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STUDIES ON ETHYLENEDIAMINE–GRAPHITE OXIDE COMPLEXES—STRUCTURAL PARAMETERS AND INTERLAYER AREA

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Abstract—Natural and synthetic graphites were oxidized using the Staudenmaier reagent. The most strongly oxidized products were graphite oxides and the others contained both graphite and graphite oxide. Ethylenediamine was intercalated by imbibing the graphite oxidation products in liquid ethylenediamine and outgassing to constant weight. X-ray diffraction diagrams and IR absorption spectra of the adducts have been studied. The intercalated ethylenediamine exhibits little interaction with the functional groups of the layers. Its state is similar to that of liquid ethylenediamine at 20°C.

Key Words—Graphite oxide, layered compounds, intercalated ethylenediamine.

1. INTRODUCTION

The interest in interlayer compounds has been increasing in recent years due to theoretical implications and technological applications. The host matrix may vary in nature[1]: layered clays, metal dichalcogenides of groups IV B, V B and VI B, layered W bronzes, graphite, graphite oxide, etc., and there are also many classes of guests. Furthermore, the intensities of the interactions between the intercalated species and the matrix range from Van der Waals forces to ionic bonds. Many intercalated graphite compounds are known[2]: graphite–alkali metals, graphite–acid salts, halogen–graphite compounds, graphite–metal halides and graphite–metal oxides.

Graphite oxide (GO) is a covalent compound of graphite which is obtained by treatment of graphite with strong oxidizing agents in a liquid medium. It has a layered structure and its oxygen functionality allows intercalation of polar molecules between the layers. The guest usually inserts itself in graphite oxides by means of weak interactions with the host, the stability of the intercalation compounds obtained is low when the temperature increases above 100°C.

A structural consequence of intercalation is sometimes a simple increase of the interlayer distance, as a result of the insertion of the guest. Frequently this effect can be visually observed during the reaction. Powder patterns furnish particularly useful information. The inclusion shifts the d_{00l} reflection set to smaller angles 2 θ[3]. Graphite oxide can include polar molecules, consequently its d_{001} distance increases. This effect does not occur with compounds which have a small dielectric constant. So Thiele[4] has shown that the GO volume increases in contact with acetone and lastly decreases when it is immersed into pentane. Many papers have been published by several authors about GO swelling. Boehm *et al.*[5] have studied intercalation of water, ethanol, ethyl ether and dioxane in GO and in methylated GO. Slabaugh and Seiler[6] have pointed out that the ammonia action in GO is more complex. Ammonia adsorption occurs in several stages. First the molecules fill the voids in the interlayer area and later the d_{001} increase is finally proportional to the ammonia uptake. Physical and chemical adsorption appear, the latter is due to the interaction between the ammonia and the acidic sites in GO. Cano Ruiz and McEwan[7] have postulated two types of complexes when the host is graphite oxide and the guest a polar molecule: in α, the guest is oriented parallel to the layers, and in β, the guest is in a vertical position inside the interlayer space.

In this paper we study some aspects of ethylenediamine intercalation in GO and in intermediate oxidation products of graphite.

2. EXPERIMENTAL

The oxidation products of graphite were obtained by reacting two different graphite samples with an oxidizing mixture of $KClO_3$, nitric and sulfuric acids. Basically the treatment was the Staudenmaier method[8]. The beaker was kept at 0°C during the reaction. Both graphite samples were ultrapure and polycrystaline materials, one natural (N-graphite) from Degussa (Germany) and the other one synthetic (A-graphite), produced by Sigri Elektrographite GmbH (Germany). The oxidation attack was interrupted at different times for each sample by dilution with distilled water at 0°C. The samples so obtained were washed and dried in an oven at 40°C and they were labeled with a letter (N or A) indicating their origin and a number indicating the reaction time in hours.

Samples with 40–60 μm particle size were chosen and dehydrated under vacuum over P_2O_5. The adducts were produced by imbibing these samples in ethylenediamine followed by evacuating at 6×10^{-3} torr until they had obtained a constant weight.

IR spectra of the graphite oxidation products and their complexes with ethylenediamine were recorded by means of a Pye-Unicam SP3-300 spectrophotometer, using KBr pellets.

Powder diagrams were obtained by means of a Siemens' set (model D-500) using CuKα radiation, an Agfa-Gevaert film Structurix (Model NDT) system, and a Philips PW 1024/30 camera with diameter equal to 114.9 mm. Debyegrams were transformed and plotted by a KD-540 microdensitometer.

3. RESULTS

The products obtained by cold oxidation of graphite were characterized by chemical analysis and by X-ray diffraction. From chemical analysis a composition was observed for the most strongly oxidized samples which was similar to that of other graphite oxides previously described by several authors.

Powder diagrams of graphite oxidation products are shown in Figs. 1 and 2. The d_{00l} spacings for GO reflections are summarized in Table 1. The assignment of Miller indices to the different reflections was easy for the original graphite samples, and it also was not difficult to find the fit for the strongly oxidized products. But it was not possible to find a simple fit for any partially oxidized products (N-24, N-76, N-84, A-12, A-24, A-48 and A-52). This was because reflections corresponding to the basal plane spacings of both graphite and graphite oxide were present simultaneously. Bearing in mind the coexistence of both substances in the partially oxidized samples, a double fit was performed in each experimental diagram. Thus we observed that (100) and (110) graphite reflections maintained their location for the most strongly oxidized samples, as has been known for a large time for GOs. The c-parameter is, however, larger in GO than in graphite. On the one hand it is well known that an expansion of the basal spacing occurs when graphite is transformed into graphite oxide, as a result of the functional group insertion between the layers, on the other Hofmann[9] has shown that the projection of C–C distances onto the layer planes of GO is only slightly larger than the C–C distances in the layers of graphite. We will use later this fact to calculate the interlayer area.

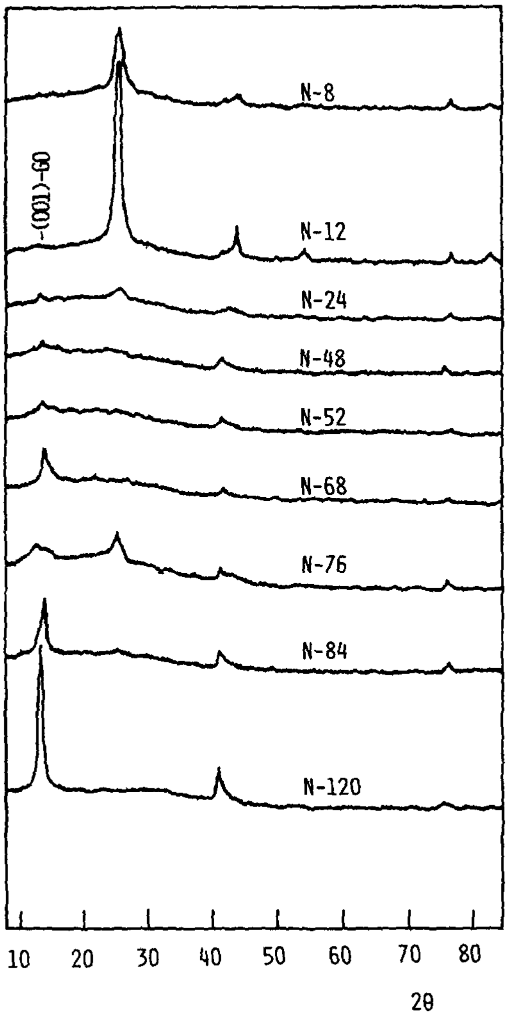

Fig. 1. Powder diagrams of graphite oxidation products. Natural series.

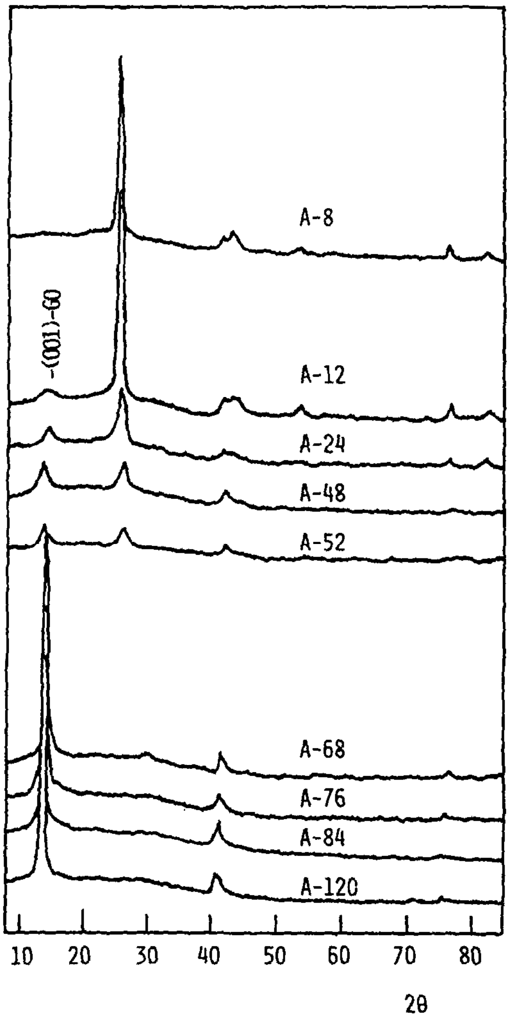

Fig. 2. Powder diagrams of graphite oxidation products. Artificial series.

When the diagrams of the partially oxidized products within a series were compared (Figs. 1 and 2), a strong decrease was observed in the crystallinity of the samples with reaction times going from 24 to 52 hr. This fact was more clearly shown in the diagrams of the samples

Table 1. d_{00l} spacing values (in Å) of GO in graphite oxidation products and in the adducts with intercalated ethylenediamine

Sample	d_{001}	d_{002}	Sample	d_{001}	d_{002}
A-8	----	----	N-8	----	----
A-12	5.93	----	N-12	----	----
A-24	5.91	----	N-24	6.17	----
A-48	6.29	----	N-48	6.06	----
A-52	6.05	----	N-52	6.31	----
A-68	5.91	----	N-68	5.92	----
A-76	5.95	----	N-76	6.58	----
A-84	6.05	----	N-84	5.92	----
A-120	5.99	----	N-120	6.12	----
A-8-en	8.63	----	N-8-en	----	----
A-12-en	8.58	----	N-12-en	----	----
A-24-en	8.40	4.15	N-24-en	8.55	3.87
A-48-en	8.57	4.22	N-48-en	9.08	3.98
A-52-en	8.61	4.17	N-52-en	8.47	4.15
A-68-en	8.64	4.29	N-68-en	8.76	4.33
A-76-en	8.78	4.32	N-76-en	8.85	4.37
A-84-en	9.06	4.49	N-84-en	8.75	4.29
A-120-en	9.06	4.51	N-120-en	8.84	4.38

belonging to the natural graphite series. Probably the reason was the strain in the boundary region of a layer where graphite and graphite oxide coexist.

Only samples N-120, A-84 and A-120 showed IR absorption spectra similar to those obtained by Hadži and Novak for graphite oxide[10]. No band that could be evaluated was observed in the IR spectra of the remaining products. It seems that the oxidation process was faster in A-graphite than in N-graphite.

Powder diagrams of the complexes show a strong influence of the ethylenediamine intercalation on the structure of the oxidation products (Figs. 3 and 4). As can be observed, the (001) graphite oxide reflection shifts its location toward smaller angles 2θ and a new second order reflection appears then. The d_{00l} spacings are listed in Table 1. The sharper and more intense (001) band of the complex as compared to the original GO band, in addition to the new second order reflection, points out further arrangement of the layers raised by the ethylenediamine inclusion. It must be emphasized, however, that a weak interaction occurs between the functional groups in the layers and ethylenediamine. Only Van der Waals forces or weak hydrogen bridges are present since ethylenediamine and graphite oxide spectra are both superposed in the IR spectra of (N-120)-en, (A-84)-en, and (A-120)-en complexes, showing a few light shifts (Fig. 5). The remaining complexes obtained did not show any band that could be evaluated. It is probably due to the lower amount of GO in the samples, so that the IR band intensities are very weak.

4. DISCUSSION

The ethylenediamine molecular dimensions can be evaluated from its structural parameters given in the literature[11] for its transconformation, using covalent radii for interatomic distances and Van der Waals radii for intermolecular intervals. If the theoretical basal spacing of the graphite oxide (4.8 Å) given by Cano Ruiz and McEwan[7] is considered, as well as the thickness increase produced by the intercalation, it can be inferred that the ethylenediamine molecules must be lying as a monolayer between the GO sheets, probably holding the C—C bond parallel to the carbonaceous layers. In this way the samples obtained by ethylenediamine inclusion into graphite oxidation products are α-type complexes.

It is not difficult to calculate the surface which is covered by an ethylenediamine molecule. We considered its projection over an ideal plane in the carbonaceous layer and we thus obtained a value of 23.8 Å^2, very similar to 25.2 Å^2, the value calculated from Emmett and Brunauer's equation. Consequently, the average area of 24.5 Å^2 has been used. The interlayer specific surface is given by the expression

$$S = 2(N_A/M)\,\tau \cdot X \quad (\text{in m}^2\text{g}^{-1}),$$

where 2τ is the area filled by an ethylenediamine molecule on both layers which it contacts, N_A is Avogadro's number, M is the molecular weight of ethylenediamine, and X is the amount of ethylenediamine which was retained

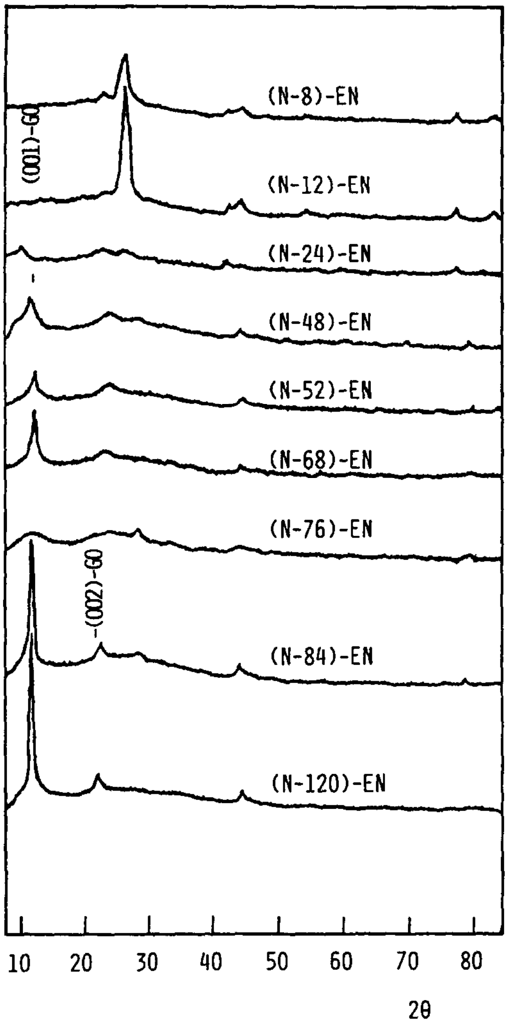

Fig. 3. Powder diagrams of ethylenediamine–graphite oxidation products. Natural series.

by the sample (in grams of ethylenediamine per gram of sample dehydrated over P_2O_5). The specific surface values which were calculated from the above equation are plotted in Figs. 6 and 7, where they are compared with other results previously calculated[12, 13]. Taking into account that these results were obtained several ways and with different guests, they agree relatively. But we must consider some divergences on a number of points. When the oxidation time increases, the amount of ethylenediamine which is retained by the sample increases the surface values towards 1500–1700 m^2g^{-1} for the most strongly oxidized products. The results obtained with other intercalated substances were similar in these samples. Nevertheless, in partially oxidized products the agreement is poor, particularly for the samples belonging to the natural graphite series. It is probably due to the labyrinthine effect since these samples are in the most disordered state. Therefore interlayer diffusion is hindered. There is an intermediate stage in the oxidation of graphite, that corresponds with the more unequal behaviour in relation to the oxidizing attack in natural and synthetic graphite due to the larger sheets in N-graphite. Later, the behaviour becomes very similar; this fact is caused by disintegration.

A careful analysis of the IR absorption spectra shows a slight shift in the GO band at 3380 cm^{-1} (ν_{OH}). The position of the band of the intercalated complex is lowered by 40 cm^{-1} relative to the maximum in GO and by 20 cm^{-1} relative to the maximum of ethylenediamine (ν_{NH}). Small shifts are also observed for the ethylenediamine bands at 1570 cm^{-1} (δ_{NH_2}) and at 1470 cm^{-1} (δ_{CH_2}). In order to corroborate the ethylenediamine state between the carbonaceous layers, the density of the ethylenediamine which is intercalated in GO has been calculated.

The unit cell of the hexagonal graphite is a rhombic base prism (a = 2.46 Å), 6.72 Å high. This cell contains four carbon atoms, and its full interlayer area is 20.98 $Å^2$/unit cell[14]. So that in the sheets of carbon atoms in graphite the area per carbon atom is 2.62 $Å^2$, and it is $S = 1315 \cdot 10^4$ cm^2 per gram of carbon. The increase in volume in 100 g of swollen GO is then

$$\Delta V = 1315 \cdot 10^4 \cdot 100p \cdot \Delta d,$$

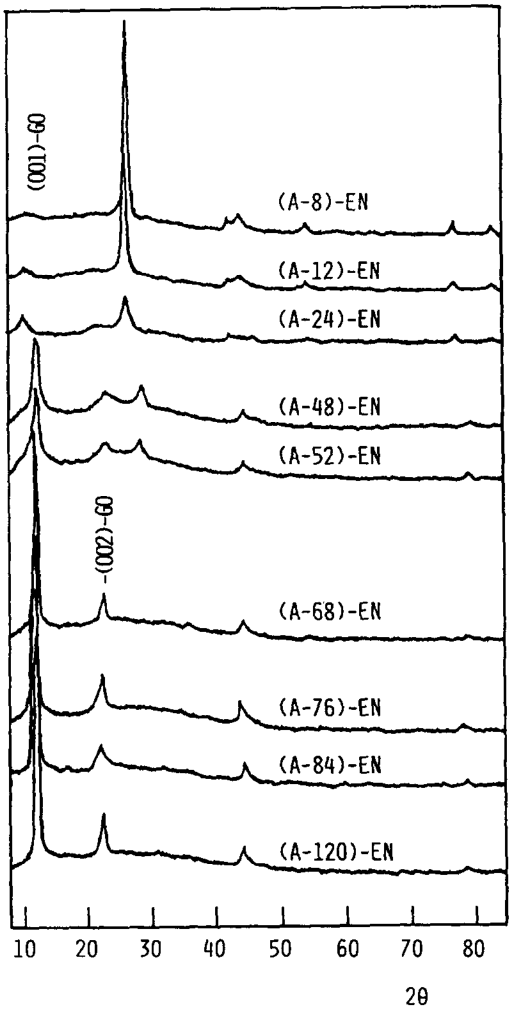

Fig. 4. Powder diagrams of ethylenediamine–graphite oxidation products. Artificial series.

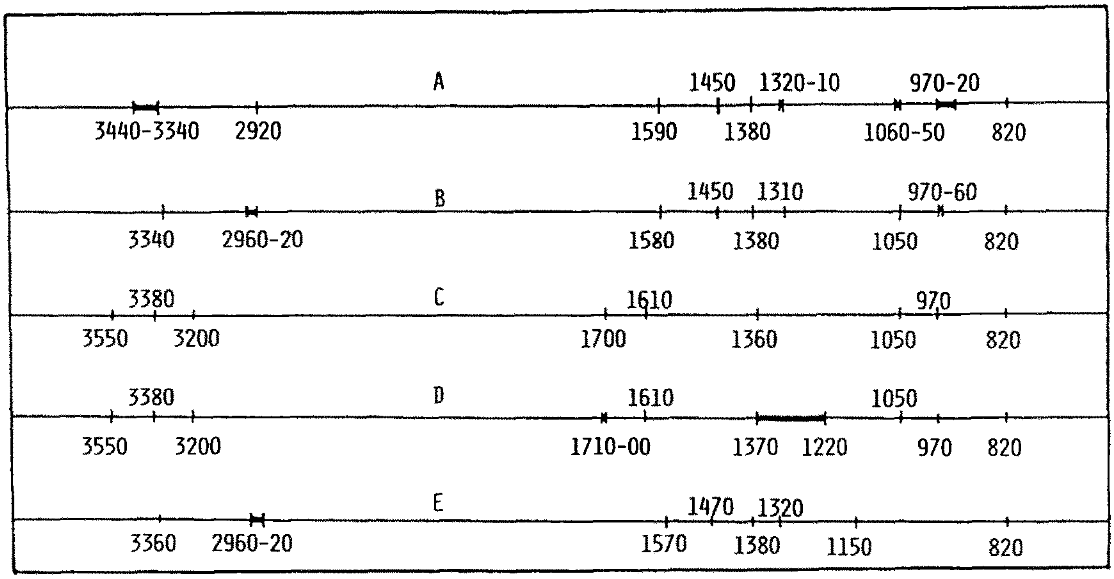

Fig. 5. IR absorption spectra. Chart of wave numbers. (a) (A-120)-en. (b) (N-120)-en. (c) A-120. (d) N-120. (e) Ethylenediamine.

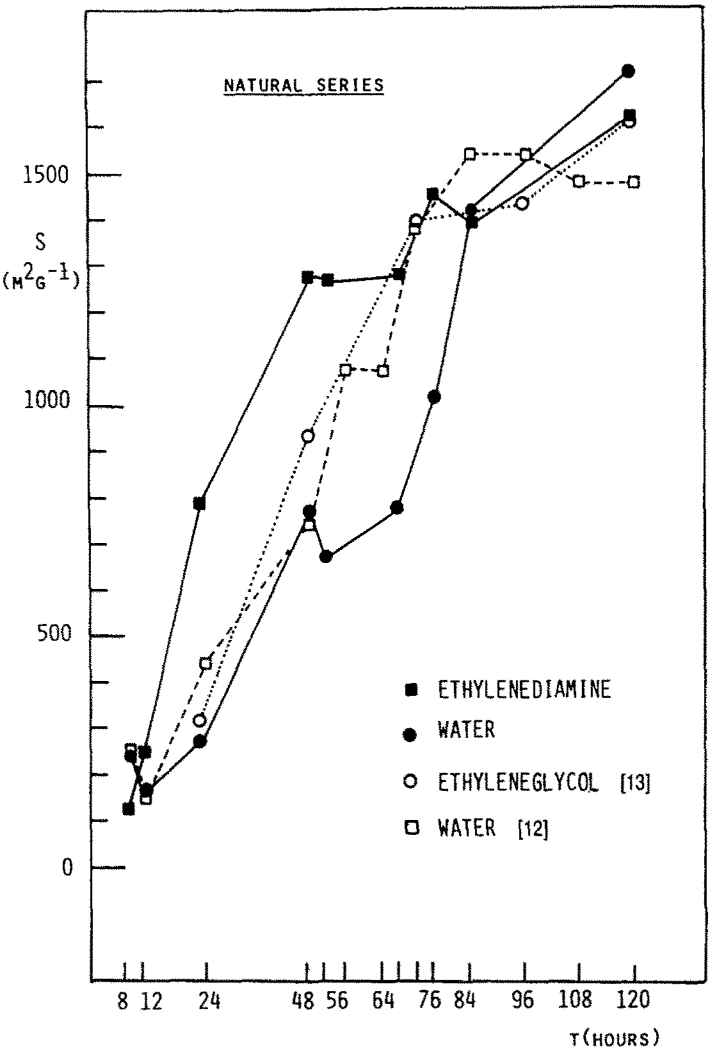

Fig. 6. Specific interlayer surface of graphite oxidation products. Natural series.

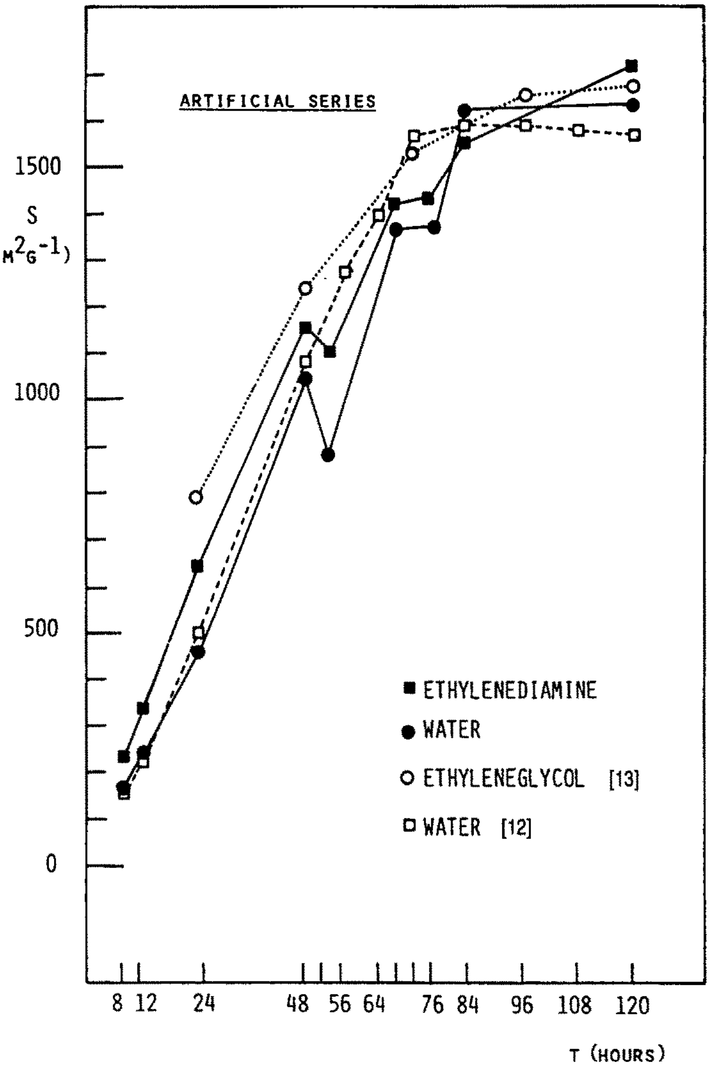

Fig. 7. Specific interlayer surface of graphite oxidation products. Artificial series.

where p is the carbon percentage in the sample and Δd is the thickness increase.

The density of the intercalated ethylenediamine then comes out as

$$\rho = \frac{\Delta m}{\Delta V} = \frac{100\ W}{1315 \cdot 10^4 \cdot 100p \cdot \Delta d}$$

where W is the retained ethylenediamine percentage.

The density values (Table 2) for a monolayer of ethylenediamine are slightly larger than its bulk density at 20°C. Assuming the theoretical basal spacing of the graphite oxide as 4.8 Å, it is possible to think that these larger values were due to the ethylenediamine filling the voids between the layers which already exist in the "dry" sample. The existence of a small amount of additional ethylenediamine which is adsorbed on edges and external surfaces must also be taken into account. (It was considered as intercalated ethylenediamine.) Another possibility is that ethylenediamine molecules form a closer packing arrangement than in the liquid at 20°C (ρ = 0.90 g · cm^{-3}).

We are studying the thermal stability of these products with ethylenediamine. Thermal stability above 100°C and

Table 2. Density of the intercalated ethylenediamine in the most strongly oxidized products

Sample	p(%)	W(%)	$\Delta d \cdot 10^8$(cm)	ρ(g.cm^{-3})
N-120	56.59	33.08	4.01	1.10
A-84	55.55	31.58	4.23	1.02
A-120	58.20	34.97	4.22	1.08

thermal decomposition seem similar to the behaviour which is shown by the oxidation products with a temperature increase[15]. In these samples there are three main stages of thermal decomposition: dehydration, internal decomposition and combustion (the last only occurs when there is an external oxidizing agent).

5. CONCLUSIONS

According to the above results the intercalation of ethylenediamine in several graphite oxidation products causes an increase of the c-parameter. Likewise a rise in the crystalline order of the layers has also been observed. The interaction between ethylenediamine and the GO layers must be weak. The ethylenediamine monolayer is packed in a similar way to liquid ethylenediamine at 20°C.

A transition stage during oxidation has been observed. Such intermediate preparations are very disordered: no or only weak (001) reflections of graphite or of GO are observed. These compounds show improved stacking order after swelling with ethylenediamine (e.g. A-48-en and A-52-en).

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