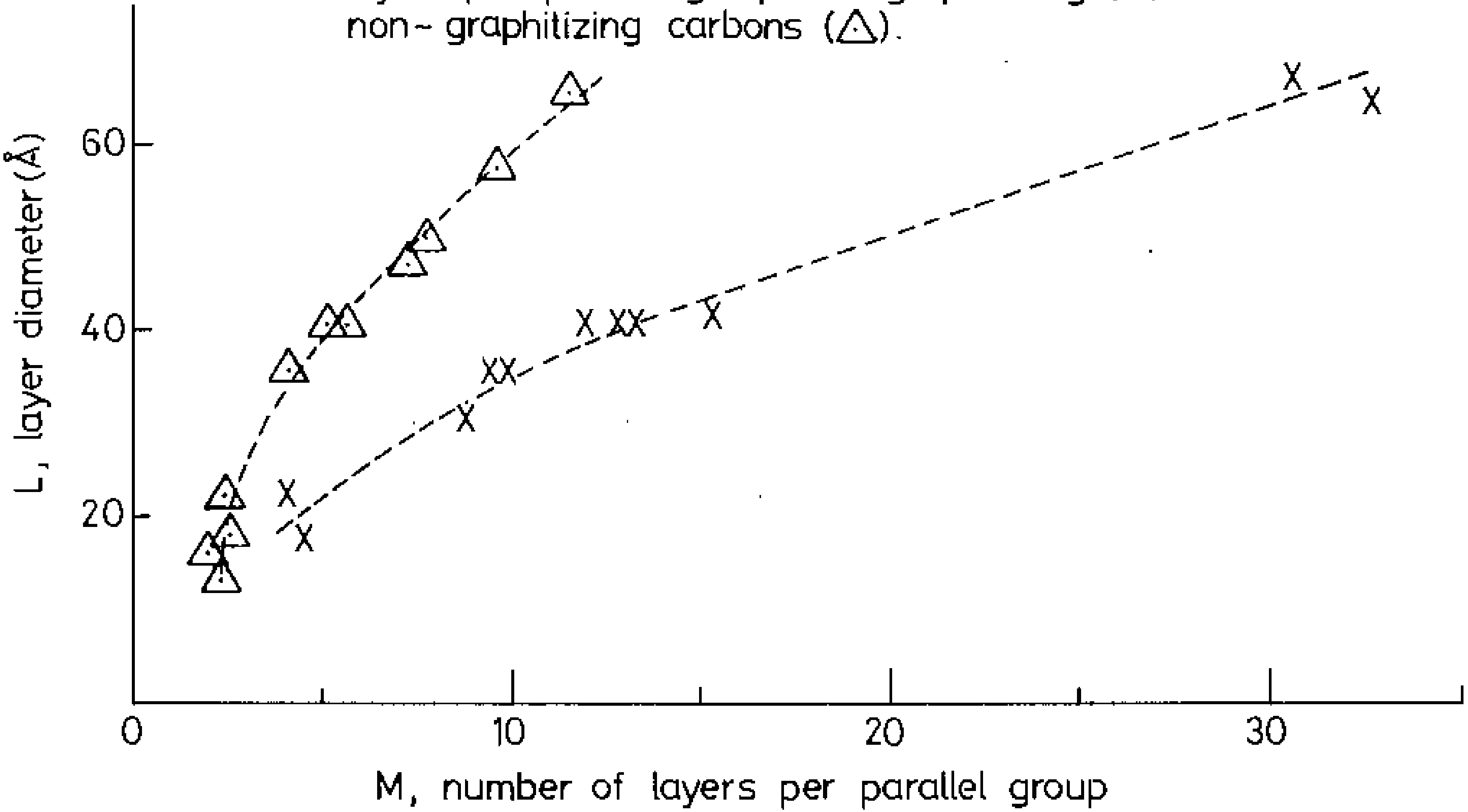


Fig. 2.4. The rhombohedral structure, showing the true unit cell and the atomic co-ordinates in the approximate hexagonal cell shown in double lines.

Fig. 2.5 Relationship between the layer diameter and the number of layers per parallel group for graphitizing (X) and non-graphitizing carbons (△).



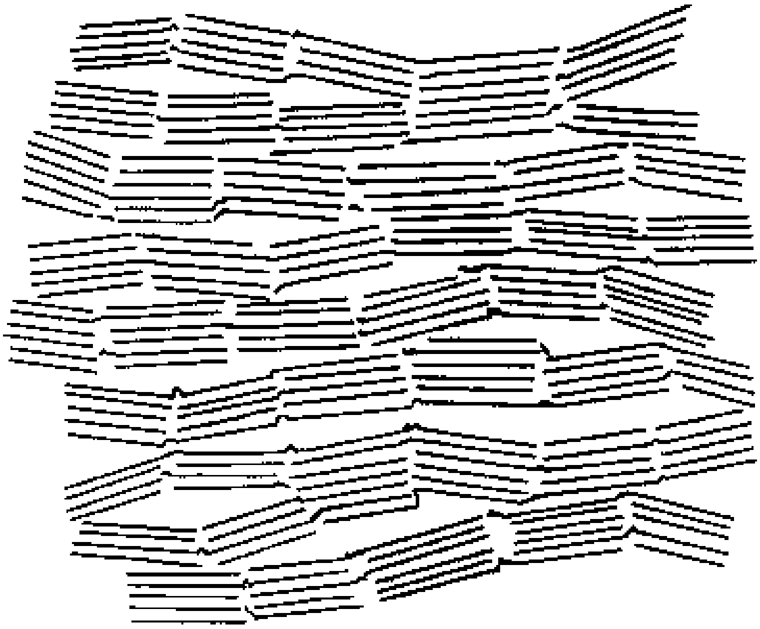


Fig. 2.6. Schematic representation of the structure of a graphitizing carbon.

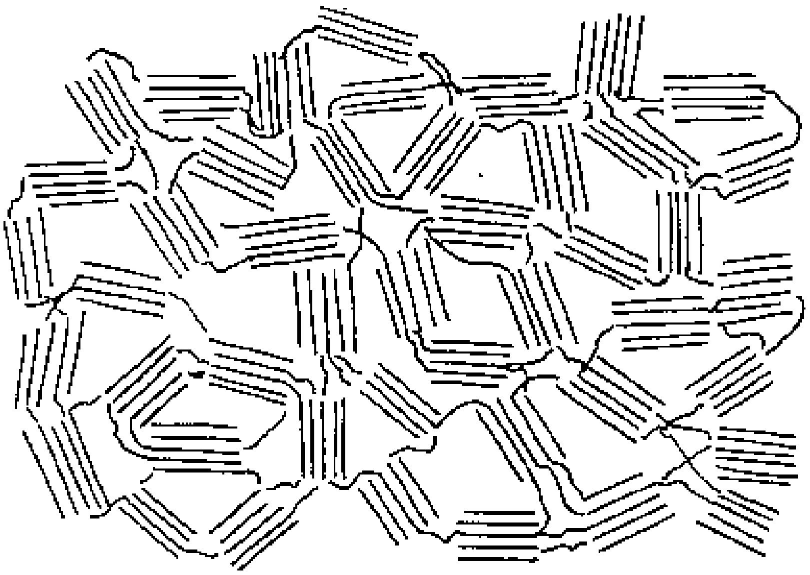


Fig.2.7. Schematic representation of the structure of a non-graphitizing carbon.

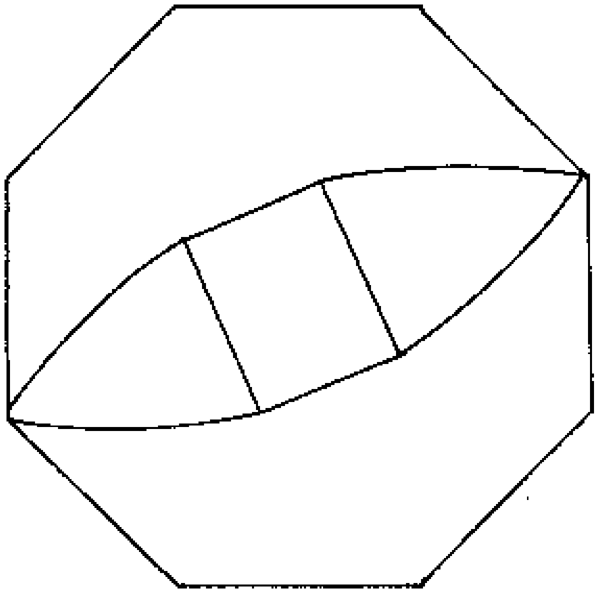


FIG. 2.8. DIAMOND STRUCTURE.

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CHAPTER 3

DIFFERENTIAL THERMAL ANALYSIS (DTA)

3.1 Introduction:

Under thermal (or heat) treatment a substance may undergo structural changes, such as physical as well as chemical changes. These changes occurring due to dehydration, transition from one crystalline variety to another, destruction of crystalline lattice, oxidation and decomposition etc. The technique of differential thermal analysis detects these changes as a function of temperature. In a physical change the chemical nature of the transformed material will be same as that of the starting material. In a chemical change the thermal treatment may rupture the chemical bonds to form new compounds. Every substance has a certain energy content. The energy content of the substance after a thermal change is different from that of the starting material; this difference may manifest itself as heat energy.

So, the technique of Differential thermal analysis is an important tool of accurately measuring the difference in the temperature between a thermocouple embedded in a sample being studied and a thermocouple in a standard inert material such as aluminum oxide while both are being heated at the uniform rate. The temperature difference arises due to the phase transition (transformation) or chemical reaction in the sample. Reaction attended by the absorption of heat are "endothermic" while those that evolve heat are 'exothermic'.

The exothermic and endothermic reactions are generally shown in the DTA trace as positive and negative deviation respectively from a base line. So, Differential thermal analysis gives a continuous thermal record of reaction occurring in a sample. This technique has recently attained considerable importance in determining the carbonizing and graphitizing properties of pure organic compounds, coals and pitches etc.

3.2 History of the method:

The technique of differential thermal analysis was first proposed by Lechatelier[1] in 1887. This method was successfully employed to investigate clays and other minerals. The thermal reactions was invented by Roberts Austin in 1899 and is popularly known as Differential thermal analysis. The Differential thermal analysis technique was mainly used in the field of metallurgy until 1913. Since then Differential thermal analysis has become an invaluable tool in clay mineralogy. But in recent years this technique has been extensively applied to chemical problems. The study of thermal behaviour of carbonising material by Differential thermal analysis was first reported at the fourth carbon conference by Nakamura and Atlas[2], Smother & chiang[3] and Mackenzie[4]. They described elaborately the theoretical basis and manifold applications of Differential thermal analysis.

3.3 DTA apparatus and its working principle:

The basic design parameter of the DTA apparatus has been fully described by Lewis and Edstrom[5,6]. A sketch of sample holder and a block diagram of controlling, detecting, amplifying and recording systems of the DTA unit are shown, in figs.3.1 & 3.2. The apparatus used in this program to detect and record these small temperature differences consists of three basic units[7].

(a) A DTA furnace and control system

(b) An atmosphere control system and

(c) Electric apparatus for amplifying and recording the temperature difference between the sample and the standard and for recording the actual temperature of the standard.

In DTA apparatus the thermo-couple which is used within the assembly consists of two matched chromel-alumel thermocouple which are supported in a porcelain tube held in position in a furnace combustion tube. The sample and the reference containers are both nickel cylinders with a thermocouple well extending into the centre of the cylinder from the bottom. With this arrangement, the thermocouple are protected from the destructive action of the hydrocarbons during carbonisation and so the thermocouple can be used repeatedly. The sample and reference cups are also isolated from each other and independent of the thermocouples. This arrangement facilitates weighing before and after heating so that weight changes can be readily determined. Approximately, 0.1 g anhydrous alumina is used in the reference cup and the sample weights varies over a range 0.05 g to 0.125g, depending on their packed density. Normally a heating rate is standardised at 10°C per minute.

All experiments are carried out at atmospheric pressure in a continuous flow of a purified inert gas, usually argon, nitrogen or helium. Gases are normally purged into the furnace chamber at the lower end through a purification train in which oxygen and water are removed by heated copper wool and exhausted from the top into a condensate trap[7] for collecting the condensable volatile products. The condensable volatile reaction products along with the unchanged starting material, if any, are thus swept by the flow of inert gas into a KBr-filled condensate trap placed in the exhaust end of the furnace. The non-condensable gases then pass through a sulphuric acid bubbler which seals the system and prevents back diffusion of air.

Normally, the DTA thermogram on carbonisation are obtained by heating continuously to 750°C at which the residue is essentially carbon.

3.4 DTA Results for carbonising and Graphitizing Materials:

It has already been mentioned that in differential thermal analysis, the rejection or absorption of heat by any material during pyrolysis is recorded and indicated by exothermic or endothermic peaks respectively in the DTA trace. The reaction temperature and the rate of reaction together give the characteristic thermal curve of that particular material.

Dollimore and Heal[8](1967) reported differential thermal analysis for the carbonization of a wide range of polymers under nitrogen flow. From the DTA results with certain exceptions in the case of chlorinated polyvinyl chloride and chlorinated rubber, it is generally seen that an exothermic portion of the DTA curve appears some where in the 1st stage of decomposition, indicating that the resulting product will be a non-graphitizing carbon. Two competing reactions are often found to occur: cross-linking producing an exothermic reaction, and chain stripping and associated reactions, producing endothermic peaks. The endothermic peaks often allows the formation of oriented aromatic rings which generally gives rise to graphitizing carbons. It should be mentioned that the exothermic reaction may be produced by some reaction of secondary importance, such as loss of absorbed water or other volatile impurities.

An additional information is helpful to supplement the DTA curve such as thermogravimetric analysis (TGA), X-ray diffraction, Infra-red absorption spectroscopy, visual phase examinations, polarized-light micrography etc, for correct interpretation of the thermogram peaks.

A combination of differential thermal analysis and polarized light microscopy[9,10,11] has proved a valuable approach to the determination of the temperature interval of mesophase formation.

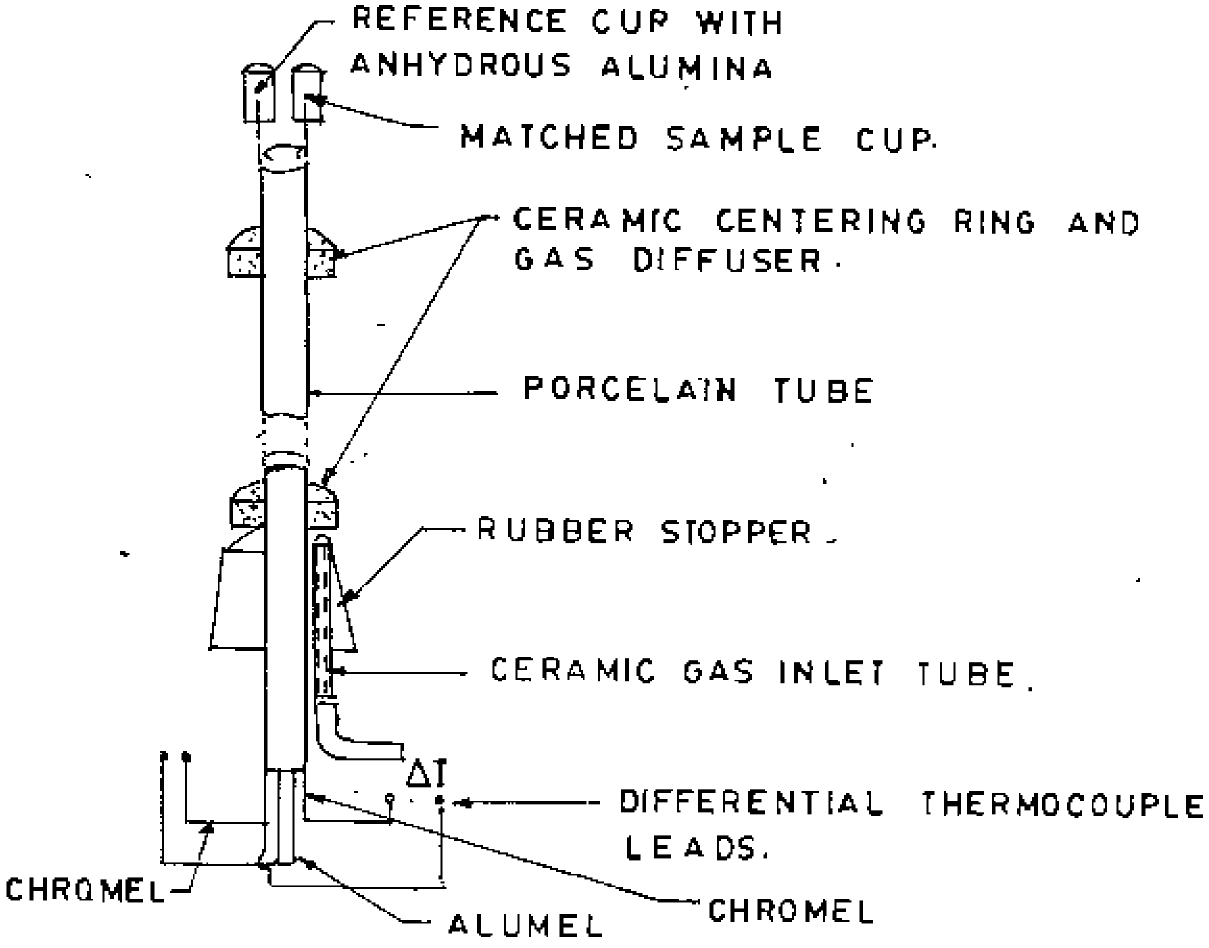

FIG. 3.1. DTA THERMOCOUPLE ASSEMBLY.

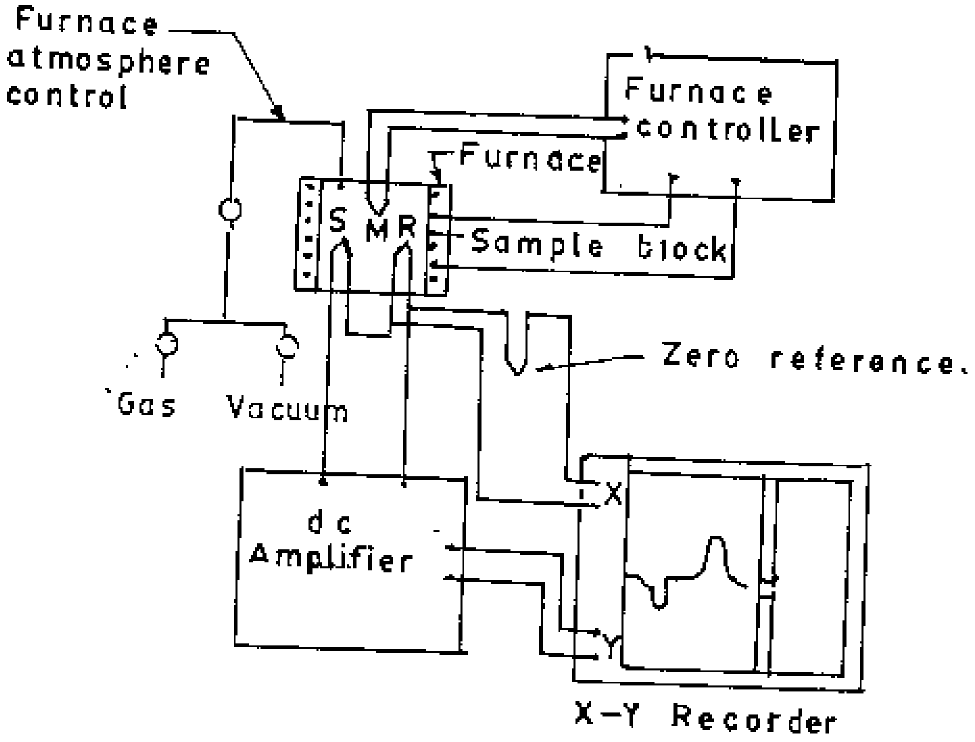

FIG. 3.2. BLOCK DIAGRAM OF A DIFFERENTIAL THERMAL ANALYSIS EQUIPMENT. (S) SAMPLE THERMOCOUPLE. (R) REFERENCE THERMOCOUPLE. (M) MONITOR THERMOCOUPLE.

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CHAPTER 4

ELECTRIC PROPERTIES OF ORGANIC SEMICONDUCTORS

4.1 Introduction:

A great number of the organic materials have been found to be electrical insulators. In recent years, a number of organic compounds having conspicuous electronic conductivity in solid state have been found[1,2]. Very little is known about the semiconducting behaviour of organic materials. The semiconducting properties of organic compounds are remarkably interesting, for, firstly they are molecular crystals and secondly they are synthetic compounds. Many varieties of electrical properties are expected due to the varieties of molecular structures. Thirdly the semiconductive properties of organic compounds should be important for the phenomena of energy transfer in some chemical reactions.

Solids are generally classified into four categories namely: metals, ionic crystals, valence crystals and molecular crystals[3]. Metals are good electrical conductors and are formed by the combination of the atoms of electro-positive elements.

Ionic crystals are formed by a combination of highly electro-positive and electro-negative elements and they possess good ionic conductivity only at high temperatures. Valence crystals, possessing homopolar bonds, are very hard and they have high melting points but poor electronic and ionic conductivities. Molecular crystals are formed by chemically inactive atoms or saturated molecules, held together by a weak force of the Vander Waals' type. Organic materials with substantial electrical conductivity are difficult to find, because they are mostly molecular crystals and the interaction between molecules is usually too weak to provide good electron transfer from one molecule to another.

Quite a good number of solids, however, have properties which correspond to a border line between two or more of these ideal types. The semiconductive materials are usually found in such a border line solids. Silicon and Germanium are remarkable examples of border line solids between covalent crystals and metals. Their crystal structures are nearly similar to that of diamond, which is a covalent crystal.

In molecular crystals, one can also find compounds which are border line to the other crystal types. Graphite consists of layer lattices of carbon atoms which are separated by a distance so large (3.35 A^0) that there can be no covalent bonds between layers. Each of the layers is a giant aromatic molecule. The superimposed molecules are held together only by weak Vander Waal's forces. The electrical resistivity at room temperature is 10^{-5} Ohm-cm along the layers and is 10^{-1} Ohm-cm in the direction perpendicular to the layers.

Measurements of electrical conductivity with temperature is a technique for detecting the semiconducting nature of an organic compounds. Thermal and optical studies of some aromatic compounds show that they consist of planer molecules[15]. The prime examples are polycyclic aromatic compounds and phthalocyanines. There is a remarkable similarity to these compounds in that they have valence π-electrons which can move through out the molecular plane. Little is known about the molecular interaction in these solids. However, it may be presumed that the molecular orbital of π- electrons are diffused and that those on neighbouring molecules overlap slightly.

From the view point of organic semiconductors, structures such as (-CH=CH-)n or (=C=C)n in linear form should be expected, because they form π-bonds. The former structure is found in diphenylpolyenes and in carotinoids. Another family of interesting compounds are those which have free radicals and they would shift their properties towards those of a borderline solid because of their unusual electronic state. Stable free radicals are found in carbonized materials, such as chars and coals, and also in solid polymers which have been treated with high energy irradiations[4].

Some organic compounds can form solid molecular complexes with halogens or alkali metals . Recently, Mulliken[5] has proposed a charge transfer mechanism to explain the interaction in the molecular addition compounds. Thus aromatic hydrocarbons, for instance, can act as electron donors or acceptors in such solid complexes. They can be seen as the border line compounds between molecular and ionic crystals. The electronic properties of the solid complexes are quite attractive from the view point of organic semiconductors.

4.2 Classes of Organic Semiconductors

Organic semiconductors are classified in three groups,

1. Compounds which have a number of delocalized electron (π-electrons) in the molecules:

2. The organic free radicals; and

3. The intermolecular addition compounds.

Substantial investigations have been conducted on the semiconducting properties of the first group, viz, the condensed polycyclic aromatic compounds, the phthalocyanines and some dyestuffs. On the coutrary, few surveys have been made on the simple free radicals. An investigation in to the electronic properties of the third group has been carried out with success.

4.3 Structure of Organic Semi-conductors

Most of the organic semiconductors have been found to consist of the conjugated and aromatic molecules. For examples, in benzene the carbon atom lie at the vertices of a plane hexagon and the six hydrogen atoms lie in the same plane directed radially outward from the carbons in such a manner that all the valence angles are 120^0. This implies that of the four valence electrons ($2S2P^3$) of the carbon atoms; three (SP^2) are hybridized in the trigonal state so that they give rise to localized C-C and C-H bonds. Both the bonds are σ-type molecular orbital which are symmetrical around the bond axis.

The fourth valence electron (Pz-electron) is unhybridized. Those six electron, one for each carbon atom, are π-electrons as their atomic orbital are all directed parallel to each other and extend perpendicularly to the molecular plane having the ± 1 component of angular momentum around the bond direction. The pairing of these neighbouring electrons leads to the molecular orbital of π-type which is symmetrical around the bond axis. However, any one of these atomic orbital overlaps on both its neighbors equally, so that the π-electrons have to occupy the molecular orbital which extends over all six carbon atoms.

The mobility of the π-electrons contributes to the important physical and chemical properties of aromatic compounds. For instance aromatic molecules show a remarkable diamagnetic anisotropy. The tiny electron currents give rise to a large diamagnetism when the magnetic field is perpendicular to the plane of molecule[6,7]. This anisotropy becomes large as the molecular size increases[8,9].

In the case of graphite, a giant aromatic molecule, its magnetic anisotropy has been interpreted with substantial success even with a simple model based on a two dimensional free electron gas[10,11]. The electron conduction in the planer lattice of graphite is presumably associated with the motion of π-electrons drifted under the electrical field[12,13].

Another important character of π-electrons arising from their mobility is that the electronic transition takes place much easier than that for π-electrons. Thus most strong absorption spectra which are observable in the visible region are the result of electronic transition from the π-bonding orbital to the π^* antibonding orbital (so called, N-V transitions). The dyestuffs which are colored compound necessarily consists of the conjugated molecules including aromatic rings. They have the mobile electrons.

It is well known that a number of lower condensed aromatic hydrocarbons, such as, naphthalene, anthracene, pyrene and chrysene are produced by extraction from a coal-tar pitch.

Recently, through the hydrogenation of a coal-tar pitch, a fairly large quantity of coronene, the seven membered aromatic has been produced[14]. Similar to coal-tar pitch aromatic hydrocarbons, such as, naphthalene, anthracene, pyrene, picene, chrysene and also coronene, the seven membered aromatic have been also found to be present in the peat complexes.

During carbonization these organic compounds give rise to ordered molecular arrangement in the temperature range of 350 to 650°C approximately and hence they show the semiconducting properties. For instance, the resistivity of some typical polycyclic aromatic compounds, such as, violanthrone and isoviolanthrone have been measured. Fig. 4.1 shows the electrical character of this matrix.

Pyrolysis of benzene, naphthalene, phenanthrene and chrysene have been carried out and it has been established that these polycyclic aromatic compounds produce planer sheets of aromatic molecules ultimately to form graphite[15].

Riley[16] determined the electrical conductivity of coke during carbonization upto a temperature of 700°C. The rapid increase of conductivity with temperature around 700°C indicates the formation of graphite crystallites.

Manchunk, R.V. et al[17] studied the electrical conductivity of carbonized peat. The addition of $AlCl_3$ to the peat decreases the electrical conductivity of the composites with silicates. The electrical conductivity increases as the composite volume fraction increases and the percentage of $AlCl_3$ decreases.

Bel'Kevich, P.E. et. al[18] found that the electrical conductivity of peat semi-coke decreased exponentially as the coking temperature increased from 200°C to 400°C.

Begum, D.A., Hossain, T.[19] have studied 84 samples of Bangladeshi coal-peats collected from Chanda and Baghia Beel of Faridpur and Kola Mouza of Khulna. Their study shows that Bangladeshi peats are poor raw materials for chemical processing but they can be used as fuel because of their high calorific value. The Differential Thermal Analysis (DTA) reveals that peats of the three areas are structurally different.

A.B.M. Shah Jalal[20] measured the electrical resistivity of Bangladeshi coal-peats found in Baghia and Chanda Beels of Faridpur and Kola Mouza of Khulna. The change of resistivity with temperature indicates that peats available in this region are semi-conducting and also graphitic in nature. In the mesophase transformation a sharp fall of resistivity indicates the semiconducting nature of the samples.

4.4 The General Properties of Semiconducting Materials

The mechanical properties of semiconductors vary greatly. However, in respect of hardness, brittleness, and fracture strength, semicouducting crystals resemble insulating crystals more than the metal do. Most semiconductors lack the high density in electrons which may help them becoming ductile and plastic in character like some metals.

One of the most important properties of the semiconducting materials is the temperature dependence of the electrical resistivity[21]. Magnetically, they may be diamagnetic, paramagnetic, or even ferromagnetic.

4.5 Theoretical consideration of Electrical conductivity measurements:

Electrical conduction is the transfer of charge carriers through a medium under the influence of an electric field or temperature gradient. The rate at which an element of charge dQ is transported over an area A in a time dt is given by the current,

$$i = dQ/dt = nqV_DA,$$

where n is the number density of charge carriers, V_D is the drift velocity under an applied field. V_D is proportional to the applied field i.e. $$V_d = \mu E \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Then

$$i = nq\mu E A$$

where μ ($cm^2\ V^{-1}\ sec^{-1}$) is the drift mobility and E ($V\ cm^{-1}$) is the applied field.

The conductivity σ ($Ohm^{-1}\ cm^{-1}$) is defined by

$$\sigma = id/VA \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where d is the sample thickness and V the applied voltage.

Assuming the electrical field E, to be uniform across the medium. i.e.

$$E = V/d \ldots\ldots\ldots\ldots\ldots (4)$$

$$\sigma = qn\mu \ldots\ldots\ldots\ldots\ldots (5)$$

If there is more than one type of charge carriers the conductivity is

$$\sigma = \sum q_1\, n_i \mu_i \ldots\ldots\ldots (6)$$

In any particular system the number mobility of the charge carriers will depend upon the material and the experimental parameters of voltage, temperature, and ambient atmosphere. If the material is crystalline or oriented, the conductivity will depend on the direction with respect to some molecular axis in which the measurement is made. These dependence can be expressed by

$$n = n\ (T,V)$$

$$\mu = \mu(T,V,Z) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

$$\sigma = \sigma(T,V,Z)$$

where T represents temperature, V the applied potential and z the direction in which the measurement is being made.

Phenomenologically the conductivity is obtained by measuring the current following through a piece of the material and using the simple dimensions to calculate σ from the equation

$$\sigma = (d/Av)\ i \ \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

where d(cm) is the sample thickness, A its area (cm^2) and V the potential across the material. Hence the dependence of either the number of carriers (n) or the carrier mobility (μ) upon the potential will be shown by a potential dependence of as defined above.

From equation (6) the conductivity is seen to be the product of two terms, n and μ , which are independent variables. Any prediction about the conduction process which assumes a dependence of n or μ upon an experimental parameter is meaningless until that assumption is proved correct. e.g., there are two extreme assumptions which can be taken with respect to equation (6): (i) to assume that the number of carriers is independent of temperature, and (ii) to assume that mobility is independent of temperature. In each case the variation of the assumed temperature dependent parameter has been used to prove some fundamental relationship between the conduction process and molecular structure.

There are many experimental difficulties involved making electrical measurements on organic polymers[22]. The high resistivity of many polymers requires the measurement of small currents. The form of the sample (powder, molded slab etc.), its purity, the presence of solvent, moisture, the ambient atmosphere, and temperature are all important. The electrodes should be ohmic; that is there should be no potential barrier at the electrode-polymer interface. Frequently it is found that the conductivity of most polymers varies exponentially[22,23] with temperature T according to the equation.

$$\sigma = \sigma_0 e^{-E_\sigma/KT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(9)$$

where K is the Boltzmann constant and E_σ is the activation energy.

Since this equation is also obeyed by inorganic semiconductors, it has been assumed that considerations used to describe inorganic semiconductors may also be used to describe electrical properties of polymers. Such an assumption is justified if it is known that charge carriers are not ionic. Bearing this in mind, the charge carriers may be generated intrinsically or from impurities, in which case they may be electrons, holes or ions.

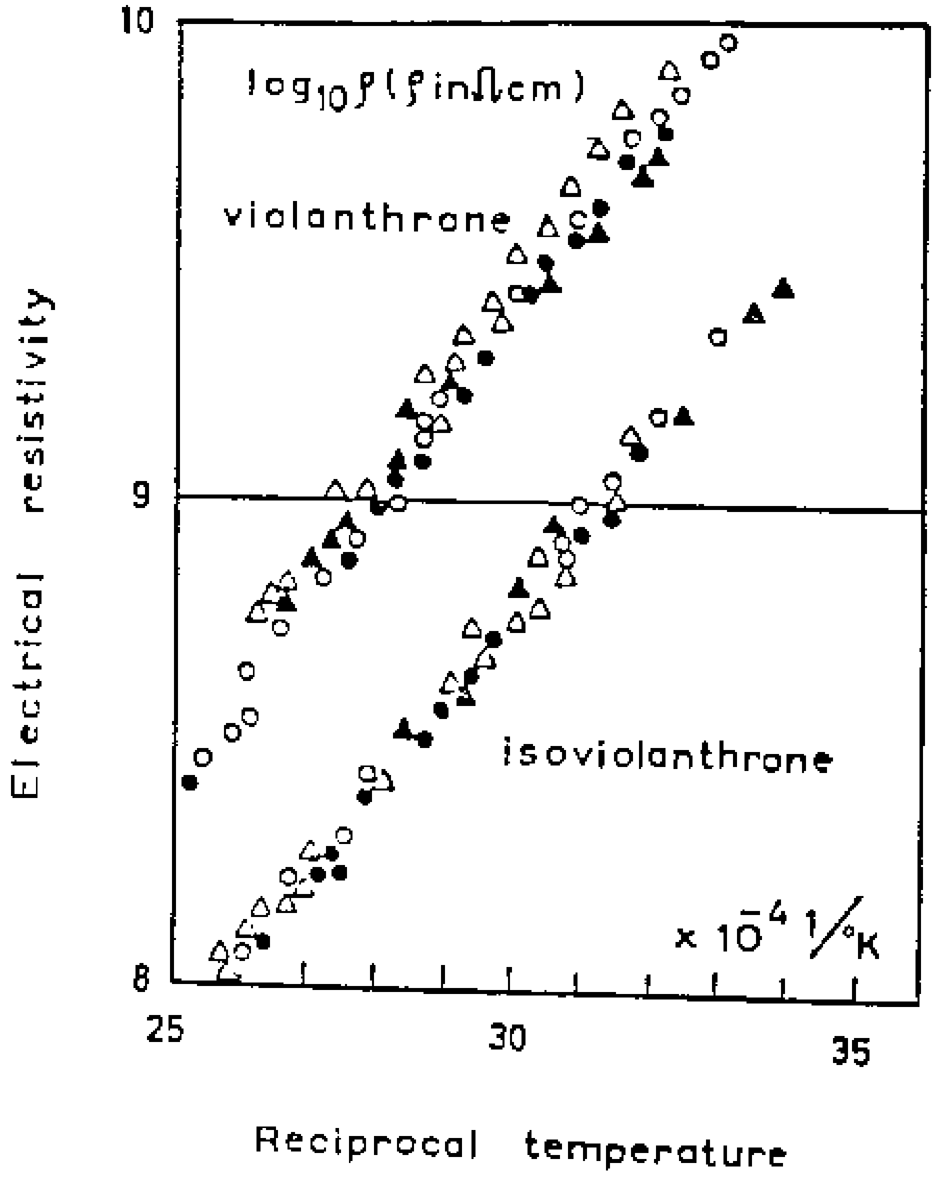

Fig..4.1 Log $_{10}\rho$ vs $\frac{1}{T}$ curves for violanthrone and and isoviolanthrone.

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CHAPTER 5

POLARIZED-LIGHT TECHNIQUE

5.1 The Polarizing microscope

The polarizing microscope[1,2,3] is essentially an ordinary compound microscope provided with calcite polarizing prisms, or more usually now, discs of 'polaroid' (or some other make of polarizing filter) above and below the stage, and some convenient means of altering the orientation of the object (usually in one plane only) with reference to the plane of vibration of the light incident upon it. Provision is also made for the insertion of auxiliary lenses and compensators into the path of the light through the instrument.

Because of its widely varying application the polarizing microscope has undergone many modifications, but in principle all types are the same and do not differ essentially from one another. However, the arrangement of the main components of a typical modern polarizing microscope are described below. The incident light passes through the polaroid disc, the polarizer, and is thus constrained to vibrate in one plane only. The polarizer can be rotated in its own plane and the angle of rotation can be read against a fixed mark from divisions on the metal ring in which it is mounted. A second polaroid disc, the analyser, is mounted in the body tube of the instrument. The analyser can be rotated or withdrawn from the field of view to enable a sample to be viewed in unpolarized light. When both the polarizer and analyser are in the 0^0-position (as marked on the scale) they are said to be in 'crossed position', and they will not permit light to reach the eye piece so long as the medium between them is entirely isotropic. This is because light emerging from the polarizer is completely extinguished by the analyser according to the principle underlying the well known Malus's experiment in optics.

The specimen under investigation, mounted in a quick-setting acrylic resin or on a glass slide, is placed on a circular stage. This specimen, which can be held in position by means of a clamp attached to the stage, is capable of movement in two perpendicular directions in the plane of the stage. To permit easy return to a certain specimen point the coordinate positions can be read against millimeter scales. The stage can be rotated in its own plane and is provided with centering screws and 'click stops' at intervals of 45^0. The angle of rotation of the stage can be measured on a degree scale. The stage is also provided with a clamp to arrest the motion if so desired.

Above the objective lens is a slot in the body tube of the instrument, through which the compensator or tint plate is inserted. The tint plate, which is a gypsum plate (sometimes called first-order red plate) is placed at an angle of 45^0 to the vibration planes of the polarizer and the analyser when they are in the crossed position.

Also contained in the microscope body is the Bertrand lens which can be swung into or out of the field of view. This lens and the eye piece act together to constitute a low power microscope which can be focussed on the upper focal plane of the objective. The chief purpose of this combination is, however, to give an enlarged image of the interference figures which are formed in this plane under certain conditions. Above the Bertrand lens is an iris diaphragm, or a pinhole stop. The purpose of which is to isolate the interference figure of the crystal occupying the centre of the field of view when several are present.

The condensing lens system is situated between the rotating stage and the polarizer. Its primary function, as in the compound microscope, is to bring the incident light to a focus in the plane of the specimen.

The eye piece lens system, fitted to the microscope body is of the binocular type, having a X10 magnification. This together with the different objectives produces an overall magnification range from X25 - X1000.

The illumination of the microscope is provided by a low voltage 100 watt quartz iodide bulb, the power supply of which is controlled from a regulating transformer. This lamp generally operates on 12 volts at 8.3 ampares. The bulb is contained in a well ventilated housing with a circular opening for the emission of light.

The body tube of the microscope allows a camera adaptor to be fitted after the analyser. The adaptor is supplied with a X10 magnifying eye piece. The camera used for photography is a 35 mm Exakta Varex 116.

5.2 Modes of Observation in a Polarizing Microscope

5.21 Orthoscopic Arrangement

The orthoscopic arrangement may be regarded as an ordinary microscope arrangement (Fig. 5.1) in which the crystal is illuminated by a series of essentially parallel, normally incident rays all of which travel along the same crystallographic direction within the crystal. In this type of observation there are three combinations of polarizer and analyser that enable three different sets of observations and measurements to be made.

Firstly, both the polarizer and analyser being removed, observations can be made on colour, crystalline form, cleavage and fracture, together with the determination of the refractive index of isotropic crystals.

Secondly, with the polarizer inserted, the principal refractive indices of anisotropic crystals can be determined. Observations on pleochroism (which is the variation in colour or tint resulting from differential absorption of white light) and twinkling (which is the variation in relief when a crystal having a large double refraction is rotated in an immersion medium whose refractive index is near to one of those of the crystal) may also be made with just the polarizer inserted.

Lastly, with the polarizer and analyser inserted in the crossed position, distinctions can be made between isotropic and anisotropic substances and measurements can be made of extinction angles.

Most of the observations on the polarizing microscope are done with both the polarizer and analyser inserted in crossed position. In accordance with their behaviour between crossed polar, all non-opaque substances can be divided into two groups, namely, isotropic and anisotropic substances. The former remain dark, like the rest of the field of the microscope whatever be their orientations. On the other hand, anisotropic substances will appear colored on rotation in most orientations and only in certain definite positions will become dark.

The reason for this difference in behaviour is that in isotropic substances light vibrates with equal ease in any direction, the wave surface being a sphere, and so, when such a substance is placed on the microscope stage between the polars, it does not interfere in any way with the direction of light vibration, and the field remains dark as if the stage is empty. Alternately, when an anisotropic substance is placed between crossed polars, the plane polarized light emerging from the polarizer is doubly refracted on entering the crystal, the two rays vibrating in planes at right angles to one another, and travelling with different velocities. Similarly, light reflected by a polished anisotropic eurface is polarized in the two principal directions at right angle to each other, the two rays travelling in different velocities. Rotation of such a crystal on the stage in either case will cause it to become dark, or extinguished at intervals of 90° and between these position of darkness the crystal will become illuminated, being brightest at 45^0 from the extinction position. The section extinguishes when the traces of its vibration directions become parallel to those of one of the polars, for in such positions, the light from polarizer is not resolved in the crystal, but passes on to the analyser nnchanged as if there is no crystal on the stage, and hence darkness results. The colour shown in the positions of illumination are known as 'polarization colors'.

The polarization colours observed through the microscope depend on the relative retardation or optical path difference, i.e. the retardation of the ordinary ray relative to the extraordinary ray. For any crystal section the amount of retardation of one wave behind the other depends on the difference in wave velocity beams in a direction normal to the plane of the section. The retardation also depends on the thickness of the crystal plate. Since the wave velocities are related inversely to their respective refractive indices, the relative retardation of the section is given by the formula: $R = (n_1-n_2)t$, where 'n_1-n_2' is the difference between the two refractive indices for the ordinary and extraordinary rays, i.e. its birefrigence and 't' the thickness of the plate. The phase difference between the two components of velocity on emergence from the crystal is given by $RX360/\lambda$, R being the relative retardation, λ the wavelength of incident light. If the sample is viewed in white light and at the same time its thickness is varied from zero to a finite quantity, a series of different colors will be seen. This is because the increasing thickness introduces a phase difference between the two components of velocity and consequently constructive and destructive interference occurs at different thickness for different wavelengths. The colour from zero thickness upwards are arranged in orders, the Newton colour scale, each one terminating and including red. As the thickness is increased still further, the colours become further and further complex, owing to the overlapping of the extinction bands for different parts of the spectrum, the fifth and sixth orders consisting mainly of pale pinks and greens. In still higher orders these colours merge in to white.

For bireflecting substance the two reflectance belonging to the principal directions in a surface may also vary independently according to the wavelength of light used. In white light the two directions then present different characteristics tints. This is sometimes called 'reflection pleochroism', since it has some analogy with pleochroism in transmitted light. The latter, however, depends substantially on the absorption, while the reflectance (ratio of the intensity of the reflected light to that of the incident beam) is determined by both absorption and refractive index. As the stage is rotated under polarized illumination the reflected light changes in tint through the admixture in varying proportions of the two component tints, each of which is seen unmixed when the vibration direction of the incident light coincides with the corresponding principal direction. The changes obtained in this way are very characteristic. In a uniaxial crystal there are two principal colours, for light vibrating parallel or perpendicular to the crystal axis and in inclined sections the tiuts remain the same. In a biaxial crystal there are three principal colours and the effects for inclined section are more complicated. An important aspect of these vibrations is that the difference between the reflectance for the two principal directions, i.e. the bireflection for the section, though small, often varies greatly with the wavelength. This is termed 'dispersion of the bireflection'. It causes very distinctive colour effects when the section is examined with the two polar at or near the crossed position.

5.22 Conoscopic Arrangement

The passage of light through a polarizing microscope when it is used as a conoscope to observe a specimen on the stage of the microscope is indicated in fig. 5.2. The conoscopic arrangement requires, in addition to the polarizer and analyser, the insertion of an Amici-Bertrand lens and a substage condensing lens. The former converts the microscope into a low power telescope focussed at infinity. The latter causes the object on the stage to be illuminated by a cone of light rather than by a bundle of near-parallel rays as it is with orthoscopic case. important additional information may be obtained by passing a strongly convergent beam of light through the crystal when it is possible, by various means, to examine the optical character in many directions at ona and the same time. This is done by viewing between crossed polar, not the image of the crystal but another optical image formed in the principal focus of the objective by the strongly convergent beams of light. This image is called the 'interference figure'. Each point in the field corresponds to a given direction through the crystal. In effect, the Bertrand lens and the eyepiece constitute a system used to examine the pattern in the back focal plane of the objective.

The interference figures produced in a conoscope can be classified into two broad divisions: those formed by the uniaxial crystal and those formed by the biaxial crystals. The former pattern consists of concentric circles[4,5,6,7] known as "isochromes" into which is superposed a pattern in the shape of a maltese cross (fig. 5.3), the arms of which are known as 'isogyres'. This pattern is produced assuming that the section of the crystal is normal to the optic axis, or in the basal section. On rotation of the stage, the pattern remain unchanged provided that the optic axis is centered and perpendicular to the stage. If a section of the crystel parallel to the optic axis is used then the isogyres only retain a broad cross shape when the optic axis is parallel to one or other of the polar. Rotetion of the stage causes the isogyres to move in and out giving rise to 'flash figures'.

In a biaxial crystal there are two optic axes, the lines bisecting their enclosed acute angle is called the 'acute bisectrix'. The interference figure obtained when viewing a section normal to the acute bisectrix consist of two 'eyes' or melatopes (fig. 5.4), which mark the points of emergence of the optic axes, surrounded by bands of equal retardation, coloured in white light. On to this pattern are superimposed the isogyres which form a cross when the trace of the optic axial plane (i.e. the line joining both melatopes) lies parallel to either polar, that arm of the cross passing through the melatopes being narrower than the other. Rotation of the crystal away from this position causes the cross to breakup into two hyperbolic brushes which are centred on the melatopes. The isogyres revolve in a direction opposite to the movement of the stage.

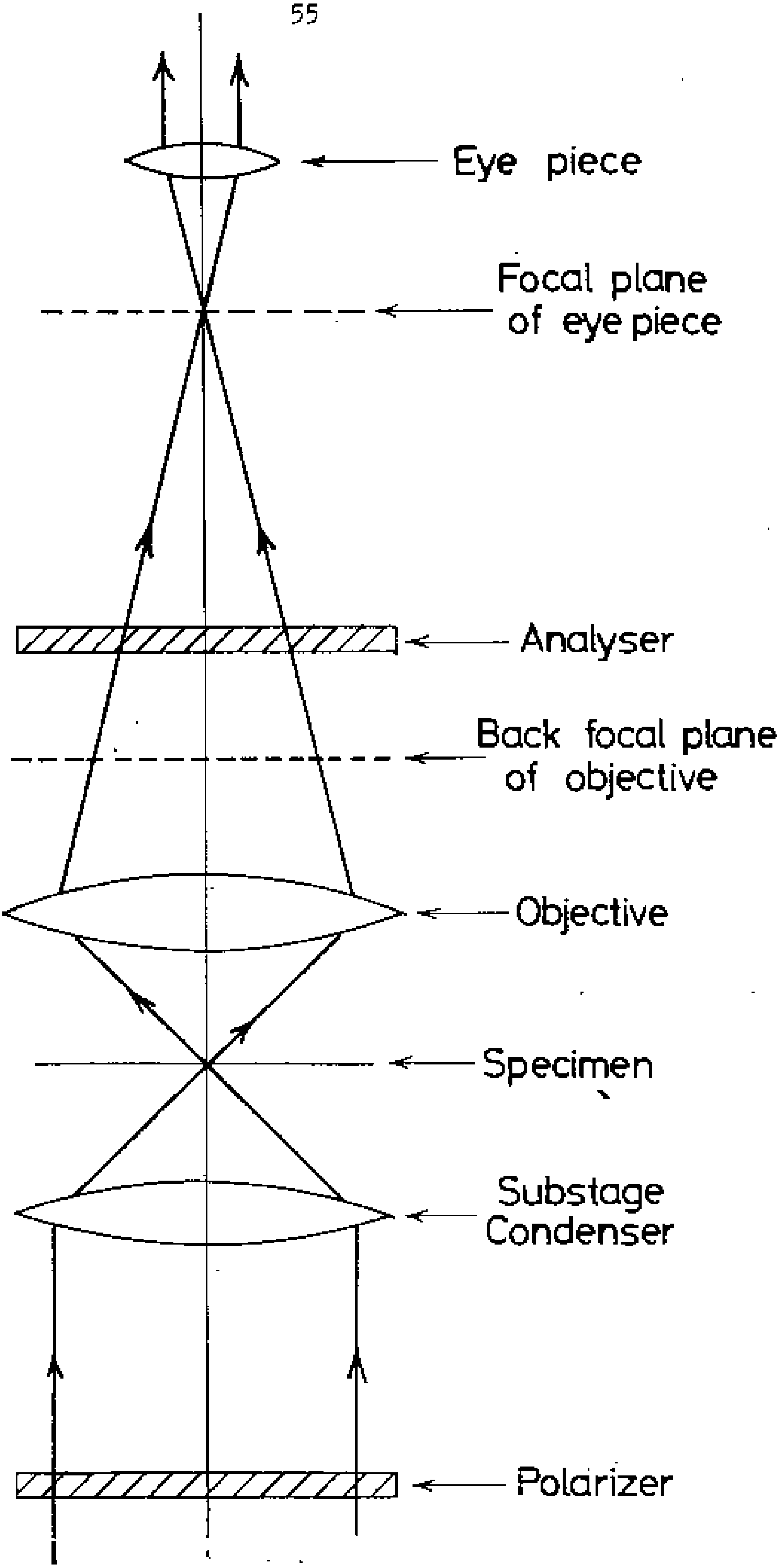

Fig. 5.1. Polarizing microscope in orthoscopic mode.

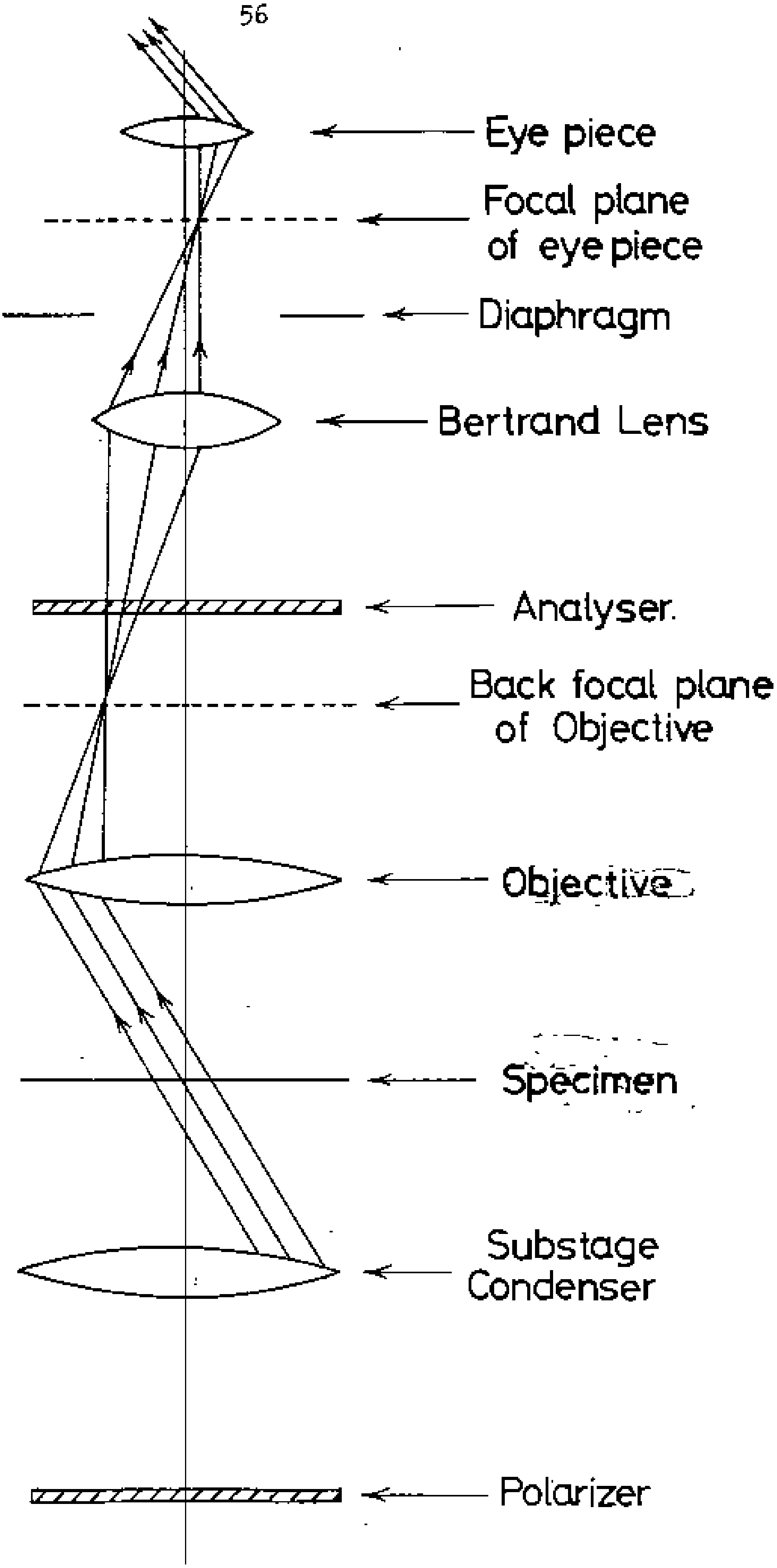

Fig. 5.2. Polarizing microscope in conoscopic mode.

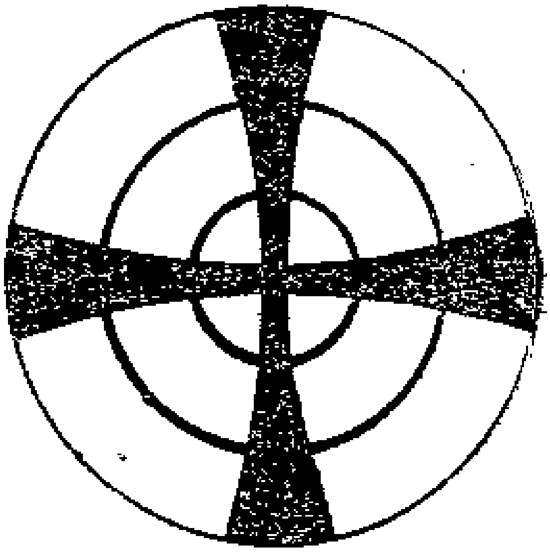

Fig. 5.3. Typical interference figure for uniaxial crystal.

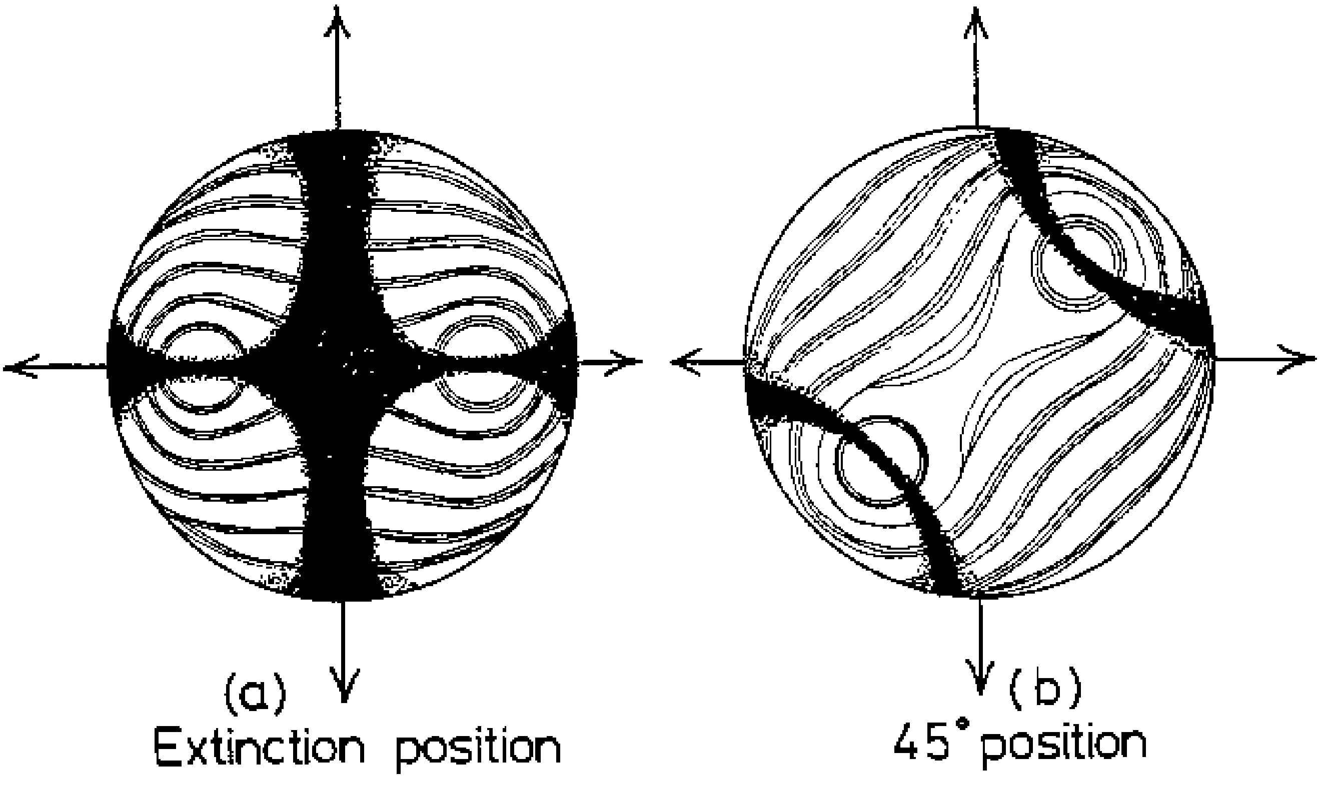

Fig. 5.4. Biaxial interference figure given by a section normal to the acute bisectrix.

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CHAPTER 6

EXPERIMENTAL RESULTS SAND DISCUSSIONS

6.1 Material preparation

6.11 Introduction

Coconuts abundently grow in almost all the regions of Bangladesh. People are mostly wasting the shells of the coconut by throwing them here and there. The carbon yield from the charring of the wasted shell is possibly the highest so far known. There are immense uses of carbon in our everyday life. The artificially prepared carbon has become important now a days because naturally occuring graphite are available only in few of the countries. Scientists are still searching for carbon rich materials to produce artificial graphite and diamond by carbonising these carbonaceous materials.

6.12 Preparation of raw-samples

Coconut-shells from different areas of Bangladesh were collected. They were then sun dried in open atmosphere. The sample when dried was ground to powder in a hand driven grinder. The powder so prepared were oven dried et 104°C for about fifteen minutes. The powders were then put inside small container and then preserved in a dessicator.

6.13 Preparation of samples for DTA, polarized-light micrography and resistivity measurement.

6.13.1 Sample preparation for DTA

Two grams of the prepared powdered samples were taken inside a sealed tube made of pyrex glass and then heat-treated inside a solenoidal horizontal furnace to the desired temperature. The pyrex tube was heavy walled, 2.5 mm in thickness in order to withstand the heavy pressure developed due to emission of various hydrocarbon gases during pyrolysis. Four samples were prepared for DTA analysis, one raw without any heat-treatment, one partially carbonized at 380°C, one at 400°C and the rest carbonised at 450°C. The sealed tubes containing the heat-treated sample were allowed to cool. When cold, they were then successively held horizontally inside the specially designed safety box and then cut one by one at the central portion of the tube with a diamond edge. Usually a strong push at the central portion from below was sufficient to break the tube. These heat-treated samples were then dried, put inside a container and then preserved inside a dessicator for DTA analysis.

Selected samples have been heat-treated in Shimadzu Micro differential thermal analyser (Model DT-30). These samples (0.1g) were heat-treated in the inconel head to 700°C with dry alumina being employed as the inert material in the reference cell.

6.13.2 Sample preparation for polarized-light micrography

Samples for polarized-light micrography were obtained by heating about 0.5 g of the original powder samples (Art 6.12) in a sealed tube inside the same solenoidal furnace to the desired temperature at which investigation was necessary. A heating rate of 10°C per min was adopted using a temperature controller. The sample was then heated to carbonise at a fixed temperature for a fixed duration. The sample was then allowed to cool. The sealed tube cooled to room temperature was these opened inside the safety box using the same technique as before. The sample removed from the tube was then dried and embedded in a cold setting mounting resin in the manner described below:

A 1.5" in length of 1.25" in O.D. and 10 s.w.g. brass tube with one end accurately machined to a flat finish was taken. A piece of metal with flat surface was also taken and its surface was smeared lightly with vaseline. The inside wall of the tube was also coated with vaseline to prevent adhesion to the mount. The heat-treated sample was then placed on the metal plate facing downwards and the tube whose inside diameter is more than the sample was placed over the sample. 1/8 inch of the plastic powder was then poured in the tube and the powders were then saturated with the liquid methyl methacrylate. In the beginning the slurry was kept stirring gently to prevent air bubbles adhering to the sample. After 20-30 minutes, the mould was lifted off the plate and the mount was tapped through with a rod and hammer.

The dried mounted sample was then ground progressively with finer grades of water proof silicon carbide paper progressing from 120 to 600 grit to expose the carbonised residue in the sample. The polishing process used is described below.

The silicon paper in the form of a disc was fixed on the top of a rotator and the sample was allowed to be rubbed by the silicon paper when the disc was kept on rotation. Light but steady pressures were applid on the sample while it was rubbed by the silicon carbide paper. The direction of polish was maintained constant except for reversals made at regular intervals by lifting and rotating the sample by 180^0 at hand. Accordingly the sample was not moved about the wheel but was only moved laterally between the centre and the peripherry. The sample was washed with tap water before using with another comparatively finer grade of carbide paper. The best results were achieved by using fresh paper for each sample and by grinding some-what further than what was necessary at each grit level to remove the scratches from the preceeding paper. After the final grinding on 600 grit paper, the surface of the sample appeared bright independent of the level of heat-treatment.

Subsequent polishing was done with Hyprez diamond lapping compounds(6 micron size followed by 1 micron size) on a wet polishing TEXMET cloth in the way described as follows:

The coarse grade Dialap diamond compound was spread over the polishing TEXMET cloth fixed on one of the rotating discs of the polisher and the sample was kept on rubbing for about five minutes and then thoroughly washed with tap water. The finer grade diamond compound was then spread over another polishing TEXMET cloth fixed on the other rotating disc of the polisher and the sample was again kept on rubbing for another five minutes.

Final polishing of the sample was carried out by high purity linde Alpha Alumina powder. The powder was first wetted with distilled water and the sample was then rubbed gently by it with hand in the same direction for about ten minutes. The final polishing resulted in a high polished surface having a bright lustre, necessary for observation by polarized light microscopy.

The polished sample when observed by a Reichert METAVERT polarizing microscope with cross-polars having the gypsum plate (red I plate) at an angle of 45^0 with one of the polars (Sensitive tint technique), either the carbonaceous mesophase appears as spherules or coalescence as a mosaic texture otherwise a complete dark background is observed.

6.13.3 Sample preparation for resistivity measurements:

Some of the prepared raw powder samples described in art 6.12 were placed inside three different pyrex glass tubes and heat-treated in exactly the same manner using the same procedure of art 6.13 except that the heat treatment temperature for the three samples were arbitrarily selected as

350^{0}C, 400^{0}C and 450^{0}C respectively. The disc shaped specimens for the d.c. conductivity measurements were prepared from these pyrolysed powders by the following method. A borosilicate glass tube of 5 mm internal diameter (I.D) and 7.24 mm outside diameter (O.D.) were used as the jig for preparing the specimens. A small solid brass cylinder of O.D. 5 mm with flat end surfaces was pnshed inside from one end of the glass tube. A thin aluminium foil was then placed on the flat surface and the required amount of pyrolysed powders were then introduced in the glass tube. On the top of the powders another thin piece of aluminium foil was placed and then another solid brass cylinder of internal diameter 5 mm was placed on top of the foil. The powders thus sandwiched between the two aluminium foils were then pressed with a hydraulic press using a pressure of 250 PSI. An intimate contact between the sample and the foil was achieved in this method. These disc shaped specimens with aluminium foil caps at the both ends were used for the conductivity measurements.

6.2 Results and Discussions

6.21 Differential Thermal Analysis (DTA)

Differential Thermal Analysis (DTA) is an efficient powerful tool for determining the graphitic and non-graphic behaviour of the organic samples[1,2,3]. An initial endotherm in the DTA trace, with a few exceptions, generally predict that the sample under investigation is graphitic in nature. Chain-stripping and associated reactions which produce endothermic peaks often allows the formation of oriented aromatic rings thereby giving rise to graphitizable carbons. On the otherhand, cross-linking producing an exothermic peak prevents the formation of oriented layers. Therefore, if an exothermic peak appears some where in the initial portion of the DTA e.g. in the first stage of decomposition curve the sample may produce carbons of non-graphitic in nature.

The DTA trace of raw coconut shell is shown in fig. 6.1. An endothermic peak in the initial portion of this curve at a temperature lower then 100^{0}C possibly indicates hydrogenation and removal of moisture-contents e.g. absorbed water or other volatile impurities. With the gradual rise of temperatures the hydrogenation and removal of moisture and absorbed water as well as volatile impurities becomes complete and ultimately an exothermic peak appears nearly at 370^{0}C.

The DTA traces for the partially carbonized coconut shell samples heat treated at 380^{0}C. 400^{0} and 450^{0}C each for two hours durations are shown in figs. 6.2, 6.3 and 6.4 respectively. In these curves no initial endothermy were observed possibly because the samples are well dried. All these curves shows an exothermic peak initially at 355^{0}, 350^{0} and 385^{0}C respectively indicating non-graphitizing character of the sample. An exothermic peak in the initial portion of the DTA curves indicates crosslinking which retards the formation of oriented layers, one of the criteria of graphitization. So, coconut shell on pyrolysis gives rise to carbons, non-graphitic in nature. The physical appearance of the carbon obtained from coconut shell are shown in plates 6.1 and 6.2.

Carbons obtained from coconut shell are found to be hard having high microporosity with relatively low density and hence they satisfy another important criteria of a non-graphitizable carbon.

6.22 Polarized-light photo-micrography

During carbonization all graphitizable organic compounds pass through a liquid crystal plastic stage called mesophase in the temperature interval 350^{0}-600^{0}C with the formation of spherule, colescence and mosaic texture[4,5,6]. This is observed by a Reichert METAVERT polarizing microscope with crosspolars having a gypsum plate at 45^{0} in between both the polar (So-called Sensitive tint method).

In the mesophase regions the coconut shell under investigation was carbonized. The samples carbonized at different temperatures for different duration of times are mounted and polised as indicated in article No. 6.13.2. The samples was observed with Reichert METAVERT polarizing microscope using reflected polarized-light by the so-called Sensitive tint technique.

The formation of spherule, growth of spherule or mosaic formation could not be observed with cross-polar. Thereby, a conclusion about its non-graphitizing character was drawn. We took some photo-micrographs of carbonized coconut-shell by the

Reichert **METAVERT** polarizing microscope using reflected polarized-light. The microscope was equipped with the 35 mm Remica III photomicrographic camera. The light source of the microscope was a 6V-15W halogen bulb. An exposure time of 10 minutes per photograph was used. The colour photomicrographs obtained by using **FUZINEOPAN** 135 mm 36 exp. film are depicted in plate No. 6.3-6.6. The analyzer and the polarizer remained parallel to each other. When the analyzer and polarizer remained cross with respect to each other with the gypsum plate at an angle of 45^0 with the analyzer, extinction occurs giving dark background. This is an indication of the fact that the sample is isotropic rather than anisotropic.

6.23 RESISTIVITY MEASUREMENTS

The disc shaped specimen prepared with the thin Aluminum foils at its opposite faces was placed between two brass electrodes. The electrodes were kept pressed on the specimen by two stainless steel springs attached with them. These electrodes worked both as the current and potential contacts on the specimen. The specimen thus rigidly held between the electrodes was placed inside a vertical mini furnace. The furnace in turn was placed inside a cylindrical metallic chamber. During experiment the top and bottom end of the metallic chamber was kept closed for maintaining a uniform temperature within the chamber. Thin mica sheets were placed arround the inside of the metallic chamber to avoid any electrical contact between the heating element of the furnace and the metallic chamber.

The specimen placed inside the mini furnace was then heated at a rate of about 3 degrees per minute. The heating rate of the specimen was controlled by controlling the current to the furnace by a variable transformer.The temperature of the specimen was monitored by a thermocouple kept closed to the specimen. The thermocouple out-put was recorded by a microvoltmeter type 53213 of Leybold Heraeus. A constant voltage of around 80 volt dc was applied across the specimen using a power supply type 6181C of Hewlett Packard and the current output across the sample was recorded by a Keithly electrometer type 614.

The measurements of the current and voltage across the specimen were taken during heating at an interval of 12.5 degrees. The measurements were performed in the temperature range of 25°C to 300°C. When one cycle is completed the specimen was allowed to cool to room temperature in the furnace. Then the measurements during the second cycle of heating were taken. Same procedure was applied for the third set of measurements. The conductivity values calculated from these measured values of voltage and current at different temperatures are given in Table 1a, 1b, 1c, 2a, 2b, 2c and 3a, 3b, 3c.

The three sets of ln σ Vs 1000/T curves obtained for the three specimens pyrolysed at three different temperatures are shown in figs.6.5 - 6.7. The results of the successive heating cycle are marked with a, b and c. The curves show that in the first heating cycle the conductivity has a peak arrounds 60°C (curves 6.5a, 6.6a. 6.7a) and then starts decreasing and reaches the lower limit around 100^{0}C. The conductivity then increases with temperature. With the repeated heating cycle the initial peak portion of the curve gets considerably reduced i.e. shallower, where as the lnσ Vs 1000/T curve for temperature above 100^{0}C remains almost identical. Similar pattern was observed for all the three specimens.

This we believe is due to the reason that water contents and may be volatile hydrocarbons were present in the prepared disc shaped specimens. When the specimens are heated the mobility of the volatile products increases and reaches a peak value around 60^{0}C. With further heating the water content starts evaporating and the evaporation is supposed to be complete at a temperature higher than the boiling temperature of water which is 100^{0}C. From the curves it appears that when the sample was allowed to cool in the furnace before taking the measurements for the second cycle of heating (curves 6.5b,6.6b,6.7b), the specimen absorbs some moisture probably just on the surface.

The absorbed moisture content is expected to be much lower than the initial amount present in the starting disc shaped sample. This is manifested by a shallower peak in the initial part of the curve. Besides it appears that a very small amount of the moisture content remains entrapped within the specimen in the first heating cycle even at elevated temperature. This is manifested by the slight reduction of the conductivity at elevated temperature during the second cycle of heating. With repeated heating cycle the entrapped moisture content gets further reduced and the conductivity values obtained at higher temperature approaches its ultimate value, attributed to the specimen only. Since the sample absorbs some moisture during cooling cycle, the conductivity at lower temperature ($<100^{0}C$) will have some contributions from the absorbed moisture content. Thus $\ln\sigma$ Vs 1000/T curve is expected not to be fitted by a single straight line through out the whole temperature range of measurements. The conductivity values obtained in the present measurements at temperatures higher than $T>100^{0}C$ are found to satisfactorily fit a straight line when drawn $\ln\sigma$ Vs 1000/T (figg. 6.5, 6.6 and 6.7).

The observed increased value of conductivity with temperature satisfying a straight line relationship for $\ln\sigma$ vs 1/T is a manifestation of the fact that all the specimens are semiconducting in nature and satisfies the relation $\sigma = \sigma_0 e^{-E_a/KT}$. This equation can be rewritten as

$$\ln\sigma = \ln\sigma_0 - Ea/KT$$

Thus when $\ln\sigma$ drawn against 1/T a straight line fit is expected with the slope equal to $-Ea/K$. The activation energy Ea of the three specimens under investigation were thus calculated from the slope of the $\ln\sigma$ Vs 1000/T curve and are tabulated in table 4.

It is seen that the specimen pyrolysed at higher temperature have lower activation energy than the one pyrolysed at lower temperature. This we believe is due to the reason that pyrolysing the specimen at higher temperature the sample gets more carbonized. As a consequence cross linking between pair of layer planes in the sample increases, and more π-bonds are created resulting in the increase in charge carriers in the valance bond and narrowing of the energy gap. This means that pyrolysing at higher temperature the materials gets more conducting. The observed activation energy for the three specimens pyrolysed at 450^0C, 400^0C and 350^0C are 9.2 Kcal, 10.6 Kcal and 13.6 Kcal. per mole respectively. These values of the activation energy are much lower than the values (about 60 Kcal/mole) obtained for graphitizing polymeric materials showing semiconducting behavior[7,8,9]. Thus we may conclude that the sample under investigation are semiconducting but non graphitizing in nature.

Table 1a

Sample:
Coconut-shell pyrolysed for 2 hours at 450°C
Dimension of the sample, Diameter : 5 mm
Thickness : 3.06 mm
Applied voltage: 82 volt d.c.

Temperature T°K	$\frac{1}{T}$ x10^{-3}	Conductivity (σ)	ln σ
298	3.355	4.955x10^{-8}	-16.82
310.5	3.220	5.910x10^{-8}	-16.64
323	3.095	6.958x10^{-8}	-16.48
335.5	2.980	6.497x10^{-8}	-16.54
348	2.873	2.534x10^{-8}	-17.49
360.5	2.773	1.448x10^{-8}	-18.05
373	2.680	1.322x10^{-8}	-18.14
385.5	2.594	1.341x10^{-8}	-18.12
398	2.512	1.455x10^{-8}	-18.04
410.5	2.436	1.682x10^{-8}	-17.90
423	2.364	1.999x10^{-8}	-17.72
435.5	2.296	2.403x10^{-8}	-17.54
448	2.232	2.972x10^{-8}	-17.33
460.5	2.171	3.755x10^{-8}	-17.09
473	2.114	4.555x10^{-8}	-16.90
485.5	2.059	5.431x10^{-8}	-16.72
498	2.008	6.747x10^{-8}	-16.51
510.5	1.958	8.673x10^{-8}	-16.26
523	1.912	1.154x10^{-7}	-15.97
535.5	1.867	1.675x10^{-7}	-15.60
548	1.824	1.949x10^{-7}	-15.45
560.5	1.784	3.095x10^{-7}	-14.98
573	1.745	4.405x10^{-7}	-14.63

Table 1b

Sample:
Coconut-shell pyrolysed for 2 hours at 450^{0}C
Dimension of the sample. Diameter : 5 mm
Thickness : 3.06 mm
Applied voltage: 80 volt d.c.

Temperature T^0K	$\frac{1}{T} x10^{-3}$	Conductivity (σ)	ln σ
298	3.355	$9.180x10^{-9}$	-18.50
310.5	3.220	$1.132x10^{-8}$	-18.29
323	3.095	$1.406x10^{-8}$	-18.07
335.5	2.980	$1.621x10^{-8}$	-17.93
373	2.680	$9.765x10^{-8}$	-18.44
383	2.610	$9.180x10^{-8}$	-18.50
385.5	2.594	$9.375x10^{-8}$	-18.48
398	2.512	$1.035x10^{-8}$	-18.38
410.5	2.439	$1.230x10^{-3}$	-18.21
423	2.364	$1.503x10^{-8}$	-18.01
435.5	2.296	$1.953x10^{-8}$	-17.75
448	2.232	$2.637x10^{-3}$	-17.45
460.5	2.171	$3.046x10^{-9}$	-17.30
473	2.114	$3.828x10^{-8}$	-17.07
485.5	2.059	$5.197x10^{-8}$	-16.77
498	2.008	$6.915x10^{-8}$	-16.48
510.5	1.958	$8.326x10^{-9}$	-16.31
523	1.912	$1.138x10^{-7}$	-15.98

Table 1c

Sample:
Coconut-shell pyrolysed for 2 hours at 450^{0}C
Dimension of the sample. Diameter : 5 mm
Thickness : 3.06 mm
Applied voltage: 80 volt d.c.

Temperature T^0K	$\frac{1}{T} \times 10^{-3}$	Conductivity (σ)	ln σ
298	3.355	1.757×10^{-9}	-20.15
310.5	3.220	2.148×10^{-9}	-19.95
323	3.095	2.929×10^{-9}	-19.64
335.5	2.980	3.906×10^{-9}	-19.36
348	2.873	4.297×10^{-9}	-19.26
360.5	2.773	4.882×10^{-9}	-19.13
373	2.680	5.664×10^{-9}	-18.98
383	2.610	6.640×10^{-9}	-18.83
385.5	2.594	7.031×10^{-9}	-18.77
398	2.512	9.180×10^{-9}	-18.50
410.5	2.439	1.132×10^{-8}	-18,29
423	2.364	1.425×10^{-8}	-18.06
435.5	2.296	1.855×10^{-8}	-17.80
448	2.232	2.520×10^{-8}	-17.49
460.5	2.171	3.183×10^{-8}	-17.26
473	2.114	4.278×10^{-8}	-16.96
485.5	2.059	5.216×10^{-8}	-16.76
498	2.008	6.896×10^{-7}	-16.48
510.5	1.958	8.658×10^{-8}	-16.26
523	1.912	1.154×10^{-7}	-15.97
535.5	1.867	1.449×10^{-7}	-15.74

Table 2a

Sample:
Coconut-shell pyrolysed for 2 hours at 400°C
Dimension of the sample. Diameter : 5 mm
Thickness : 4.06 mm
Applied voltage: 82 volt d.c.

Temperature T°K	$\frac{1}{T}$x10^{-3}	Conductivity (σ)	ln σ
310.5	3.316	3.810x10-$^{-8}$	-17.08
314.5	3.184	4.980x10-$^{-8}$	-16.81
326.5	3.062	3.810x10-$^{-8}$	-17.08
339	2.949	1.092x10-$^{-8}$	-18.33
344	2.906	8.994x10-$^{-8}$	-18.52
351.5	2.844	9.273x10-$^{-8}$	-18.49
364	2.747	1.013x10-$^{-8}$	-18.40
376.5	2.656	1.232x10-$^{-8}$	-18.21
389	2.570	1.600x10^{-8}	-17.95
401.5	2.490	2.027x10^{-8}	-17.71
414	2.415	2.645x10^{-8}	-17.44
426.5	2.344	3.273x10^{-8}	-17.23
439	2.277	4.101x10^{-8}	-17.00
451.5	2.214	5.235x10^{-8}	-16.76
464	2.155	6.631x10^{-8}	-16.52
476.5	2.098	8.183x10^{-8}	-16.31
489	2.044	1.067x10^{-7}	-16.05
501.5	1.994	1.398x10^{-7}	-15.78
514	1.945	1.926x10^{-7}	-15.46
526.5	1.899	2.666x10^{-7}	-15.13
539	1.855	3.558x10^{-7}	-14.84
551.5	1.813	5.208x10^{-7}	-14.46
564	1.773	7.092x10^{-7}	-14.15

Table 2b

Sample:
Coconut-shell pyrolysed for 2 hours at 450^{0}C
Dimension of the sample. Diameter : 5 mm
Thickness : 3.06 mm
Applied voltage: 82 volt d.c.

Temperature T^{0}K	$\frac{1}{T}$ x10^{-3}	Conductivity (σ)	ln σ
300	3.333	9.654x10^{-10}	-20.75
312.5	3.2	1.430x10^{-9}	-20.36
325	3.076	1.989x10^{-9}	-20.03
337.5	2.962	2.782x10^{-9}	-19.70
350	2.857	3.750x10^{-9}	-19.40
362.5	2.758	5.106x10^{-9}	-19.09
375	2.666	6.707x10^{-9}	-18.82
387.5	2.580	8.841x10^{-9}	-18.54
400	2.5	1.166x10^{-8}	-18.26
412.5	2.424	1.595x10^{-8}	-17.95
425	2.352	2.106x10^{-8}	-17.67
437.5	2.285	2.896x10^{-8}	-17.35
450	2.222	3.847x10^{-8}	-17.07
462.5	2.162	5.058x10^{-8}	-16.79
475	2.105	6.784x10^{-8}	-16.50
487.5	2.051	8.818x10^{-9}	-16.24
500	2.0	1.184x10^{-7}	-15.94
512.5	1.951	1.510x10^{-7}	-15.70
525.5	1.904	1.949x10^{-7}	-15.45
537.5	1.860	2.469x10^{-7}	-15.21
550	1.818	3.278x10^{-7}	-14.93

Table 2c

Sample:
Coconut-shell pyrolysed for 2 hours at 450°C
Dimension of the sample. Diameter : 5 mm
Thickness : 3.06 mm
Applied voltage: 82 volt d.c.

Temperature T^0K	$\frac{1}{T} \times 10^{-3}$	Conductivity (σ)	$\ln \sigma$
300	3.333	5.401×10^{-10}	-21.33
312.5	3.2	7.690×10^{-10}	-20.98
325	3.076	1.111×10^{-9}	-20.61
337.5	2.962	1.633×10^{-9}	-20.23
350	2.857	2.456×10^{-9}	-19.82
362.5	2.758	3.348×10^{-9}	-19.51
375	2.666	4.488×10^{-9}	-19.22
387.5	2.580	6.070×10^{-9}	-18.91
400	2.5	7.896×10^{-9}	-18.65
42.5	2.424	1.080×10^{-8}	-18.34
425	2.352	1.502×10^{-8}	-18.01
437.5	2.285	1.978×10^{-8}	-17.73
450	2.222	2.649×10^{-8}	-17.44
462.5	2.162	3.575×10^{-8}	-17.14
475	2.105	4.990×10^{-8}	-16.81
487.5	2.051	6.430×10^{-8}	-16.55
500	2.0	8.539×10^{-8}	-16.27
512.5	1.951	1.140×10^{-7}	-15.98
525	1.904	1.470×10^{-7}	-15.73
537.5	1.860	1.851×10^{-7}	-15.50
550	1.816	2.518×10^{-7}	-15.19

Table 3a

Sample:
Coconut-shell pyrolysed for 2 hours at 350°C
Dimension of the sample. Diameter : 5 mm
Thickness : 4.60 mm
Applied voltage: 81 volt d.c.

Temperature T^0K	$\frac{1}{T} \times 10^{-3}$	Conductivity (σ)	ln σ
301.5	3.316	5.535×10^{-10}	-21.31
311	3.215	5.267×10^{-19}	-21.36
314	3.184	4.375×10^{-10}	-21.54
319	3.134	4.017×10^{-10}	-21.63
326.5	3.062	4.642×10^{-10}	-21.49
339	2.949	6.666×10^{-10}	-21.12
348.5	2.869	7.113×10^{-10}	-21.06
351.5	2.844	6.666×10^{-10}	-21.12
364	2.747	5.148×10^{-10}	-21.38
376.5	2.656	3.601×10^{-10}	-21.74
389	2.570	2.797×10^{-10}	-21.99
389.75	2.565	2.767×10^{-10}	-22.00
401.5	2.490	3.422×10^{-10}	-21.79
414	2.415	4.613×10^{-10}	-21.49
426.5	2.344	6.458×10^{-10}	-21.16
439	2.277	9.293×10^{-10}	-20.79
451.5	2.214	1.395×10^{-9}	-20.38
464	2.155	2.119×10^{-9}	-19.97
476.5	2.098	2.979×10^{-9}	-19.63
489	2.044	4.473×10^{-9}	-19.22
501.5	1.994	7.023×10^{-9}	-18.77
514	1.945	9.673×10^{-9}	-18.45
526.5	1.899	1.446×10^{-8}	-18.05
539	1.855	2.059×10^{-8}	-17.69
551.5	1.813	3.000×10^{-8}	-17.32

Table 3b

Sample:
Coconut-shell pyrolysed for 2 hours at 350^0C
Dimension of the sample. Diameter : 5 mm
Thickness : 4.60 mm
Applied voltage: 82 volt d.c.

Temperature T^0K	$\frac{1}{T} \times 10^{-3}$	Conductivity (σ)	ln σ
300.25	3.330	6.097×10^{-11}	-23.52
312.75	3.197	6.968×10^{-11}	-23.38
325.25	3.074	9.872×10^{-11}	-23.03
337.75	2.960	1.626×10^{-10}	-22.53
350.25	2.855	2.235×10^{-10}	-22.22
362.75	2.756	2.555×10^{-10}	-22.08
375.25	2.664	2.903×10^{-10}	-21.95
387.75	2.578	3.048×10^{-10}	-21.91
400.25	2.498	3.803×10^{-10}	-21.68
412.75	2.422	4.994×10^{-10}	-21.41
425.25	2.351	6.794×10^{-10}	-21.10
437.75	2.284	9.843×10^{-10}	-20.73
450.25	2.220	1.329×10^{-9}	-20.43
462.75	2.160	1.832×10^{-9}	-20.11
475.25	2.104	2.630×10^{-9}	-19.75
487.75	2.050	3.768×10^{-9}	-19.39
500.25	1.999	4.968×10^{-9}	-19.12
512.75	1.950	6.591×10^{-9}	-18.83
525.25	1.903	9.466×10^{-9}	-18.47
537.75	1.859	1.356×10^{-8}	-18.11
550.25	1.817	2.041×10^{-8}	-17.70

Table 3c

Sample:
Coconut-shell pyrolysed for 2 hours at 350°C
Dimension of the sample. Diameter : 5 mm
Thickness : 4.60 mm
Applied voltage: 82 volt d.c.

Temperature $T^{\circ}K$	$\frac{1}{T}\times10^{-3}$	Conductivity (σ)	ln σ
300	3.333	6.387×10^{-11}	-23.47
312.5	3.2	6.968×10^{-11}	-23.38
325	3.076	7.839×10^{-11}	-23.26
337.5	2.962	1.045×10^{-10}	-22.98
350	2.857	1.509×10^{-10}	-22.61
362.5	2.758	1.713×10^{-10}	-22.48
375	2.666	1.800×10^{-10}	-22.43
387.5	2.580	2.032×10^{-10}	-22.31
400	2.5	2.322×10^{-10}	-22.18
412.5	2.424	3.048×10^{-10}	-21.91
425	2.352	4.239×10^{-10}	-21.58
437.5	2.285	5.981×10^{-10}	-21.23
450	2.222	8.681×10^{-10}	-20.86
462.55	2.162	1.213×10^{-9}	-20.52
475.25	2.105	1.160×10^{-9}	-20.18
487.5	2.051	2.546×10^{-9}	-19.78
500	2.00	3.510×10^{-9}	-19.46
512.5	1.951	4.997×10^{-9}	-19.11
525	1.904	7.085×10^{-9}	-18.76
537.5	1.859	1.016×10^{-8}	-18.40
550	1.817	1.556×10^{-8}	-17.97
562.5	1.777	2.575×10^{-8}	-17.47
575	1.739	4.653×10^{-8}	-16.88

TABLE - 4

Pyrolysis temperature	Activation energy Kcal/mole
450°C	9.2
400°C	10.6
350°C	13.6

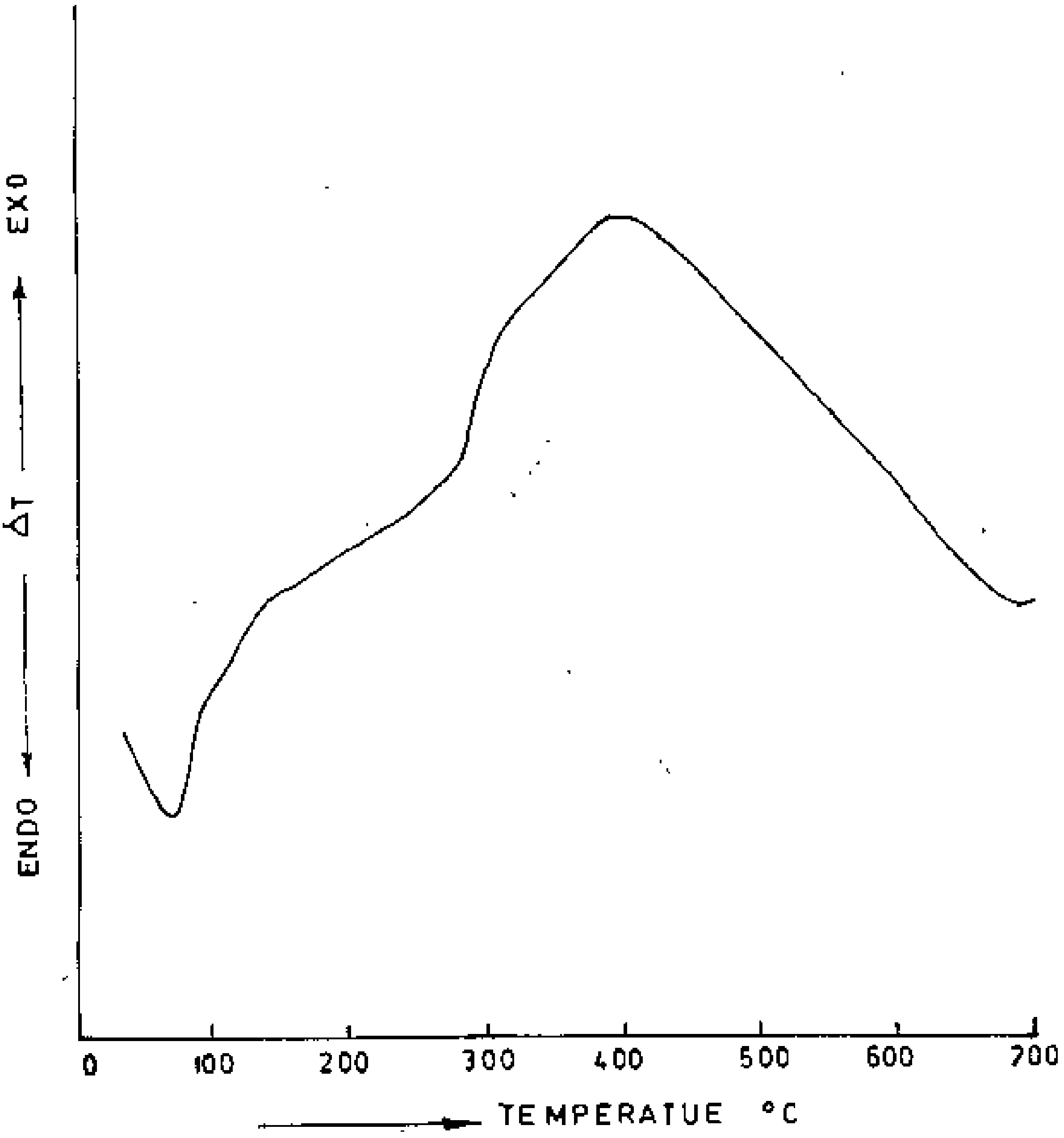

FIG. 6.1. DTA CURVE OF RAW SAMPLE OF COCONUT-SHELL.

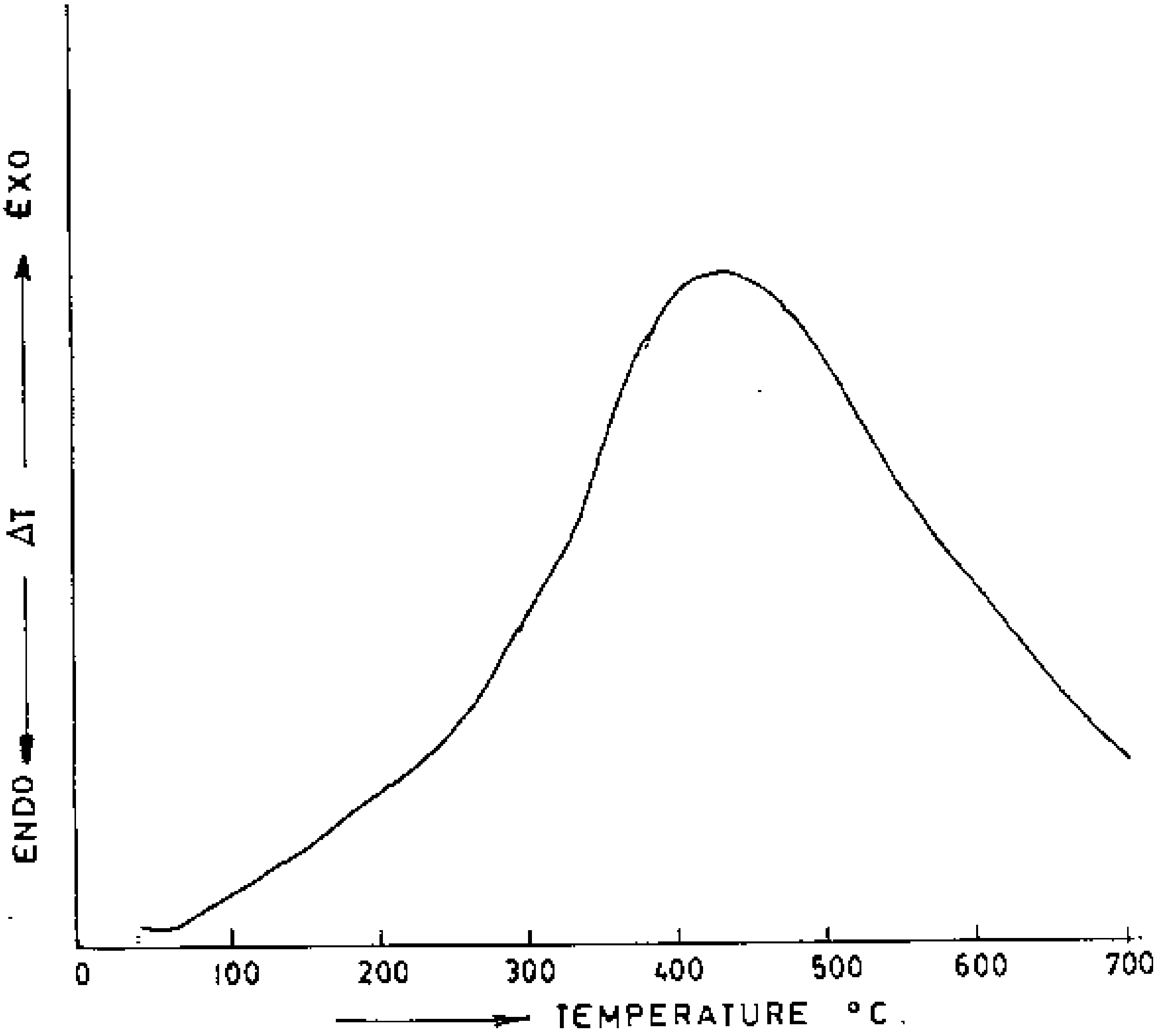

FIG. 6.2. DTA CURVE OF PARTIALLY CARBONISED COCONUT-SHELL HEAT-TREATED TO 380°C FOR TWO HOURS.

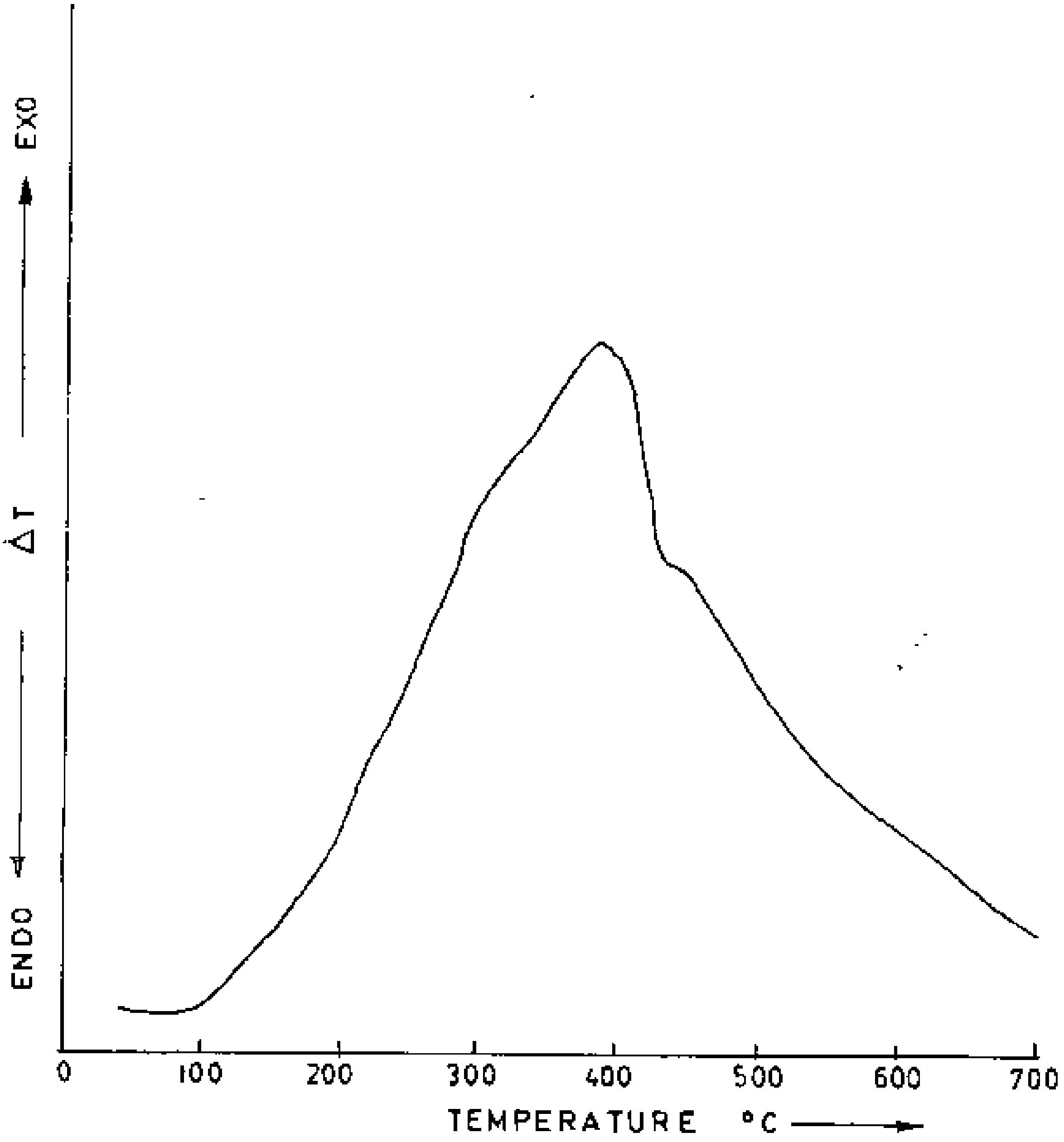

FIG. 6.3. DTA CURVE OF PARTIALLY CARBONISED COCONUT-SHELL HEAT-TREATED TO 400°C FOR 2 HOURS.

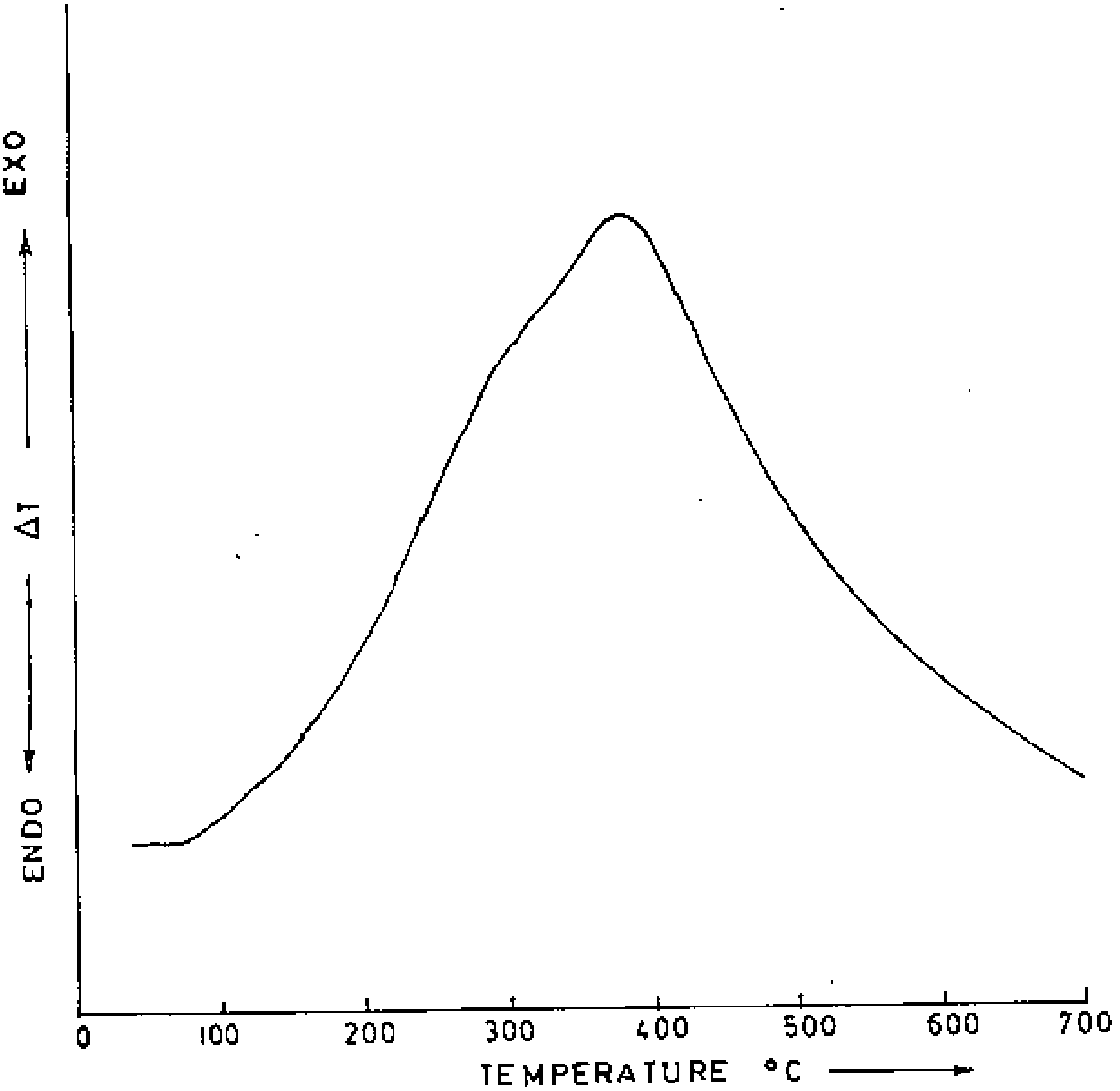

FIG.6.4. DTA CURVE OF PARTIALLY CARBONISED COCONUT-SHELL HEAT-TREATED TO 450°C FOR 2 HOURS.

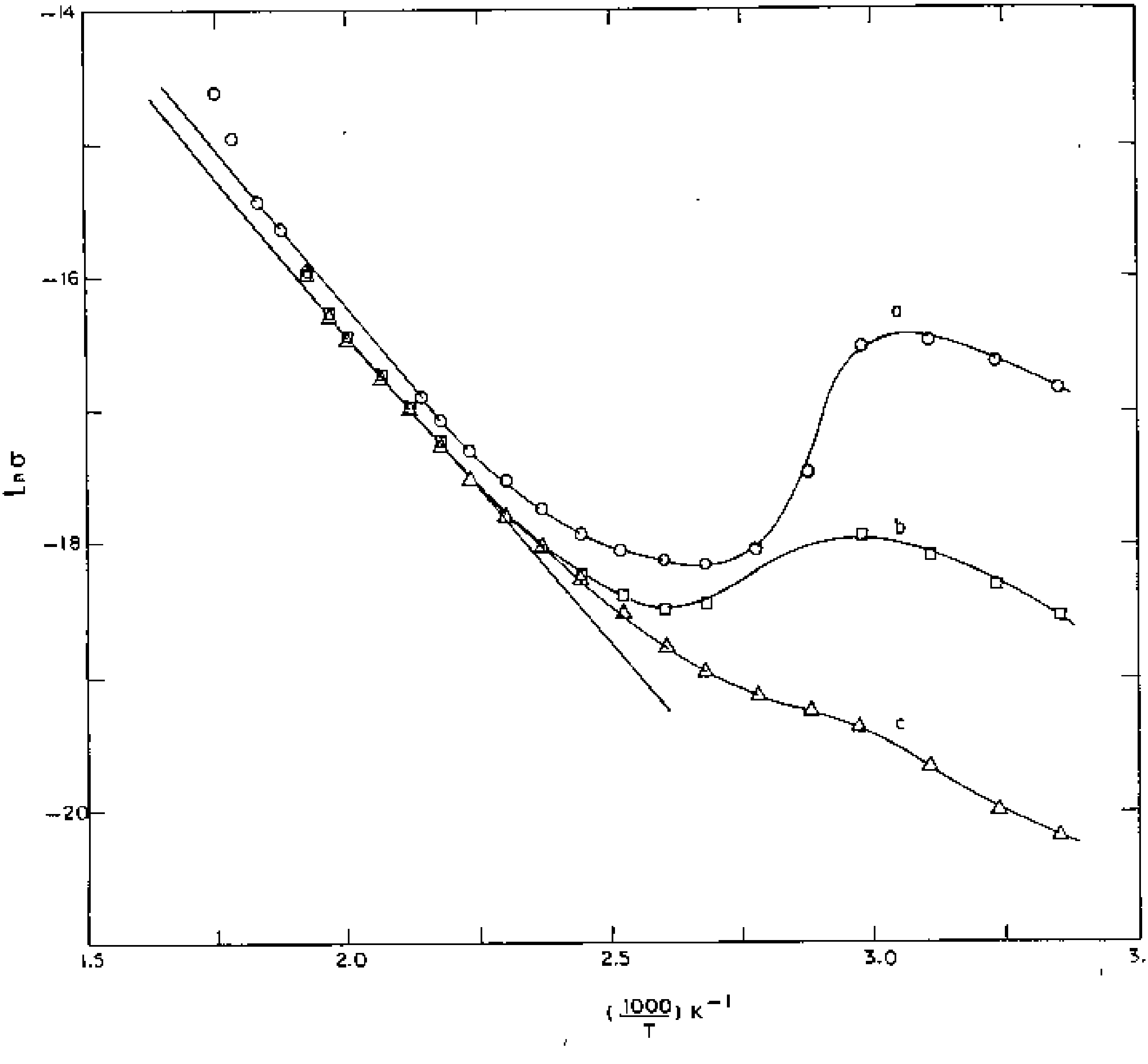

Fig.6.5 The temperature dependence of the conductivity of carbonised coconut-shell sample prepared from powders pyrolysed for two hours at 450°C (a, b, c represent the successive heating cycle)

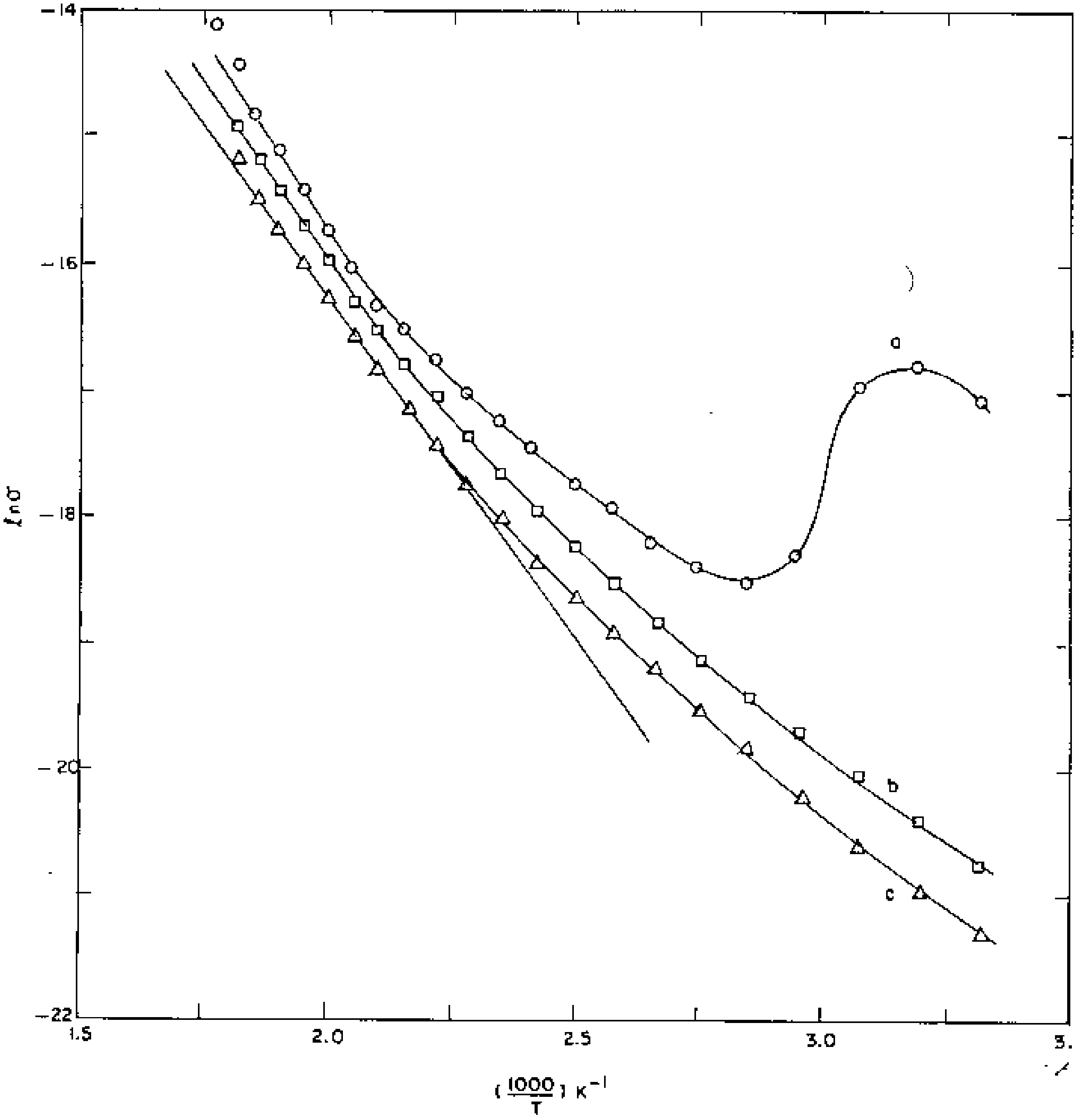

Fig 6.6 The temperature dependence of the conductivity of carbonised coconut-shell sample prepared from powders pyrolysed for two hours at 400°C (a, b, c represent the successive heating cycle)

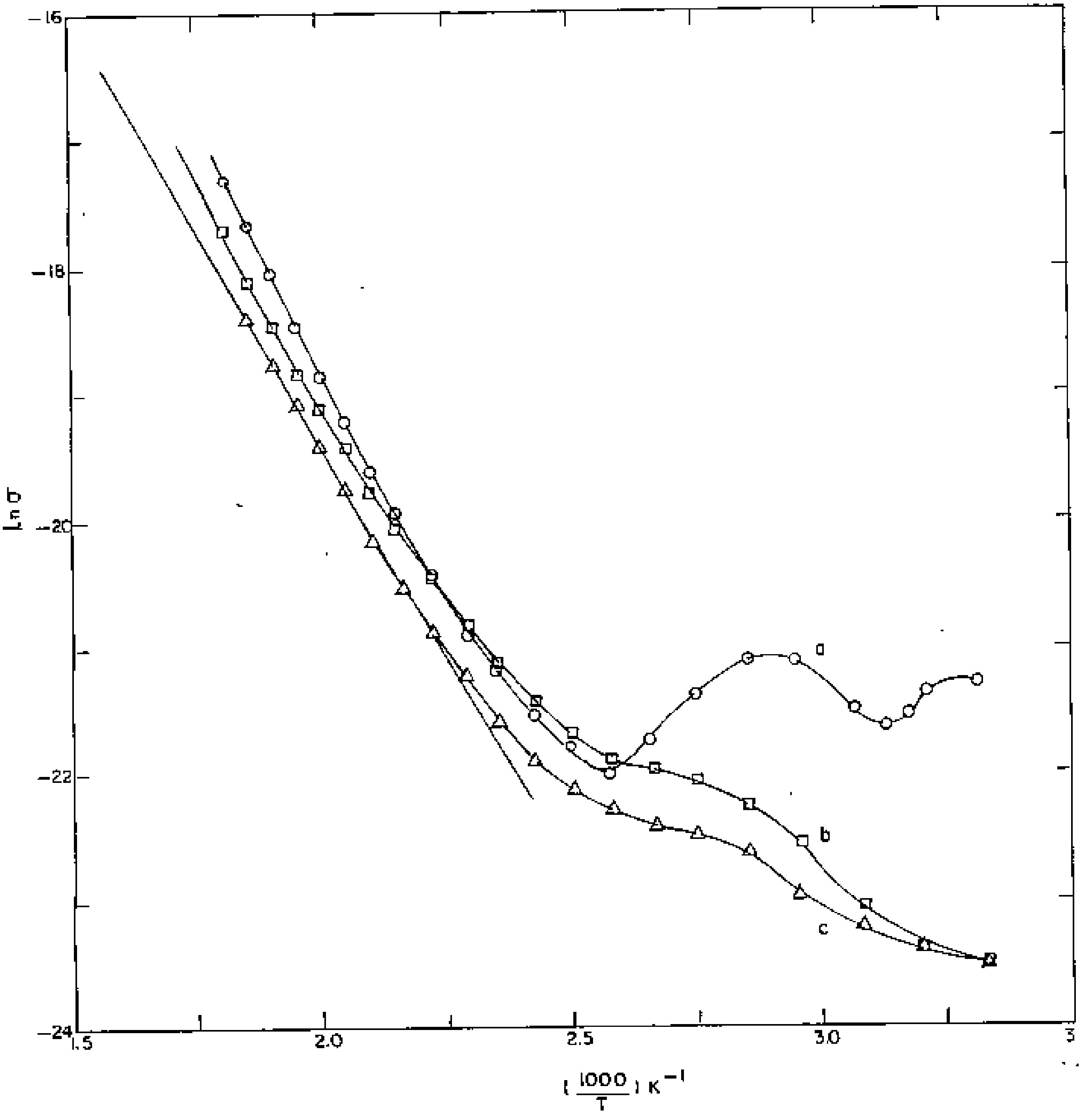

Fig. 6.7 The temperature dependence of the conductivity of carbonised coconut-shell sample prepared from powders pyrolysed for two hours at 350 °C (a, b, c represent the successive heating cycle)

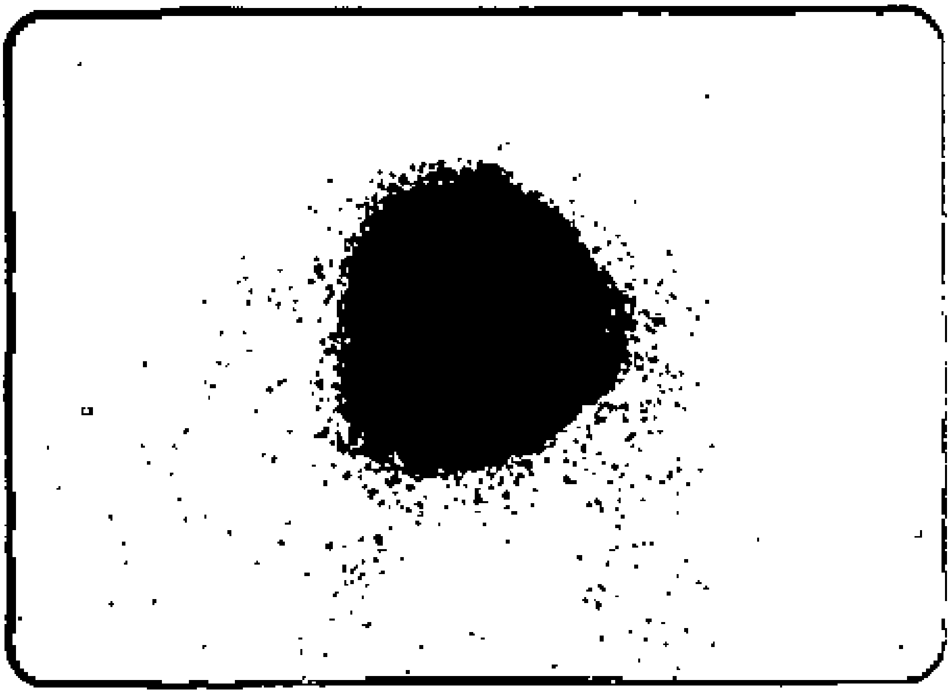

Plate 6.1: Physical appearance of powdered carbons prepared from coconut-shell.

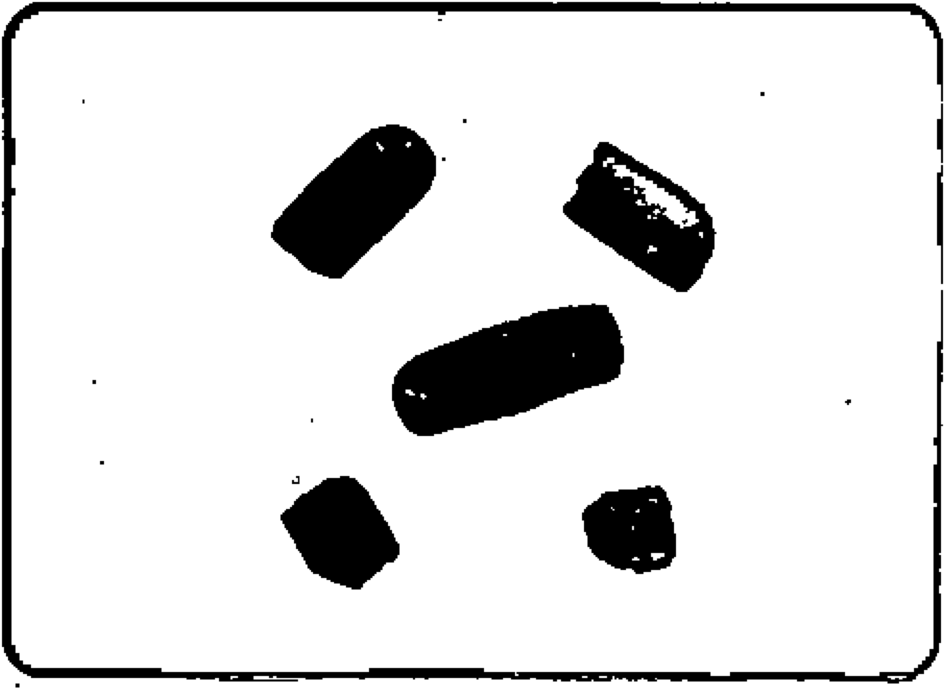

Plate 6.2: Physical appearance of carbons having microporosity prepared from coconut-shell.

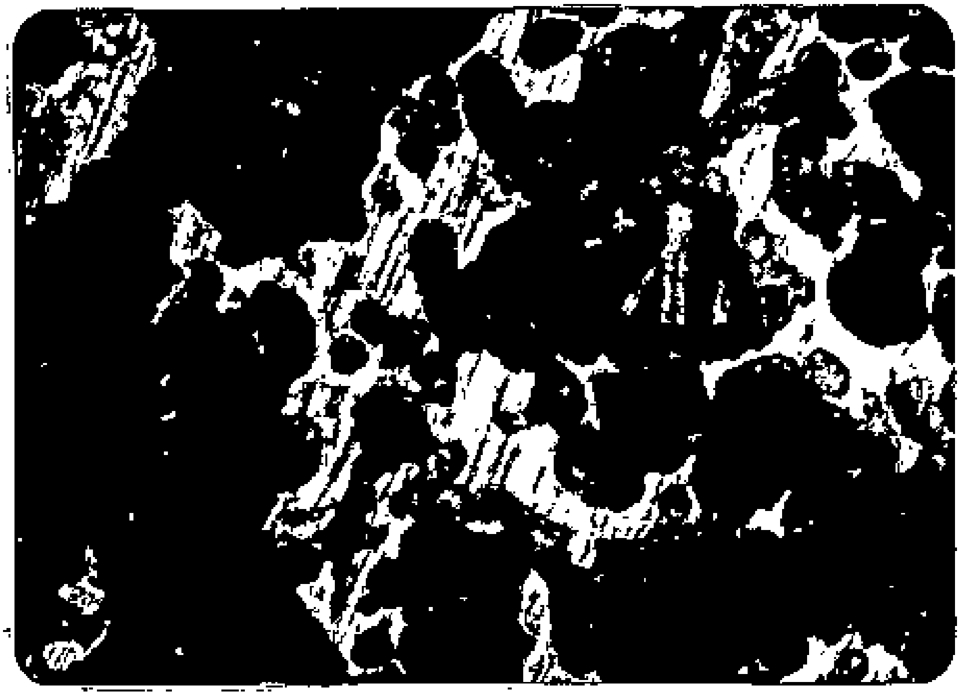

Plate 6.3: Polarized-light photomicrographs of coconut-shell heat-treated to 350°C for 2 hours.

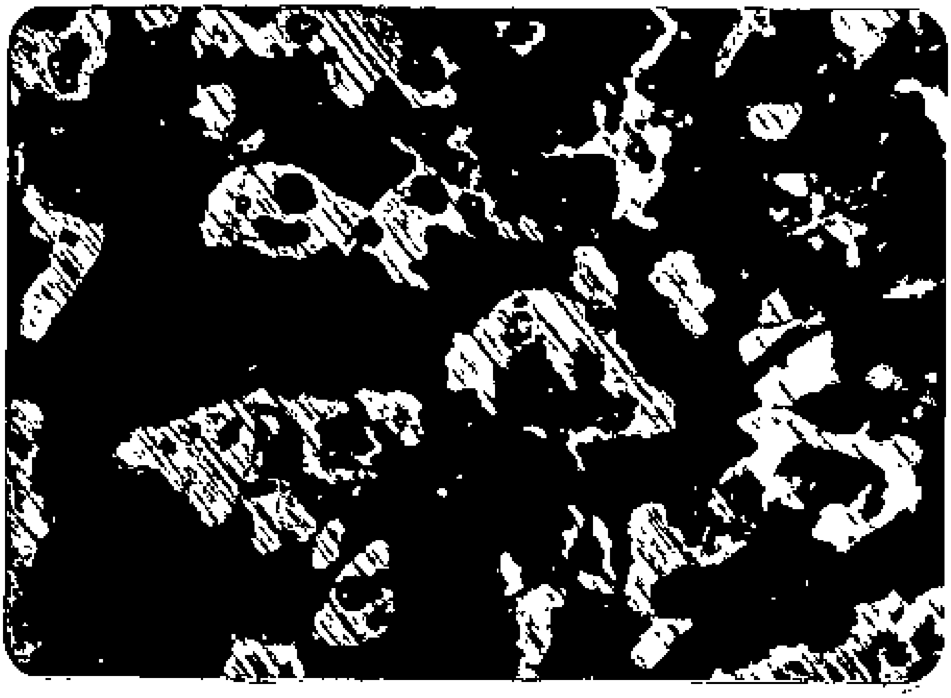

Plate 6.4: Polarized-light photomicrographs of coconut-shell heat-treated to 380°C for 2 hours.

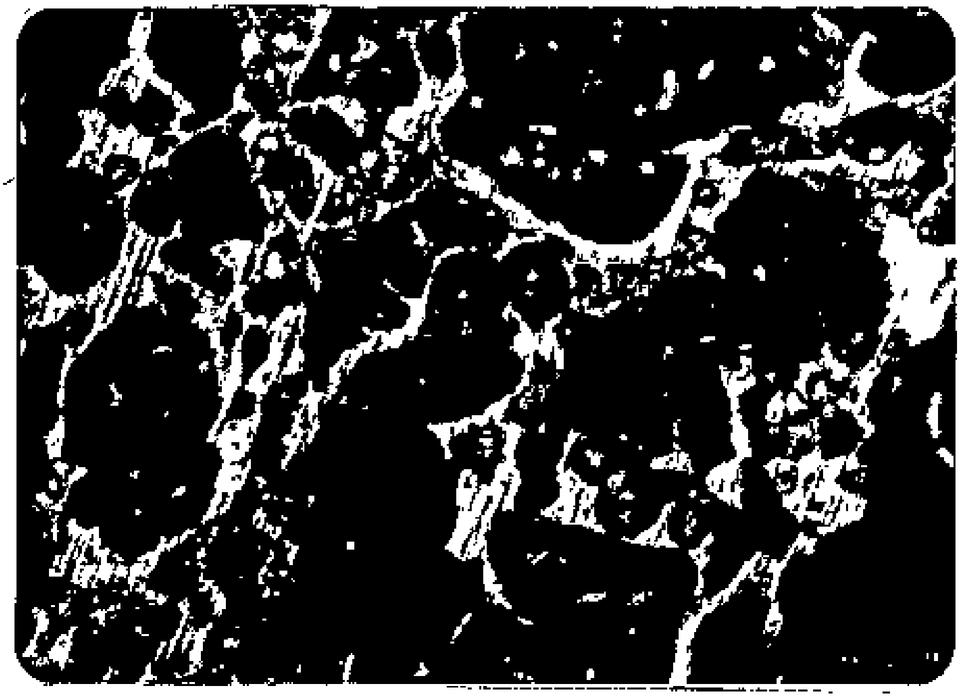

Plate 6.5: Polarized-light photomicrographs of coconut-shell heat-treated to 400°C for 2 hours.

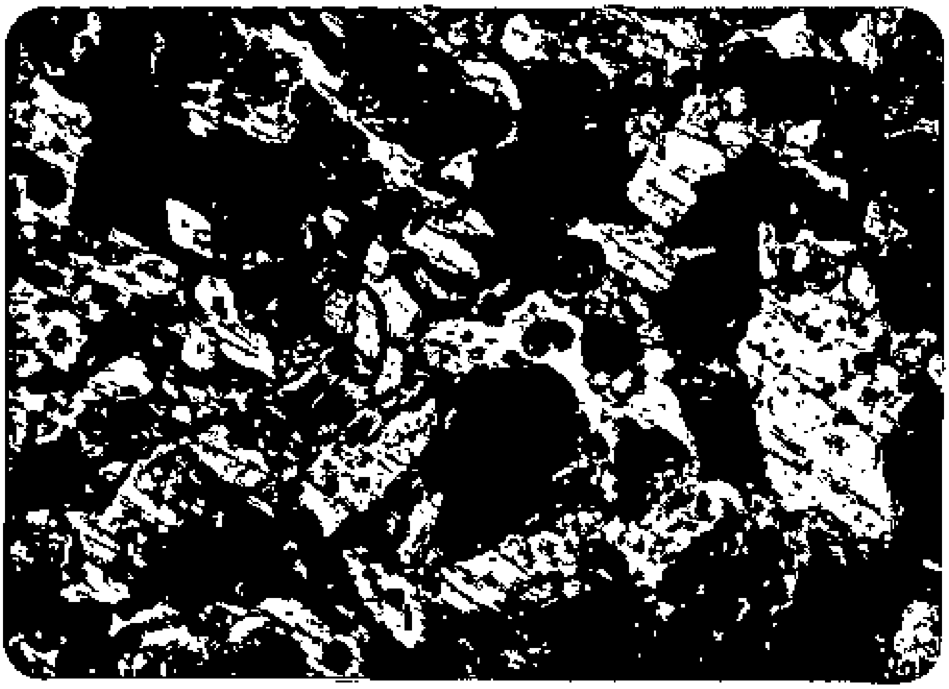

Plate 6.6: Polarized-light photomicrographs of coconut-shell heat-treated to 450°C for 2 hours.

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CHAPTER 7

CONCLUSIONS

If we review the criteria of a non-graphitizable organic compound, we can summarize:

(1) Non-graphitizable organic compounds does not pass through carbonaceous mesophase transformation in which large planer molecules become aligned in a parallel array to form an anisotropic liquid crystal with the formation of spherules , coalescence and mosaic texture. On the other hand, they give rise to carbons of optical isotropy during pyrolysis in the initial stage of carbonization. When observed by a reflected polarizing microscope with cross-polars with the sensitive tint plate at 45° with one of the polars complete darkness occurs signifying the fact that the sample under test give rise to non-grphitizing carbons.

(2) Non-graphitizable organic samples on heat-treatment depict a competing reaction:

Cross-linking producing an exothermic reaction. This cross-linking prevents the formation of oriented aromatic rings. So an exothermic portion of the DTA curve somewhere in the initial stage of decomposition indicates that the resulting product will be a non-graphgitizing carbon.

(3) Graphitic carbons physically appears as soft, black, shiny having low microporosity. Obviously, non-graphitizing

carbons are generally hard, comparatively less black and shiny with high microporosity and of low apparent density.

(4) For Graphitizable materials [illegible] endothermal process of decomposition are typical with the values of the effective activation energy exceeding 60 Kcal/mole For non-graphitizable one exothermal process of cross linking are observed with low values of the activation energy about 20 kcal/mole or less. The polarized-light photomicrographs (plates 6.3-6.6) obtained for the samples on heat-treatment at different temperatures and time indicate that they satisfy the first criteria of the non-graphitizable organic compound e.g. the compound do not pass through the carbonaceous mesophase transformation. So the carbons obtained from coconut shell by pyrolysis are non-graphiting in character.

Again the DTA traces (Figs. 6.2-6.4) having exothermic peak in the initial portion clearly indicate that the carbons obtained from coconut-shell by pyrolysis are non-graphitizing in character.

The physical appearance of carbons obtained from coconut-shell on pyrolysis (Plates 6.1,6.2) are found to be hard with high microporosity. They are not very much black and shiny. So the carbons obtained from coconut-shell are obviously non-graphitizing in character.