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1542 (A-3)

POLYMER-GRAPHITE COMPOSITE LOUDSPEAKER DIAPHRAGM

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Polymer-graphite Composite Loudspeaker Diaphragm

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ABSTRACT

A polymer-graphite composite has been developed which has both a high E/ρ ratio and a large internal loss factor. The specific modulus (E/ρ) of the composite is higher than that of aluminum or titanium, and the internal loss, $\tan \delta$, is larger than that of cone paper.

Since the composite exhibits good formability it can be molded into various shapes of low- and high-frequency loudspeaker diaphragms. By the use of the composite superior loudspeakers have been realized that have smooth frequency response, very low harmonic distortion characteristics and wide dynamic range.

INTRODUCTION

Desirable properties of materials for loudspeaker diaphragms are high Young's modulus, low density and large internal loss. For mid-range and high-frequency loudspeaker diaphragms light metals such as aluminum, titanium or beryllium have been employed. Since they all have high values of the ratio of Young's modulus to density (E/ρ), the high frequency limit can be extended.

In low-frequency loudspeakers cone papers with large internal losses have been employed which result in smooth frequency responses. Paper diaphragms, however, are apt to break up at relatively low frequencies because of their low Young's modulus and produce large distortions when high level signals are supplied to them.

In these situations loudspeaker diaphragms, particularly low-frequency diaphragms, which have both a high E/ρ ratio and large internal losses have been desired for many years. To realize these desirable properties the possibilities of a new composite material have been studied and a superior material has been realized.

This material consists of fine graphite granules and several specific polymers. By the employment of these polymer-graphite composite diaphragms (P.G.) loudspeakers which have superior sound quality can be produced.

This paper describes the development process, the structure and the physical properties of the composite and the characteristics of several loudspeakers using P.G. diaphragms.

GRAPHITE

Graphite is one form of the carbon crystal and has a laminar structure which consists of large layers linking many hexagonal rings of carbon atoms [graphene] as shown in Figs. 1a & 1b. The covalent bonding of carbon atoms in the 'a-b' dimension layer plane is so strong that it produces a Young's modulus greater than 1,100 GPa. (5). Contrastingly, layer planes are only weakly bonded to each other by the van der Waals force and this weak bonding between 'C' axis layer planes results in slipperiness. Carbon fibers having a high Young's modulus exploit the firm a-b plane bonding of graphite.

In the case of loudspeaker diaphragms using carbon fibers, adequate strength is not produced because of the lack of solid bonding between carbon fibers caused by the slipperiness of the C-axis carbon fiber surfaces.

In our early developmental stages a chemical vapor deposition (C.V.D.) method was employed to obtain a carbon diaphragm. A carbon film deposited by the C.V.D. method has the special feature that the a-b layer planes of the deposited carbon are oriented parallel to the substrate surface if the C.V.D. conditions are suitable.

Carbon particles were deposited on a substrate, which had the shape of the diaphragm and which was heated to a temperature over 1000° C. The carbon diaphragm was obtained by separation from the substrate. A loudspeaker using this carbon diaphragm produced a very smooth frequency response.

A scanning electron micrograph of the fracture cross section of the diaphragm revealed a laminar structure in the deposited film diaphragm. The C.V.D. method is very difficult to use in actual production because of its high manufacturing cost.

However, graphite with a laminar structure contributes to a high Young's modulus and is very suitable for loudspeaker diaphragms.

POLYMER-GRAPHITE COMPOSITE

In order to realize laminar structures in diaphragm materials, composites were investigated using graphite crystallite granules having parallel layer planes. The following several points were taken into consideration in the development processes of the composite:

1. - Dispersion of graphite granules into matrix polymers.
2. - Orientation of laminar graphite granules parallel to the surface of the diaphragm.
3. - Development of matrix polymers that can be applied to the diaphragm and can tightly bond graphite granules to each other.
4. - Mixing ratio of graphite granules to matrix polymers.

All these factors exert mutual influences, therefore the physical properties of the composites have many variations. As a result of many experiments on numerous combinations of the above factors, a superior composite was realized. The composite has both a high E/ρ ratio and a large internal loss factor, $\tan \delta$. A block diagram of the composite production process is shown in Fig. 2.

STRUCTURE OF THE COMPOSITE

A scanning electron micrograph of the fracture cross section of the composite sheet is shown in Fig. 3. A laminar structure parallel to the surface is observed and this resulted from the orientation imparted thru the calendaring process in the composite production.

PHYSICAL PROPERTIES OF THE COMPOSITE

To compare the composite with other materials used for diaphragms, the physical properties are shown in Tables 1a and 1b. Particularly, the comparison data concerning internal loss and sound velocity of each material are plotted in Fig. 4. The sound velocity of the composite is higher than that of aluminum or titanium and is about three times that of cone paper.

The decay patterns of free vibrations of the composite, aluminum and cone paper reeds are shown in Fig. 5. It is recognized that the composite is an excellent material for diaphragms having both a high E/ρ ratio and larger internal loss. This kind of material has never been previously obtained. Since the composite has good formability, it can be molded into various shapes of diaphragms for either low-frequency or high-frequency loudspeakers. Because the fine graphite granule layer planes are oriented parallel to the diaphragm surfaces, isotropy of the physical properties can be obtained in the direction of the surfaces. Being stable in humidity, by which cone paper is degraded, the composite can have stability with high strength for a very long time.

CHARACTERISTICS OF LOUDSPEAKERS WITH P.G. DIAPHRAGMS

In order to effectively use P.G. diaphragms, several types of loudspeakers have been developed by the use of Finite Element Analysis and laser holography.

1 – 400mm Cone Type Low-Frequency Loudspeaker – Comparisons of the characteristics between a 400mm cone type loudspeaker employing the P.G. diaphragm and a 400mm loudspeaker employing a paper diaphragm of the same shape are shown in Figs. 7 and 8.

Fig. 7 shows an output sound pressure level of 90dB and Fig. 8 shows an output sound pressure level of 115dB. The harmonic distortion of the loudspeaker with the P.G. diaphragm at 90dB is markedly lower than 0.03%, and at a very high sound pressure level of 115dB is lower than 0.3% in the frequency range of 100Hz to 800Hz. Furthermore, the high frequency limit of the loudspeaker with the P.G. diaphragm is an octave higher than that seen from the paper diaphragm.

The peak at the high frequency resonance of the diaphragm using the composite material is hardly noticeable both at 90dB and 115dB sound pressure levels. Thus the P.G. diaphragm loudspeaker produces a very smooth frequency response and very low harmonic distortion..

2 – High Frequency Loudspeaker – The frequency responses and harmonic distortion characteristics of two 66mm cone type high-frequency loudspeakers, one with the P.G. diaphragm and the other with a paper diaphragm of the same shape are compared in Fig. 9. The frequency response of the loudspeaker with the P.G. diaphragm is markedly smoother in the frequency range from 1kHz to 43kHz.

The frequency responses of two 25mm dome type high-frequency loudspeakers, one with a P.G. diaphragm and the other with a titanium diaphragm of the same shape are compared in Fig. 10. The frequency response of the loudspeaker with the P.G. diaphragm reaches 35kHz which is higher by about 5kHz than the titanium diaphragm and the peak at the high frequency resonance of the loudspeaker using the P.G. diaphragm is lower in both amplitude and Q, thus a smoother high frequency response is achieved by the P.G. diaphragm.

CONCLUSION

The polymer-graphite composite with a laminar structure has both a high E/ρ ratio and a large internal loss factor. Therefore, loudspeakers employing P.G. diaphragms provide smooth frequency response and low harmonic distortion over a wide frequency range.

The composite will be applied to other components in various fields.

ACKNOWLEDGEMENT

The authors wish to thank Dr. Sugio Ohtani, Professor at Gunma University, who gave us helpful suggestions, and Messrs. Toshikazu Yoshino, Masami Kimura Jiro Nakazono, Kunio Imai and Hiroyuki Hamada who greatly assisted in this work.

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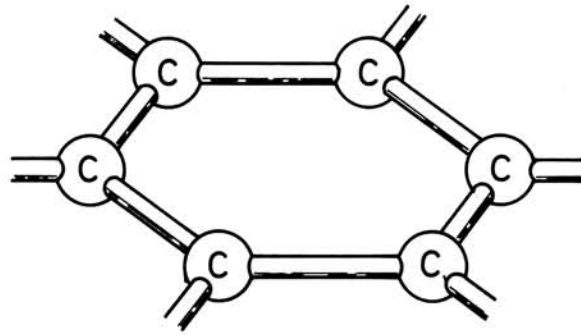


Fig. 1a. Schematic model of bonding of carbon atoms

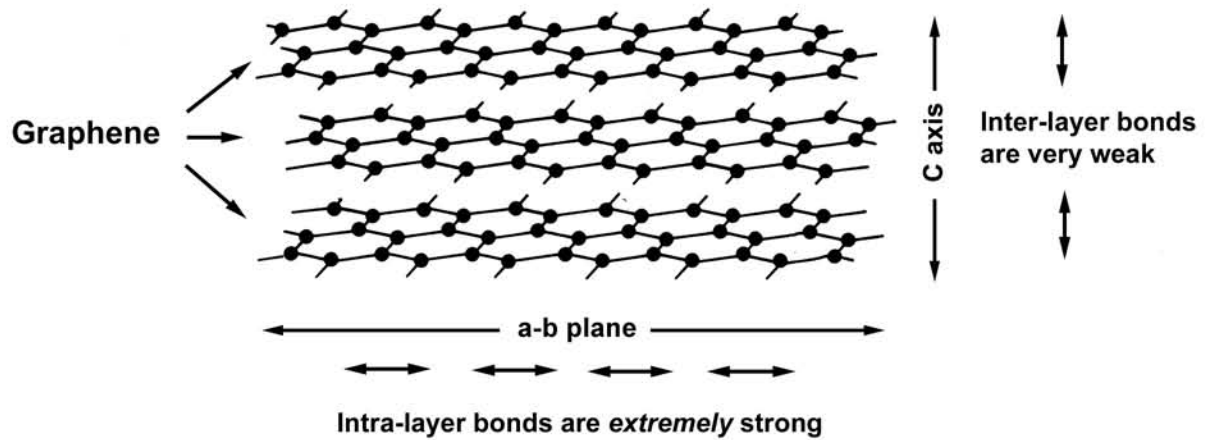
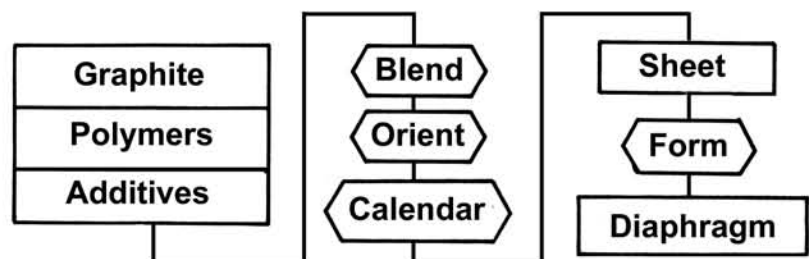


Fig. 1b. Schematic model of laminar structure of graphite crystal

Fig. 2. Flow diagram of the production process of polymer-graphite composite.



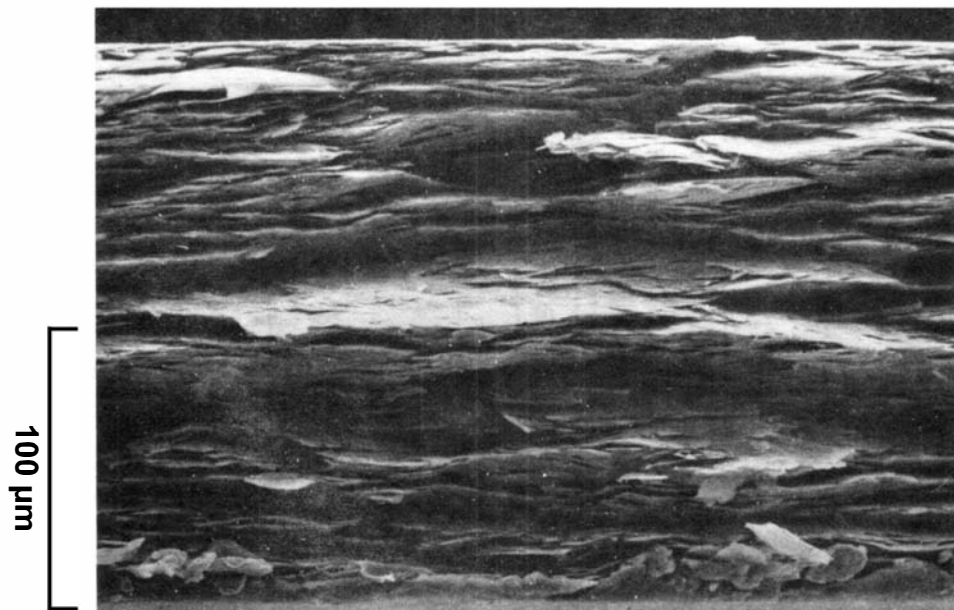


Fig. 3. Scanning electron micrograph of fracture cross-section of the polymer-graphite composite.

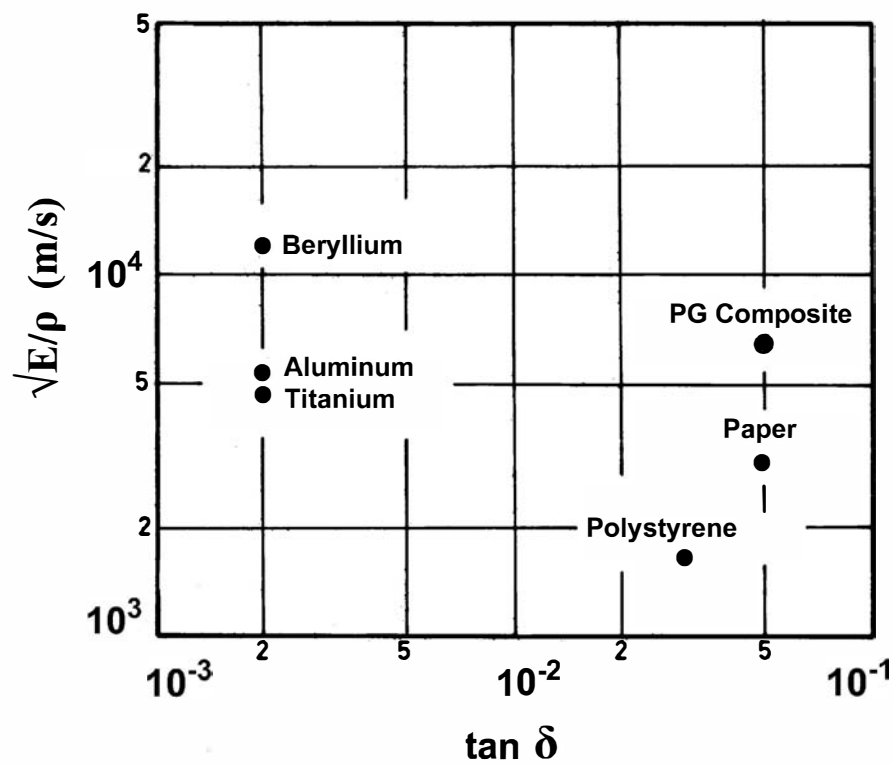
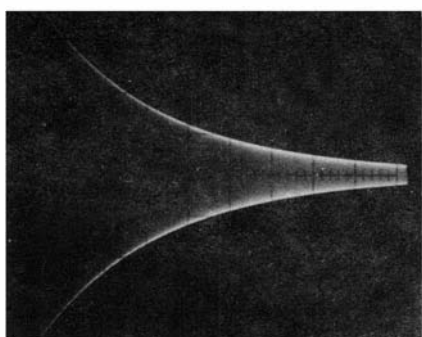



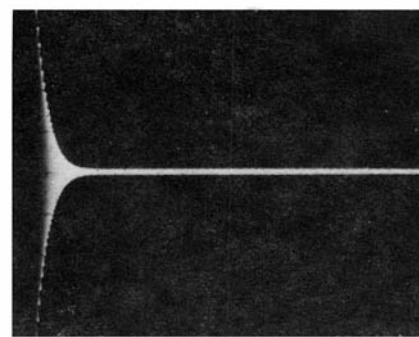
Fig. 4. Comparison of the composite with other materials in respect of internal loss and sonic velocity.

Fig. 5. Decay Patterns of Free Vibration

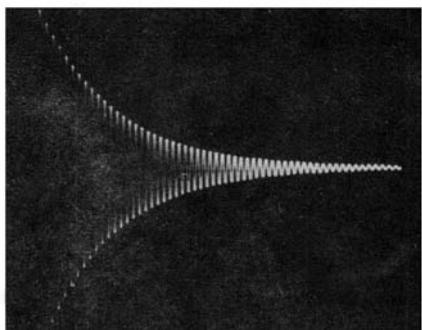


a) Aluminum



500mSec

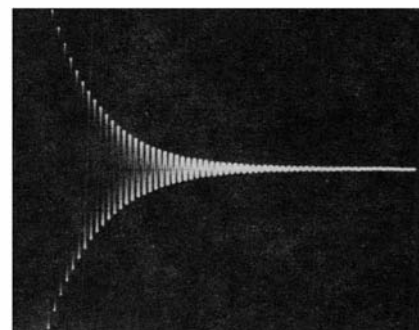


P.G. Composite



b) Cone Paper


100mSec



P.G. Composite



Fig. 6. 400 mm cone type loudspeaker using the polymer-graphite composite diaphragm.

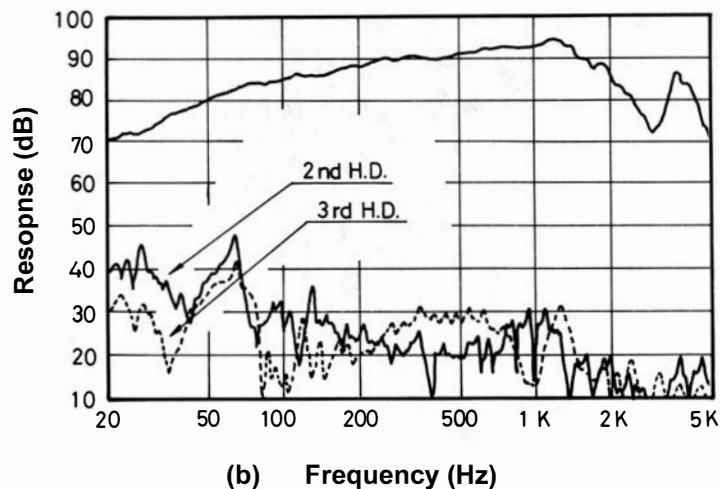
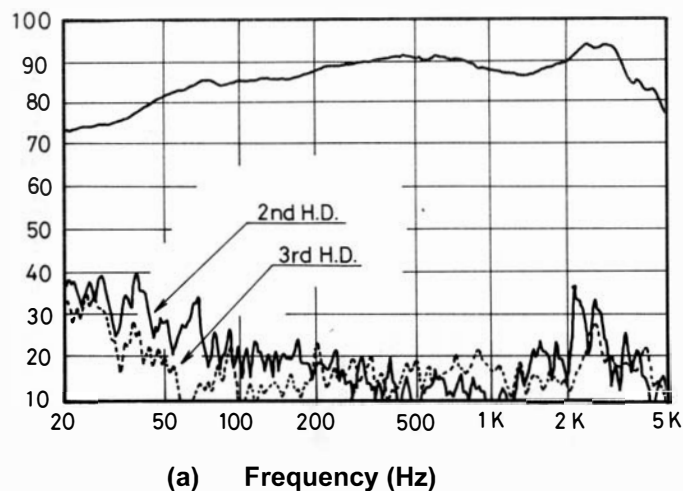


Fig. 7. Frequency responses and harmonic distortion characteristics of 400mm cone type loudspeakers at an output sound pressure of 90dB @ 1M for:
a) the polymer-graphite composite diaphragm and,
b) a paper cone diaphragm

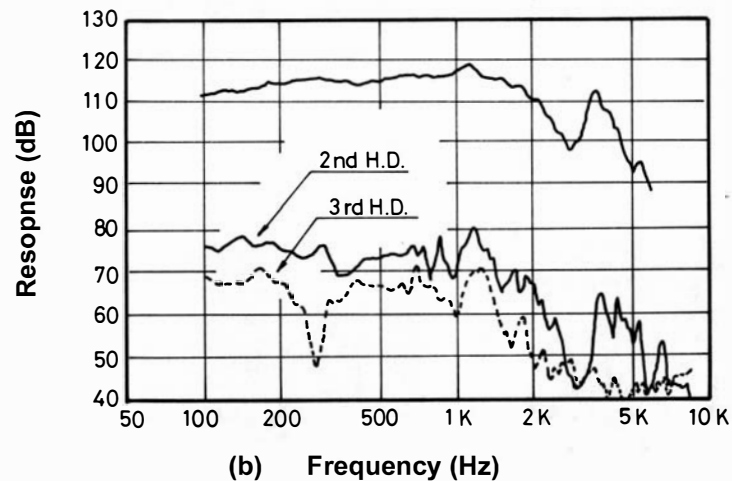
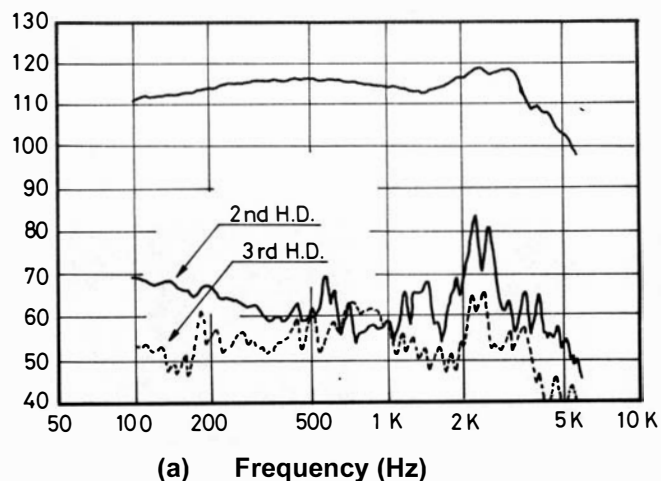


Fig. 8. Frequency responses and harmonic distortion characteristics of 400mm cone type loudspeakers at an output sound pressure of 115dB @ 1M for:
a) the polymer-graphite composite diaphragm and,
b) a paper cone diaphragm

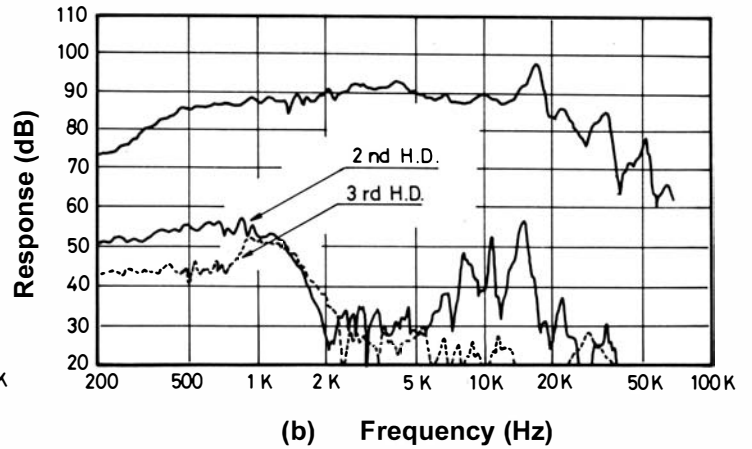
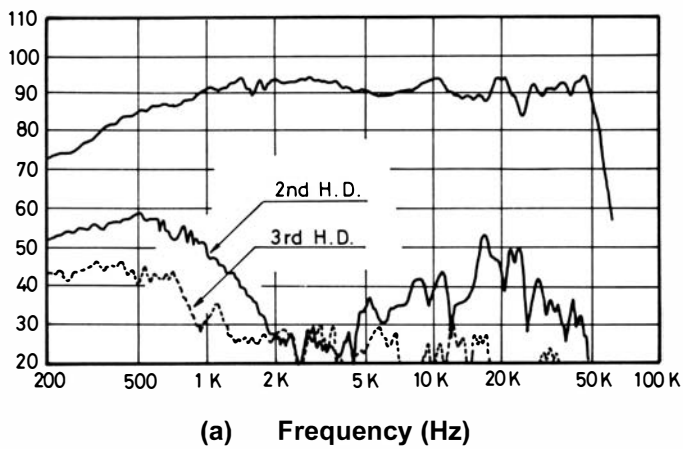


Fig. 9. Frequency responses and harmonic distortion characteristics of 66mm cone type loudspeakers for:
a) the polymer-graphite composite diaphragm
b) cone paper diaphragm.

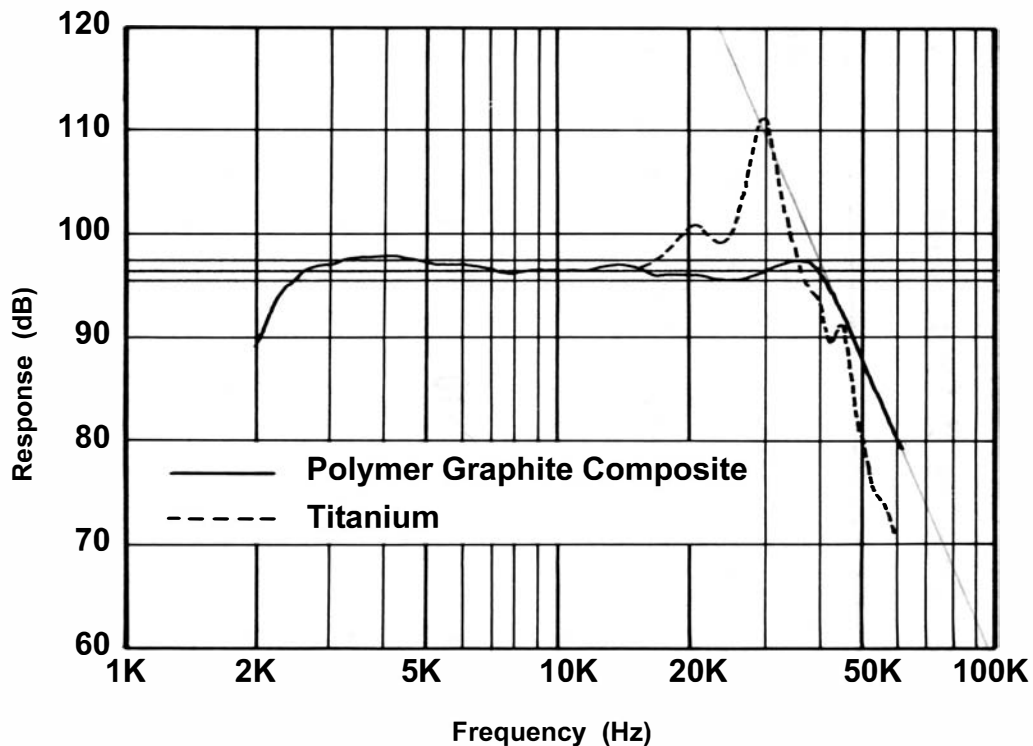


Fig. 10. Frequency responses of two 25mm tweeters; a polymer-graphite domed unit and a titanium domed unit.
Note the almost complete lack of HF resonance in the P.G. unit and its almost textbook smooth, 30dB/octave rolloff beyond 40KHz.

Table 1. Physical properties of several materials for diaphragms

	Young's Modulus E: GPa	Density ρ : gm/cc	Sonic Velocity $\sqrt{E/\rho}$: m/s	Internal Loss: $\tan \delta$
Composite	70	1.8	6.2×10^3	0.05
Aluminum	70	2.7	5.1×10^3	0.002
Titanium	110	4.5	4.9×10^3	0.002
Cone Paper	2.0	0.5	2.0×10^3	0.05

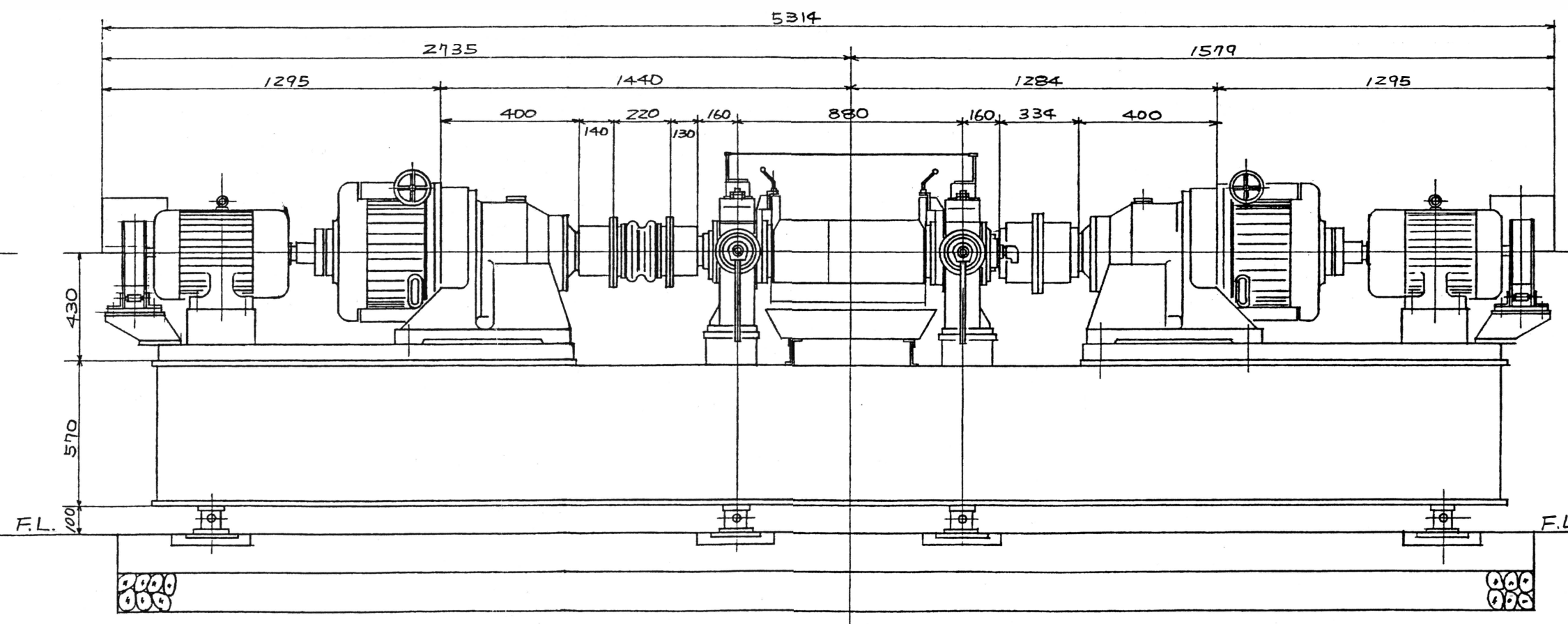
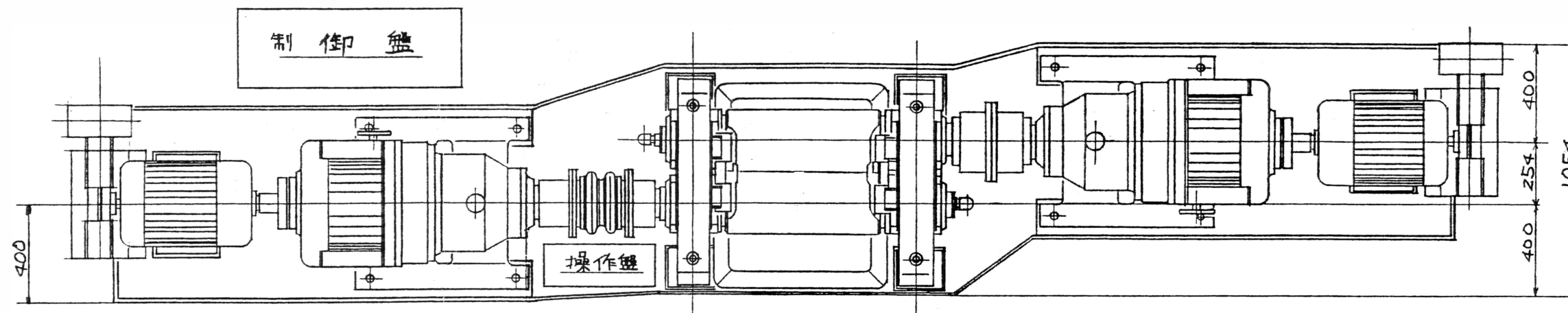
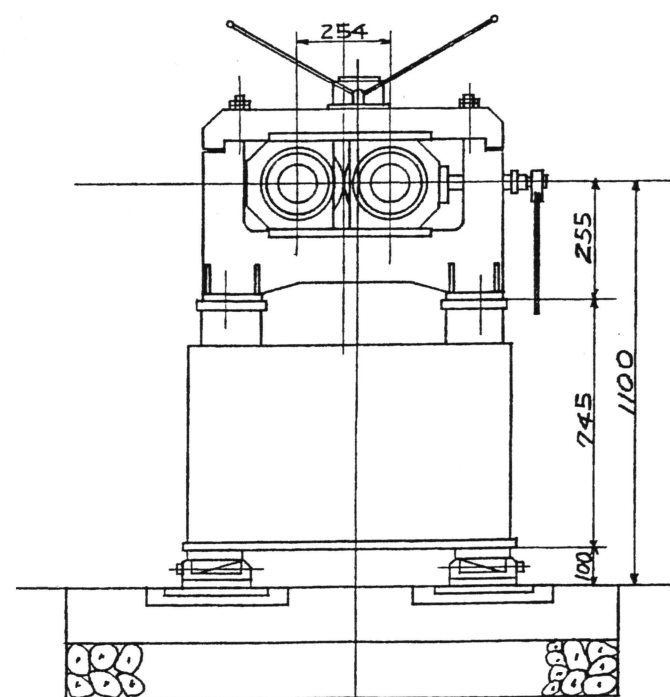
Table 1 Physical properties of materials for diaphragms.

Material	Young's modulus $E, \times 10^{10} \text{N/m}^2$	Density $\rho, \times 10^3 \text{kg/m}^3$	Specific modulus $E/\rho, \times 10^7 (\text{m/s})^2$	Sound velocity $\sqrt{E/\rho}, \times 10^3 \text{m/s}$	Internal loss $\tan \delta$	Melting point $^{\circ}\text{C}$
Beryllium	28	1.85	15	12	0.002	1284
Boron	40	2.34	17	13	0.002	2225
Aluminum	7.0	2.7	2.6	5.1	0.002	660
Titanium	10	4.5	2.2	4.7	0.002	1668
Boronized titanium	25	4.5	5.6	7.5	0.002	
Carbon fiber	23	1.74	13	11.5		
CFR-olefin	0.37	0.45	0.82	2.9	0.025	
Polymer-graphite	7.0	1.8	3.9	6.2	0.05	
Cone paper	0.1~0.2	0.5	0.2~0.4	1.4~2.0	0.02~0.05	
Graphite Glass	35	1.4	25	15.8	.005	

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By J. D. BERNAL, B.A.

(Communicated by Sir William Bragg, F.R.S.—Received July 28, 1924.)

The crystallographic information on the subject of graphite is scanty. It has generally been accepted as hexagonal with a well-marked basal cleavage; but besides the cleavage face few other faces have ever been observed on it. Kenngott,* the earliest observer, seems to have obtained the best crystal, and measured planes, to which he gave the indices $10\bar{1}1$ and $11\bar{2}1$, making angles of 58° and $70^\circ 18'$ respectively with the basal plane 0001. (These results are strikingly confirmed by X-ray measurements, which make the corresponding angles $58^\circ 8'$ and $70^\circ 13'$.) Nordenskiöld† considered graphite monoclinic, on account of the variability of its angles; but his conclusions were questioned by Sjögren,‡ who, in a very full paper, adduced a number of reasons (twinning, percussion and etch figures, thermal conductivity) to show that it was hexagonal. Quite recently the researches of Gaubert§ have added a knowledge of the optical properties of graphite. In very thin flakes it is transparent, uniaxial and negatively birefringent, with a refractive index of about 2. This settles definitely that it has trigonal hexagonal symmetry.

The X-ray analysis of graphite has lagged considerably behind that of the

* Hintze, 'Mineralogie,' vol. 1.

† 'Pogg. Ann.,' vol. 96, p. 110 (1855).

‡ 'Min. Mag.' (Aug., 1885).

§ 'Comptes Rendus,' vol. 177, pp. 1123–1125 (1923).

diamond. Bragg* in 1914 made a measurement of the spacing of the cleavage planes, finding it to be 3.42 A.U., while Ewald,† in the same year, took a Laue photograph of a crystal, perpendicular to the axis, confirming its hexagonal symmetry. The fuller interpretation of its structure was attempted by Hull‡ and by Debye and Scherrer§ in 1917 by the powder method. Both were able to assign a structure to the element, but these structures have different lattices and belong to different crystal systems. An examination of the original papers shows that the observations of neither investigator are in very good agreement with the structure they propose, and the observations only show the roughest agreement with each other. This is especially marked in the matter of intensities. On the whole, Hull's results are more plausible, because he separated the K_α and K_β lines of Mo by screening, whereas Debye and Scherrer often mistook α for β lines, as will be shown subsequently. Since then Backhurst|| has made some measurements on graphite, from the point of view of its expansion and the effect of temperature on the reflection intensities.

It seemed to me that the essence of the problem lay in determining the orientation of the planes giving rise to the spacings observed in the powder photographs. For this a single crystal was necessary. I had the good fortune to secure from Prof. Gordon, of King's College, a specimen of Ceylon graphite, from which, by careful dissection and picking out, I obtained a few crystalline fragments which, though very far from perfect, were sufficiently so for my purpose.

The method of analysis employed was that of the rotating crystal with a concentric cylindrical film. The actual apparatus is shown in the diagram, fig. 1. The rays from the X-ray tube (of the Shearer¶ type, with copper anticathode) passed through the brass tube A, through the two diaphragms B B', which were either holes or slits, and fell upon the rotating crystal C. The crystal was mounted on a goniometrical holder, such as that described by Bragg.** The diffracted rays fall upon the film, which is placed on the inside of the small cylindrical brass camera, D. A small camera, radius 2.25 cm., was used, because the imperfections of the crystals prevented any very sharp

* 'X-Rays and Crystal Structure,' 4th Ed., p. 131.

† 'Sitzungsberichte, Münch.' (1914).

‡ 'Physical Review,' vol. 10, p. 661 (1917).

§ 'Physikalische Zeitschrift,' vol. 18, p. 291 (1917).

|| 'Roy. Soc. Proc.,' A, vol. 102 (1922).

¶ 'X-Rays and Crystal Structure,' 4th Ed., p. 33.

** 'X-Rays and Crystal Structure,' 4th Ed., p. 20.

reflections, and a larger camera would have decreased the intensity without adding to the accuracy.

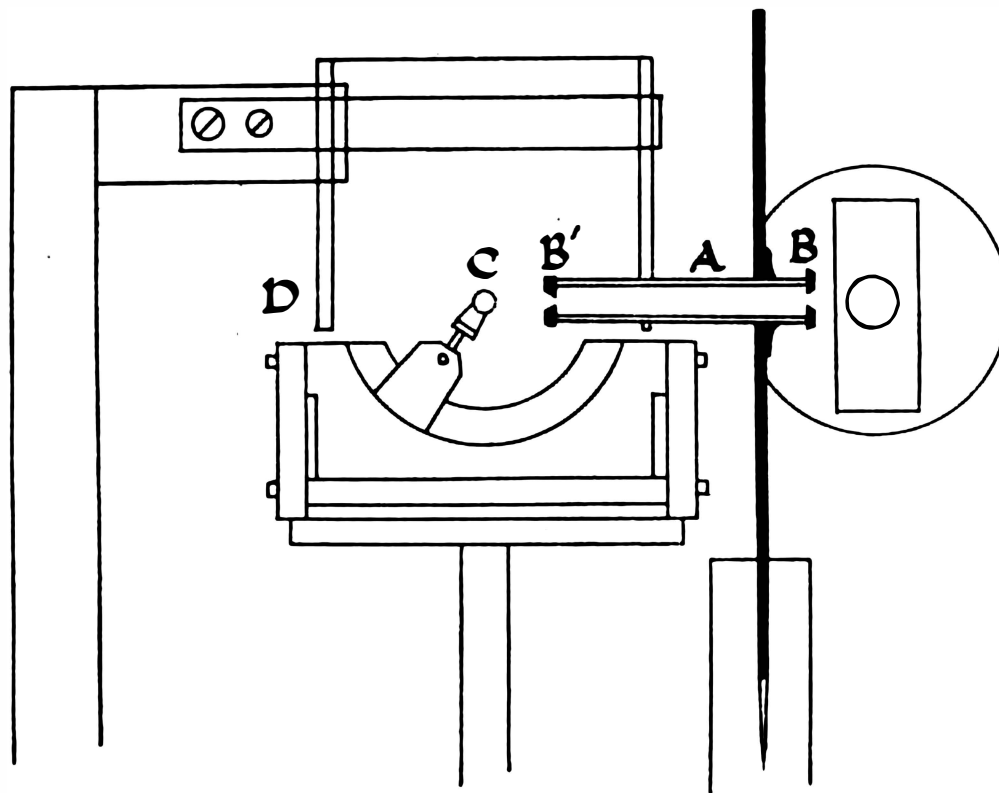


FIG. 1.

Theory.

The theory of the method is much simplified by the use of polar co-ordinates r, χ, ϕ (see fig. 2) (χ is measured from the equator and takes the place of θ , as the latter is reserved for the glancing angle). Take the axis of rotation of the crystal as the axis $\chi = \pi/2$. The incident beam, supposed perpendicular to it, as $\chi = 0, \phi = 0$. Let the incident ray of wave-length λ impinge upon a crystal plane of spacing d , the normal to which makes an angle α with the axis of rotation. In general, at some point of its revolution, this plane will come into position where it reflects the incident beam. Its normal then makes with the incident beam an angle $\pi/2 + \theta$, where θ is given by the familiar formula $\sin \theta = \lambda/2d$.

The reflected beam makes an angle 2θ with the incident beam and its χ, ϕ co-ordinates are given by the two formulæ

$$\cos \chi \cos \phi = \cos 2\theta, \quad \sin \chi = 2 \sin \theta \cos \alpha.$$

From these equations it can be seen that if χ and ϕ are one solution corresponding to fixed values of θ and α , so are χ and $-\phi$; and as the plane α is indistinguishable from that $\pi - \alpha$. The values $-\chi, \phi$ and $-\chi, -\phi$, also

satisfy the equation. The reflecting position is, in general, reached in four positions of the plane giving four reflected directions, symmetrically distri-

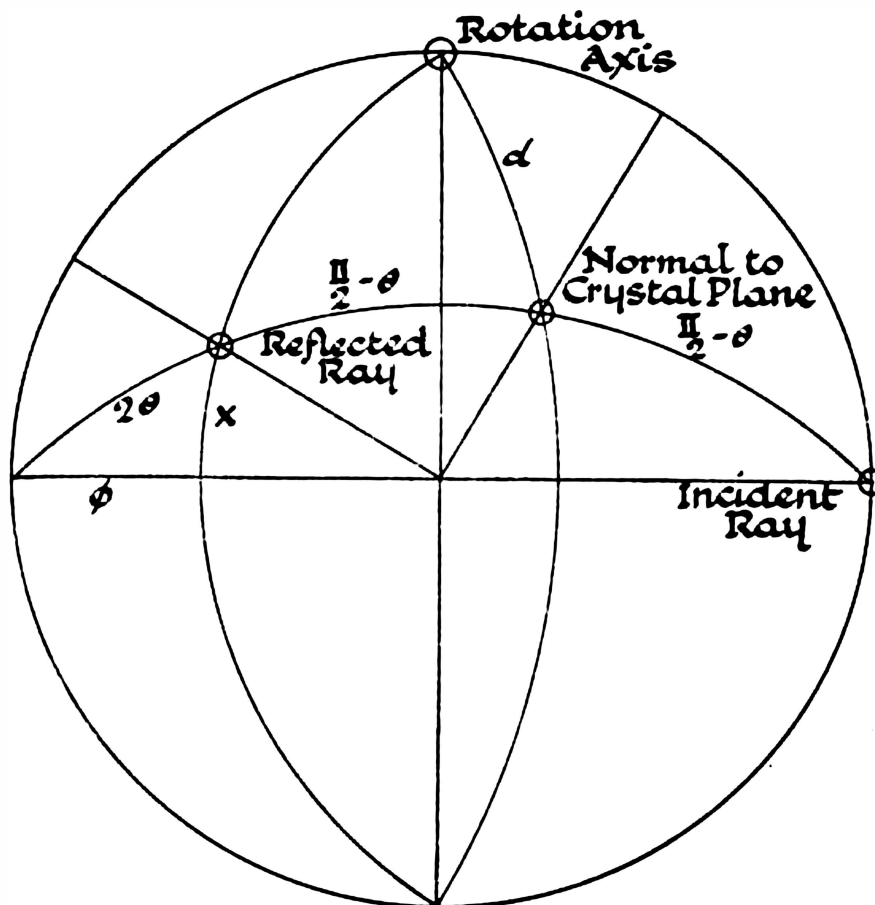


FIG. 2.

buted about the equator and the plane containing the incident ray and the axis. If $\sin \theta \cos \alpha > \frac{1}{2}$ there is no real value χ, ϕ that can satisfy the equations. No reflection is therefore possible. This occurs for small spacings and planes nearly perpendicular to the axis of rotation. If $\alpha = 0$, i.e., the plane is parallel to the axis, $\chi = 0$. There are only two reflections, both in the equatorial plane.

Now consider a cylindrical film of radius a . The reflected ray meets it at the point $a/\sin \chi, \chi, \phi$. If the cylinder is flattened out the xy co-ordinates of this point referred to axes in, and perpendicular to, the equator are $x = a \phi$, $y = a \tan \chi$. That is, by measuring the co-ordinates of the spots on the film we can obtain χ and ϕ and thence θ and α .

These calculations are, however, rather laborious, and the procedure can be simplified by a graphical method. Actually x and y were calculated for a cylinder of 10 cms. radius, and for every five degrees in the values of θ and α . These were plotted and the curves $\theta = \text{const}$ and $\alpha = \text{const}$ drawn for every

five degrees. The first set are, of course, the familiar Debye curves; the second resemble lemniscates in form. (See fig. 3.) The films were projected on to this chart with suitable magnification, and θ and α read off directly to an accuracy of about one degree.

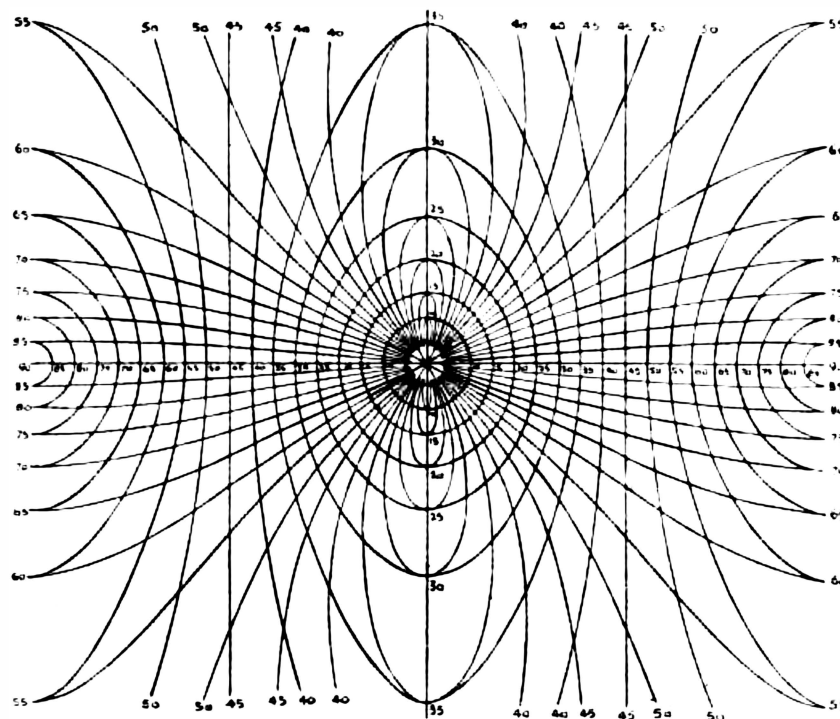


FIG. 3.

Two photographs of a crystal in different settings are theoretically sufficient to account completely for its structure, but to avoid complications these settings are so chosen that the axis of rotation coincides with some important axis of the crystal, and preferably in turn with two axes at right angles. The same planes can always be identified in the two photographs from the fact that they have the same spacing. Allowance has, however, to be made for planes belonging to the same form, and this is usually effected by the setting of the crystal, in which the spots due to such planes are made to superpose their effects. From the two values α_1 , α_2 of the inclination of the normal of the plane to the axis, the position of the plane relative to the axes can be calculated, and from two pairs of such values the angle between the two corresponding planes in the crystal can be found. It is easier, however, and for the purpose quite accurate enough, to prepare from the measurements a stereographic projection of the crystal in the manner described below.

Let the primitive be chosen to include the two axes of rotation 1 and 2 (see fig. 4), the poles of which are at A_1 and A_2 . About A_1 and A_2 describe small circles of angular diameter α_1 and α_2 .

Where they meet is the projection of the plane. In this way the whole stereographic projection may be mapped out and from it the symmetry and

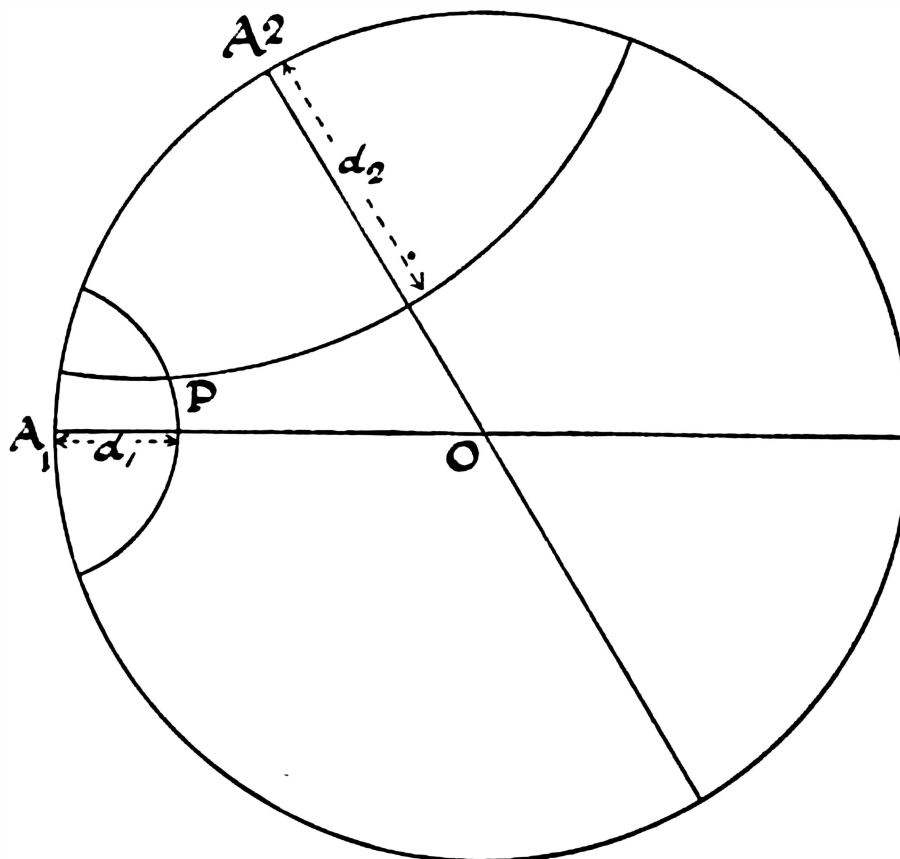


FIG. 4.

axial ratios of the crystal determined. The case is much simplified when the axes are at right angles. Here one axis may be taken as the axis of the primitive and the other to lie in it.

Experimental Procedure.

The first requirement is a single crystal, or one approximately so; that is, a crystal one of whose constituent pieces is so much greater than the others that the spots on the plate due to it can easily be separated. To secure this several crystals were mounted in turn in an arbitrary manner and photographed with relatively short exposures. Most were found to give a great number of spots due to the cleavage plane, such as photographs, and were consequently rejected. At last one was found which gave an intense single spot reflection with a much fainter halo and subsidiary spots. This crystal was used in most of the subsequent work. It will be referred to as crystal I. The crystal was a small fragment of a cleavage plane, of irregular outline and fairly thick as graphite crystals go. (See fig. 5.) It was first set with its cleavage plane

perpendicular to the axis, giving photograph No. 1. The photograph shows eleven principal planes (not counting the arc of the cleavage powder and the vertical brush due to reflections of white radiation by the cleavage plane).

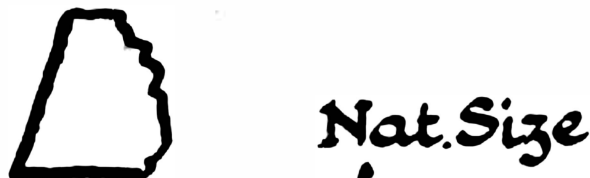


FIG. 5.

The values of θ and α_1 for each of these are shown in Table I, together with the calculated values on the basis of the Hull lattice.

This photograph is in itself sufficient to determine the graphite lattice, on the sole assumption that it has a trigonal or hexagonal symmetry, for it shows reflections of planes at the spacings and angles demanded by the Hull lattice (see Table I), whereas, according to the Debye and Scherrer lattice, for instance, the spacing of the $(01\bar{1}0)$ planes should have been one-third of that which appears on the plate.

The crystal was then turned through 90° and another photograph taken. Here the normal to the cleavage plane is in the equator, and it was seen that the planes $\bar{1}011$, $1\bar{1}01$ and other planes in that zone gave reflections near each other, showing that the $\bar{1}2\bar{1}0$ and $\bar{1}\bar{1}20$ zones are nearly, but not quite, at 30° to the axis. The angle of mis-setting is 8° , but the method gives no hint of which sense this mis-setting is in, so that the next photograph, where the crystal has been turned through that amount, shows that it has only made things worse. However, in the next (No. 2) the final result is achieved, and the crystal is now set with the zone $2\bar{1}\bar{1}0$ parallel to the axis.

This photograph shows a large number of planes, the most important being those in the equatorial zone. The definition is sufficiently good to be able to measure 11 planes in this zone, and thus to estimate their spacings to within 1 per cent., i.e., nearly as accurately as Hull's measurements, and at the same time to leave no possibility of doubt in the great majority of cases as to the indices of the plane dealt with. In Table II a comparison is given between Hull's spacing and these, and the agreement is excellent. In the same table there are also given spacings recalculated from Debye and Scherrer's measurements, taking some lines given as β lines as α lines and using a more correct value for λ K $_{\alpha}$ Cu. This procedure gets rid of some of the most glaring differences; but there are some lines, notably those at spacing 1.48, 1.21 and 0.92, which cannot be accounted for, either as α or as β lines. All of these lines are marked weak and may conceivably be due to some impurity.

By turning the crystal through 30° the $2\bar{1}1n$ zone is brought into the equatorial plane. The photograph taken in this position shows these reflections, but, unfortunately, showed at the same time that the crystal was not a simple one, but consisted of two crystals having the cleavage plane in common but turned through about 28° with respect to each other—probably twins. There is, however, no difficulty in separating the spots due to the main crystal, and the values of θ and α_2 are given in Table I.

Subsequently other photographs have been taken with crystal II (No. 3). This had the advantage of not being twinned and, as it was larger than crystal I, of showing up faint spots better. The results from these photographs are incorporated in Tables I and II.

It can be seen from the tables that of the 25 planes that can reflect copper rays only four have been unaccounted for, and all of these are planes of high indices.

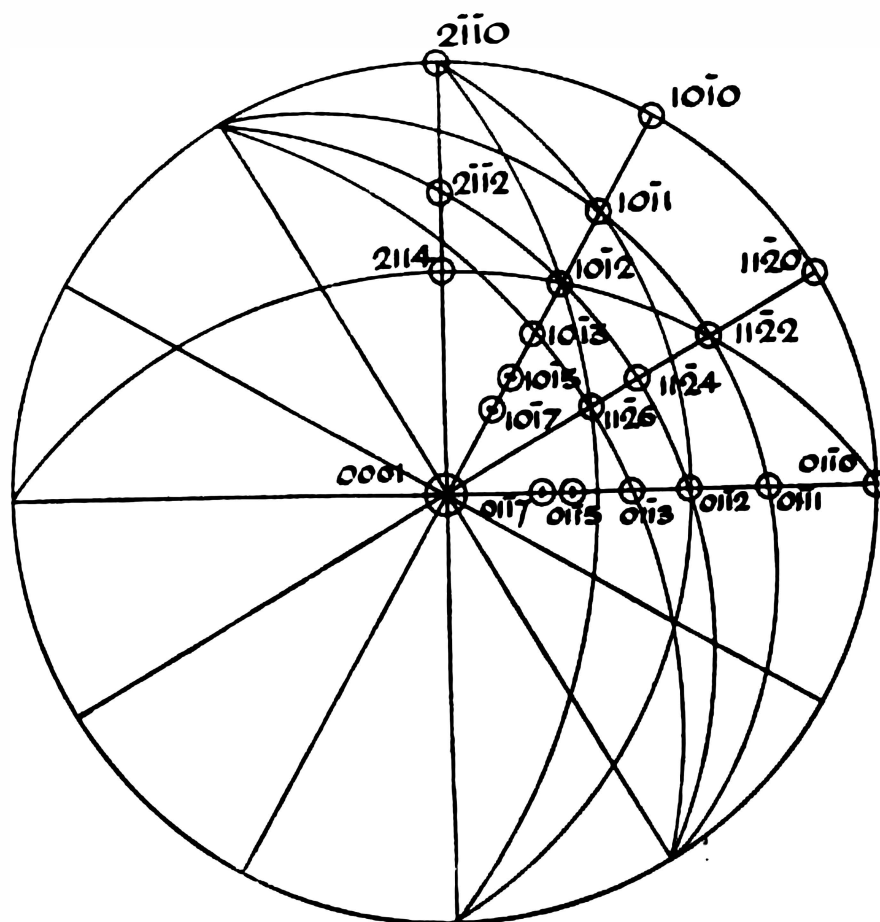


FIG. 6.

All these measurements are relative to the cleavage spacing, the four orders of whose reflections calibrate the photograph. It is difficult to obtain a direct value of the radius of the film, as it is a duplitised one, and its thickness and

that of its paper envelopes are commensurate with that of the camera itself.

The values of α_1 , α_2 , α_3 observable on the photographs are combined to give a stereographic projection of the crystal in the manner described above. This is shown in fig. 6. It will be seen that the points lie as closely as might be expected to their calculated position.

Measurements by the Ionisation Spectrometer.

Once the crystal can be set up so that an important zone lies in the equatorial plane, the crystal holder can be removed as one piece on to the table of the ionisation spectrometer.

Mr. Astbury was kind enough to make some measurements of the crystal set up as for photographing, *i.e.* with the zone $11\bar{1}n$ in the equatorial plane. He was able to detect three orders of the cleavage plane and also the plane $01\bar{1}1$, the angle between it and the cleavage plane being measured and found to be $72^\circ 30'$ as against $72^\circ 44'$ calculated. Mr. Wood also, using a larger and more imperfect crystal, observed three orders of the cleavage plane, giving a spacing of 3.41 A.U. These measurements will be referred to again in the discussion of the intensity questions. Subsequently Miss Yardley, using crystal II, was able to measure five orders of the cleavage plane reflections, giving a mean value of 3.41 A.U.

Laue Photograph Measurements.

Mr. Astbury has very kindly taken four Laue photographs of graphite : (i) with crystal II, No. 4; (ii) with crystal IV, which was unfortunately destroyed; (iii) with crystal V; and (iv) with the thick crystal VI. In all cases the cleavage plane is perpendicular to the beam, and the distance between plate and crystal was 2 cms. All the photographs are similar in that they show prominent spots due to the $01\bar{1}1$ planes, and fainter ones, due to the $2\bar{1}12$. These spots are reduplicated on all the plates except one, on account of the twinning to be discussed in a later paper. Besides these spots there are others which from their position and appearance must be referred to distorted portions of the crystal. All the photographs show the hexagonal symmetry.

The large size of the spots, due to imperfections of the crystal, did not permit of accurate measurements. The values of the axial ratio as calculated from photographs (i), (ii), (iii) and (iv) are 2.65, 2.64, 2.63, 2.60. The value from other measurements is 2.77.

Ewald's Laue photograph of graphite taken in 1914 shows a very similar appearance, but it was obviously taken from a better crystal than any at my

disposal. He referred the crystal to different axes, but re-calculating his results gives an axial ratio of 2.79, much closer to the other values.

Fundamental Lattice.

All the measurements from the photographs agree with the lattice suggested by Hull, namely, a hexagonal lattice, with length of side of elementary triangle 2.4 A.U. and of height 6.8 A.U. This lattice is shown drawn to scale in fig. 7.

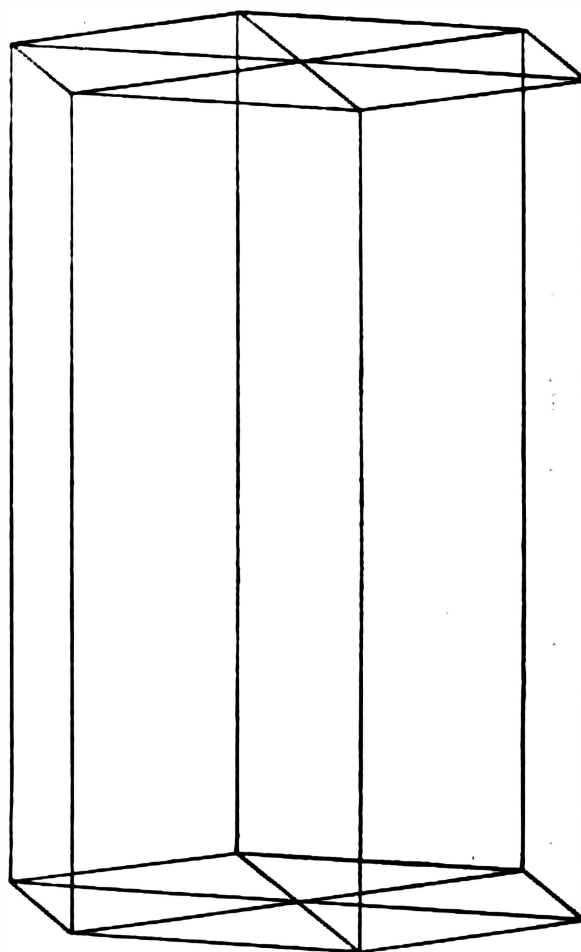


FIG. 7.

To determine the dimensions of this lattice better than could be done by the small circular camera employed, the crystal (in this case crystal II) was mounted on a Müller spectrometer, so that the $01\bar{1}n$ zone was in the equatorial plane. Three spacings were measured, 0002, $01\bar{1}0$, and $01\bar{1}1$. The last two gave rather wide bands even with fine slits, but their spacings could be measured to an accuracy of 1 per cent., while the cleavage plane, which gave sharper reflections, could be measured to an accuracy of $\frac{1}{2}$ per cent.

The spacings are :—0002	$3.40 \pm .01$	A.U.
$01\bar{1}0$	$2.13 \pm .02$	A.U.
$01\bar{1}1$	$2.02 \pm .02$	A.U.

Taking account of the other values of the cleavage-plane spacing, which are all over 3·40, we may take it as 3·41. From this and the values of the other two spacings we arrive at two values for the base length of the elementary triangle, 2·46 and 2·44. We may, therefore, take as the dimensions of the cell of graphite at ordinary temperatures and pressures:—

Height	6·82 ± 0·04 A.U.
Length of sides	2·45 ± 0·03 A.U.
Axial ratio, c : a	2·77

Measurements on Artificial Graphite.

Through the kindness of Mr. Robert Lennox, of the Lennox Foundry Company, London, I have been able to obtain crystals of artificial graphite which occur loose in pockets in the heads of certain silicon-steel castings. These crystals, while much smaller than the natural crystals employed, were large enough to give photographs by the rotation method, showing four of the most prominent graphite planes in identical positions to those of the natural graphite. A comparison photograph, in which a flake of natural graphite was mounted side by side with one of artificial graphite in a Müller spectrometer, showed that the cleavage spacings of the two forms do not differ by as much as 0·3 per cent. We may, therefore, assume that artificial and natural graphite are identical in structure.

Position of the Atoms.

The volume of the unit cell of graphite is

$$6\cdot82 \times 2\cdot45^2 \times 3/2 = 35\cdot5 \text{ A.U.}$$

The specific gravity of graphite is 2·2. If there are N atoms of weight $12 \times 1\cdot66 = 20\cdot0$ A.U. per cell; then

$$20\cdot N = 35\cdot5 \times 2\cdot2 = 78. \quad N = 4.$$

There are four atoms in the unit cell. The distribution of the four atoms in the cell can only be determined on the basis of the intensities of the reflections from the various planes.

The most important plane, and the only one from which quantitative intensities have been measured, is the cleavage plane. The spacing for this plane is 3·41 A.U. half the height of the unit cell. This shows that in each cell the four atoms must have heights, 0, $t/2$, $\frac{1}{2}$, $1 + t/2$, above the basal plane of the cell (these heights refer to fractions of the actual height of the cell). If we consider only half the cell it is clear that the atoms must lie in two planes, the

basal plane and one at a so-far indeterminate height t above it. To estimate this height we have the intensities of the successive orders of reflection from the cleavage plane. The results of the various measurements are given in Table III. Those of Miss Yardley are the most complete, giving as far as the fifth order. The ionisation spectrometer measurements agree fairly closely with each other, and the photographic measurements bear them out as far as they go. In order to obtain higher orders photographically, I used both a molybdenum and a silver anti-cathode, but in neither case could any order higher than the fifth be detected.

In comparison with the observed values are shown the intensities calculated for various values of t ; 0 , $\frac{1}{9}$, $\frac{1}{7}$. The intensities are given between rather wide limits, the upper being based on the behaviour of the diamond, the lower on the theoretical decrease with $\text{cosec}^2 \theta$. It can be seen that none of these calculated values fit the whole of the observed values; for instance, $t = \frac{1}{7}$ fits the observations fairly well until the fourth order, after which it gives too high values, whereas $t = 0$ is consistently higher than the observed values. The fact that only on the latter hypothesis each order is weaker than the one before it is very strongly in its favour, and the more rapid falling-off of the intensities of the successive orders may well be accounted for by the following considerations. In fig. 8 curves plotted from Miss Yardley's results are given.

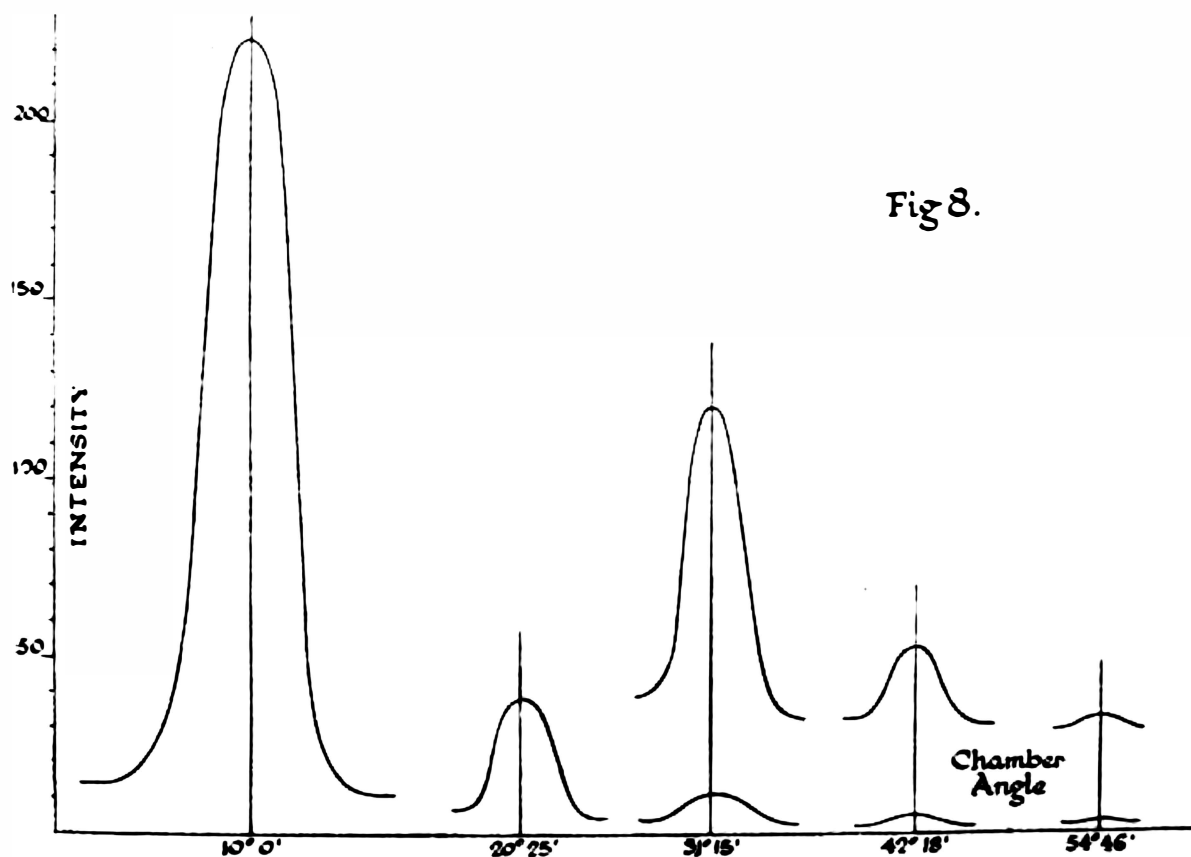


Fig 8.

The vertical scale of the third, fourth and fifth orders is shown multiplied ten-fold, but the horizontal angular scale is the same for all, and it can be seen that the breadths of the peaks, instead of increasing with the higher orders as they would in a more perfect crystal, actually decrease. The explanation of this is that the reflections from the small crystals nearly coincident with the main crystal contribute to the large peaks of the first orders, but in the higher orders, where the peaks themselves are small, their effect is lost in the general white radiation. At the same time the imperfections of the crystal probably abolish that extinction effect which in the diamond reduces the intensities of the first orders. (Another but more speculative cause for this apparent rapid falling-off of intensity will be dealt with when we consider the positions of the electrons.) If we assume that the first of the above causes is alone operative, it can be allowed for by multiplying the heights of the peaks of the ionisation curves by the corresponding order, and taking the result as the true measure of intensity. The results taken from Miss Yardley's measurements are given in the table, and will be seen to agree much more closely than any of the others with the theoretical values.

Returning now to the interpretation of the intensities, we see that there is a fairly strong probability that all the carbon atoms lie in the basal planes of the cells, and that it is almost certain that half of them do not lie at a distance more than one-ninth of the cleavage spacing from the plane containing the other half.

Whatever the actual symmetry of graphite is, it certainly has a trigonal axis perpendicular to the cleavage plane. This ensures that all the atoms

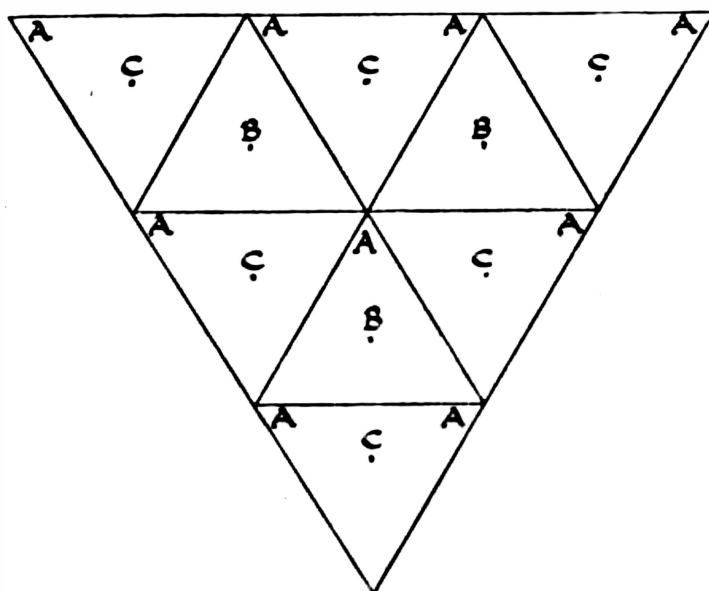


FIG. 9.

must lie either on the axes through the points of the lattice or on axes passing through the centres of the triangles of the hexagonal net (the points A, B, C in fig. 9). Any other arrangement would either not give trigonal symmetry or would lead to more than four atoms in the cell.

We may now consider the evidence of the intensities of reflection from planes of the type $2\bar{1}1n$. The graphite crystal must, in conformity with what has been said above, present the appearance of fig. 10 when viewed along the

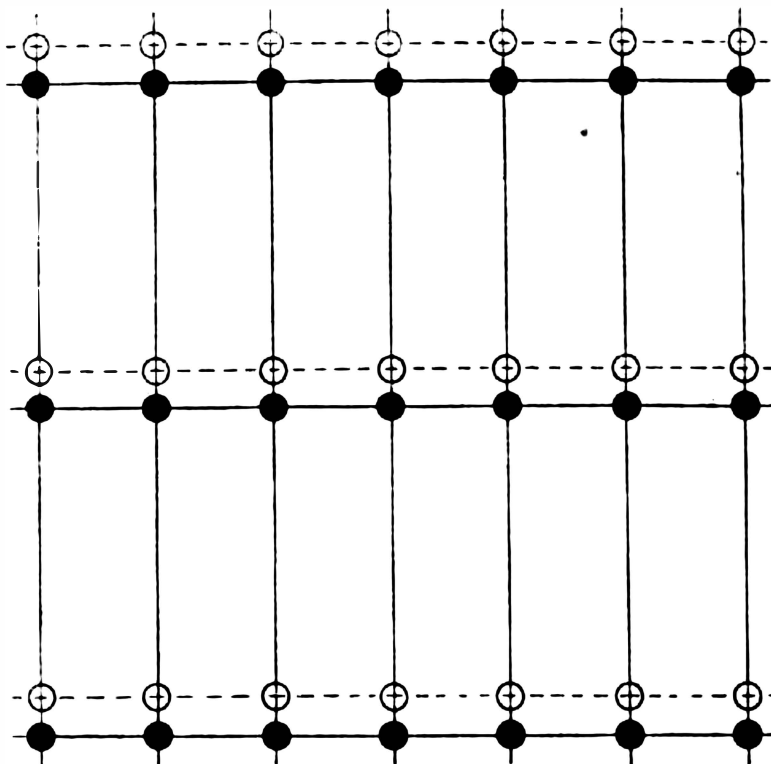


FIG. 10.

common axis of these planes. (In this figure, and in figures 11 and 12, the white circles represent the positions of atoms governed by the undetermined parameter t , drawn for values of $t = \frac{1}{3}$ and $t = 0$.) It will be seen at once that the planes for which n is odd are halved. Of the planes of even indices four appear on the photographs: $2\bar{1}10$, $2\bar{1}12$, $2\bar{1}14$, and $2\bar{1}16$; the others are beyond the range of copper rays. All these planes give strong reflections. Debye and Scherrer also mark them all as strong; Hull, however, gives the intensities as 35, 50, 15, 2. A plausible explanation for this disagreement is given by the following considerations, to which sufficient notice has not always been given. In the classical expression for intensity

$$\frac{N^2 \lambda^3}{\sin 2\theta} \frac{1 + \cos^2 2\theta}{2} e^{-B \sin 2\theta} F^2 \frac{e^4}{m^2 c^4} \delta V$$

the term $\frac{1}{\sin 2\theta}$ is not generally taken into account, and quite rightly, since

it only makes a small difference in the result if the glancing angles are small, that is, if hard rays are used. But Debye and Scherrer used copper rays and a camera of a circular kind, in which the values of θ approached 180, which vastly increased the intensity of the reflected beam in these cases. This effect is very noticeable on Debye photographs of nearly all substances; the circle surrounding the opposite point of entry of the X-ray beam being nearly as intense as those surrounding the central spot. The effect is also noticeable in my photographs, notwithstanding the fact that the spots are very much spread out, owing to the large geometrical dispersion and distortion in his part of the field.

To avoid the difficulties these considerations entail it is best to compare only the intensities of points in the same part of the field. Judged in this way the $2\bar{1}1n$ planes still give strong reflections, or at any rate there is no marked falling off. Theoretically the intensities of these planes should be affected in the ratio of $1 : 1 + \cos 2\pi t : 1 + \cos 4\pi t : 1 + \cos 6\pi t$.

If $t = \frac{1}{3}$ this would be $1.0 : 1.76 : 1.17 : 0.5$, and $2\bar{1}16$ would only be one-third as strong as $2\bar{1}12$, which would be quite sufficient to show photographically. *A fortiori*, if $t = \frac{1}{4}$, as Hull's model makes it, the effect would be unmistakably present. It is only on the assumption that $t = 0$ that $2\bar{1}12$, $2\bar{1}14$, $2\bar{1}16$ would all give the same intensity. Thus the evidence from the $2\bar{1}1n$ planes corroborates that obtained from the cleavage plane.

We have shown that the four carbon atoms can only lie on three axes in the cell (the axes marked A, B, C in fig. 9), and that their heights above the base of the cell are $0, t/2, \frac{1}{2}, \frac{1}{2}(1+t)$. If we place the first atom on the axis A and at height 0, we have to find how to place the remaining three atoms. Consider the atom at height $t/2$, it might be placed on axis A or on axis B or C. There is a good reason why it should not lie on A. The distance between the first two atoms would then be less than $1/9$ of $3.41, 0.38$ A.U.; $\frac{1}{4}$ of the diameter of the carbon atom and much smaller than the diameter of any atom. We must therefore place the second atom on the axis through B or C, which of the two is immaterial.

The third atom, height $\frac{1}{2}$, may now be placed on A, B or C—there is nothing so far to say which—and the fourth, height $\frac{1}{2}(1+t)$, on any axis on which the third is not placed. If the third atom is placed on A the fourth can only be placed on C; to place it on B would be to repeat the arrangement of the first two atoms and thus halve the height of the lattice. If the third atom is placed on B the fourth can only be placed on A, because the fourth atom must be related to the first of the cell above, as the second atom is to the third,

otherwise the perfect halving of the basal plane could not be maintained; to place the third atom on B and the fourth on C would upset this relation. Similarly, if the third atom is placed on C the fourth must be on B; but this arrangement is essentially the same as the one first mentioned, with B in the place of A, so we are left with only two possible structures, shown in figs. 11, 12.

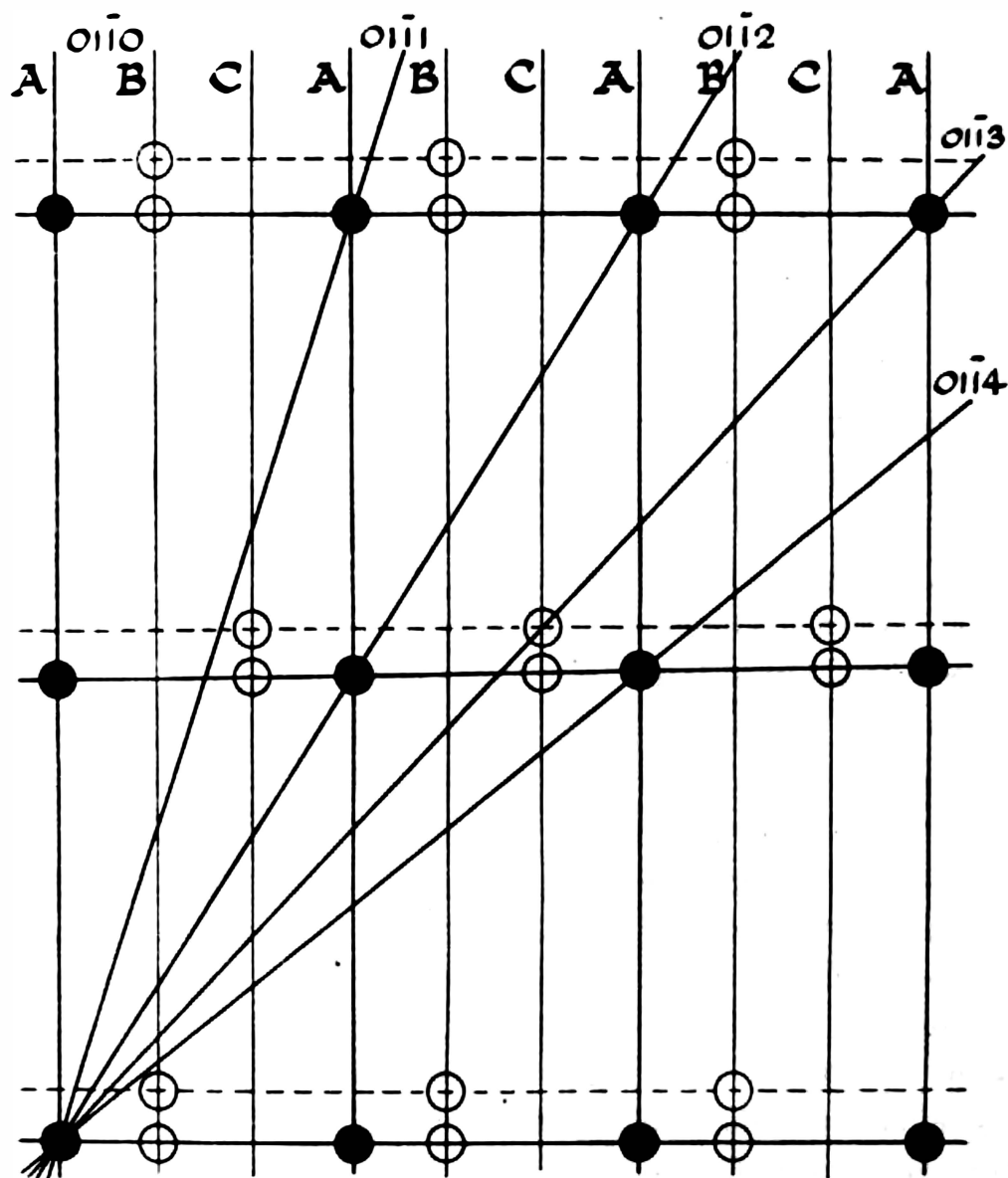


FIG. 11.

To distinguish between them we have the intensities of the planes of the type $011n$. The appearance of the two structures (which we will call structures I and II), viewed along their common axis, is shown in figs. 11 and 12. As can be seen, the structure II would degenerate into one with half the lattice height if $t = 0$, but this we are not yet justified in assuming. If we calculate

the ratios in which the reflection intensities of various planes of the type $01\bar{1}n$ would be affected by interleaving in each of the structures we get :—

		For Structure I.	For Structure II.
When n is odd	$\frac{3}{16}$	$\frac{3}{4} \sin^2 \frac{1}{2} (n\pi)$
When n is even	$\frac{1}{16} + \frac{1}{2} \sin^2 \frac{1}{2} (n\pi)$	$\frac{1}{4} \cos^2 \frac{1}{2} (n\pi)$

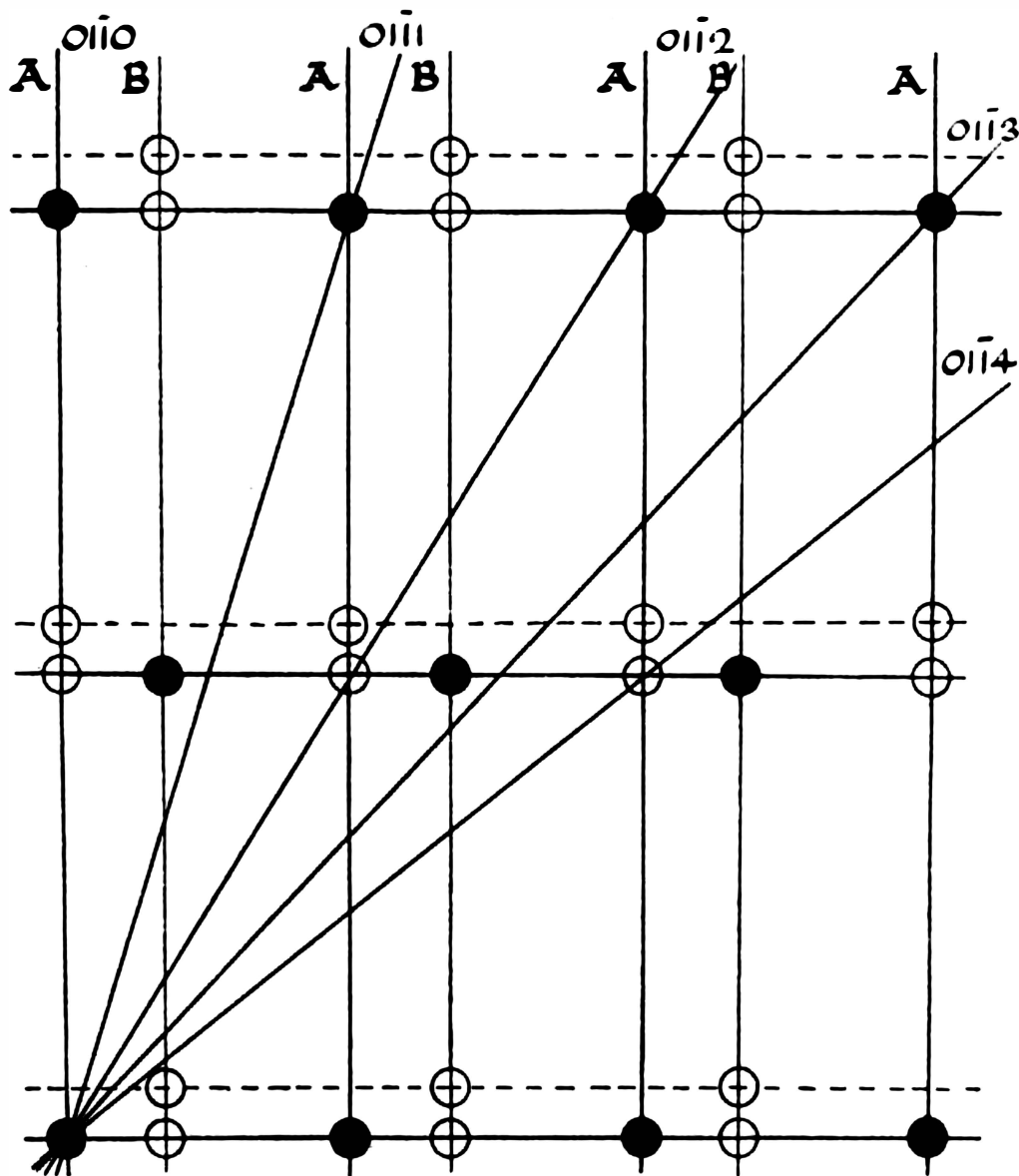


FIG. 12.

Now $t \gtrsim 1/9$, so that the reflections from such planes as $01\bar{1}1$, $01\bar{1}3$, should according to model LI be very small, much less than those of $01\bar{1}0$ and $01\bar{1}2$. The observed intensities show unequivocally that the reverse is the case. $01\bar{1}1$ gives a very strong reflection indeed, the next after the cleavage plane in fact; $01\bar{1}3$ is also strong; while both $01\bar{1}0$ and $01\bar{1}2$ are distinctly weak. Structure II must, consequently, be rejected without further consideration.

According to model I, on the other hand, all planes such as $01\bar{1}1$, $01\bar{1}3$, $01\bar{1}5$,

0117, should be equally affected by interleaving; this is borne out by the photographs, which show no marked difference in intensities. On the other hand, the reflections from the 0112 n planes should, except when $t = 0$, increase in intensity with n in a rapid manner. The photographs do not show such an increase and the intensities are less than those from the 011(2 $n + 1$) set. This enables us to fix an upper limit for t . The reflection from the 0117 plane is certainly stronger than that from 0116 (it is probably more than twice as strong). From this we have the inequality :—

$$\begin{aligned} \frac{3}{16} &> \frac{1}{16} + \frac{1}{4} \sin^2 3\pi t : \\ \sin^2 3\pi t &< \frac{1}{4} \\ |\sin 3\pi t| &< \frac{1}{2} \\ 3\pi t &< \pi/6 \\ t &< \frac{1}{18}. \end{aligned}$$

This limitation of t is much more rigid than the two previously employed. The comparison between the reflections of the odd and the even planes avoids all the allowances for the angle of reflection, the absorption, or any of the general factors which affect intensity.

It may be seen that none of the results, except that from the ionisation spectrometer, suggest that $t \neq 0$; and this method, without the allowances suggested, would equally disagree with any other value of $t < \frac{1}{18}$. 0 is a much more probable value than any fraction $< \frac{1}{18}$, particularly for reasons of symmetry, and we may therefore adopt it without much fear of error.

In this way the structure of graphite has been completely determined. The model arrived at is shown in fig. 13. It may be described as follows :—

The atoms of carbon in graphite lie in planes in which they form nets of hexagons. These nets are in successive planes, superposed so that half the atoms in one net lie normally above half the atoms of the net beneath, while the other half lie normally above the centres of the hexagons of this net. Alternate nets lie atom for atom normally above each other. The symmetry of graphite is hexagonal holohedral, belonging to the space group D_{6h}^3 . It will be seen that this model, while it accepts Hull's lattice, has the carbon atoms arranged in plane nets, as in the model of Debye and Scherrer, so that it agrees and disagrees with both equally.

The model put forward, though fairly well established by X-ray data, is open to objections on physico-chemical grounds. The first and most obvious of these is that the atoms are actually closer together in the hexagonal nets of graphite than they are in diamond, their centres being 1.42 instead of 1.53 A.U.

apart. This should not be surprising, as in the absence of other carbon atoms in the immediate vicinity the atoms in the rings might be considered to draw

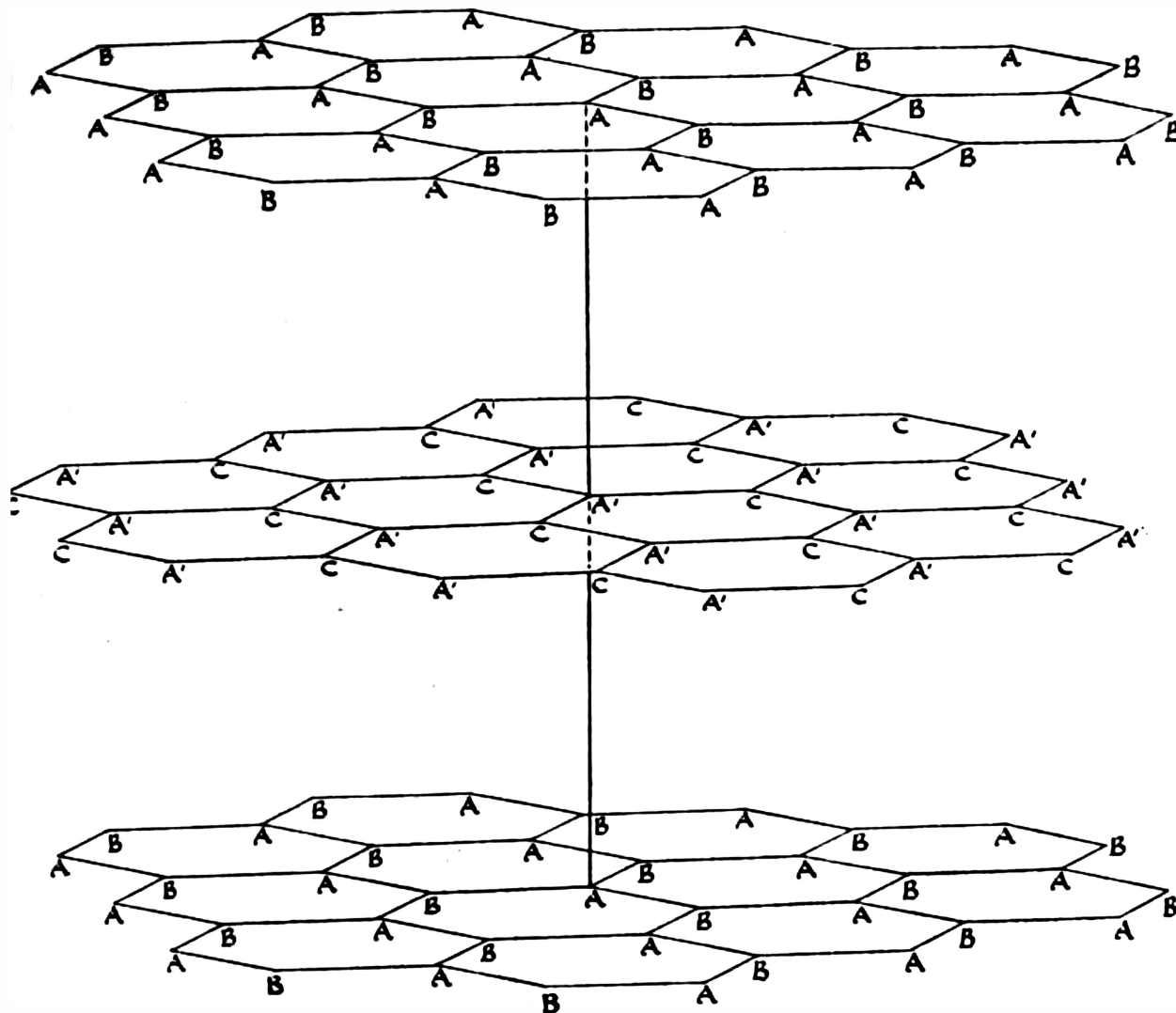


FIG. 13.

closer together than they do in diamond. The great difference between the mechanical properties of graphite and diamond (hardness, flexibility, etc.) is due to the fact that the atoms are linked closely in a two-dimensional net in the former and in a three-dimensional lattice in the latter, and, in fact, graphite exhibits in the plane of the cleavage sheets considerable hardness and tenacity.

Another objection is that the carbon atom in the structure proposed would lose that tetrahedral symmetry so well exhibited in diamond and in organic substances. This is inevitable in any explanation of graphite structure. The relatively large gap between the carbon atoms in successive cleavage planes can only be explained by some virtual extension of the carbon atom along one axis, thus destroying its tetrahedral symmetry.

The third objection is one which was urged against Hull's structure and which

applies in a lesser degree to the one proposed. It is that it makes the carbon atoms fall into two classes. It can be seen from fig. 13 that the carbon atoms at A and A' are geometrically differently placed than those at B and C. This is undeniably displeasing to our sense of the homogeneity of elementary substances. However, this difference is not very great. In fig. 14 we see

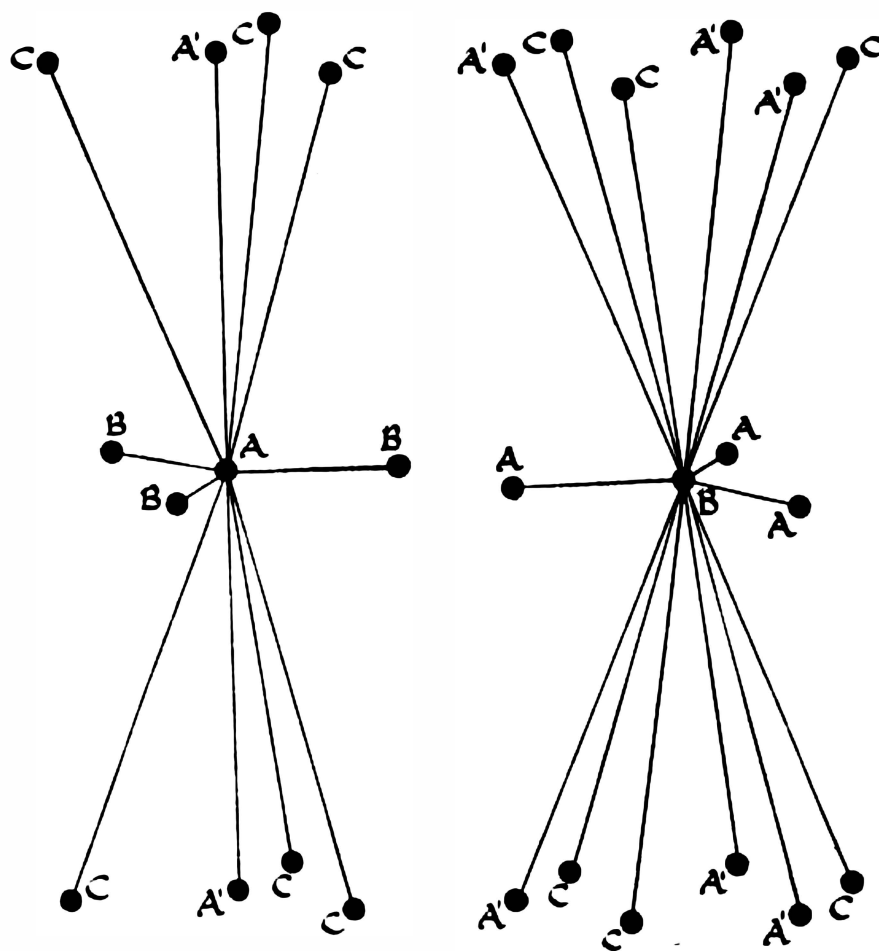


FIG. 14.

the arrangement of the neighbours of a carbon atom in an A and B position ; in both cases the immediate neighbours are three atoms in the equatorial plane at a distance of 1.42 A.U. The next nearest are, in the case of an A atom, two atoms on the vertical axis at a distance of 3.41, and six symmetrically distributed about it at a distance of 3.70 A.U. In the case of a B atom there are 12 at a distance of 3.70 A.U. It is probable that an atom loses most of its directive attraction at distances as large as 3.4 A.U., and the resultant non-directive forces must be very much the same in both cases, so that it must be nearly an indifferent matter whether a carbon atom takes an A or B position. This is borne out by the twinning and glide planes of graphite, in which interchanges of A and B positions take place.

The proposed structure fits in well with the later ideas of Bohr on the

structure of the carbon atom. Instead of the four L electrons being distributed in 2_1 orbits whose planes intersect at the tetrahedral angle, he now postulates as the more stable form an atom with only three 2_1 orbits and one 2_2 orbit. This form would possess trigonal symmetry only. Such atoms would fit very naturally together in the graphite nets, giving the appearance of fig. 15,

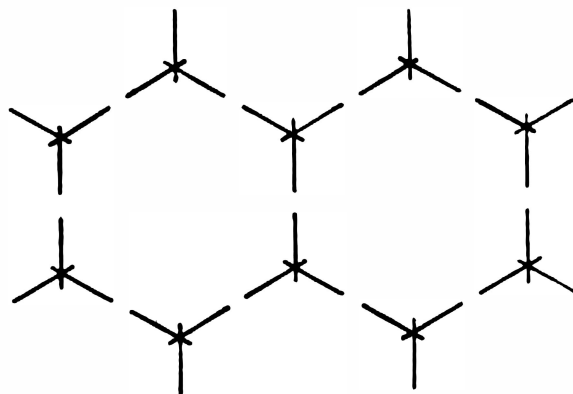


FIG. 15.

the orbits being seen edgewise. The fourth L orbit is not shown, it being doubtful in what form it would persist in the solid, but the existence of such a loosely bound electron would explain at once the relatively large distance between successive planes of atoms and would help to account for the rapid falling-off of the intensities of the orders of reflection from this plane. It would also explain the metallic properties of graphite, such as its thermal and electrical conductivities and its very high absorption of light. A test for this hypothesis would be a determination of the resistances of graphite crystals in different directions: it would be expected that the resistance would be much greater across the cleavage layers than along them. It is hoped that experiments at the Cryogenic Laboratory at Leyden may clear up this point.

Diamond may be considered to consist of atoms with four 2_1 orbits, and this would explain both its higher symmetry and its non-metallic qualities. The orbits in diamond would thus suffer more mutual screening action than those of graphite, and might consequently be expected to be larger; this would explain the closer packing of the graphite nets. The existence of two forms of carbon atom in diamond and graphite, analogous to the two forms of helium, may tend to explain the extreme difficulty of converting graphite (obviously the more stable form) into diamond, in a way that no mere difference of arrangement of similar atoms could do.

The chemical bearings of the structure of graphite are still obscure; strictly speaking, its elucidation throws no new light on the vexed question of the plane or puckered benzene ring. Before turning carbon in any form into

any organic substance in any ordinary way, such high temperatures are used that the structure is completely broken up, and we have no more reason for assuming that the flat ring of graphite should persist rather than the puckered one of diamond.

There remains, however, one avenue along which the transition is more gradual. Gaubert,* in his investigations of the optical properties of graphite, observed its change into graphitic acid under the microscope, and remarked that the crystals of the latter retained the orientation of the original graphite crystals. It is hoped in the future, by X-ray investigation of the transformation graphite—graphitic acid—mellitic acid, to relate the structure of graphite to that of the benzene ring.

Acknowledgments.

The author wishes to express his indebtedness to Sir William Bragg for his suggestions and the use of some of his unpublished papers; to the workers of the Davy Faraday Laboratory who materially assisted the course of the research; and to the Master and Fellows of Emmanuel College, Cambridge, whose financial help made the work possible.

Summary.

The structure of graphite has been examined by the method of the rotating single crystal. Sufficient evidence has been found to establish the lattice proposed by Hull rather than that proposed by Debye and Scherrer. This is confirmed by measurements by the ionisation spectrometer and from Laue photographs. The structure has also been completely determined. It is essentially that of Hull, but with all the carbon atoms lying in the cleavage plane, as in the Debye and Scherrer model.

Table I.

lices of plane.	1			2			3			θ (d)
	Rotation Axis 0001.			Rotation Axis 2110.			Rotation Axis 0110.			
	θ (obs.)	α_1 (obs.)	α_1 (cal.)	θ (obs.)	α_2 (obs.)	α_2 (cal.)	θ (obs.)	α_3 (obs.)	α_3 (cal.)	
0002	°	'	° 0'	13° 0'	90° 0'	90° 0'	13° 0'	90° 0'	90° 0'	13°
0004			0	27° 0'	90° 0'	90° 0'	27° 10'	90° 0'	90° 0'	26°
0006			0	43° 0'	90° 0'	90° 0'	43° 15'	90° 0'	90° 0'	42°
0008			0	63° 0'	90° 0'	90° 0'	65° 30'	90° 0'	90° 0'	64°
0110				21° 0'	90° 0'	90° 0'			0	
1010	21° 0'	90° 0'	90° 0'	21° 30'	29° 30'	30° 0'	21° 30'	59° 0'	60° 0'	21°
1100										

* *Loc. cit.*, p. 1.

Table II.

Indices of Reflecting Plane.	Spacings.				Intensities.		
	Observed.	Observed by Hull.	Observed by Debye and Scherrer (recalculated).	Calculated.	Estimated.	Estimated by Hull.	Estimated by Debye and Scherrer.
Cleavage plane.	Assumed.				Ionisation spectrometer measurements.		
0002	3.41	3.37	3.36	3.41	I 100	100	St
0004	1.71	1.69	1.70	1.71	St 13	3	m
0006	1.14	1.13	1.14	S-m 2.5		W
0008	0.85	0.851	0.85	S-m 0		
Zone	Observed.				Order of intensity.		
011 _n							
0110	2.13	2.11	2.23	2.12	m (5)	30	VW
0111	2.00	2.03	2.06	2.03	St (1)	60	St
0112	1.79	1.81	1.76	1.80	m (6)	1	m
0113	1.55	1.56	1.66	1.55	St (2)	2	m
			1.48 β				S-m
0114	1.35	1.31 ?	1.33	VW (7)		VW
0115	1.15	1.21	1.14	S-m (3)		VW
0116	1.01 ?	0.990	1.01 ?	1.00	VW (7)		
		(2114)					
0117	0.888	0.865	0.88	S-m (3)		VW
0118	0.794 ?	0.79 ?	0.79	VW ? (9)		
Zone							
022 _n							
0220	—			1.06		
0221	1.06	1.05	1.06	1.04	W	3	
0222	1.00 ?	0.990 ?		1.00	VW ?		
0223	0.95	0.96	0.96	W		
			0.92 ?				
0224	—		0.89		
0225	0.84 ?		0.84	W ?		
Zone							
2112 _n							
2110	1.23	1.227	1.25	1.23	S-m (4)	35	St
2112	1.16	1.155	1.18	1.15	St (1)	50	St
2114	1.00	0.990	1.01	0.99	St (2)	15 pt	St
		(0116)					
2116	0.837	0.827	0.838	0.83	St (2)	2	St
Zone							
123 _n							
1230	0.80	0.800 }		0.80	S-m	} 5	
1231	0.79	0.800 }	0.79 ?	0.80	S-m		

Table III.—Cleavage Plane Reflections.

1st Order.	2nd Order.	3rd Order.	4th Order.	5th Order.	6th Order.	Observed by
100	3	0	—	—	—	Hull (photo-metric).
100	16	6	0	—	—	Debye and Scherrer.
100	13.5	2.4	0	—	—	Astbury.
100	12.5	2.1	0	—	—	Wood.
100	12.4	2.0	0.4	0.08	0	Yardley.
100	33	12	4.4	1.5	—	Yardley (corrected).
						Calculated.
100	40 → 25	25 → 11	15 → 6	→ 4	→ 3	No interleaving $t = 0$.
100	26 → 16	7 → 3	0.5 → 0.2	→ 0.13	→ 0.8	Interleaving $t = \frac{1}{2}$.
100	19 → 12	1.6 → 0.7	1.0 → 0.4	→ 2.0	→ 2.8	Interleaving $t = \frac{1}{2}$.

Über die Kristallstruktur des Graphits.

Von **O. Hassel** und **H. Mark** in Berlin-Dahlem.

I. Mitteilung.

(Aus dem Kaiser Wilhelm-Institut für Faserstoffchemie.)

Mit fünf Abbildungen. (Eingegangen am 31. März 1924.)

Einleitung: Die erste Angabe über die Struktur des Graphits findet sich bei P. P. Ewald¹⁾, welcher aus einer Laue-Aufnahme auf einen hexagonalen Elementarkörper mit dem Achsenverhältnis 1,633 schloß.

Die nächste Bestimmung stammt von Debye und Scherrer²⁾, die auf Grund eines Debye-Scherrer-Diagramms mit Kupferstrahlung zum Ergebnis kamen, daß Graphit (es wurde Flinzgraphit und Ceylongraphit untersucht) trigonal kristallisiert und im rhomboedrischen Elementarkörper mit der Kantenlänge $4,69 \text{ \AA}$ 12 C-Atome enthält; über den Rhomboederwinkel ist an dieser Stelle nichts angegeben.

In einer zweiten ausführlichen Arbeit³⁾ über dieses Thema haben dieselben Autoren vier verschiedene Graphitpräparate mit Kupferstrahlung nach der Pulvermethode untersucht und gefunden, daß alle vier Präparate identische Diagramme ergaben, in welchen etwa 25 unabhängige Linien vermessen werden konnten, die auf einen rhomboedrischen Elementarkörper mit $r = 4,48 \text{ \AA}$ und $\alpha = 68^\circ 26'$ schließen lassen, der 8 C-Atome enthält.

In demselben Jahre hat A. W. Hull⁴⁾ eine Strukturbestimmung veröffentlicht, welche er an natürlichem und künstlichem Graphit ebenfalls nach der Pulvermethode durchgeführt hat. Es erwiesen sich die Bilder des künstlichen und natürlichen Graphits als identisch. Aus 19 vermeßbaren Linien⁵⁾ kommt Hull zu dem Schluß, daß von allen Strukturen, welche er mit diesem Befund in Einklang zu bringen versuchte, am besten die folgende paßt: Ein hexagonales Gitter, welches aus drei einfachen trigonalen Prismen zusammengesetzt ist;

¹⁾ P. P. Ewald, Sitzungsber. d. Münch. Akad., 4. Juli 1914.

²⁾ Debye u. Scherrer, Phys. ZS. **17**, 277, 1916.

³⁾ Ebenda **18**, 291, 1917.

⁴⁾ A. W. Hull, Phys. Rev. **10**, 661, 1917.

⁵⁾ Bei sieben dieser Linien ist eine eindeutige Indizierung nicht mehr möglich gewesen.

$c = 6,80 \text{ \AA}$, $b = 2,47 \text{ \AA}$, das Achsenverhältnis γ ist also gleich 2,76. Die Koordinaten der Atomschwerpunktslagen sind:

$$\begin{array}{ccc} m & n & p \cdot \gamma \\ m + \frac{1}{3} & n + \frac{2}{3} & \left(p + \frac{1}{14}\right)\gamma \\ m & n & \left(p + \frac{1}{2}\right)\gamma \\ m + \frac{2}{3} & n + \frac{1}{3} & \left(p + \frac{8}{14}\right)\gamma. \end{array}$$

Dieses Gitter erscheint dem Diamantgitter in bezug auf den Abstand aufeinanderfolgender Basisebenen, den Abstand der nächsten Atome in der Basis, und den kürzesten Abstand von Gitterpunkten überhaupt sehr ähnlich (vgl. Tabelle 1).

Tabelle 1. Beziehungen zwischen dem Gitter des Diamanten und des Graphits nach Hull.

	Graphit	Diamant
Abstand aufeinanderfolgender nächster 0001-Ebenen	0,48	0,51
Atomabstand in der 0001-Ebene	2,47	2,52
Kürzester Atomabstand im Gitter überhaupt	1,50	1,54

Das Fehlen einiger Interferenzen: $(10\bar{1}4)$, $(10\bar{1}5)$ in erster, $(10\bar{1}0)$, $(10\bar{1}1)$ in zweiter und (0001) in vierter Ordnung wird aus der Atomordnung nicht verständlich; man müßte zur Erklärung dieses Befundes Annahmen über die Beugungsfähigkeit der Atome als Folge ihrer inneren Struktur — also über den Laueschen ψ -Faktor — machen.

In einer zweiten kurzen Mitteilung¹⁾ ergänzt Hull seine Angaben dadurch, daß weitere genauere Aufnahmen seine obige Struktur bestätigt haben und daß es nicht möglich sei, diese Aufnahmen mit dem Debye-Scherrerschen Gitter in Einklang zu bringen.

Diese über die Graphitstruktur bestehende Ungewißheit ließ es wünschenswert erscheinen, unter Heranziehung sämtlicher Röntgeninterferenzmethoden sowohl an Einkristallen als auch an polykristallinem Material neue experimentelle Beiträge zu dieser Frage zu liefern.

1. Das verwendete Material und die verwendeten Methoden.

Es standen uns zwei Sorten von Einkristallen zur Verfügung:

1. Künstlicher Graphit in Blättchen aus dem Graphitwerk Kropfmühl in Oberbayern, für dessen Überlassung wir Herrn Eugen Ryschkewitsch zu bestem Danke verpflichtet sind, und

¹⁾ Referat eines am 22. April 1922 in Washington gehaltenen Vortrages. Phys.

2. natürlicher Graphit ins Muttergestein eingesprengt, ebenfalls in schön ausgebildeten Blättchen, aus Parainen (Parsby), Finnland, den uns Herr Prof. Dr. Aarne Laitakari in Helsingfors in liebenswürdigster Weise zur Verfügung gestellt hat.

Als polykristallines Material verwendeten wir natürlichen Graphit aus Ceylon, aus Krumau und fein gepulverten böhmischen Graphit von C. A. F. Kahlbaum.

Beide Einkristallpräparate zeigten auf der Blättchenebene zwei Systeme von Streifungen; das eine bestand aus drei Scharen paralleler Geraden, welche, wie Tabelle 2 erkennen läßt, miteinander Winkel

Tabelle 2. Die am Drehtisch mit Mikroskop und Fadenkreuz abgelesenen Winkel der Streifungen eines Graphitblättchens.

Abgelesene Winkel	Differenz	
	Streifung I	Streifung II
195° 42'	—	—
256 42	61° 0'	—
316 0	120 18	—
16 12	180 30	—
105 0	—	269° 18'
136 54	301 12	—
195 42	360 0	—
315 48	480 6	—

von 60° einschließen. Dieses System ist auf fast allen Stücken ziemlich deutlich ausgeprägt; das andere war nur stellenweise zu erkennen und bestand aus zwei bis drei Scharen paralleler Geraden, welche miteinander ebenfalls einen Winkel von 60° bilden. Die beiden Systeme waren zueinander um 30° verdreht.

Bei der Vorbereitung der Graphitkriställchen zu den Röntgenaufnahmen haben wir besonderen Wert darauf gelegt, das äußerst weiche Material möglichst wenig zu berühren, um Deformationen des Gitters, wie sie von Debye-Scherrer bei gepreßten Stäbchen festgestellt wurden, zu vermeiden. Auch die Aufnahmen am polykristallinen Graphit haben wir nicht mit gepreßten Stäbchen durchgeführt, sondern indem wir das in feinen Schuppen oder als Pulver vorliegende Material mit Hilfe von Kollodium an einen dünnen Wollfaden brachten, welcher dann an der Achse der Kamera befestigt wurde.

Es wurden nun zunächst an mehreren Einkristallen mit verschiedenen charakteristischen Strahlungen Drehdiagramme (im ganzen zwölf) hergestellt und mit der Polanyischen Gleichung drei Identitätsperioden in wichtigen kristallographischen Richtungen direkt vermessen.

Um über die Lage der höchstzähligen Achse Aufschluß zu erhalten, wurden ebenfalls an verschiedenen Präparaten Laue-Diagramme senkrecht zur Blättchenebene aufgenommen.

Zur möglichst genauen Vermessung des Netzebenenabstandes der Blättchenebene haben wir dann in einer Seemann-Kamera mit großer Aufspaltung diese Ebene nach der Braggschen Methode zur Reflexion gebracht, um so auch das Intensitätsverhältnis der aufeinanderfolgenden Ordnungen dieser wichtigsten Netzebene genau vermessen zu können.

Zur Beurteilung der Intensitätsverhältnisse aller Reflexionen endlich wurden Debye-Scherrer-Diagramme hergestellt und mit Hilfe eines Kochschen Registrierphotometers die quantitative Vermessung ausgeführt.

Es sei nun zunächst das durch die Kombination dieser Methoden erhaltene experimentelle Material mitgeteilt und dann an seiner Hand die kristallographische Diskussion durchgeführt.

2. Bestimmung des Elementarkörpers.

Schon die genaue Gleichseitigkeit der Dreiecksstreifung in der Blättchenebene deutet darauf hin, daß diese Ebene als Basis des trigonalen oder hexagonalen Elementarkörpers aufzufassen ist. Zur Sicherstellung dieser Vermutung wurden senkrecht zur Blättchenebene an mehreren Präparaten Laueaufnahmen gemacht, welche erkennen ließen, daß eine mindestens dreizählige Achse parallel der Strahlrichtung lag¹⁾. Durch Drehung um diese Richtung wurde hierauf der Identitätsabstand auf dieser Achse bestimmt; die diesbezüglichen Zahlen sind in Tabelle 3²⁾ enthalten. Es wurden vier Präparate in verschiedenen Kameras durchleuchtet. Das Mittel der Bestimmungen I., III. und IV. war: $c = 6,79 \text{ \AA}$.

Als nächste kristallographische Richtung wurde die am stärksten hervortretende Streifung in der Basisebene gewählt; zwei an verschiedenen Kristallen aufgenommene Diagramme ergaben die in Tabelle 4 enthaltenen Zahlen.

Endlich wurden noch zwei Drehdiagramme um die schwächer ausgeprägte Streifung angefertigt, welche die in der Tabelle 5 enthaltenen Identitätsperioden ergaben.

¹⁾ Bezüglich der Diskussion dieser Aufnahmen und bezüglich der Frage, ob trigonale oder hexagonale Symmetrie vorliegt, sei auf Abschnitt 4 verwiesen.

²⁾ Bezüglich der Translationsgruppenbestimmung und der dabei verwendeten Bezeichnungen sei auf die Arbeit von K. Weissenberg und dem einen von uns (ZS. f. Phys. **16**, 1, 1923) verwiesen.

Tabelle 3. Drehdiagramm um die höchstzählige Achse.

I. Aufnahme: $\lambda = 1,54 \text{ \AA}$; $2r = 5,72$.

$2e$	$\frac{2e}{2r}$	$\cos \mu$	J	J -Mittel
1,33	0,232	0,226	6,81	6,78
2,97	0,518	0,458	6,74	
5,25	0,920	0,678	6,83	

II. Aufnahme: $\lambda = 1,54 \text{ \AA}$; $2r = 5,75$.

1,40	0,244	0,237	6,51	6,60
3,06	0,536	0,473	6,53	
5,34	0,435	0,683	6,76	

III. Aufnahme: $\lambda = 1,54 \text{ \AA}$; $2r = 5,72^1$.

1,34	0,235	0,229	6,73	6,78
2,98	0,521	0,460	6,75	
5,25	0,920	0,678	6,83	

IV. Aufnahme: $\lambda = 0,876 \text{ \AA}$; $2r = 5,72$.

0,74	0,129	0,129	6,80	6,81 ₅
1,52	0,268	0,258	6,81	
2,35	0,410	0,383	6,86	
3,50	0,613	0,525	6,70	
4,68	0,820	0,638	6,87	
7,00	1,220	0,770	6,85	

Tabelle 4. Drehdiagramm um die deutliche Basisstreifung.

I. Aufnahme: $\lambda = 1,54$; $2r = 5,72$.

$2e$	$\cotg \mu$	$\cos \mu$	J	J -Mittel
2,26	0,395	0,368	4,19	4,25
5,84	1,02	0,714	4,31	

II. Aufnahme: $\lambda = 1,54$; $2r = 5,70$.

2,28	0,400	0,371	4,15	4,25
5,74	1,00	0,707	4,35	

Das Mittel aus beiden Bestimmungen ist: $4,25 \text{ \AA}$.

Tabelle 5. Drehdiagramm um die schwächere Streifung der Basisebene.

I. Aufnahme: $\lambda = 1,54$; $2r = 5,72$.

$2e$	$\cotg \mu$	$\cos \mu$	J
4,58	0,800	0,625	2,46

II. Aufnahme: $\lambda = 1,54$; $2r = 5,72$.

4,60	0,804	0,622	2,47
------	-------	-------	------

Das Mittel aus beiden Versuchen ergibt: $2,46_5$.

¹⁾ Wie man sieht, weicht der aus dieser Aufnahme sich ergebende Wert für c um etwa 3 Proz. vom Mittelwert der anderen Bestimmungen ab. Wir haben versucht, diese Abweichung durch verschiedene Fehlerquellen zu erklären (Zentrierung des Präparates, Lage des Films usw.), ohne daß das befriedigend gelungen wäre.

Aus den bisherigen Versuchen geht also hervor: Die Identitätsperiode auf der höchstzähligen Achse beträgt $6,79 \text{ \AA}$; in der darauf senkrechten Ebene gibt es zwei kurze Perioden, welche miteinander 30° einschließen, $a = 4,25$ und $b = 2,46$; wie man sieht, verhält sich a zu b wie $1,725$, also sehr annähernd wie $\sqrt{3}:1$.

Die Zahlen lassen es am natürlichsten erscheinen, für die Bildung der quadratischen Form dieses Gitters einen orthohexagonalen Elementarkörper $b = 2,46$, $c = 6,79$, $a = 4,25$ zugrunde zu legen ¹⁾. Setzt man für die Dichte einen mittleren Wert von $2,20$, so enthält dieser Elementarkörper

$$n = \frac{71 \cdot 2,20}{12 \cdot 1,649} = 7,91 \sim 8 \text{ C-Atome } ^2).$$

Die orthohexagonale quadratische Form lautet für die gefundenen speziellen Werte:

$$\sin^2 \frac{\vartheta}{2} = 0,0325_5 h^2 + 0,0975 k^2 + 0,0129_8 l^2. \quad (1)$$

Mit ihr wurden sämtliche Diagramme durchindiziert. Auf allen Aufnahmen ³⁾ erwies sich ein Punkt mit dem Reflexionswinkel $\frac{\vartheta}{2} = 13^\circ 10'$ als der stärkste. Um zu sehen, ob diese Reflexion, wie zu erwarten war, von der Blättchenebene herrührt, haben wir folgende Versuche durchgeführt: Es wurde zunächst ein Kriställchen um eine in der Blättchenebene liegende kristallographische Richtung, nämlich $[100]$ eingestellt und dann diese Richtung um einen bekannten Winkel, 40° bzw. 50° gegen die Drehachse geneigt. In dem bei Durchleuchtung dieser Anordnung erhaltenen Diagramm befand sich dann die Reflexion, welche auf dem Debye-Scherrer-Kreis mit $13^\circ 10'$ liegt, nicht auf dem Äquator, sondern war ebenfalls um 40° bzw. 50° dagegen geneigt. Daraus geht hervor, daß diese Reflexion tatsächlich von der Blättchenebene herrührt, also in orthohexagonaler Indizierung an den Ebenen (001) erfolgt. Den in den Diagrammen gefundenen $\sin \frac{\vartheta}{2}$ -Werten sind in Tabelle 6 die aus der quadratischen Form (1) berechneten gegenübergestellt.

Für die Photometrierung wurden noch Debye-Scherrer-Diagramme mit Kupferstrahlung hergestellt, deren Vermessung in Tabelle 7

¹⁾ Die Bezeichnung der Achsen erfolgte nach P. Niggli.

²⁾ Nimmt man hier die neuerdings von E. Ryschkewitsch und A. Köstermann bestimmte Dichte von $2,23$ an, so wird n genau gleich 8 .

³⁾ Mit Ausnahme der Drehdiagramme um die hochzählige Achse.

Tabelle 6. Drehdiagramm um $[001]^1$.

$2e$ in cm	$\frac{\vartheta}{2}$	Äquator		Indizierung	Intensität geschätzt
		$\sin \frac{\vartheta}{2}$ gefunden	$\sin \frac{\vartheta}{2}$ berechnet		
4,23	21° 9'	0,361	0,361	$\begin{Bmatrix} 110 \\ 200 \end{Bmatrix}$	mst
7,75	38 45	0,626	0,625	$\begin{Bmatrix} 020 \\ 310 \end{Bmatrix}$	mst
9,35	46 46	0,728	0,722	$\begin{Bmatrix} 400 \\ 220 \end{Bmatrix}$	schw
14,58	72 54	0,955	0,951	$\begin{Bmatrix} 420 \\ 130 \end{Bmatrix}$	mst
I. Schichtlinie.					
4,35	22° 32'	0,383	0,378	$\begin{Bmatrix} 111 \\ 201 \end{Bmatrix}$	s st
9,50	47 26	0,736	0,731	$\begin{Bmatrix} 221 \\ 401 \end{Bmatrix}$	schw
15,05	73 56	0,961	0,961	$\begin{Bmatrix} 421 \\ 131 \end{Bmatrix}$	st
II. Schichtlinie.					
4,50	25°	0,423	0,425	$\begin{Bmatrix} 112 \\ 202 \end{Bmatrix}$	st
8,37	42 8'	0,671	0,665	$\begin{Bmatrix} 022 \\ 312 \end{Bmatrix}$	s st
10,02	49 46'	0,763	0,756	$\begin{Bmatrix} 222 \\ 402 \end{Bmatrix}$	s schw
III. Schichtlinie.					
4,82	30° 22'	0,505	0,498	$\begin{Bmatrix} 113 \\ 203 \end{Bmatrix}$	st
11,20	52 56	0,798	0,798	$\begin{Bmatrix} 403 \\ 223 \end{Bmatrix}$	schw
IV. Schichtlinie.					
10,85	51°	0,771	0,775	$\begin{Bmatrix} 024 \\ 314 \end{Bmatrix}$	mst

Drehdiagramm um die b -Achse.

Äquator.					
2,33	11° 39'	0,202	0,205	002 β	st
2,63	13 9	0,228	0,228	002	s st
4,32	21 36	0,368	0,361	200	mst
4,46	22 18	0,379	0,378	201	mst
4,83	24 9	0,409	0,405	004 β	s
5,01	25 3	0,424	0,425	202	s
5,38	26 54	0,450	0,451	004	st
5,91	29 33	0,493	0,498	203	s
7,08	35 24	0,579	0,583	204	ss

¹⁾ Die orthohexagonale Indizierung der in diesem Diagramm auftretenden Ebenen ist in zweifacher Weise möglich; in diese Tabelle sind beide Möglichkeiten eingetragen. Das Vorhandensein zweier Indizeskombinationen bei einer Reflexion bedeutet also hier nicht eine Vieldeutigkeit in der Zuordnung der Interferenzen.

$2c$ in cm	$\frac{\vartheta}{2}$	$\sin \frac{\vartheta}{2}$ gefunden	$\sin \frac{\vartheta}{2}$ berechnet	Indizierung	Intensität geschätzt
7,62	38 6	0,617	0,616	006 β	ss
8,48	42 27	0,675	0,674	205	ss
8,62	43 9	0,684	0,684	006	mst
9,31	46 33	0,726	0,722	400	s
9,78	48 54	0,754	0,756	402	ss
10,18	50 54	0,776	0,772	206	s
10,58	52 54	0,798	0,798	403	s
11,19	55 57	0,829	0,826	008 β	ss
11,76	58 39	0,854	0,855	404	ss
12,31	61 33	0,879	0,876	207	s
13,32	66 36	0,917	0,917	008	ms
13,44	67 12	0,922	0,920	405	s

I. Schichtlinie.

1,86	21° 13'	0,362	0,361	110	mst
2,36	22 10	0,377	0,378	111	st
3,58	25 23	0,429	0,425	112	s
4,96	29 18	0,490	0,498	113	s
7,34	38 24	0,619	0,625	310	mst
8,12	41 33	0,664	{0,665 0,660	{312 214}	mst
10,35	50 48	0,775	{0,772 0,775	{116 314}	s
12,13	68 48	0,932	{0,926 0,931	{217 316}	ss

Drehdiagramm um [100].

2,41	12°	0,209	0,205	002 β	st
2,69	13 24'	0,232	0,228	002	s st
4,96	24 48	0,420	0,405	004 β	mst
5,52	27 30	0,463	0,450	004	st
6,61	33 3	0,546	0,555	014	ss
7,90	39 34	0,636	0,625	020	mst
8,53	42 39	0,678	0,665	022	mst
8,88	44 24	0,700	0,683	006	s
10,40	52	0,788	0,775	024	ms
11,64	58 12	0,850	0,845	008 β	ss
13,70	68 30	0,930	0,918	008	s

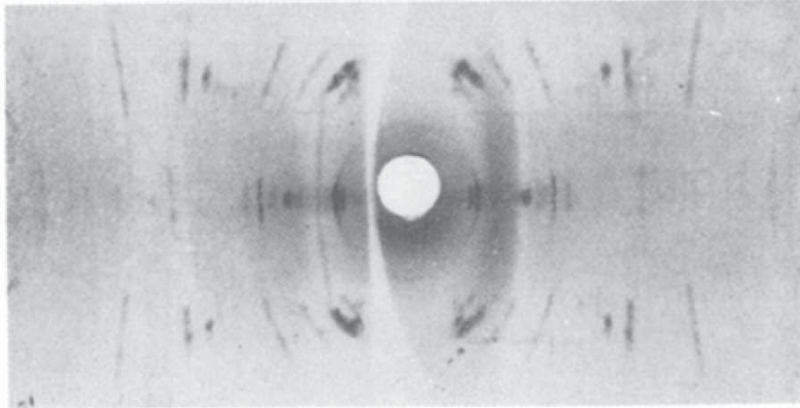
I. Schichtlinie.

3,80	21° 36'	0,368	0,361	110	s
4,12	22 43	0,386	0,378	111	st
4,80	25 42	0,433	0,425	112	mst
5,91	30 43	0,511	0,498	113	s
7,23	36 47	0,598	{0,583 0,596	{114 105}	ss
8,68	43 30	0,688	0,674	115	s

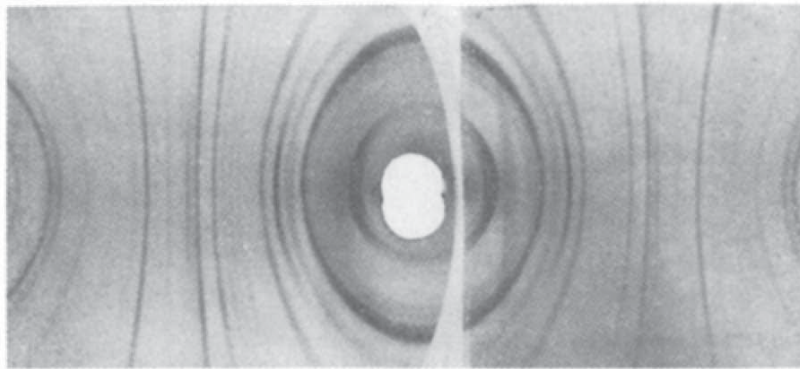
wiedergegeben ist. In der letzten Spalte dieser Tabelle sind die von Debye und Scherrer experimentell gefundenen $\sin \frac{\vartheta}{2}$ -Werte angegeben¹⁾; man sieht, daß die beiden Diagramme recht gut über-

¹⁾ Phys. ZS. 18, 291, 1917.

einstimmen. Der vorliegende Film scheint etwas stärker belichtet zu sein, da verschiedene Linien auftreten, welche von Debye und Scherrer nicht verzeichnet worden sind. Der experimentelle Befund ist in beiden Fällen der gleiche; die Indizierung der Interferenzen



a



b

Fig. 1.

- a) Drehdiagramme um die *b*-Achse mit der Cu-Strahlung aufgenommen.
 b) Natürlicher Graphit aus Ceylon mit deutlich erkennbarer Faserstruktur (Cu-Strahlung).

aber weicht von der Debye-Scherrerschen ab. Es liegt also hier ein Fall vor, in dem zwei verschiedene quadratische Formen, nämlich die von Debye und Scherrer benutzte rhomboedrische

$$\sin^2 \frac{\vartheta}{2} = 0,03724 (h^2 + k^2 + l^2) - 0,02001 (hk + kl + hl) \quad (2)$$

und die in Gleichung (1) enthaltene die experimentellen Daten eines Pulverdiagramms gleich gut wiedergeben. Dieses experimentelle Material reicht also für eine Entscheidung zwischen den durch die verschiedenen quadratischen Formen bedingten verschiedenen Deutungen nicht aus. Das Ergebnis der direkten Vermessung der Identitätsperioden auf der trigonalen Achse ist aber mit dem Debye-Scherrerschen Elementarkörper nicht verträglich; es führt vielmehr zu dem durch die Gleichung (1) gegebenen Elementarkörper.

Tabelle 7.

$2e$	Indi- zierung	Geschätzte Intensität	$\frac{\vartheta}{2}$	$\sin \frac{\vartheta}{2}$ gefunden	$\sin \frac{\vartheta}{2}$ berechnet	$\sin \frac{\vartheta}{2}$ D u. S
2,35	002 β	st	11°45'	0,204	0,205	0,205
2,63	002	s st	13 9	0,228	0,228	0,228
3,68	110 β	s schw	18 24	0,316	0,325	—
3,88	111 β	schw	19 24	0,332	0,340	0,331
4,14	110	mst	20 51	0,356	0,361	0,349
4,38	{ 111 202 β }	st	21 54	0,373	{ 0,378 0,382 }	0,373
4,81	004 β	schw	24 3	0,408	0,405	0,413
5,00	202	schw	25	0,423	0,425	—
5,37	{ 004 203 β }	st	26 51	0,451	{ 0,450 0,448 }	0,451
5,63	210	ss schw	28 9	0,472	0,478	0,464
5,90	203	mst	29 30	0,492	0,498	—
6,39	204 β	s schw	31 57	0,529	0,525	0,521
6,79	310 β	s schw	33 57	0,558	0,563	0,556
7,08	204	schw	35 24	0,579	0,583	—
7,30	{ 312 β 205 β }	schw	36 30	0,595	{ 0,596 0,607 }	0,590
7,65	{ 310 006 β }	mst	38 15	0,619	{ 0,625 0,616 }	0,616
7,90	020	schw	39 30	0,636	0,626	0,635
8,29	{ 312 400 β 401 β }	mst-st	41 27	0,662	{ 0,665 0,658 0,662 }	0,655
8,49	205	schw	42 27	0,675	0,674	—
8,65	006	mst	43 15	0,685	0,684	0,683
8,83	206 β	s schw	44 9	0,697	0,695	0,697
9,21	403 β	s schw	46 3	0,720	0,718	0,719
9,37	{ 400 401 }	schw	46 51	0,729	{ 0,722 0,731 }	—
9,80	402	schw	49	0,755	0,756	—
10,13	{ 206 024 }	mst	50 39	0,773	{ 0,772 0,775 }	0,766
10,60	403	schw	53	0,799	0,798	0,806
11,20	008 β	s schw	56	0,829	0,826	0,829
11,42	{ 025 316 β }	s schw	57 6	0,840	{ 0,836 0,838 }	0,834
11,77	404	s schw	58 51	0,856	0,855	—
12,07	420 β	ss s	60 21	0,869	0,861	—
12,35	207	schw	61 45	0,881	0,876	{ 0,889 0,910 }
13,34	{ 008 405 }	mst	66 42	0,918	{ 0,918 0,920 }	0,919
13,72	316	st	68 36	0,931	0,931	0,934
14,26	031	s schw	71 18	0,947	0,945	0,946
14,58	{ 510 420 }	schw	72 54	0,956	{ 0,950 0,951 }	0,951
15,02	421	schw	75 6	0,966	0,956	0,974

Zur genauen Vermessung des Netzebenenabstandes der Basis-ebene haben wir in einer Seemann-Kamera mit 30 cm Durchmesser Kupferstrahlung an der Blättchenebene reflektiert. Aus der zweiten und vierten Ordnung ergab sich als Mittel der Wert $d_{001} = 3,79$, also $\frac{J_{001}}{2}$.

Zwei andere, mit Sr-Strahlung bzw. Mo-Strahlung aufgenommene Diagramme ergaben einen übereinstimmenden Befund, so daß wir von der Wiedergabe der Vermessungen absehen ¹⁾.

Die folgende Tabelle 8 enthält eine Zusammenstellung der gefundenen Netzebenen nebst den geschätzten Intensitäten:

Tabelle 8. Basis, Prismen und Pyramiden.

002 s st	200 = 110 mst	400 = 220 s	421 s
004 st	201 = 111 st	401 = 221 s	
006 s	202 = 112 st	402 = 222 ss	
008 s	203 = 113 s	403 = 223 s	
	204 = 114 ss	404 = 224 ss	
	205 = 115 ss	405 = 225 s	
	206 = 116 s	020 = 310 mst	
	207 = 117 s	022 = 312 mst	
	420 = 130 s	024 = 314 mst	
		026 = 316 st	

Dieser Statistik, welche aus einer Reihe unabhängiger Versuche hervorgegangen ist, im Zusammenhang mit den direkt vermessenen Identitätsperioden entnehmen wir nun zunächst für die Raumgruppenbestimmung folgendes:

1. Die Basis tritt in ungeraden Ordnungen nicht auf, wohl aber in allen möglichen geraden, am stärksten in der zweiten.

2. Die Rhomboederbedingung ist nicht erfüllt, denn es treten folgende Ebenen auf: 201, 204, 207, 402, 405.

3. Ebenen (h01) mit geradem h treten in erster Ordnung sicher auf: 201, 203, 205, 207, 401, 403, 405.

4. Die Identitätsperiode auf [001] ist doppelt so groß als der Netzebenenabstand (001).

3. Die Diskussion der in Frage kommenden Raumgruppen.

Da die Kristallklasse des Graphits nicht bekannt ist, seien die Raumgruppen sämtlicher hexagonalen, rhomboedriscen und trigonalen Klassen in die Diskussion einbezogen. Die Tatsache,

¹⁾ Da wir auf keiner einzigen Aufnahme Anzeichen für einen größeren Elementarkörper finden konnten, haben wir der folgenden Diskussion die kleinstmögliche Basis als die richtige zugrunde gelegt.

daß die Basis erst in zweiter Ordnung auftritt im Verein mit dem Umstande, daß die Rhomboederbedingung nicht erfüllt ist und daß Ebenen ($h0l$) mit geradem h in erster Ordnung auftreten, gestattet es, eine große Zahl von Gruppen streng auszuschließen, d. h. es sind Reflexionen experimentell beobachtet, welche mit den von dieser Gruppe geforderten Auslöschungen unverträglich sind. Es bleiben dann nur noch bestehen:

hexagonal	D_{6h}^4 ,	D_6^6 ,	C_{6h}^2 ,	C_{6v}^4 ,	C_6^6 ,
rhomboedrisch	C_{3v}^4 ,	C_{3v}^3 ,	C_{3i}^1 ,		
trigonal	D_{3h}^4 ,	D_{3h}^2 ,	C_{3h}^1 .		

In jeder dieser Gruppen mögen nun sämtliche Lokalisierungsmöglichkeiten für vier Atome im gewöhnlich hexagonalen (acht im orthohexagonalen) Elementarkörper an Hand der Tabellen von P. Niggli¹⁾ und R. W. G. Wyckoff diskutiert werden²⁾.

D_{6h}^4 . Es bestehen zwei Möglichkeiten vier C-Atome im hexagonalen Prisma zu lokalisieren:

1. Die Atome sind gleichwertig und kommen dann in die Lage mit einem Freiheitsgrad und der Eigensymmetrie C_{3v} entweder

a) auf die trigonalen Drehachsen und haben die Koordinaten

$$00u, 00\bar{u}, 00\frac{1}{2}-u, 00\frac{1}{2}+u \text{ oder}$$

b) auf die hexagonalen Schraubenachsen mit den Koordinaten

$$\frac{1}{3}\frac{2}{3}u, \frac{2}{3}\frac{1}{3}u + \frac{1}{2}; \frac{2}{3}\frac{1}{3}\bar{u}, \frac{1}{3}\frac{2}{3}\bar{u} + \frac{1}{2}.$$

Die erste Alternative gibt zwei gegeneinander längs der c -Achse um $2u$ verschobene c -kantenzentrierte Gitter. Die Identitätsperiode auf der c -Achse müßte hier gleich dem Netzebenenabstand sein, was dem experimentellen Befund

$$J_{001} = 2d_{001}$$

widerspricht. Diese Möglichkeit fällt also fort (da sie auch in vielen anderen Raumgruppen vorkommt, sei sie im folgenden kurz als Anordnung A bezeichnet).

Bei der zweiten Alternative bilden die Komplexe $\frac{1}{3}\frac{2}{3}u$ und $\frac{2}{3}\frac{1}{3}u + \frac{1}{2}$ bzw. $\frac{2}{3}\frac{1}{3}\bar{u}$ und $\frac{1}{3}\frac{2}{3}\bar{u} + \frac{1}{2}$ je ein Gitter der „hexa-

¹⁾ P. Niggli, Geomtr. Kristallogr. des Diskont. 1919.

²⁾ R. W. Wyckoff, The analytical expression etc. 1922.

gonalen dichtesten Kugelpackung“; diese beiden Gitter sind gegeneinander um $00\frac{1}{2} - 2u$ verschoben; die Struktur hat einen Freiheitsgrad u und sei Anordnung B genannt.

2. Es sind zweierlei C-Atome mit verschiedenem Reflexionsvermögen vorhanden. Jede Art kommt mit der Eigensymmetrie D_{3d} oder D_{3h} in eine der vier zweizähligen Lagen:

$$(a) \begin{matrix} 0 & 0 & 0 \\ & & 0 & 0 & \frac{1}{2} \end{matrix}, \quad (b) \begin{matrix} 0 & 0 & \frac{1}{4} \\ & & 0 & 0 & \frac{3}{4} \end{matrix}, \quad (c) \begin{matrix} \frac{1}{3} & \frac{2}{3} & \frac{1}{4} \\ & & \frac{2}{3} & \frac{1}{3} & \frac{3}{4} \end{matrix}, \quad (d) \begin{matrix} \frac{1}{3} & \frac{2}{3} & \frac{3}{4} \\ & & \frac{2}{3} & \frac{1}{3} & \frac{1}{4} \end{matrix},$$

und das Gitter entsteht durch Kombination von je zwei dieser Lagen.

$a + b$, $a + c$ und $a + d$ führen auf Gitter, in welchen bei annähernd gleichem Reflexionsvermögen der C-Atome die zweite Ordnung der Basis sehr geschwächt, die vierte sehr verstärkt erscheinen müßte. Da dies keineswegs der Fall ist, fällt diese Anordnung (C) weg. $b + c$ und $b + d$ führen auf je ein c -kantenzentriertes Gitter, gegen welches eine dichteste Packung um $\frac{1}{3} \frac{2}{3} 0$ bzw. $\frac{2}{3} \frac{1}{3} 0$ verschoben ist (D).

$c + d$ bilden zwei ohne Parameter ineinander gestellte „hexagonale dichteste Kugelpackungen“ mit C-Atomen von verschiedenen Reflexionsvermögen in den Lagen (E)

$$\begin{matrix} 0 & 0 & 0 \\ & & \frac{1}{2} \end{matrix} \quad \text{und} \quad \begin{matrix} 0 & 0 & \frac{1}{2} \\ & & 0 \end{matrix}.$$

In (D) und (E) könnte es gelingen, durch geeignete Wahl des Verhältnisses der beiden Reflexionsvermögen R_1 und R_2 in Übereinstimmung mit den experimentellen Ergebnissen zu gelangen. Die Anordnungen (A) und (C) widersprechen also den experimentellen Befunden, während B , D und E noch geprüft werden müssen. Die Eigensymmetrien in den verschiedenen Lagen sind in dieser Raumgruppe:

$$\begin{array}{ll} A & C_{3v}, \\ B & C_{3v}, \\ C & D_{3d} \text{ und } D_{3h}, \\ D & D_{3h}, \\ E & D_{3h}. \end{array}$$

D_6^6 . Hier sind möglich:

A mit der Atomsymmetrie	C_3 ,
B " " "	D_3 ,
C " " "	D_3 ,
D " " "	D_3 ,
E " " "	D_3 .

Andere Anordnungen gibt es nicht.

C_6^2 . Hier kommen in Frage:

A mit der Eigensymmetrie	C_3 ,
B " " "	C_3 ,
C mit der	C_{3i} und C_{3h} ,
D " " "	C_{3h} ,
E " " "	C_{3h} .

Andere Anordnungen sind nicht möglich.

C_6^4 . Es gibt hier folgende Anordnungen:

A mit der Eigensymmetrie C_{3v} und zwei ungleichwertigen C-Atomen, deren Abstand auf der c -Achse p beträgt (A_1); fällt aus demselben Grunde fort wie A , da man die Verschiedenheit der Reflexionsvermögen der ungleichwertigen C-Atome nicht gut so groß annehmen ($\frac{R_1}{R_2} \sim 3$) kann, daß die gefundene große Intensität von (111) erklärt wird.

B mit C_{3v} und zwei ungleichwertigen C-Atomen. Diese Struktur hat einen Parameter p längs der C -Achse und zwei verschiedene Reflexionsvermögen R_1 und R_2 . Die Lagen der ungleichwertigen C-Atome sind entweder

$$R_1 \begin{matrix} 0 & 0 & 0 \\ 2/3 & 1/3 & 1/2 \end{matrix}, \quad R_2 \begin{matrix} 0 & 0 & p \\ 2/3 & 1/3 & 1/2 + p \end{matrix} \quad \text{oder} \quad R_1 \begin{matrix} 0 & 0 & 0 \\ 0 & 0 & 1/2 \end{matrix}, \quad R_2 \begin{matrix} 1/3 & 2/3 & p \\ 2/3 & 1/3 & p + 1/2 \end{matrix}.$$

Es sind dies diejenigen Anordnungen, welche als nächste in Betracht kommen, falls es nicht gelänge, durch E , D oder B in Übereinstimmung mit den experimentellen Zahlen zu kommen, da sie außer dem Parameter p noch das Verhältnis der beiden Reflexionsvermögen als Freiheit enthalten. Die eine Anordnung ist ein c -kanten-zentriertes Gitter mit R_1 kombiniert mit einer um $1/3 \cdot 2/3 p$ verschobenen dichtesten Packung mit R_2 , die andere besteht aus zwei verschiedenartig reflektierenden, gegeneinander um $00p$ verschobenen hexagonalen dichtesten Kugelpackungen (B_1). Andere Fälle gibt es in dieser Gruppe nicht.

C_6^6 . Hier kommen nur in Betracht:

A_1 mit der Symmetrie	C_3 ,
B_1 „ „ „	C_3 .

Damit sind sämtliche hexagonalen Gruppen erschöpft und haben zu den Anordnungen D , E , B und B_1 geführt.

Die Diskussion der trigonalen Gruppen ergibt folgendes:

D_{3h}^4 . Es sind vorhanden:

A mit der Symmetrie	C_3 ,
B „ „ „	C_3 ,
C , D und E mit	D_3 bzw. C_{3h} .

In D_{3h}^2 gibt es:

A mit der Atomsymmetrie C_3 ,

dann C , D und E mit der Symmetrie D_3 bzw. C_{3v} ;

außerdem gibt es hier noch zwei c -kantenzentrierte Gitter mit R_1 und R_2 , die um $\frac{1}{3} \frac{2}{3} 0$ bzw. $\frac{2}{3} \frac{1}{3} 0$ gegeneinander verschoben sind (P).

Von den rhomboedrischen Gruppen ergeben C_{3v}^4 und C_{3v}^3 zwei c -kantenzentrierte Gitter mit R_1 und R_2 um $0 0 p$ bzw. $\frac{1}{3} \frac{2}{3} p$ oder $\frac{2}{3} \frac{1}{3} p$ gegeneinander verschoben (Q).

C_{3i}^1 . Hier lassen sich vier Punkte folgendermaßen lokalisieren:

Zwei Arten von Kohlenstoffatomen in $[[000]]$ einerseits und in $\left[\left[\frac{1}{2} \frac{1}{2} \frac{1}{2}\right]\right]$, $\left[\left[0 \frac{1}{2} \frac{1}{2}\right]\right]$, $\left[\left[\frac{1}{2} 0 \frac{1}{2}\right]\right]$. Da (001) in ungeraden Ordnungen nicht auftritt, würde aus dieser Anordnung folgen, daß $R_1:R_2 \sim 3$ wäre, was ein sehr unwahrscheinliches Ergebnis ist und gegen diese Anordnung spricht. Sonst ergeben sich nur Möglichkeiten mit mehr als zwei Freiheiten.

C_{3h}^1 . Hier ergibt sich eine Möglichkeit mit drei Freiheiten, wenn man viererlei C-Atome in je eine der einzähligen Lagen bringt; wählbar sind hier die Verhältnisse der Reflexionsvermögen.

Außerdem gibt es eine Möglichkeit mit drei Freiheiten bei zwei verschiedenen C-Atomen, deren eines in eine der einzähligen Lagen kommt, während das andere in die dreizählige Lage mit zwei Parametern lokalisiert wird.

Zusammenfassend läßt sich also das Ergebnis dieser Diskussion so darstellen: Es gibt keine einzige Anordnung, bei welcher vier gleichwertige C-Atome in Punktlagen ohne Freiheitsgrad liegen. Die Struktur besitzt also auf alle Fälle mindestens eine frei wählbare Größe, entweder einen Verschiebungsparameter oder ein Verhältnis von Reflexionsvermögen verschiedenartiger C-Atome.

Strukturen mit einer frei wählbaren Größe sind:

1. Ein c -kantenzenetriertes hexagonales Gitter mit dem Reflexionsvermögen R_1 kombiniert mit einem um $\frac{1}{3} \frac{2}{3} 0$ dagegen verschobenen Gitter der „hexagonalen dichtesten Kugelpackung“ mit dem Reflexionsvermögen R_2 ; frei wählbar ist $\frac{R_1}{R_2} (D_{6h}^4, D_6^6, C_{6h}^2, D_{3h}^4, D_{3h}^2)$.

2. Zwei hexagonale dichteste Packungen mit R_1 und R_2 gegeneinander um $0 0 \frac{1}{2}$ verschoben; frei wählbar $\frac{R_1}{R_2} (D_{6h}^4, D_6^6, C_{6h}^2, D_{3h}^4, D_{3h}^2)$.

3. Zwei c -kantenzenetrierte Gitter mit R_1 und R_2 gegeneinander um $\frac{1}{3} \frac{2}{3} 0$ bzw. $\frac{2}{3} \frac{1}{3} 0$ verschoben; wählbar $\frac{R_1}{R_2} (D_{3h}^2)$.

4. Zwei dichteste Packungen mit gleichem Reflexionsvermögen gegeneinander verschoben um $0 0 p$; frei wählbar $p (D_{6h}^4, D_6^6, C_{6h}^2, D_{3h}^4, D_{3h}^2)$.

Strukturen mit zwei Größen sind:

5. Ein c -kantenzenetriertes Gitter mit R_1 gegen eine dichteste Packung mit R_2 verschoben um $\frac{1}{3} \frac{2}{3} p$; frei wählbar sind p und $\frac{R_1}{R_2} (C_{6v}^4, C_6^6, C_{3v}^4, C_{3v}^3)$.

6. Zwei dichteste Packungen mit R_1 und R_2 verschoben um $0 0 p$; frei wählbar sind p und $\frac{R_1}{R_2} (C_{6v}^4, C_6^6, C_{3v}^4, C_{3v}^3)$.

Strukturen mit drei Freiheitsgraden gibt es nur in den Raumgruppen C_{3h}^1 und C_{3i}^1 :

7. Zwei c -kantenzenetrierte Gitter mit R_1 und R_2 gegeneinander verschoben um $0 0 p$ bzw. $\frac{1}{3} \frac{2}{3} p (C_{3v}^3, C_{3v}^4)$; wählbar $\frac{R_1}{R_2}$ und p .

Damit sind sämtliche geometrischen Möglichkeiten erschöpft.

Es seien nun zunächst die Anordnungen mit einem Freiheitsgrad an Hand des Strukturfaktors diskutiert.

4. Die Vermessung und Berechnung der Intensitäten.

Da sich bei verschiedenen Aufnahmen von natürlichem polykristallinen Graphit (aus Ceylon und Tikonderoga) herausgestellt hatte, daß diese Präparate ziemlich starke Anisotropiestruktur zeigten¹⁾,

¹⁾ Die Richtung $[100]$ war mit einer Streuung von etwa 30° parallel der Schichtung der polykristallinen Präparate eingestellt.

haben wir zur Erzielung gleichmäßiger Verteilung aufgeschlemmten böhmischen Graphit vorsichtig an Wollfäden gebracht und damit Debye-Scherrer Diagramme hergestellt, welche keinerlei Anisotropie mehr zeigten. Diese wurden in einem Kochschen Registrierphotometer photometriert und die Intensitäten der einzelnen Linien mit Hilfe einer gleichzeitig hergestellten Schwärzungsskala berechnet. Das Ergebnis der aus drei verschieden lang exponierten Diagrammen erhaltenen Vermessungen enthält Tabelle 9.

Tabelle 9.

$2e$	Gemessene Intensität	Indizierung	$2e$	Gemessene Intensität	Indizierung
2,64	82	002	8,64	48	006
3,88	15	111 β	8,82	3	206 β , 024 β
4,14	32	110	9,20	3	403 β
4,38	52,5	111	9,35	15	400, 401
4,81	20	004 β	9,79	5	402
5,00	20	202	10,12	50	206, 024
5,38	52	004, 203 β	10,58	10	403
5,64	4	210	11,19	5,5	008 β , 405 β
5,90	45	203	11,40	7	316 β
6,79	7	310 β	11,77	4	404
7,06	10	204	12,06	4,5	420 β
7,30	9,5	312 β , 205 β	12,35	15,5	207
7,65	43	310, 006 β	13,34	39,5	008, 405
7,90	5	020	13,70	46,5	316
8,27	51	312, 400 β , 400 β	14,62	20	420
8,48	9	205	15,02	44,5	421

Mit Hilfe dieser Zahlen lassen sich die Fälle 2 und 3 (S. 332) ausschließen; wollte man bei der Kombination 2 etwa das richtige Intensitätsverhältnis von (111) zu (110) herausbekommen, so müßte man $R_1:R_2$ gleich 2,5 oder 0,4 annehmen, was als äußerst unwahrscheinlich gelten muß; bei der Struktur 3 müßten alle Ebenen mit ungeradem l verschwinden, was keineswegs zutrifft. Diese beiden Anordnungen widersprechen also schon im groben den gefundenen Intensitäten.

Zur Diskussion der Anordnungen 1 und 4 greifen wir nun aus den in Tabelle 9 enthaltenen Reflexionen diejenigen heraus, welche folgende Bedingungen erfüllen:

1. Soll die Reflexion mit keiner anderen α -Reflexion so koindizieren, daß sie nicht im Photogramm noch deutlich unterscheidbar wäre (den Einfluß der β -Linien haben wir mit Hilfe eines mit Nickelfolie aufgenommenen Diagramms festgestellt und in Abzug gebracht).

2. Soll der Ablenkungswinkel in der Umgebung von 90° liegen, da hier die gestreute Bremsstrahlung am wenigsten stört.

Man findet neun dieser Ebenen in Tabelle 10 zusammengestellt.

Die Anordnung 4 führt zu den in Fig. 2 gezeichneten Intensitätsverläufen für die ausgewählten Ebenen; es sind nur diejenigen Parameterwerte eingetragen, welche am ehesten für eine richtige Wiedergabe in Betracht kommen; bei allen dazwischenliegenden Werten ist die Übereinstimmung noch schlechter. Man sieht, daß hier nur der Parameter 0,04 den gefundenen Gang der Intensitäten einigermaßen wiedergibt; dieser Wert ergibt aber für (111) eine viel zu schwache Intensität, steht also auch nicht in hinreichender Übereinstimmung mit den experimentell gefundenen Werten.

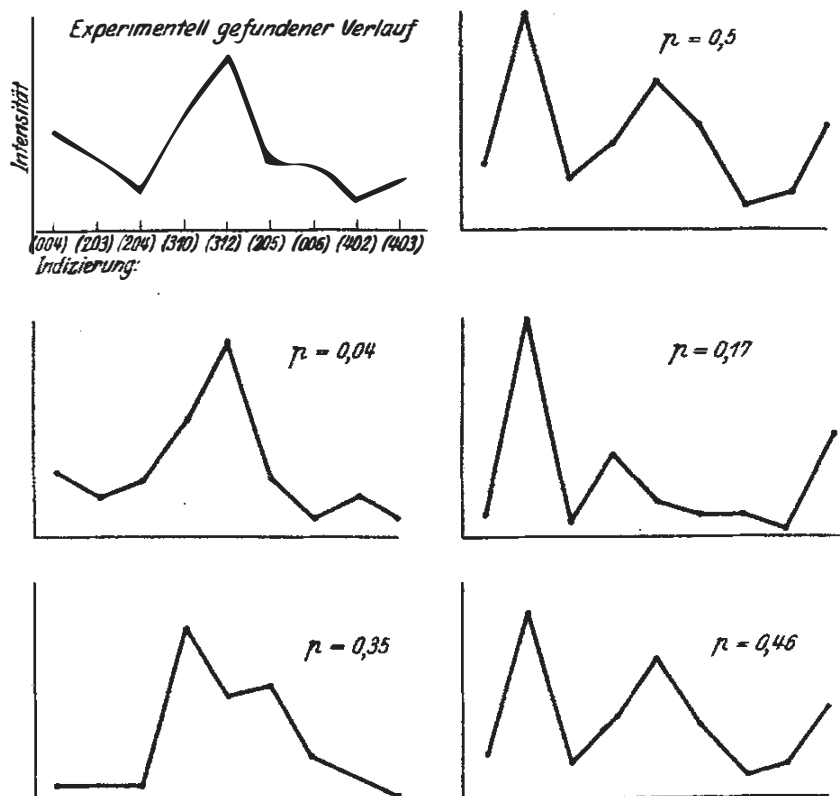


Fig. 2.

Bei der Anordnung 6, welche mit 4 nahe verwandt ist, gelingt es nicht, durch einen von 1 abweichenden Wert des Verhältnisses $\frac{R_1}{R_2}$ besseren Anschluß an die Versuchsergebnisse zu erhalten.

Der Strukturfaktor der Anordnung 1 ergibt unter der Annahme $R_1 = R_2$ das in Fig. 3 wiedergegebene Intensitätsverhältnis, welches den Gang der gefundenen Intensitäten ziemlich gut wiedergibt. Auch die übrigen Ebenen fügen sich mit befriedigender Annäherung in dieses Schema.

Bei Wahl der Anordnung 5 hat man es in der Hand, durch Annahme eines bestimmten Wertes von p diese Annäherung noch etwas zu verbessern; hierbei kann man p zwischen 0 und 0,1 variieren.

Die Anordnung 5 mit p zwischen 0 und 0,1 gibt also sämtliche experimentellen Befunde mit genügender Näherung richtig wieder. Die Frage, ob das Gitter hexagonale oder trigonale Symmetrie besitzt, läßt sich allerdings hieraus nicht entscheiden, da die Anordnung 5 sowohl in trigonalen als auch in hexagonalen Raumgruppen

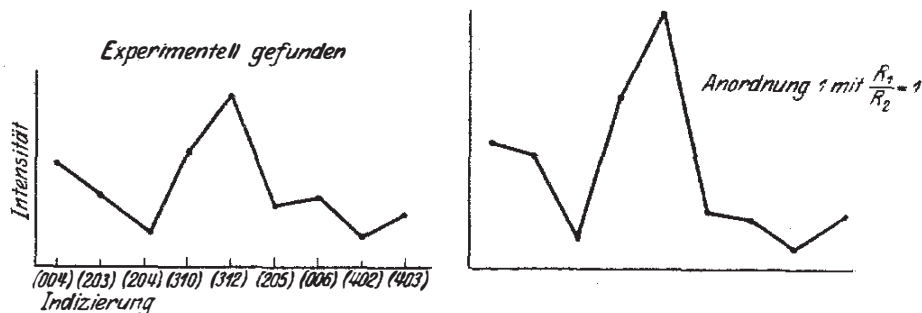


Fig. 3.

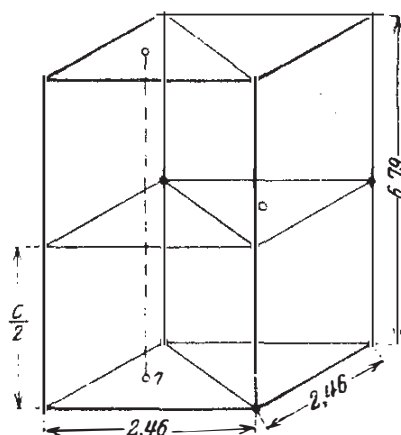


Fig. 4.

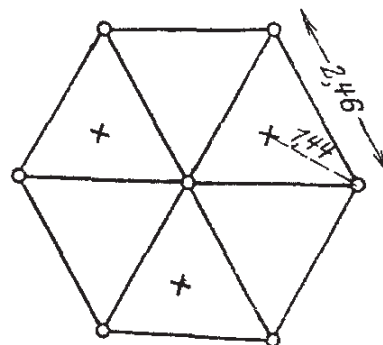


Fig. 5.

Hexagonaler Elementarkörper des Graphits. Lage der C-Atome in der Basisebene.

realisierbar ist. Das Laue-Diagramm zeigt in bezug auf alle vorhandenen Punkte 6-Zähligkeit, ist aber nicht besonders punktreich. Auf die Mitteilung seiner Vermessung sei hier verzichtet, da keine neuen Ebenen in ihm aufgefunden wurden.

Der hexagonale Elementarkörper des Graphits ist in Fig. 4 dargestellt. Die Lagen der hexagonalen dichtesten Kugelpackung sind als leere, die des kantenzentriertes Gitters als volle Kreise eingezeichnet.

Diese Anordnung macht den blättchenförmigen Habitus und das Auftreten von (001) als Gleit- und Spaltebene verständlich. Greift man ein beliebiges Kohlenstoffatom heraus, etwa das Atom 1 in Fig. 4, so sind die Entfernungen zu den nächstliegenden Atomen folgende.

Drei nächstgelegene (ungleichwertige) Atome in derselben Ebene im Abstand von $1,45 \text{ \AA}$; sechs zweitnächstgelegene in derselben Ebene im Abstand von $2,46 \text{ \AA}$ wie in Fig. 5 gezeichnet.

Im Abstand von $3,39 \text{ \AA}$ liegt die nächste gleichbelastete Ebene, welche gegen $(001)_0$ um $\frac{2}{3} \frac{1}{3}_0$ verschoben ist und erst im Abstand von $6,79 \text{ \AA}$ folgt eine identische Ebene.

Wir haben nun noch zu zeigen, daß die hier mitgeteilte Struktur auch mit den experimentellen Feststellungen, auf welchen die eingangs zitierten Gitterbestimmungen beruhen, im Einklang steht. Von der Lage der Interferenzen ist dies für das von Debye und Scherrer zu ihrer Strukturbestimmung benutzte Zahlenmaterial bereits in Tabelle 7 gezeigt worden. Es stimmen aber auch die von Debye und Scherrer gemessenen Intensitäten mit denen von uns gefundenen gut überein, so daß die hier durchgeführte Diskussion des Parameters auch an dem Photogramm von Debye und Scherrer durchgeführt werden kann. Die Tabelle 10 enthält die Intensitäten derjenigen Ebenen, welche wir zur Parameterbestimmung herangezogen haben, und zwar in der zweiten Spalte nach Debye und Scherrer, in der vierten nach unserer Tabelle 9. Man sieht, daß die beiden Befunde übereinstimmen.

Tabelle 10.

Indizierung nach Debye-Scherrer	Intensität	Indizierung nach Tabelle 9	Intensität
222	m	004	12,0
—	—	203	8,5
—	—	204	4,5
$0\bar{2}2$	st	310	13,5
$\bar{1}13$	st	312	20,0
—	—	205	7,0
333	s	006	7,5
—	—	402	3,5
$\bar{1}33$	ss	403	6,0

Die Atomanordnung in den einzelnen (001) -Ebenen ist in beiden Fällen die gleiche (Fig. 5). Während aber nach Debye und Scherrer identische (001) -Ebenen erst im Abstand von $10,22 \text{ \AA}$ aufeinanderfolgen, ist dies bei der hier angegebenen Struktur schon nach $6,79 \text{ \AA}$ der Fall.

Auch der experimentelle Befund von P. P. Ewald kann als Stütze für unseren Elementarkörper angesehen werden, da sich aus ihm ein Achsenverhältnis von 1,63 ableiten läßt; dieses Verhältnis

stimmt mit dem von uns angegebenen Verhältnis $\frac{c}{a}$ gleich 1,61 innerhalb der Fehlergrenzen überein.

Die Hullsche Struktur endlich ist mit der angegebenen dann identisch, wenn man in ihr zwei C-Atome kristallographisch ungleichwertig macht¹⁾; sie wird dann zur Anordnung 5 mit $p = \frac{1}{14}$.

Es zeigt sich also, daß die in Fig. 4 dargestellte Struktur (Anordnung 5 mit p zwischen 0 und 0,1) mit sämtlichen experimentellen Daten in befriedigender Übereinstimmung steht. Über Versuche zur genaueren Bestimmung des Parameters und zur Feststellung der natürlichen und künstlichen Anisotropiestrukturen des Graphits wollen wir in einer zweiten Mitteilung berichten.

Zusammenfassung.

Durch Kombinationen mehrerer Röntgeninterferenzmethoden wurde das Gitter des Graphits an verschiedenen Graphiteinkristallen mit verschiedenen Strahlungen untersucht. Der kleinstmögliche orthohexagonale Elementarkörper besitzt die Abmessungen $a = 2,47$, $b = 4,25$, $c = 6,70$ und enthält acht Atome. Die Anordnung ist in Fig. 4 wiedergegeben.

Das bei den bisherigen Strukturbestimmungen von P. P. Ewald, P. Debye, P. Scherrer und A. W. Hull verwendete experimentelle Material steht mit der von uns angegebenen Struktur im Einklang.

Dem Elektrophysikausschuß der Notgemeinschaft danken wir auch an dieser Stelle bestens für die gewährte Unterstützung, mit deren Hilfe die vorliegende Arbeit ausgeführt wurde.

Anmerkung bei der Korrektur. Wie Herr Prof. P. P. Ewald uns freundlichst mitteilt, ist er auf Grund recht detailreicher Aufnahmen an dem bereits früher von ihm untersuchten Graphitkristall zu einer vollen Bestätigung unserer Strukturbestimmung gelangt. Die Reproduktion und Diskussion dieser Laueaufnahmen wird demnächst in der Zeitschrift für Kristallographie erfolgen.

¹⁾ Die von Hull angegebene Punktlage mit lauter kristallographisch gleichwertigen C-Atomen kommt unter den strukturtheoretisch möglichen Fällen nicht vor.

THE THERMAL EXPANSION OF GRAPHITE FROM 15° C. TO 800° C.: PART I. EXPERIMENTAL

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ABSTRACT. The variation with temperature of the a and c unit-cell dimensions of hexagonal Ceylon graphite has been measured over the temperature range 15°–800° C. by the x-ray powder method. At 14°·6 C.,

$$a = 2.4562 \pm 0.0001 \text{ kx.} \quad c = 6.6943 \pm 0.0007 \text{ kx.}$$

The carbon-carbon bond length,

$$\text{C} - \text{C} = 1.4210 \pm 0.0001 \text{ \AA.}$$

The a dimension shows a slight contraction up to about 400° C., a small expansion occurring above this temperature. The thermal expansion in the c direction is large; the average value for α over the temperature range is 28.3×10^{-6} . The complex nature of the expansion in both directions is discussed qualitatively.

§ 1. INTRODUCTION

A STUDY of the thermal expansion of graphite is of interest for two main reasons. The first is the need for extending our knowledge of the solid state in the field of anisotropic crystals; the second is the importance of precise information concerning the effect of heat on elementary carbon in connection with the technological processes of carbonization and coking. The x-ray method is the only suitable one for an investigation of this character. Other methods, the results of which are summarized in § 2, are not able to do more than measure the *mean* linear expansion of the crystal. Such information is of little significance thermodynamically, the essence of the problem being the *anisotropy* of the structure. The work reported here shows how valuable a tool x-ray

diffraction methods can be in measuring the effect of temperature on such structures.

§ 2. PREVIOUS WORK

Previous x-ray work comparable to ours has been carried out by Backhurst (1923) in the course of an investigation of the variation in intensity of x-ray reflections with temperature. He measured with the ionisation spectrometer and molybdenum radiation the shift of the 0004 reflection (called by him 0001) on heating from 17° to 870° c. In this way an average value over this range of 26.7×10^{-6} was derived for $\alpha_{||}$, the coefficient of linear expansion in the c direction.* This value is somewhat lower than the average value of 28.3×10^{-6} found by us. He did not measure the coefficient in the a direction, α_{\perp} , but surmised that a contraction and not an expansion might occur.

Hirata (1931) has investigated the behaviour of carbon in an incandescent arc at a temperature of about 4000° c. Even at this temperature, no measurable expansion in the a direction occurred, but by observing the shift of the 0002 reflection (with copper radiation) he derived these average values for $\alpha_{||}$ over this large temperature range :

$\alpha_{||} = 39.1 \times 10^{-6}$ assuming a temperature of 4200° c. by measurements of surface brightness.

$\alpha_{||} = 45.1 \times 10^{-6}$ assuming an average temperature of 3700° c.

The thermal expansion of graphite has also been measured by various other methods, and the following values have been recorded :

	Expansion coefficient	Temperature (°c.)
Fizeau (1869)	7.86×10^{-6} 7.96×10^{-6}	40° 50°
Muraoka (1881)	3.8×10^{-6}	26° to 302°
Day and Sosman (1912)	$0.55 \times 10^{-6} + 3.2 \times 10^{-9}t$	0° to 1800°
Hidnert and Sweeney (1927)	2.7×10^{-6} 3.7×10^{-6}	20° to 600°
Erfling (1939)	2.34×10^{-6} 6.695×10^{-6}	-195° to -183° +20° to +40°
Dewar (1902)	7.33×10^{-6} (vol. coeff.)	-190° to +17°

In no case was a single crystal of graphite used. As the specimens probably consisted of aggregations of small graphite crystals variously oriented, the values can only refer to the mean coefficient of linear expansion $\bar{\alpha}$. In a hexagonal crystal

$$\bar{\alpha} = \frac{2}{3}\alpha_{\perp} + \frac{1}{3}\alpha_{||}$$

and, using our data, $\bar{\alpha} \approx 8 \times 10^{-6}$ at 20° c. Several of the values are much too low and probably refer to the expansion of the aggregated solid as a whole rather than to the expansion of the individual crystals. It is interesting that Fizeau,

* The symbols $\alpha_{||}$ and α_{\perp} refer to the coefficients of linear expansion parallel and perpendicular to the hexagonal axis

who was the first to measure the thermal expansion of graphite in the course of his classical researches, was also responsible for the best value of $\bar{\alpha}$.

The work of Erfling requires special comment. Employing an optical method, he attempted to measure α_{\perp} by taking care to orient the crystals in the specimen. In spite of his precautions Erfling must have been measuring the mean coefficient of expansion. His value of 6.695×10^{-6} at 20° to 40° c. is probably a low value for $\bar{\alpha}$; it is much too large to be α_{\perp} , which we have found to be a small negative quantity over this range.

§ 3. APPARATUS

The camera used was the high-temperature 19 cm.-diameter powder-camera described by Wilson (1941). The camera angle θ_k for this instrument has been carefully determined by Wilson and Lipson (1941). The use of this camera in the determination of accurate unit-cell dimensions had been previously investigated (Nelson and Riley, 1945). The method of measuring the temperature of the specimen was essentially that of Wilson. We found, however, that the melting point of aluminium filings did not provide a satisfactory high-temperature calibration as the aluminium reacted with the silica capillary in which it was contained. Antimony (Hilger H.S.), with a melting point of $630^{\circ}.5$ c., was used in its place. It can be said that the error in temperature measurement did not exceed $\pm 1^{\circ}$ c. at the highest temperature investigated and was certainly less than this at the lower temperatures.

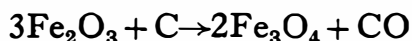
§ 4. PREPARATION OF THE SPECIMEN

Some difficulty was encountered in obtaining a specimen of graphite which combined high purity with the ability to give the sharp diffraction lines necessary for accurate measurements.

An examination of powder photographs of available graphites ("Kish", Acheson, Mexican, Bavarian, Travancore, Ceylon) showed that the Ceylon specimen gave the sharpest lines, although the purity was not of the highest (4% ash). It was felt, however, that purification by the usual chemical treatments (boiling with NaOH, H_2SO_4 or HF solution) was to be avoided because of the ease with which graphite forms complexes which show an appreciably altered c dimension. The Ceylon graphite was therefore chosen in spite of its low purity.

After reducing the material to pass a 300-mesh B.S.S. sieve, several silica capillary tubes of bore approximately equal to 0.05 cm. and a wall thickness of 0.003 cm. were filled. It was thought advisable to remove traces of adsorbed gases by heating to about 850° c. during the evacuation of the filled capillaries. However, as soon as even gentle heating was applied to them, the graphite powder was completely swept out, presumably by gases released during the heating. This made it necessary to heat the powdered graphite in bulk in a large-bore (1.5 cm.) continuously evacuated silica tube. Heating for 30 minutes at approximately 850° c. was found to be an ample treatment for completely removing the gas. Photographs of the graphite taken in an ordinary powder camera showed that the only extra lines discernible, besides those due to a small amount of the rhombohedral modification of graphite, were those of Fe_3O_4 in the heat-

treated material and hydrated Fe_2O_3 in the untreated. It seems fairly certain, therefore, that the evolution of gas is connected with the reaction



together with the evolution of water vapour.

No trouble was encountered in evacuating, heating and sealing off the capillaries after heat-treatment. The sealed-off capillary with the smallest bore and thinnest, most uniform wall thickness was selected for the exposures, which were made in order of descending temperature. Its bore, as measured by a microscope ocular micrometer, was 0.048 cm. and the wall thickness 0.0025 cm.

Subsequent precision measurements of both the a and c dimensions of the heat-treated and untreated graphites at room temperature were in excellent agreement. It would appear, therefore, that the impurities present (chiefly oxide of iron) have no influence on the measurements as they simply form a mixture with the graphite itself.

§ 5. THE X-RAY PHOTOGRAPHS

X-ray photographs were taken at the following temperatures: $14^\circ.6$, 150° , 300° , 450° , 600° , 700° , 800° c.

The temperature fluctuation during the exposure was greater the higher the temperature, but in no case did it exceed $\pm 0^\circ.5$ c. The photographs were taken with unfiltered manganese radiation with exposures of about 200 ma. hrs.

The high-angle portions of the x-ray photographs are reproduced in figure 1. Even a qualitative comparison leads to some interesting conclusions. The $hki0$ reflections ($11\bar{2}0$ and $20\bar{2}0$) do not move with change of temperature, while the 0006 doublet moves towards the low-angle end of the film quite markedly with increasing temperature. It can also be observed with the $hkil$ reflections that as the l index increases ($11\bar{2}2$, $11\bar{2}4$, $10\bar{1}5$), the rate of line shift with temperature also increases. The thermal expansion of the lattice is clearly anisotropic, the expansion occurring along the c axis. It should be noted that, at 15° c., the 553 doublet of Fe_3O_4 is practically coincident with the $11\bar{2}4$ β line of graphite. Resolution is effected at higher temperatures due to the different thermal expansions.

Another effect which is clearly visible concerns the relative intensities of the diffraction lines. The relative intensity of the 0006 reflections compared with the intensities of the $hki0$ reflections ($11\bar{2}0$, $20\bar{2}0$) shows a progressive diminution with temperature. This fading of the 0006 line is due to the large amplitude of thermal vibrations perpendicular to the layers, and obviously is in agreement with the pronounced anisotropy of thermal expansion. The $10\bar{1}5$ reflection shows a similar effect because of the high l index.

There are also nine extra lines due to the Fe_3O_4 previously mentioned, although only one (553 doublet) can be seen in figure 1. The identity of this compound was established by comparison of the interplanar spacings and intensities of the lines observed with that of pure Fe_3O_4 . To obtain the true cell dimensions, the calculated apparent length of the cubic unit cell was plotted against the extrapolation function $\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}$ for the four strongest lines on both the room

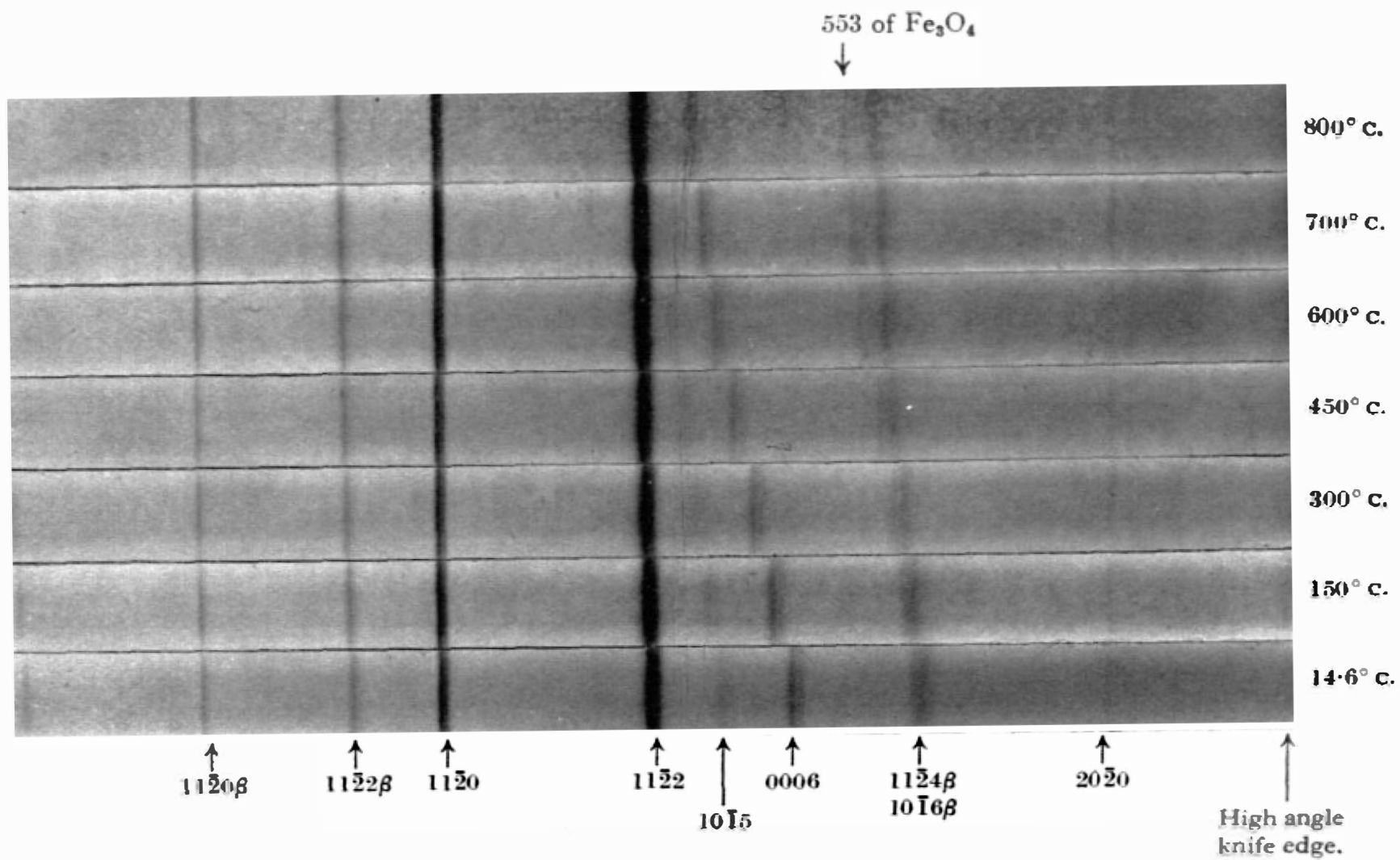


Figure 1. X-ray photographs of graphite at various temperatures.

temperature and 800° c. films. The results are as follows :

Temperature (°c.)	<i>a</i> (kx.)
15	8.378
800	8.475
20 (pure Fe ₃ O ₄ , Wyckoff and Crittenden 1925)	8.37 ± 0.01

Mean linear coefficient of thermal expansion, 14.7×10^{-8} (range 15° to 800° c.)

§6. MEASUREMENT OF UNIT-CELL DIMENSIONS AND DERIVATION OF EXPANSION COEFFICIENTS

The best radiation to use (manganese) gives the $20\bar{2}0$ α -doublet at $\theta = 80^\circ$ to 81° and the 0006 α -doublet at $\theta \approx 70^\circ$ at room temperature. These angles, and particularly the latter one, are not as high as is desirable in precision measurements, but it is impossible to effect any improvement in this case by change of x-ray wave-length. Hence, particular attention had to be paid to the extrapolation procedure adopted.

Work described elsewhere (Nelson and Riley, 1945) has shown that a reliable linear extrapolation is obtained down to $\theta \approx 30^\circ$ if the unit cell dimension under consideration is plotted against $\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}$. The apparent *c* dimensions given by the 0004 ($\theta = 38^\circ.9$ at room temperature) and 0006 reflections were therefore plotted against this function. A linear extrapolation to $f(\theta) = 0$ gave the *c* value quoted for each temperature. As the extrapolation lies through only two points, the accuracy claimed is mainly dependent on the suitability of the function of θ used in the plot. We have assigned an error of about one part in 10,000 to the *c* values derived in this way. The 0004 lines were accompanied by a weak satellite line on all the films. This feature was shown to arise from a preferred orientation of the graphite crystals in the specimen. The effect of this on the accuracy of the determination of the *c* dimension has already been discussed (Nelson and Riley, 1945).

In order to obtain the best value for the *a* dimensions at each temperature, the apparent *a* values derived from the following lines were plotted against $\frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta}$:

$$\begin{aligned} &20\bar{2}0 \alpha_1, \alpha_2. \\ &11\bar{2}0 \alpha_1, \alpha_2, \beta. \\ &10\bar{1}0 \alpha, \beta. \end{aligned}$$

At room temperature, the θ values for the $10\bar{1}0$ α and β lines were roughly $29^\circ.6$ and $26^\circ.6$ respectively. We did not assign them much weight in the extrapolation, but they serve to confirm its general trend. The error assigned to any given *a* dimension is approximately one part in 25,000. The refraction correction for *a* or *c* is negligible in comparison with the probable experimental error.

The values derived for the *c* dimensions at the various temperatures are given in table 1. A plot of *c* against temperature gives a smooth curve deviating only

slightly from linearity. An expression in t and t^2 was adopted to represent this curve, and the results were analyzed by the method of least squares. The best-fitting relation was found to be

$$c = 6.6915_4 + 180.70 \times 10^{-6}t + 12.63 \times 10^{-9}t^2, \quad \dots\dots(1)$$

where t is expressed in $^{\circ}\text{C.}$ and c in kx.

Table 1. c dimensions of graphite at various temperatures, in kx

Temperature ($^{\circ}\text{C.}$)	Observed	Calculated	Difference (calc.-obs.)
14.6	6.6943	6.6941 ₈	-1.2×10^{-4}
150	6.7185	6.7189 ₃	+4.3
300	6.7474	6.7468 ₈	-5.2
450	6.7752	6.7754 ₁	+2.1
600	6.8046	6.8045 ₁	-0.9
700	6.8240	6.8242 ₂	+2.2
800	6.8443	6.8441 ₈	-1.2

The values of c calculated from this equation are also given in the table. The deviations between the calculated and observed values are too large for equation (1) to be considered a satisfactory expression. The mean deviation is 2.4×10^{-4} , and c is therefore expressed with an average accuracy of only one part in 2800, whereas the observed values themselves are accurate to about one part in 10,000. That the assumption of a parabolic expression for c is not justified is confirmed by examining the variation with temperature of the expansion coefficient. Equation (1) leads to the following linear expression for the coefficient

$$\alpha_{||} = \frac{1}{c} \cdot \frac{\partial c}{\partial t} : \quad \alpha_{||} = 27.00 \times 10^{-6} + 3.05 \times 10^{-9}t \quad \dots\dots(2)$$

The straight line of equation (2) is compared with values of $\alpha_{||}$ derived directly from the experimental data in figure 2.

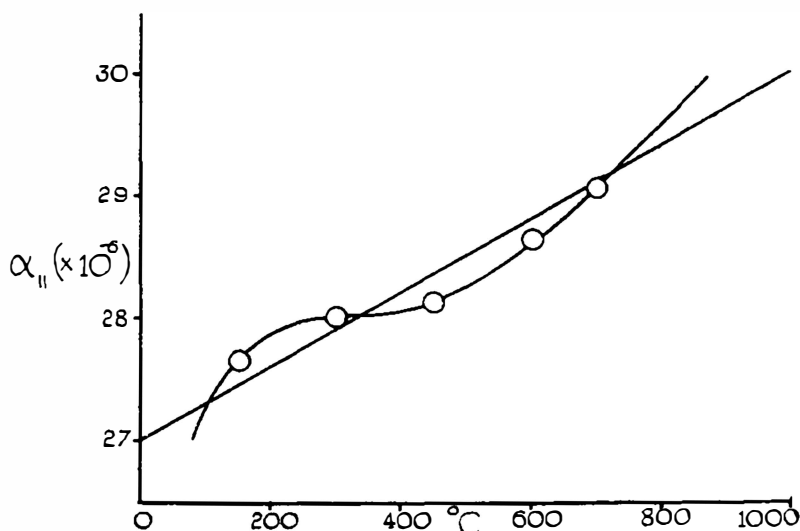


Figure 2. Comparison of observed $\alpha_{||}$ values with the best linear representation.

These values of $\alpha_{||}$ were derived in the following way. From the values c_1, c_2, c_3 of the c dimension at neighbouring temperatures t_1, t_2, t_3 , two extreme

values for $\frac{\Delta c}{\Delta t}$ at the middle temperature t_2 were obtained. The mean of these, divided by c_2 , was taken as the best value of $\alpha_{||} = \frac{1}{c} \cdot \frac{\Delta c}{\Delta t}$ at the temperature t_2 .

Owing to the large values of Δt involved, this derivation of $\alpha_{||}$ cannot be very accurate and, in particular, it is impossible to judge its course at either end of the temperature range.

It would appear from figure 2, however, that the temperature variation of $\alpha_{||}$ is of a complex form and is only approximately represented by a linear expression in t . A more exact representation is derived on theoretical grounds in Part II. The average value for $\alpha_{||}$ over the temperature range is 28.3×10^{-6} .

The measurements of the a dimension at the various temperatures showed that a shrinkage followed by an expansion occurred. In order to check this, the films were measured independently by each of us, and the best extrapolated a values are given in table 2.

Table 2

Temperature (°C.)	a dimensions in kx.	
	Measurement A	Measurement B
14.6	2.45626	2.45617
150	2.45575	2.45564
300	2.45570	2.45563
450	2.45577	2.45571
600	2.45574	2.45574
700	2.45607	2.45602
800	2.45613	2.45619

It will be seen that the agreement between the two sets of measurements is good. Two further checks were carried out in order to confirm the general nature of the effect.

(a) In measurement A the θ values for $20\bar{2}0$ α_1 at 15° and 300° c. are $80^\circ.419$ and $80^\circ.499$ respectively. The difference is therefore $0^\circ.080$ which corresponds to a line shift of 0.27 mm. This distance lies outside the limits of error in observing line positions (± 0.10 mm.). Therefore we conclude that there is a real change in angle and a real diminution in the a dimension.

(b) The measured θ values for the $20\bar{2}0$ and $11\bar{2}0$ lines were plotted against temperature for both sets of measurements, A and B. A general rise and then fall in θ was observed, in accordance with the shrinkage and subsequent expansion of a . This showed that the extrapolations could not be systematically in error.

Rough values of the thermal contraction and thermal expansion coefficients can be derived from table 2, and are :

Temperature range	α_{\perp}
0° to 150° c.	-1.5×10^{-6}
ca. 400° c.	0
600° to 800° c.	$+0.9 \times 10^{-6}$

The a dimension first contracts and then expands. It reaches its lowest value of approximately 2.4557 kx. at a temperature of about 400° C.

The unit cell dimensions at 15° C. are

$$a = 2.4562 \pm 0.0001 \text{ kx} ; \quad c = 6.6943 \pm 0.0007 \text{ kx.}$$

and the carbon-carbon bond length, expressed in Å., is

$$\text{C—C} = 1.4210 \pm 0.0001.$$

We found no evidence that the rhombohedral modification of graphite (Lipson and Stokes, 1942) has a different thermal expansion from that of the hexagonal variety. Our measurements, however, refer specifically to the latter.

§ 7. DISCUSSION

A qualitative explanation of the above results will be given first, in which the treatment of Grüneisen and Goens (1924) (see also Roberts (1940)) of the thermal expansion of hexagonal crystals will be followed.

Graphite is a perfect example of a layer structure. Each layer consists of a very large number of carbon atoms covalently linked to form what may be considered to be a huge polynuclear aromatic macromolecule. Each layer is planar, or very nearly so. The carbon atoms within a layer are very strongly linked, the C—C distance being about 1.42 Å. The bonding between adjacent layers, however, is weak, as is indicated by the large interlayer spacing of about 3.35 Å. It is probable that the interlayer forces are mainly of a van der Waals type, although they may not be entirely so. The graphite structure is therefore one of great anisotropy, and this will be reflected in all its directional physical properties.

The elastic deformability parallel to the principal Z axis will be much larger than that perpendicular to it owing to the tighter interatomic bonding within the layers. This may be written in terms of the elastic moduli as $s_{33} \gg s_{11}$.

Under the influence of temperature and of zero-point energy the atoms will vibrate, and the limiting frequency ν_{m_z} for vibrations parallel to the axis will be much smaller than for those perpendicular to it, ν_{m_x} . The solid will therefore possess two characteristic temperatures defined by these two limiting frequencies.

$$\Theta_z = \beta \nu_{m_z},$$

$$\Theta_x = \beta \nu_{m_x},$$

where

$$\beta = \frac{h}{k}$$

h = Planck's constant, k = Boltzmann's constant

and

$$\Theta_x > \Theta_z.$$

At low temperatures, quantum theory requires nearly all the thermal energy to be absorbed in oscillations parallel to the axis because of the low value of Θ_z as compared with Θ_x . These oscillations will, therefore, have much the greater amplitude and the thermal expansion parallel to the axis, $\alpha_{||}$, will be appreciable, whereas that perpendicular to the axis, α_{\perp} , will be negligible.

Thus the lattice is effectively being stretched in one direction only and a lateral contraction (Poisson contraction), proportional to the modulus s_{13} , will

accompany the stretching. At low temperatures, the lateral contraction will be greater than the small thermal expansion within the layers, and α_{\perp} will therefore be negative. As the temperature increases, more energy will go into vibrations perpendicular to the axis, until a temperature T_m is reached when the thermal expansion exactly balances the lateral contraction. At this temperature $\alpha_{\perp} = 0$. Above this temperature the thermal expansion within the layers will increasingly outweigh the lateral contraction, and α_{\perp} will be positive and increase with temperature. When this is the case an elastic contraction parallel to the axis ($\propto s_{13}$) will be contributed, which will have the effect of diminishing the rate of increase of α_{\parallel} and at a high enough temperature may cause α_{\parallel} to diminish after passing through a maximum. The apparent flattening of the curve for graphite between 250° and 450° c. (figure 2) can be explained in this way.

Grüneisen and Goens (1924) observed with zinc and cadmium similar effects to those for graphite but at lower temperatures. Zinc and cadmium are hexagonal layer structures but their anisotropy is not so pronounced as that of graphite. The data for the metal are compared with those for graphite in the following table.

	T_m	Θ_x	Θ_z
Cadmium <i>ca</i>	45° K.	214	160
Zinc „	80° K.	320	200
Graphite „	660° K.	2280	760

The values of Θ for graphite are those given by Magnus (1923).

It will be noted that Θ_x for graphite is very much higher than for Zn or Cd as is the ratio Θ_x/Θ_z . It would therefore be expected that T_m also would be very much higher. Grüneisen and Goens themselves suggest, when briefly discussing the implications of their work in the case of graphite, that this substance would have α_{\perp} negative up to higher temperatures than does Zn or Cd.

§8. ACKNOWLEDGMENTS

We wish to thank Professor Sir Lawrence Bragg, F.R.S., for giving us hospitality and working facilities in the Cavendish Laboratory. The work constitutes part of a research programme of the British Coal Utilisation Research Association on the structure and properties of carbon and carbon derivatives, and we are grateful to Dr. D. H. Bangham for his encouragement and interest. Dr. A. R. Stokes gave us access to his collection of graphite samples and x-ray photographs, and we are indebted to him and to Dr. H. Lipson for several helpful discussions.

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EXTENDED DISLOCATIONS IN THE ANISOTROPIC ELASTIC CONTINUUM APPROXIMATION*

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Eshelby, Read and Shockley's theory of dislocations in an anisotropic elastic continuum has been applied to dislocations in the basal plane of hexagonal crystals to derive the dependence of stacking fault energy γ_F on the width w and orientation with respect to the Burgers vector of extended dislocations, on the width and orientation of triple partial ribbons, and on the radius of curvature r of extended nodes. The effect of "image" forces on the width of extended dislocations near a plane, stress-free surface has been investigated. The dependence of w on depth from the surface has been calculated for a 30° extended dislocation and a symmetrical, screw triple partial ribbon in an anisotropic plate. A procedure for correcting the widths observed in electron microscopy of thin films is given. For graphite the surfaces decrease w by less than 10% if the plate thickness is greater than 300 Å for extended dislocations and greater than 1000 Å for ribbons, when the dislocations are near the middle of the plate. All three methods of determining γ_F for graphite yield results, based on values of w and r reported by experimentalists, which are consistent with the value 0.6 ± 0.2 erg/cm². The reported error is only an estimate based on the uncertainty in the values of the elastic constants and differences in experimental results.

I. INTRODUCTION AND NOTATION

This work arose from the need of formulas which are not based on the approximation of elastic isotropy to use in the interpretation of electron micrographs of dislocations in thin films of graphite. In another paper¹ the stress components of straight dislocations in certain directions in infinite crystals have been derived by using Eshelby, Read and Shockley's² theory of dislocations in an anisotropic elastic continuum. From these the dependence of stacking fault energy on (i) the width of extended dislocations, (ii) the width of triple partial ribbons, and (iii) the radius of curvature of a large extended node can be calculated for dislocations in an infinite crystal. The effect of the stress-free surfaces of an anisotropic plate on the widths of 30° extended dislocations and of screw triple partial ribbons

lying parallel to the plane sides of the plate can be determined. These results are applied to dislocations in graphite. Numerical estimates of the stacking fault energy of graphite are made by the three methods mentioned above, based on experimental information reported by electron microscopists. The effect of the stress-free surfaces on dislocation widths in graphite is estimated and procedures are given for calculating the width in an infinite crystal from the observed width in thin films.

Let c_{ij} be the elastic stiffness constants with respect to a set of Cartesian coordinates chosen such that the x_3 -axis is parallel to the direction of a straight, infinitely long dislocation. The standard elastic stiffness constants with respect to the crystallographic axes will be denoted by c°_{ij} . The relation between the c_{ij} and the c°_{ij} depends on the orientation of the x_i -axes with respect to the crystallographic axes. A set of elastic constants c_{ij} for which the only nonzero constants are c_{11} , c_{12} , c_{13} , c_{22} , c_{23} , c_{33} , c_{44} , c_{55} and c_{66} will be referred to as Type I constants.

* This research was sponsored in part by the Air Research and Development Command and the Air Material Command, United States Air Force.

¹ G. B. Spence, *J. Appl. Phys.* **33**, 729 (1962).

² J. D. Eshelby, W. T. Read, and W. Shockley, *Acta Met.* **1**, 251 (1953).

For convenience of reference we shall use the following notation due to Fujita and Izui⁷. An edge dislocation in the direction of the c -axis is designated as Type 1, a screw dislocation along the c -axis as Type 2, a dislocation with a basal slip plane as Type 3, and an edge dislocation in the basal plane with Burgers vector perpendicular to the basal plane (prismatic slip plane) as Type 4. The relative abundance of each type is determined by the core energy, the elastic field energy, the Peierls stress to move the dislocation in the crystal, and the nature of the sources.

Type 3 dislocations should have the lowest core energy and Peierls stress because no C—C bonds in the layer planes are broken for this type. This is confirmed by the fact that Type 3 dislocations are by far the most common type observed by electron microscopy, even though their elastic field energy U is roughly twice as great as that of Type 2 dislocations. Type 2 dislocations can be produced by a spiral growth mechanism and have been observed by Tsuzuku⁸. Type 4 dislocations, possibly in conjunction with the easily produced Type 3, also are produced by growth mechanisms either at the edge of extra layer half planes, as observed by Fujita and Izui⁷, or at condensed vacancy disks, as observed by Amelinckx and Delavignette⁹. It is not known at present whether Types 2 and 4 dislocations can be moved in the crystal by external stresses. Since for a Type 1 dislocation the Peierls stress and both the core and elastic field energy are high and the probability of formation by growth is small, this type of dislocation should be very rare; and, in fact, it has not been definitely identified experimentally.

Applications of the line energy formulas to estimation of stacking fault energy are made in Section III.

III. STACKING FAULT ENERGY

A. Analytical Results

The force per unit length \mathbf{f}' on a dislocation D' with Burgers vector \mathbf{b}' due to its interaction with an external stress field $\boldsymbol{\tau}$ is given by the known formula $\mathbf{f}' = (\mathbf{b}' \cdot \boldsymbol{\tau}) \times \mathbf{v}'$, in which \mathbf{v}' is a unit vector in the direction of D' . If the external stress field is due to a dislocation D along the x_3 -axis, then $\boldsymbol{\tau}$ is given by the formulas of reference 1 for Type I elastic constants.

Consider a straight, extended dislocation of width w in the basal plane of a hexagonal crystal, as shown schematically in Fig. 1.

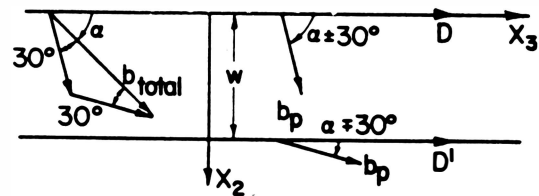


FIG. 1. Schematic drawing of the Burgers vectors of an extended dislocation.

Let γ_F be the average stacking fault energy per unit area, assumed to be a constant. From the condition of equilibrium $\gamma_F = f'$, we obtain

$$\gamma_F w = \frac{1}{2} b_p^2$$

$$[C_2 + C_1/\delta_1 + 2(C_2 - C_1/\delta_1) \cos 2\alpha], \quad (2)$$

in which b_p is the magnitude of the Burgers vector of a partial dislocation and α is the angle between the dislocation direction and the total Burgers vector of the extended dislocation. It is sometimes convenient to write this in the form

$$\gamma_F w_{45^\circ} = \frac{1}{2} b_p^2 (C_2 + C_1/\delta_1) \quad (3)$$

and

$$w = \left(1 + 2 \frac{C_2 - C_1/\delta_1}{C_2 + C_1/\delta_1} \cos 2\alpha \right) w_{45^\circ},$$

where w_{45° is the width of a 45° extended dislocation and also is the average width

⁷ F. E. Fujita and K. Izui, *J. Phys. Soc. Japan* **16**, 214 (1961).

⁸ T. Tsuzuku, *J. Phys. Soc. Japan* **12**, 778 (1957); *Proc. Third Carbon Conf.*, Pergamon Press, New York (1959), p. 433.

⁹ S. Amelinckx and P. Delavignette, *Phys. Rev. Letters* **5**, 50 (1960).

of extended dislocations. These formulas differ from those for isotropic materials only in the values of C_1 , C_2 , and δ_1 .

Amelinckx and Delavignette^{10,11} have observed both symmetrical and unsymmetrical extended dislocation ribbons in graphite consisting of three parallel partial dislocations with the same Burgers vector. The two parts of an unsymmetrical ribbon have different stacking fault energies γ'_F and γ''_F . Their analysis of an isotropic material can easily be generalized for an anisotropic material. We consider only those cases for which the elastic constants are Type I when the x_2x_3 plane is the plane of the ribbon. Since the interlayer distance is only a few angstroms while the widths w' and w'' of the two parts of the ribbon are several thousand angstroms in graphite, the simplifying approximation that all dislocations lie in the same plane can be made with negligible error. Equating the force of repulsion between partial dislocations to the effective surface tension of the stacking fault yields two independent equations of equilibrium. From these it follows that

$$\gamma'_F = B(2w' + w'')/ww'$$

and

$$\gamma''_F = B(2w'' + w')/ww'',$$

where

$$w = w' + w''$$

is the total width of the triple partial ribbon and

$$B = \frac{1}{2}b_p^2$$

$$[C_2 + C_1/\delta_1 + (C_2 - C_1/\delta_1) \cos 2\alpha].$$

In this α is the angle between the direction of the dislocation ribbon and the Burgers vector of the partials. The widths can be

expressed in terms of the stacking fault energies by

$$w' = 3B/(2\gamma'_F - \gamma''_F + \Gamma)$$

$$w'' = 3B/(2\gamma''_F - \gamma'_F + \Gamma)$$

$$w = B(\gamma'_F + \gamma''_F + \Gamma)/\gamma'_F\gamma''_F,$$

where

$$\Gamma = (\gamma'^2_F - \gamma'_F\gamma''_F + \gamma''^2_F)^{1/2}.$$

For a symmetrical triple partial ribbon, for which $w = 2w' = 2w''$ and $\gamma'_F = \gamma''_F = \gamma_F$, these formulas reduce to

$$\gamma_F w = 3B. \quad (4)$$

Comparison of (4) with (2) shows that the average width $w_{45^\circ, \text{rib}}$ at $\alpha = 45^\circ$ of a symmetrical triple partial ribbon is related to the average width $w_{45^\circ, \text{ext}}$ of an extended dislocation of equal stacking fault energy by $w_{45^\circ, \text{rib}} = 6w_{45^\circ, \text{ext}}$. Similarly, it follows that $w_{0^\circ, \text{rib}} = 6w_{30^\circ, \text{ext}}$ and $w_{90^\circ, \text{rib}} = 6w_{60^\circ, \text{ext}}$.

The stacking fault energy is related to the line tension U of a partial dislocation and the radius of curvature r of a large extended node by the known formula

$$\gamma_F = U/r. \quad (5)$$

The line tension may be estimated by assuming it is the same as the line energy per unit length of the dislocation, given by formula (1) for Type I elastic constants. In (1) $b = b_p$ and α is the angle between the Burgers vector and the partial dislocation at its midpoint. The major difficulty in applying (5) is in estimating the factor $\ln R/r_0$. Presumably R is approximately the average distance between total dislocations and r_0 is approximately b_p , but there is no unique way of determining these quantities.

B. Numerical Results

In the preceding section three formulas based on anisotropic elasticity theory have been presented for estimating the stacking fault energy from observations made on electron micrographs. At the present time

¹⁰ S. Amelinckx and P. Delavignette, *J. Appl. Phys.* **31**, 2126 (1960).

¹¹ S. Amelinckx and P. Delavignette, in *Direct Observation of Imperfections in Crystals*, J. B. Newkirk and J. H. Wernick, eds., *Interscience*, New York (1962), p. 295.

there are not enough experimental observations on well-annealed crystals of low dislocation density to obtain good experimental averages. Furthermore, since the thicknesses of the crystal plates are not known, we must neglect the effect of the stress-free surfaces on the widths and radius of curvature and assume that the observed lengths are the same as those in an infinite crystal. Even so, there is substantial agreement between the values of γ_F obtained from the three methods.

Williamson¹² and Amelinckx and Delavignette¹⁰ have reported that the average width of extended dislocations in graphite is about 1000 Å, which by (3) yields a value of γ_F of about 0.62 erg/cm². From observations on single, gently curving extended dislocations Siems, Delavignette and Amelinckx¹³ report that within their experimental error w varies as $\cos 2\alpha$ with $w_{90^\circ}/w_{0^\circ} = 2.6$ and $w_{45^\circ} = 850$ Å, for which the present theory gives $\gamma_F = 0.73$ erg/cm². The present theory predicts that $w_{90^\circ}/w_{0^\circ} = 2.1$.

Delavignette and Amelinckx¹⁴ have observed symmetrical triple partial ribbons with average total widths of $w_{0^\circ} = 5300$ Å and $w_{60^\circ} = 7000$ Å, which by (4) both yield a value of γ_F of 0.58 erg/cm². The exact agreement is fortuitous, as the uncertainty in γ_F is roughly $\pm 20\%$.

On electron micrographs taken by Williamson and by Amelinckx and Delavignette the radius of curvature of extended nodes has varied from 0.9 to 1.7 μ . Where it has been measured, the partials have been in screw orientation at their midpoint; the average distance between dislocations is roughly 1 μ . Taking $\alpha = 0^\circ$, $R = 1$ μ , and $r_o = b_p = 1.42$ Å, we find from (1) and (5) that γ_F is from 0.25 to 0.50 erg/cm². These computed values of γ_F should be less than

the true value because the repulsion between the three partials in an extended node has been neglected in the theory.

It appears that all three methods of determining the stacking fault energy in graphite yield results which are consistent with the value

$$\gamma_F = 0.6 \pm 0.2 \text{ erg/cm}^2.$$

IV. EFFECT OF STRESS-FREE SURFACES

A. A 30° Extended Dislocation in an Anisotropic Plate

From Fig. 1 we see that for a 30° extended dislocation the Burgers vector of one of the two partial dislocations is in the pure screw orientation. For Type I elastic constants the edge and screw components of dislocations do not interact with one another. Consequently, the force of repulsion between the partials of a 30° extended dislocation lying parallel to the stress-free surfaces of a flat anisotropic plate can be computed from the stress components of a screw partial dislocation in an anisotropic plate. These are given in reference 1 for Type I elastic constants.

Let d be the thickness of the plate, a be the distance from one of the two stress-free surfaces to the extended dislocation, and w be its width, as indicated in Fig. 2. Equating the stacking fault energy to the force of

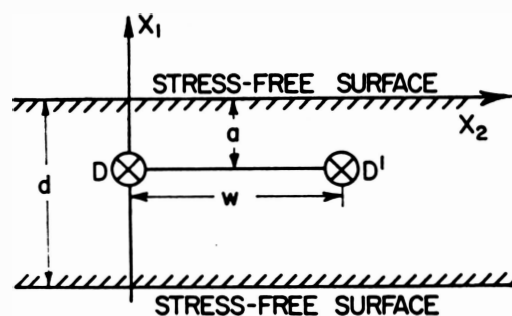


FIG. 2. Schematic drawing of an extended dislocation in a plate.

repulsion between partials, we obtain γ_F as a function of w , a and d . It is convenient

¹² G. K. Williamson, *Proc. Roy. Soc. (London)* A257, 457 (1960).

¹³ R. Siems, P. Delavignette, and S. Amelinckx, *Z. Physik* 165, 502 (1961).

¹⁴ P. Delavignette and S. Amelinckx, *J. Nuclear Materials* 5, 17 (1962).

to express the results in terms of the dimensionless quantities

$$W = w/w_\infty, \quad (6)$$

where w_∞ dislocation in an infinite crystal. From (2) we see that

$$\gamma_F = C_2 b_p^2 / 2w_\infty. \quad (7)$$

On equating the two expressions for γ_F , one obtains a transcendental equation which cannot be solved to give the explicit dependence of w on w_∞ ,

it is convenient, particularly for applications, to introduce a dimensionless parameter Ω defined by

$$\Omega = \pi \delta_3^{1/2} w/d, \quad (8)$$

which by (6) is equivalent to $\Omega = \pi \delta_3^{1/2} W/D$. This relation and the transcendental equation can then be put in the parametric form

$$W = \Omega f(\Omega, a/d) \quad (9)$$

$$D = \pi \delta_3^{1/2} W/\Omega, \quad (10)$$

where

$$f(\Omega, a/d) = \frac{\sinh \Omega}{2} \left[\frac{1}{\cosh \Omega - 1} - \frac{1}{\cosh \Omega - \cos 2\pi a/d} \right] \quad (11)$$

is a dimensionless function. For $a = d/2$ Eqs. (9) and (11) reduce to

$$W = \Omega / \sinh \Omega. \quad (12)$$

Equations (9) to (11) yield the dependence of W on Ω and the dependence of W on D at a constant a/d ratio. Since $a/d = A/D$, the dependence of W on A at constant D can also be obtained.

To apply these results to the analysis of 30° extended dislocations observed by electron microscopy, it is necessary to measure w , d , and a . Then one can compute, in turn,

Ω , f , W , and $w_\infty = W/w$; and the stacking fault energy can be determined from (7). At the present time it seems to be impossible to measure the distance a of the dislocation from the surface. However, for a given plate thickness d the dislocations in the center are widest; so it should be safe to conclude that $a = d/2$ for the widest of a large number of experimentally determined dislocation widths in films of the same thickness. Then W can be computed from (12) and the stacking fault energy obtained as before.

Measurements of w and d for the same film of graphite do not appear to have been made, although this should be possible. Estimates of d for films used by different experimentalists have ranged from, say, 200 to 2000 Å. To get an estimate of the effect

assume that $a = 0.5d$ for the observed dislocations. For the elastic constants of graphite given above, $\Omega = 0.23 w/d$. The W vs. Ω curves for several different a/d ratios are shown in Fig. 3 for the range of Ω

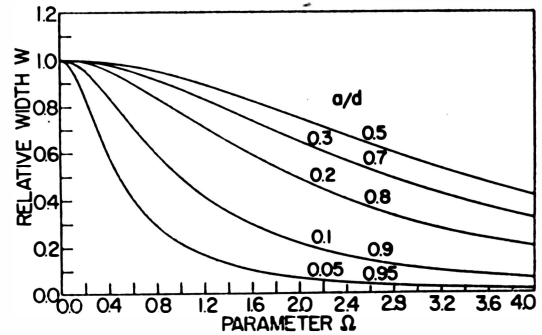


FIG. 3. Width of a 30° extended dislocation in a graphite plate versus the parameter Ω .

of most interest for a 30° extended dislocation in a graphite plate. For $a = 0.5d$ and, say, $W = 0.90$, the parameter Ω is 0.80; for which $d = 290$ Å when $w = 1000$ Å. This indicates that the stress-free surfaces decrease the width by less than 10% if $d > 300$ Å. If $d > 1000$ Å and $w = 1000$ Å, then the width in the center of the film is decreased by less than 1%. On the other

hand, if $d < 300 \text{ \AA}$, then there is a significant decrease in the dislocation width*.

Figure 4 shows the variation of W with A for several film thicknesses of interest

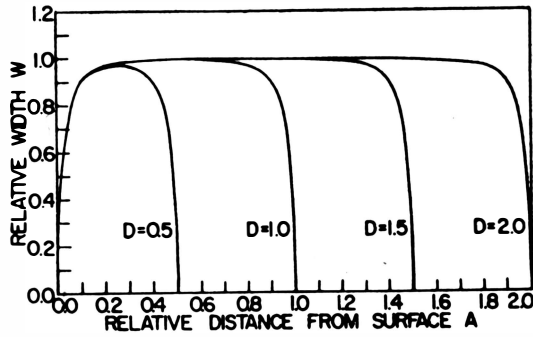


FIG. 4. Width of a 30° extended dislocation in a graphite plate as a function of depth from surface and thickness of plate.

for graphite. For all $D > 0.5$ the curves have a rather flat maximum. Consequently, the width of almost all extended dislocations in graphite will be within a few per cent of w_∞ in films of thickness $d > 0.5 w_\infty$.

B. Screw Triple Partial Ribbon in an Anisotropic Plate

For Type I elastic constants, the symmetrical, screw triple partial ribbon can be treated in a manner analogous to that for the 30° extended dislocation. We again introduce relative distances, W , A , and D by (6); except that now w_∞ is the total width of a symmetrical, screw triple partial ribbon in an infinite anisotropic crystal and is related to the stacking fault energy by

$$\gamma_F = 3C_2 b_p^2 / w_\infty. \quad (13)$$

Equation (9) is replaced by

$$W = \frac{1}{2} \Omega [f(\Omega, a/d) + f(\Omega/2, a/d)];$$

equations (8), (10) and (11) are still applicable.

These results can be applied to the widths

*Orientation studies in a semi-infinite isotropic solid [ref. 1] indicate that when the width of a 30° extended dislocation is decreased by only a few per cent, then the widths of extended dislocations of all orientations will be reduced by only a few per cent; but when the width of a 30° extended dislocation is reduced by more than 10%, then the reduction in width of extended dislocations depends strongly on the orientation.

of symmetrical, screw triple partial ribbons observed by electron microscopy by the procedure discussed for 30° extended dislocations.

The W versus Ω curves for several values of a/d are shown in Fig. 5 for the range of Ω

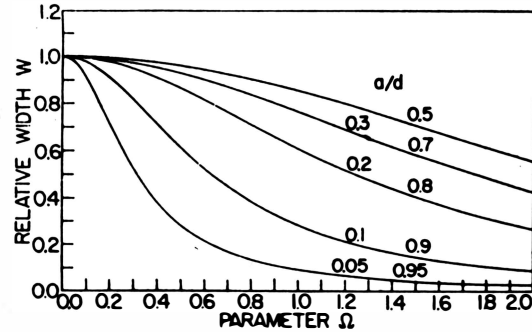


FIG. 5. Width of a symmetrical, screw triple partial ribbon in a graphite plate versus the parameter Ω .

of most interest for a symmetrical, screw triple partial ribbon in a plate of graphite. In order to illustrate the method we shall arbitrarily assume that the 5300 \AA wide ribbon observed by Amelinckx and Delavignette was in the center of the film. Then for a 1000 \AA film thickness, one obtains $\Omega = 1.22$ and $W = 0.89$. The width in an infinite crystal would be 6000 \AA , which by (13) gives a stacking fault energy of $\gamma_F = 0.51 \text{ erg/cm}^2$. For a 2000 \AA thick film, $\Omega = 0.61$ and $W = 0.97$. The width in an infinite crystal would be 5500 \AA , which gives $\gamma_F = 0.55 \text{ erg/cm}^2$. These are to be compared with the value of $\gamma_F = 0.58 \text{ erg/cm}^2$ for an uncorrected width of 5300 \AA . From these results it appears to be desirable to apply a correction to the widths of triple partial ribbons observed in films less than about 2000 \AA in thickness.

Figure 6 shows the variation of W with A for several film thicknesses of interest for graphite. For a film thickness of 1000 \AA , D is about 0.2. The curves of W versus A are not so flat topped as the curves of Fig. 4 for extended dislocations. Consequently, it is necessary to observe a larger number of

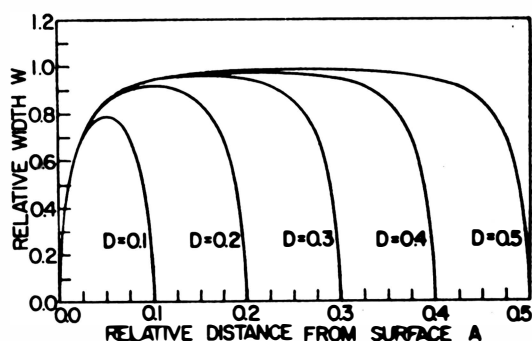


FIG. 6. Width of a symmetrical, screw triple partial ribbon in a graphite plate as a function of depth from surface and thickness of plate.

triple partial ribbons to be sure that the widest of these lies at or close to the center of the film.

V. DISCUSSION

Formulas based on the anisotropic elastic continuum theory of dislocations have been derived for estimating the stacking fault energy of hexagonal crystals from the width of extended dislocations, from the width of triple partial ribbons, and from the radius of curvature of large extended nodes. The effect of the stress-free surfaces of the thin films used in electron microscopy on the widths of 30° extended dislocations and symmetrical, screw triple partial ribbons has been calculated and procedures are indicated for making a correction to the observed width. For graphite this correction is greater

than a few per cent for 30° extended dislocations in films thinner than 500 \AA and for symmetrical, screw triple partial ribbons in films thinner than 2000 \AA .

The calculation of the stacking fault energy by different methods, the variation in width of dislocations and ribbons with orientation, and the effect of the surfaces of thin films are phenomena which can be accurately checked by experimental observations with the electron microscope. This provides an unusual opportunity to either verify the correctness of the anisotropic elastic continuum theory of dislocations as here applied or else to show that other factors must also be considered. For example, even in annealed crystals the equilibrium positions of partials may be influenced by the local stresses of point imperfections, the long-range thermal and applied stresses, and the fact that the crystals may warp or be small enough in lateral extent that the crystal edges perpendicular to the basal plane must be considered. In view of the widespread use of thin film microscopy to infer the behavior of dislocations in bulk material, it is important to determine all the factors which strongly influence the dislocations.

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IN THIS ISSUE...

**BROADCAST
COMPANDER**

LOUDSPEAKERS

**MICROPHONE
PLACEMENT**

ROOM ACOUSTICS

**AES SUSTAINING
MEMBERS**

Polymer-Graphite Composite Loudspeaker Diaphragm*

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A polymer-graphite composite has been developed which has both a large E/ρ ratio and a large internal loss factor. The specific modulus E/ρ of the composite is greater than that of aluminum or titanium, and the internal loss $\tan \delta$ is greater than that of cone paper. Since the composite forms well, it can be made into various shapes of low-frequency or high-frequency loudspeaker diaphragms. With this material, superior loudspeakers have been made having smooth frequency response, very low harmonic-distortion characteristics, and wide dynamic range.

0 INTRODUCTION

Desirable material properties for loudspeaker diaphragms are a high Young's modulus, low density, and large internal loss. For mid-range or high-frequency diaphragms light metals such as aluminum, titanium, or beryllium have been used. As they all have a large ratio of Young's modulus to density E/ρ , the high-frequency limit can be extended.

Low-frequency loudspeakers have used cone papers with large internal losses, which result in smooth frequency response. Paper diaphragms, however, are apt to break up at relatively low frequencies because of their small Young's modulus, producing large distortions in response to high-level signals.

Consequently loudspeaker diaphragms, particularly at low frequency, having both a large E/ρ ratio and large internal losses, have long been wanted. To realize these desirable properties, we have studied a new material, and a superior material has been obtained. The polymer-graphite material consists of fine graphite granules and several polymers.

This paper describes the development process, structure, and physical properties of the composite, and the characteristics of loudspeakers using polymer-graphite diaphragms.

1 GRAPHITE

Graphite is a form of carbon crystal and has a laminar structure consisting of large layers linking many hexagonal rings of carbon atoms, as shown in Fig. 1 [1-3].

The covalent bonding among carbon atoms in an *ab-plane* layer is so strong that it produces a Young's modulus greater than 1.1×10^3 GPa [4]. In contrast, when *ab-plane* layers are only weakly bonded to each other by the *c-axis* Van der Waals' forces between them, slipperiness results.

Carbon fibers having a large Young's modulus use this firm bonding, but in loudspeaker diaphragms containing carbon fibers, adequate strength is not produced because of weak bonding between fibers and the slipperiness of the fiber surfaces.

In a first attempt a chemical-vapor deposition method was used to obtain a carbon diaphragm. A film deposited by this method has the special feature that the layers of deposit are oriented parallel to the sub-

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strate surface if the chemical-vapor deposition conditions are suitable.

Carbon was deposited on a substrate having the shape of the diaphragm and heated to over 1000 °C. The diaphragm was separated from the substrate. A loudspeaker using this diaphragm produced a very smooth frequency response. A scanning electron micrograph of the fracture cross section revealed a laminar structure in the deposited film. Graphite with a laminar structure contributes to a large Young's modulus. However, the chemical-vapor deposition method is undesirable for use in production because of its high cost.

2 POLYMER-GRAPHITE COMPOSITE

Composites were next investigated using graphite crystallite granules having parallel-layer planes.

The following factors were considered in the development process:

- 1) Dispersion of graphite granules into matrix polymers
- 2) Orientation of laminar granules parallel to the diaphragm surface
- 3) Development of polymers which can be applied to the diaphragm and can tightly bond the granules to each other
- 4) Mixing ratio of granules to polymers

All of these factors were interrelated, and therefore the physical properties of composites have many variations. Following many experiments on numerous combinations, a superior composite was realized having both a large E/ρ ratio and a large internal loss factor.

A block diagram of the production process is shown in Fig. 2.

3 COMPOSITE STRUCTURE

A scanning electron micrograph of the fracture cross section of the composite sheet is shown in Fig. 3.

A laminar structure parallel to the surface is observed and resulted from the orientation process in production.

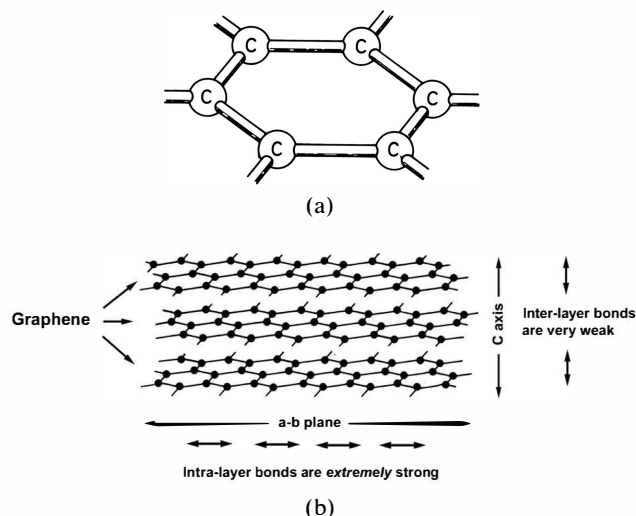


Fig. 1. Schematic models: (a) Bonding of carbon atoms. (b) Laminar structure of graphite crystal.

4 PHYSICAL PROPERTIES

To compare the composite with other materials, the physical properties are shown in Table 1. Comparative data concerning internal loss and sound velocity of each material are plotted in Fig. 4. The sound velocity of the composite is greater than that of aluminum or titanium and is about three times that of cone paper.

Decay patterns of free vibrations of composite, aluminum, and cone-paper reeds are shown in Fig. 5.

Since the composite forms well, it can be made into various shapes of diaphragms for either low-frequency or high-frequency loudspeakers.

The graphite-granule layer planes are oriented parallel to the diaphragm surfaces, so that isotropy of physical properties can be obtained in the direction of the surfaces.

The material is stable in a humid atmosphere (in which cone paper is degraded) and can therefore maintain high strength for a long time.

5 LOUDSPEAKERS WITH POLYMER-GRAPHITE DIAPHRAGMS

In order to use polymer-graphite diaphragms effectively, several loudspeakers have been developed with the use of a computer and laser holography.

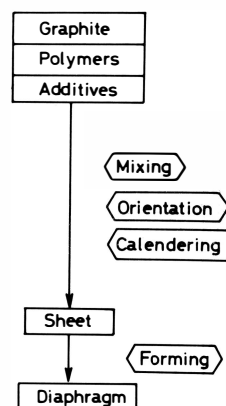


Fig. 2. Block diagram of production process of the polymer-graphite diaphragm.

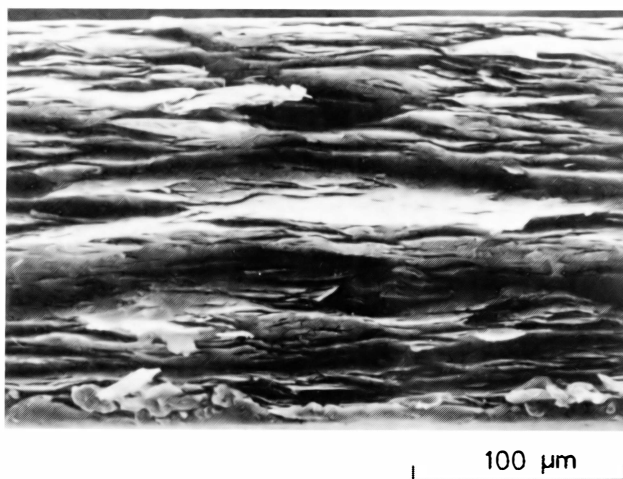


Fig. 3. Scanning electron micrograph of fracture cross section of polymer-graphite.

Table 1. Physical properties of several materials for diaphragms.

	Young's Modulus E (GPa)	Density ρ (gm/cm ³)	Sound Velocity $\sqrt{E/\rho}$ (m/s)	Internal Loss $\tan \delta$
Polymer-graphite	70	1.8×10^3	6.2×10^3	0.05
Aluminum	70	2.7×10^3	5.1×10^3	0.002
Titanium	110	4.5×10^3	4.9×10^3	0.002
Cone paper	2	0.5×10^3	2.0×10^3	0.05

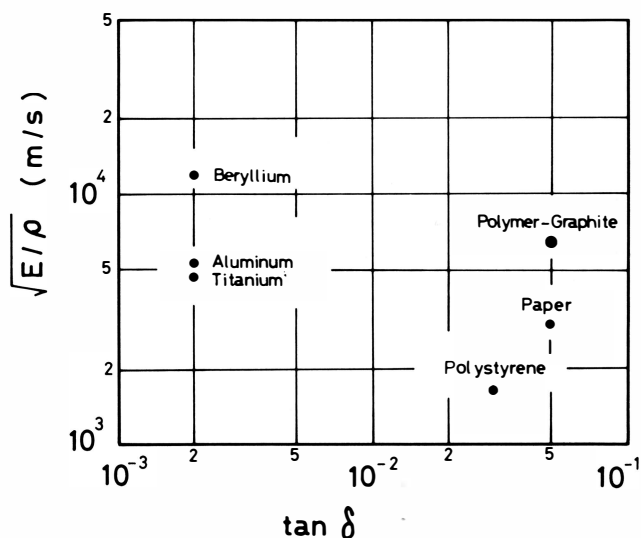


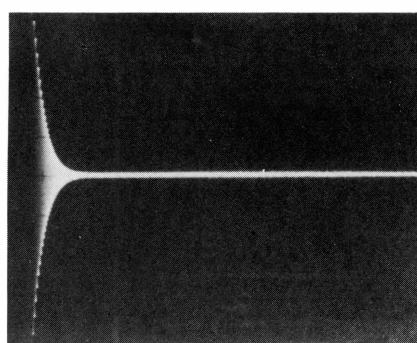
Fig. 4. Comparison of the polymer-graphite with other materials relative to internal loss and sound velocity.

5.1 40-cm Cone-Type Low-Frequency Loudspeaker

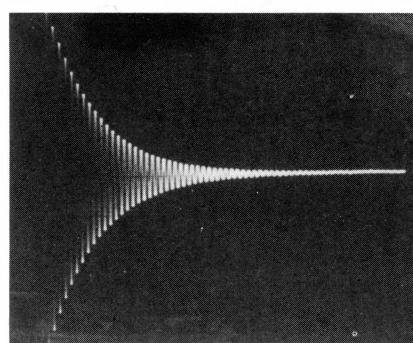
Comparisons of a 40-cm cone-type loudspeaker using the polymer-graphite diaphragm (Fig. 6) with a 40-cm loudspeaker using a paper diaphragm of the same shape are shown in Figs. 7 and 8 for output sound-pressure levels of 90 and 115 dB, respectively. The harmonic distortion of the loudspeaker with the polymer-graphite diaphragm at 90 dB is markedly less than 0.3%, and at a very high sound-pressure level of 115 dB it is less than 0.3% in the frequency range of 100–800 Hz.

Furthermore the high-frequency limit of the loudspeaker with the polymer-graphite diaphragm is twice that using a paper diaphragm.

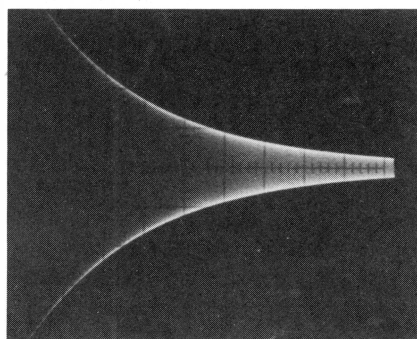
The peak in the high-frequency resonance of the diaphragm using the composite material is hardly noticeable at either the 90-dB or the 115-dB sound-pressure



Polymer - Graphite



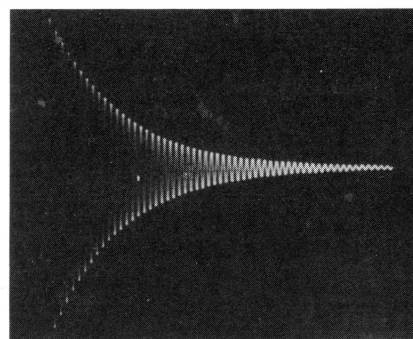
Polymer - Graphite



Aluminum

0.5 s
↔

(a)



Cone Paper

0.1 s
↔

(b)

Fig. 5. Decay patterns of free vibration. (a) Polymer-graphite compared with aluminum. (b) Polymer-graphite compared with cone paper.

levels. Thus the polymer-graphite loudspeaker produces a very smooth frequency response and low harmonic distortion.

5.2 High-Frequency Loudspeaker

Frequency responses and harmonic-distortion characteristics of 6.6-cm cone-type high-frequency loudspeakers, one with the polymer-graphite diaphragm, the other with a paper diaphragm of the same shape, are compared in Fig. 9. The frequency response of the polymer-graphite loudspeaker is smoother in the frequency range from 1 to 43 kHz.

Frequency responses of 2.5-cm dome-type high-frequency loudspeakers, one with a polymer-graphite diaphragm, the other with a titanium diaphragm of the same shape, are compared in Fig. 10. The frequency response of the polymer-graphite loudspeaker reaches



Fig. 6. 40-cm cone-type loudspeaker using polymer-graphite diaphragm.

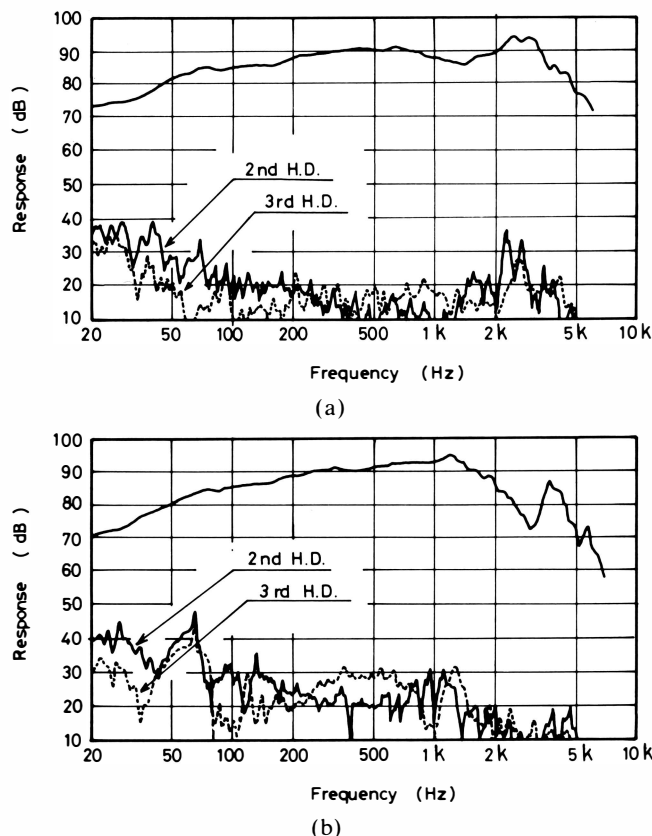


Fig. 7. Frequency responses and harmonic-distortion characteristics of 40-cm cone-type loudspeakers at output sound-pressure level of 90 dB. (a) Polymer-graphite diaphragm. (b) Cone paper diaphragm.

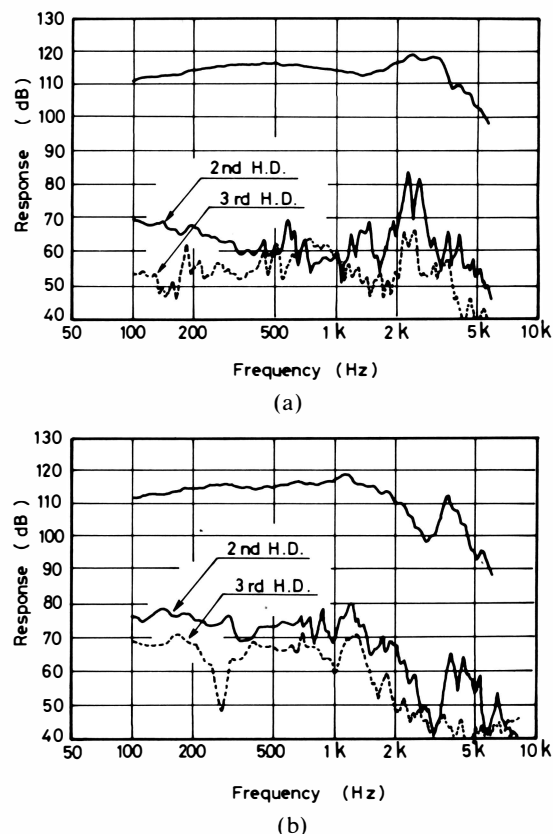


Fig. 8. Frequency responses and harmonic-distortion characteristics of 40-cm cone-type loudspeakers at output sound-pressure level of 115 dB. (a) Polymer-graphite diaphragm. (b) Cone paper diaphragm.

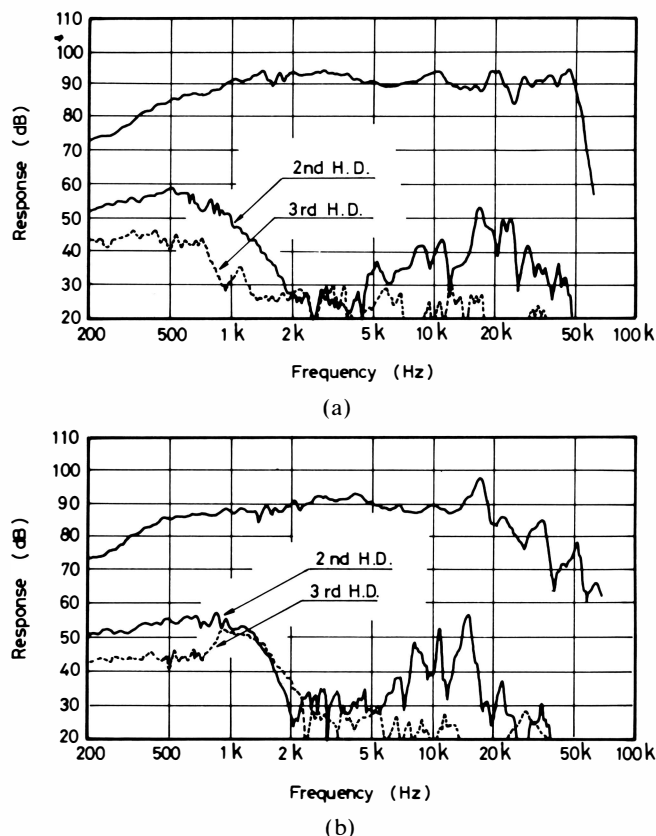


Fig. 9. Frequency responses and harmonic-distortion characteristics of 6.6-cm cone-type loudspeakers. (a) Polymer-graphite diaphragm. (b) Cone paper diaphragm.

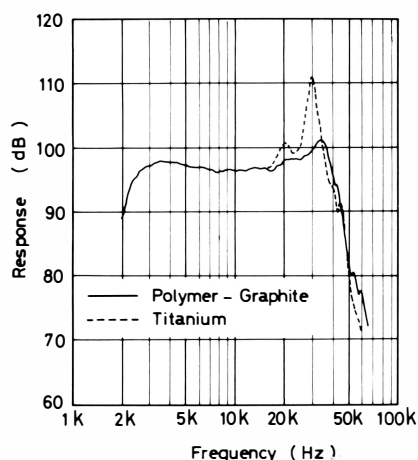


Fig. 10. Frequency responses of 2.5-cm dome-type loudspeakers.

35 kHz, which exceeds by about 5 kHz that using the titanium diaphragm, and the peak at the high-frequency resonance of the polymer-graphite loudspeaker is lower.

6 CONCLUSION

The polymer-graphite composite with a laminar

structure has both a large E/ρ ratio and a large internal loss factor. Loudspeakers using polymer-graphite diaphragms provide smooth frequency response and low harmonic distortion over a wide frequency range. The composite will be applied to other components in various fields.

7 ACKNOWLEDGMENT

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New Materials for Loudspeaker Diaphragms and Cones — An Overview —

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Desirable properties of materials for loudspeaker diaphragms are high specific Young's modulus E/ρ (E : Young's modulus, ρ : density), large flexural rigidity EI (I : moment of inertia of section) and large internal loss $\tan\delta$. In order to obtain large flexural rigidity, honeycomb structured diaphragms or porous metal diaphragms have been used. For the purpose of realizing ideal loudspeaker diaphragms which can be easily produced, however, the material itself should have high values of E/ρ and $\tan\delta$.

This paper is a review on recent developments of materials for loudspeaker diaphragms in Japan. There are beryllium and boronized titanium diaphragms which are suitable for the high frequency loudspeakers because of their high specific Young's modulus, and carbon fiber reinforced olefin and polymer-graphite composite diaphragms which are suitable for the low frequency loudspeakers because of their high specific Young's modulus and internal loss and also production easiness of large diaphragms.

1. INTRODUCTION

Acoustical performances of loudspeakers are mainly dependent upon the physical properties of the vibrating systems. The diaphragm is the principal factor for the performance of the loudspeaker within the vibrating system. There are three desirable properties for materials of loudspeaker diaphragms, as follows,

1. large specific Young's modulus E/ρ to get wider frequency range,
2. large flexural rigidity EI to reduce harmonic distortions,
3. large internal loss $\tan\delta$ to suppress breakups of the diaphragms.

From the above points of view, paper cones produced from natural pulps have been used as loudspeaker diaphragms for 50 years. This is because that paper cones satisfy the above three requirements somehow. However, there are large deviations of properties among mass-produced paper cones because they are produced one by one through many processes such as beating, felting, drying and pressing. Moreover, it is not so easy to obtain stable paper cones because they are sensitive against humidity. In this situation, new diaphragms for loudspeakers, which have superior and stable properties over paper cones and can be mass-produced, have been desired for many years.

In order to improve the properties of paper cones, newly developed high Young's modulus fibers; inorganic fibers such as glass fiber, carbon fiber and alumina fiber, or organic fibers such as polyamid fiber, have been mixed into natural pulps. Because of the weakness of cross linking forces between reinforcing fibers and natural pulps, however, much progress has not been achieved yet.

Recently, some inorganic materials such as beryllium and boron with high specific Young's modulus have been developed and used as diaphragms for mid-range and high frequency loudspeakers. Composite diaphragms such as carbon fiber reinforced olefin diaphragm and polymer-graphite composite diaphragm with high specific Young's modulus and proper internal loss have also been developed and used for low frequency loudspeakers.

There are developments concerning honeycomb structured diaphragms and porous metal diaphragms which provide low frequency loudspeaker diaphragms with large flexural rigidity. However, there seems some production difficulties in these diaphragms.

In this paper, recent developments in materials for loudspeaker diaphragms in Japan are presented. These are beryllium and boronized titanium diaphragms for mid-range and high frequency loudspeakers, and carbon fiber reinforced olefin and polymer-graphite composite diaphragms for low frequency loudspeakers. This paper describes also their production processes, physical properties and performances of the loudspeakers using the new diaphragms.

2. NEW DIAPHRAGMS WITH HIGH SPECIFIC YOUNG'S MODULUS

Materials with high specific Young's modulus are desirable for diaphragms of mid-range and high frequency loudspeakers because wider frequency range is the most important factor for these loudspeakers. Beryllium and boron are suitable materials for this purpose. And these physical properties are shown in Table 1. Unfortunately, it is nearly impossible to make diaphragms of pure beryllium or pure boron by mechanical processes because of their hardness and low ductility and their activity in higher temperature state. Relatively inexpensive mass production processes of beryllium and boron diaphragms have been developed. These diaphragms have several superior properties comparing with ordinary diaphragms.

2.1 Beryllium diaphragm

2.1.1 Production process

There are several methods such as chemical vapor deposition, frame jet spraying and electro-plating to produce beryllium diaphragms. However, these methods are not practical because of their low productivity. Taking account of low melting temperature and high vapor pressure of beryllium, Yuasa et al. have adopted vacuum deposition method⁽¹⁾.

Fig. 1 shows the vacuum deposition apparatus for

massproduction of beryllium diaphragms. The substrate should satisfy the following requirements, such as easiness in forming, stability in high temperature atmosphere, and easiness in removing from the deposited beryllium. After several tests, Yuasa et al. found that a chemical dissolution of the substrate is the most practical method to remove the substrate considering these requirements, they adopted copper as the substrate material. The deposition process is as follows,

1. put beryllium ingots produced in a vacuum induction furnace into a hearth,
2. put copper substrates mounted to substrate holders into the vacuum deposition chamber, apply negative electrical potential of 1000 ~ 2000Volts, and heat the substrates up to 300°C ~ 500°C,
3. evacuate the vacuum chamber up to $3 \times 10^{-3} \sim 8 \times 10^{-4}$ Pa,
4. focus the electron beam onto the beryllium ingot to evaporate it in a deposition rate of $1 \sim 2 \mu\text{m}/\text{min}$,
5. after deposition, heat the substrates up to 600°C to anneal and sinter the diaphragms,
6. chemically dissolve the copper substrates away from the beryllium diaphragms by an aqueous solution of nitric acid,
7. deposit SiO_2 to protect the beryllium surfaces.

Fig. 2 is the experimental results of relations between substrate temperature and Young's modulus of the beryllium diaphragm. Fig. 3 are scanning electron micrographs of deposited beryllium surfaces at various substrate temperatures. This figure shows that the crystalline grain size grows up as the temperature increases. The substrate temperature during the deposition process has been decided to 300°C ~ 500°C because the beryllium diaphragm becomes brittle when the substrate temperature exceeds 600°C.

Fig. 4 shows a thickness variation over the beryllium diaphragm. A substantially uniform thickness can be obtained by adjusting direction of the substrate holder, mechanisms of rotation and revolution of the substrate holder and the electrical potential applied to the substrate.

2.1.2 Characteristics of loudspeakers with beryllium diaphragms

Fig. 5 shows a comparison of sound pressure level frequency responses of 2.5cm dome type high frequency loudspeakers with the same shape beryllium diaphragm and titanium diaphragm.

By the use of beryllium diaphragms, mid-range and high frequency loudspeakers with wide and flat frequency responses and excellent transient responses can be obtained.

2.2 Boronized titanium diaphragm

A development of boron deposited titanium diaphragm by a vacuum deposition method has been reported⁽²⁾. However, the method doesn't seem suitable to be used as a mass production process of boron deposited diaphragms, because boron has exceedingly high melting temperature and its vapor pressure is very low.

Utilizing the activity of boron at high temperatures, a diffusion process of boron into steel has been recently established. In the case of boronizing of titanium, however, titanium is apt to become brittle because titanium reacts easily with oxygen and nitrogen at temperatures over 800°C. Tsukagoshi et al. have developed a boronizing process adap-

table for titanium and succeeded in mass-producing the high specific Young's modulus diaphragms at a reasonable cost⁽³⁾.

2.2.1 Boronizing process

Substrates for this boronizing process should have low density, easy formability and small deformation at high temperatures. Accordingly titanium is the most suitable material for the substrate.

Fig. 6 shows a new apparatus to produce boronized titanium diaphragms. Titanium diaphragms are buried into a mixed powder of boron (70wt%), carbon (20wt%) and sodium carbonate (10wt%) within the graphite case. The chamber is evacuated up to 1 Pa to prevent titanium from oxidation, and then the graphite case is heated by a high frequency induction furnace. Carbon and sodium carbonate functions as an activator and oxidation suppressor for boron and titanium. Activated boron diffuses into the titanium and boronized layers are produced at the titanium surfaces.

Fig. 7 shows the Young's modulus of a 25 μm boronized titanium diaphragm as a function of treating temperatures and treating times. Proper treating temperature is determined from 1000°C to 1200°C because diffusing rate is too slow under 1000°C and substrates deform over 1200°C. Fig. 8 is an X-ray diffraction pattern of the boronized titanium diaphragm at 1200°C for 10 minutes. Only titanium borides in the forms of TiB and TiB_2 are recognized. Fig. 9 is a scanning electron micrograph of the same specimen. A result of atomic analysis of boron and titanium by an electron probe microanalyzer along the marked line is shown in Fig. 10. As a result of these analyses, it is recognized that boronized layers of TiB_2 are produced on both surfaces of the substrate, and spikes of TiB are developed towards the center of the substrate. These spikes prevent the layer from exfoliation. Several physical properties of typical boronized titanium and pure titanium are listed in Table 1. The boronized titanium has 2.6 times higher specific Young's modulus than that of pure titanium.

2.2.2 Characteristics of loudspeakers with boronized titanium diaphragm

Fig. 11 shows a comparison of sound pressure level frequency responses of 2.5cm dome type high frequency loudspeakers with a same shape boronized diaphragm and titanium diaphragm. The high frequency resonance of the boronized diaphragm reaches 37kHz which is 1.6 times higher than that of titanium one. The ratio of the high frequency resonances almost coincides with the ratio of speeds of sound in both materials. Fig. 12 shows a sound pressure level frequency response of 12cm cone type mid-range loudspeaker using the boronized titanium diaphragm. The frequency response is fairly flat and smooth in the frequency range from 300Hz to 12kHz and the harmonic distortion is very low in the frequency range from 500Hz to 7 kHz.

As the results, using the newly developed boronizing process, we can achieve,

1. diaphragm with 2.6 times higher specific Young's modulus than that of titanium,
2. diaphragm with a reasonable cost because an inexpensive amorphous boron and relatively simple apparatus can be used, and large number of diaphragms can be treated at a time.

Boronized titanium diaphragm can provide mid-range

and high frequency loudspeakers with wide and smooth frequency response and low harmonic distortion.

3. NEW DIAPHRAGMS WITH HIGH SPECIFIC YOUNG'S MODULUS AND INTERNAL LOSS

For the applications to low frequency loudspeaker diaphragms, some new materials are desirable, which can be mass-produced into large diaphragms and provide a wide frequency range of piston motion and a smooth roll off frequency response above the cut off frequency. For this purpose, materials with high specific Young's modulus and large internal loss are required. Moreover, to get diaphragms with small variations and stability against various weather conditions, synthesized materials should be used.

Recently, there have been many researches and developments on the composite materials which consist of plastic matrices and inorganic fillers. And these composite materials have excellent properties and can be mass-produced in a reasonable cost. Examples of the developments are on the carbon fiber reinforced olefin diaphragm by Niiguchi et al. which consists of synthesized pulp and carbon fiber, and polymer-graphite composite diaphragm by Tsukagoshi et al. which consists of polyvinylchloride resin and graphite flakes.

3.1 Carbon fiber reinforced olefin diaphragm

Niiguchi et al. have developed carbon fiber reinforced (CFR-) olefin diaphragm using high density polyethylene with lowest density within polymers as a matrix and high modulus carbon fiber as a filler⁽⁴⁾.

3.1.1 Production process

Synthesized pulp of the high density polyethylene have been used as a matrix. In order to adapt to a wet process, the pulp is treated to be given a hydrophilicity. High modulus carbon fiber with small radius has been selected as a filler so as to keep good formability. Physical properties of the high modulus carbon fiber are shown in Table 1.

Fig. 13 is the mass production process of CFR-olefin diaphragms. Beaten and fibrilized pulp and chopped carbon fiber are mixed. From this mixture, continuous composite sheets are produced by felting process same as in the ordinary paper. Various kinds of loudspeaker diaphragms can be produced continuously from the sheet by the apparatus shown in Fig. 14. The composite sheet as felted has low Young's modulus because of weak cross linking forces between fibers. Through the hot forming process, however, a composite diaphragm with strong structure and light weight is produced because the synthesized pulp is melted and tightly links to the carbon fiber. Therefore, CFR-olefin diaphragm has a higher Young's modulus and stability against heat and humidity comparing to the paper cone. Fig. 15 is the scanning electron micrographs of the composite sheet before and after the heat treatment. After the heat treatment, carbon fibers are buried completely into the matrix.

Fig. 16 shows the relation between Young's modulus and density of the CFR-olefin diaphragm and the weight content of carbon fiber. Fig. 17 shows the variation of internal loss by the weight content. Taking account of the above mentioned results and the formability, 20wt% of carbon fiber content seems optimum. Table 1 indicates the physical properties

of CFR-olefin diaphragm at 20 wt% of carbon fiber. CFR-olefin diaphragm has three times larger specific Young's modulus comparing to that of paper cone.

3.1.2 Characteristics of loudspeakers with CFR-olefin diaphragms

Fig. 18 shows a comparison of sound pressure level frequency responses of 10cm cone type loudspeakers with the same shape CFR-olefin diaphragm and paper cone.

By the use of CFR-olefin diaphragm, a flat frequency response and a low harmonic distortion characteristic have been realized.

3.2 Polymer-graphite composite diaphragm

Tsukagoshi et al. have developed polymer-graphite (PG) composite diaphragm having a graphite-like structure and a high Young's modulus⁽⁵⁾. The structure is based on completely different idea from that of other conventional fiber reinforced plastics.

3.2.1 Production process

Graphite is one form of the carbon crystal and has a laminar structure. The layers of the laminar structure consist of strongly linked many hexagonal rings of carbon atoms as shown in Fig. 19. And this structure gives an extremely high Young's modulus. Because graphite is easily exfoliated between the layers by applying shearing forces, thin graphite flakes can be easily produced. The graphite-like structure has been realized in PG composite by orienting the graphite flakes parallel to the surfaces of the diaphragm. Polyvinylchloride was selected as a matrix, because it can strongly adhere graphite flakes by a strong polarity, inspite of poor adhesiveness of graphite.

Fig. 20 shows the flow chart of the production process of PG composite diaphragms. The most important processes are mixing and orientation. In the mixing process, delamination of the graphite flakes is caused by strong sheering force applied to PG composite material, consequently fresh and active surfaces of the graphite flakes can be rigidly bound with polyvinylchloride. In the orientation process, through repeated rollings, the graphite flakes are oriented parallel to the surfaces of a PG composite sheet, and results in a graphite-like structure and a high specific Young's modulus. Various shapes of loudspeaker diaphragms can be produced from PG composite sheets by vacuum forming.

Fig 21 shows the relation between Young's modulus of a PG composite sheet and mixing ratio of graphite to polyvinylchloride matrix by weight. Considering the above results and the formability, optimum mixing ratio is about two. A PG composite sheet has a higher sound velocity than that of titanium or aluminum and has a comparable internal loss to that of a cone paper as shown in Table 1.

Fig. 22 shows the relation between Young's modulus and the orientation of graphite flakes. Reed specimens are prepared by slicing at various inclined angles θ from the surface of a block produced by lamination of PG composite sheets. This figure shows that a specimen parallel to the surface has the maximum Young's modulus. The scanning electron micrograph of the fracture cross section of a PG composite sheet is shown in Fig. 23. A laminar structure parallel to the surface is observed. According to the above mentioned results, it was confirmed that the high Young's modulus of the PG composite sheet is originated from the extremely high orien-

tation of graphite flakes. Fig. 24 shows the decay patterns of free vibration of PG composite, aluminum and cone paper reed. The decay of vibration in PG composite is faster than that in aluminum and is comparable to that in cone paper. Therefore, it is apparent that PG composite has a relatively large internal loss.

3.2.2 Characteristics of loudspeakers with Polymer graphite composite diaphragm

Because PG composite has a good formability, it can be formed into various shapes and sizes of diaphragms for either low frequency or high frequency loudspeakers.

Fig. 25 shows a 40cm low frequency loudspeaker using a PG cone with corrugations and a PG dust cap. Fig. 26 shows a comparison of sound pressure level frequency responses of 40cm low frequency loudspeakers with the same shape PG composite diaphragm and paper cone. The low frequency loudspeaker with PG composite diaphragm realizes flat frequency response and lower harmonic distortion.

Fig. 27 shows a comparison of sound pressure level frequency responses of 2.5cm dome type high frequency loudspeakers with the same shape PG composite diaphragm and titanium one. High frequency resonance of the loudspeaker with PG composite diaphragm is about 20% higher than that with titanium diaphragm. This ratio is proportional to the ratio of sound velocities of both materials. The peak in the frequency response of the loudspeaker with PG composite diaphragm at the high frequency resonance almost disappears.

As discussed above, by the use of PG composite, superior diaphragms with high specific Young's modulus, large internal loss, and stability against humidity can be obtained in various shapes and sizes at a lower cost comparable to paper cone.

4. CONCLUSION

This paper presents the production processes, physical properties and performances of the newly developed diaphragms in Japan, such as beryllium diaphragm, boronized titanium diaphragm, and carbon fiber reinforced olefin diaphragm and polymer-graphite composite diaphragm.

The former two diaphragms are suitable for mid-range and high frequency loudspeaker because of their high specific Young's modulus. The latter two are applicable to various loudspeakers because of their high specific Young's modulus and relatively large internal loss. In the latter two materials, specific sheets such as carbon fiber reinforced olefin sheets and polymer-graphite composite sheets are produced at first, and then the sheets are formed into diaphragms with various shapes and sizes.

Polymer-graphite diaphragms furnish loudspeakers which can respond faithfully to pulsive signals included in digital audio signals without a delay or a distortion. This means the loudspeaker can produce high fidelity sounds. Moreover, the polymer-graphite diaphragms can offer loudspeakers which would be necessary in the future digital audio era.

However, newer materials and structures for loudspeaker diaphragms which have lighter weight and larger flexural rigidity should be developed continuously.

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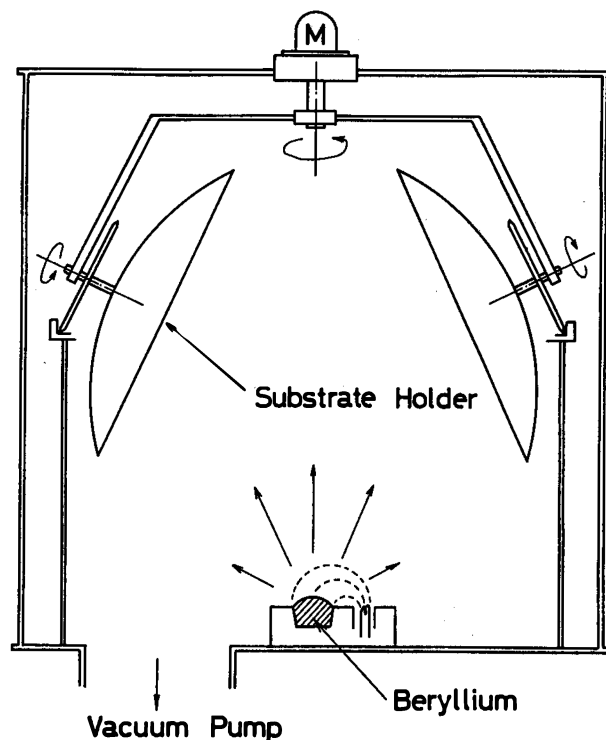


Fig. 1 Vacuum deposition apparatus for mass production of beryllium diaphragms.

Table 1 Physical properties of materials for diaphragms.

Material	Young's modulus $E, \times 10^{10} \text{N/m}^2$	Density $\rho, \times 10^3 \text{kg/m}^3$	Specific modulus $E/\rho, \times 10^7 (\text{m/s})^2$	Sound velocity $\sqrt{E/\rho}, \times 10^3 \text{m/s}$	Internal loss $\tan \delta, -$	Melting point $^{\circ}\text{C}$
Beryllium	28	1.85	15	12	0.002	1284
Boron	40	2.34	17	13	0.002	2225
Aluminum	7.0	2.7	2.6	5.1	0.002	660
Titanium	10	4.5	2.2	4.7	0.002	1668
Boronized titanium	25	4.5	5.6	7.5	0.002	
Carbon fiber	23	1.74	13	11.5		
CFR-olefin	0.37	0.45	0.82	2.9	0.025	
Polymer-graphite	7.0	1.8	3.9	6.2	0.05	
Cone paper	0.1~0.2	0.5	0.2~0.4	1.4~2.0	0.02~0.05	
Graphite Glass	35	1.4	25	5.0	.005	

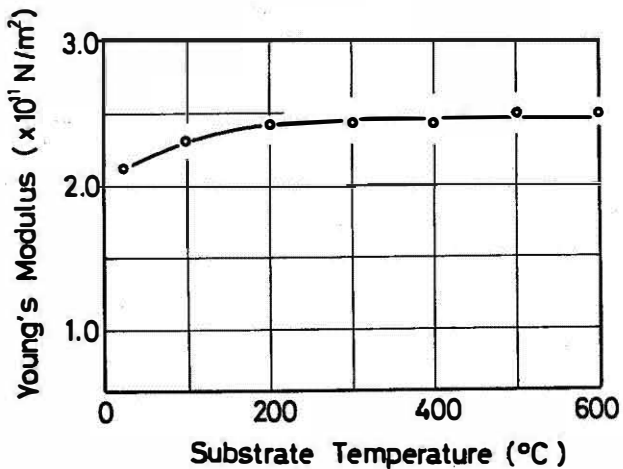


Fig. 2 Relation between substrate temperature and Young's modulus of beryllium diaphragm.

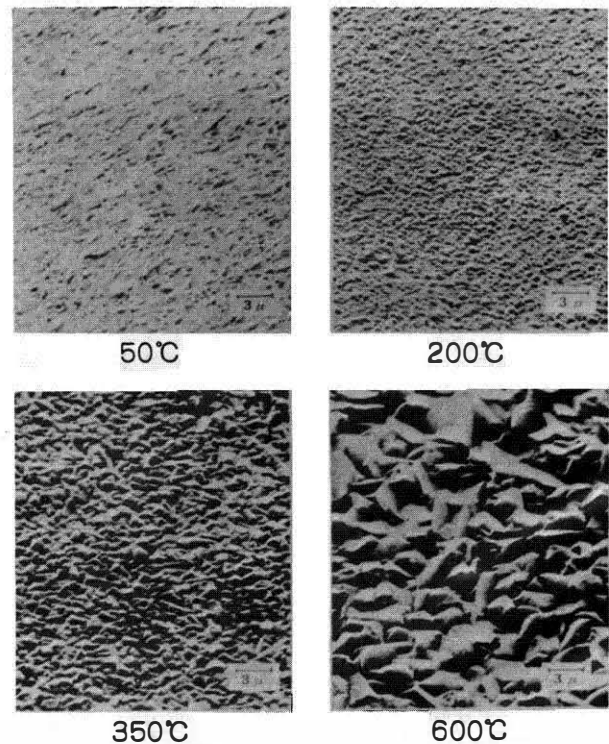


Fig. 3 Scanning electron micrographs of deposited beryllium surfaces at various substrate temperatures.

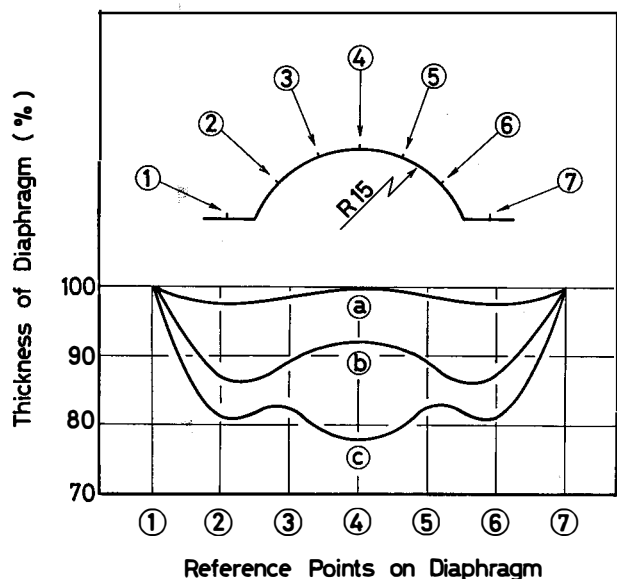


Fig. 4 Thickness variation over diaphragms.

- a) Deposited beryllium diaphragm.
- b) Pressed aluminum diaphragm.
- c) Pressed beryllium diaphragm.

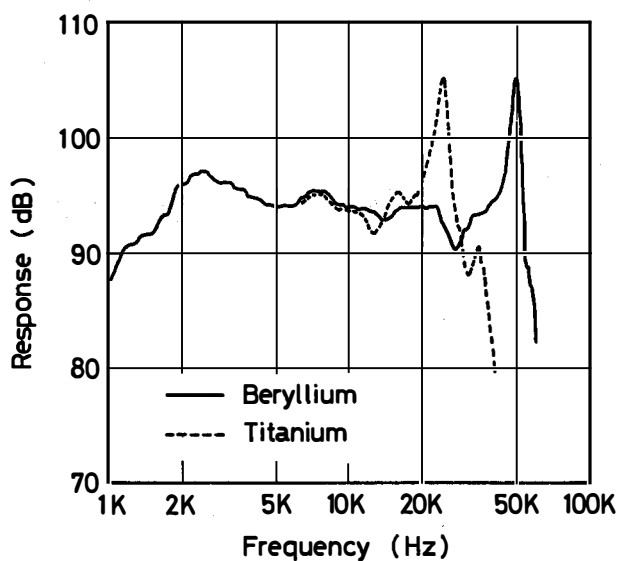


Fig. 5 Comparison of sound pressure level frequency responses of 2.5cm dome type high frequency loudspeakers with beryllium diaphragm (a), and titanium diaphragm (b).

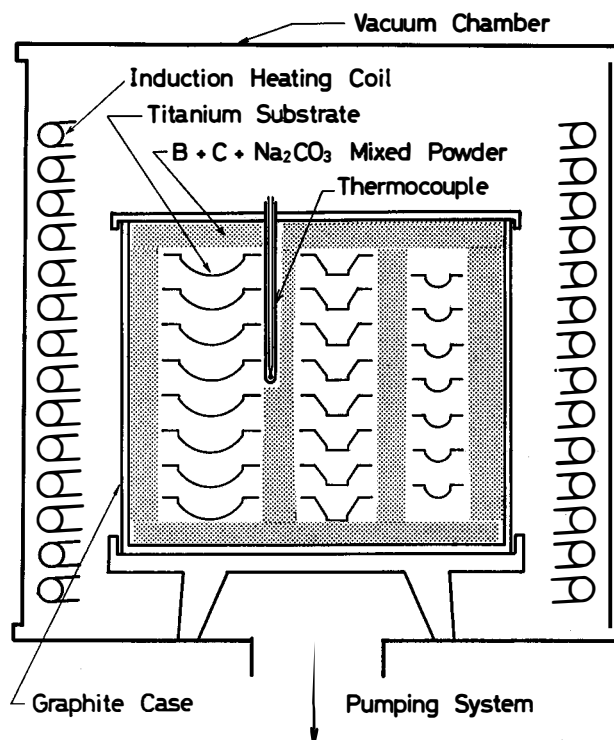


Fig. 6 Apparatus for production of boronized titanium diaphragms.

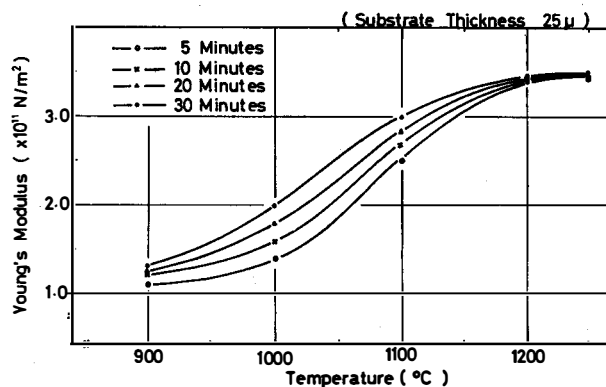


Fig. 7 Young's modulus of 25μm-thick boronized titanium diaphragm as function of treating temperatures and treating times.

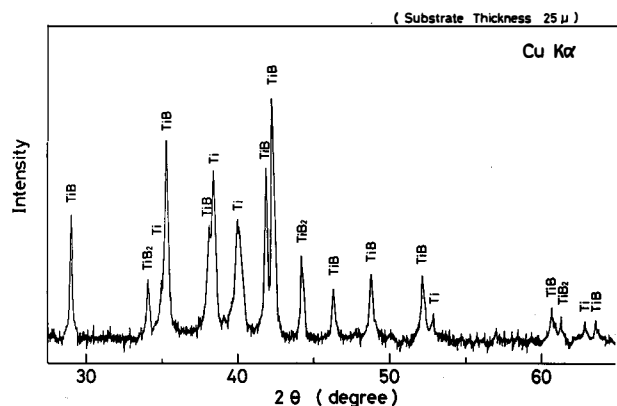


Fig. 8 X-ray diffraction pattern of boronized titanium diaphragm at 1200°C for 10 minutes.

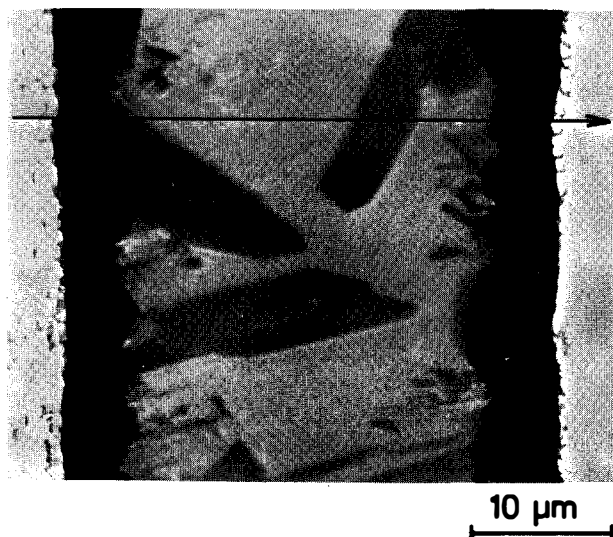


Fig. 9 Scanning electron micrograph of cross section of boronized titanium (1200°C, 10 min.).

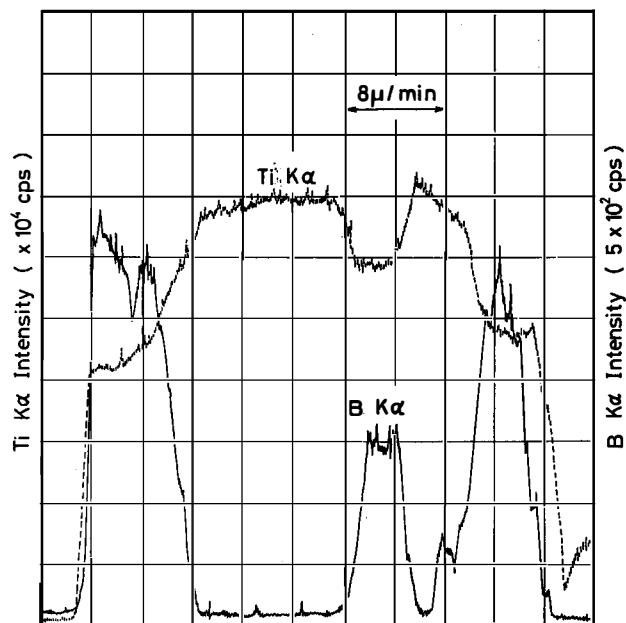


Fig. 10 Atomic analysis of boron and titanium by electron probe microanalyzer along the line marked on Fig. 9.

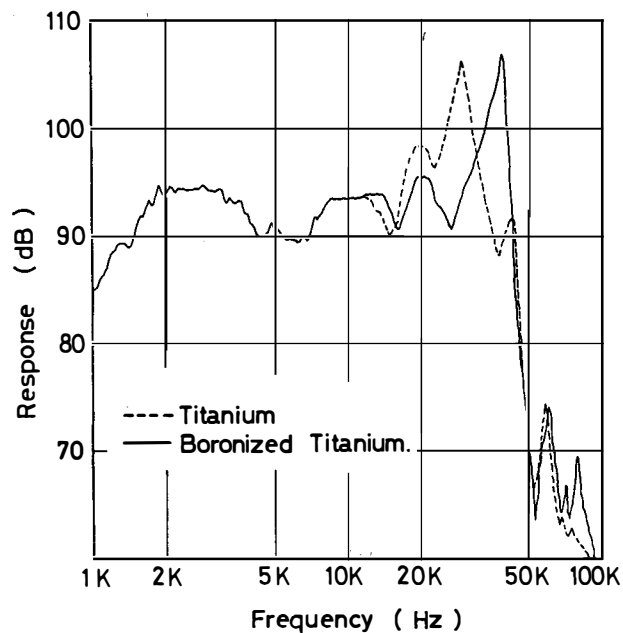


Fig. 11 Comparison of sound pressure level frequency responses of 2.5cm dome type high frequency loudspeakers with boronized titanium diaphragm (a), and titanium diaphragm (b).

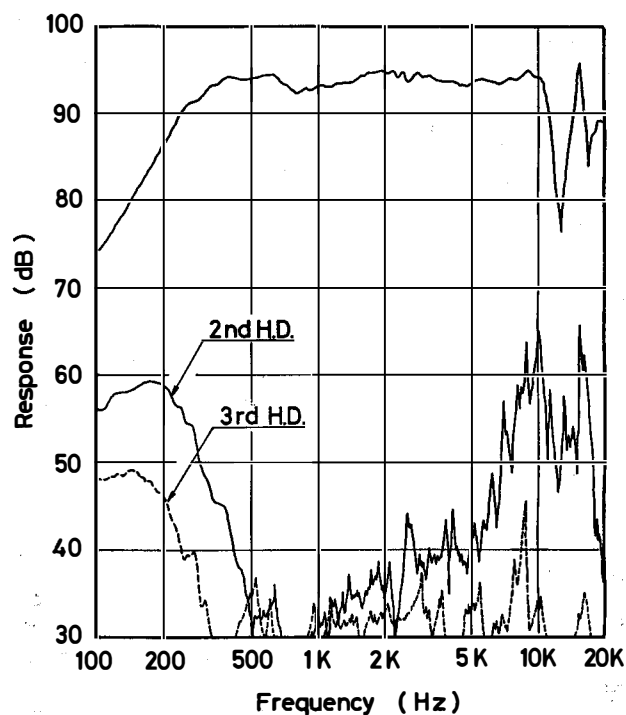


Fig. 12 Sound pressure level frequency response of 12cm cone type mid-range loudspeaker with boronized titanium diaphragm.

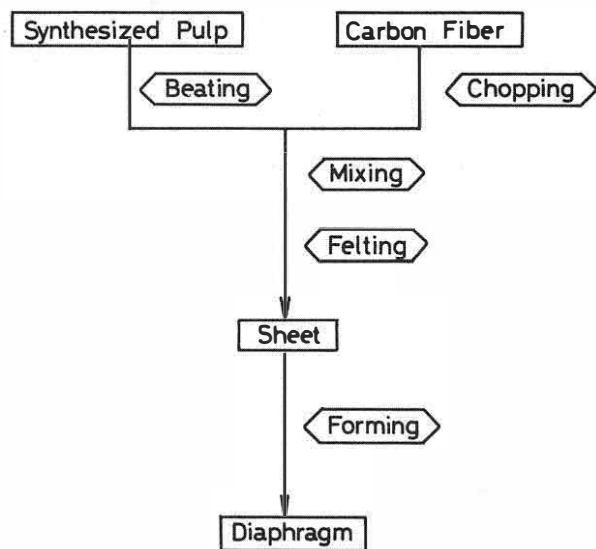


Fig. 13 Flow chart of mass production process of CFR-olefin diaphragms.

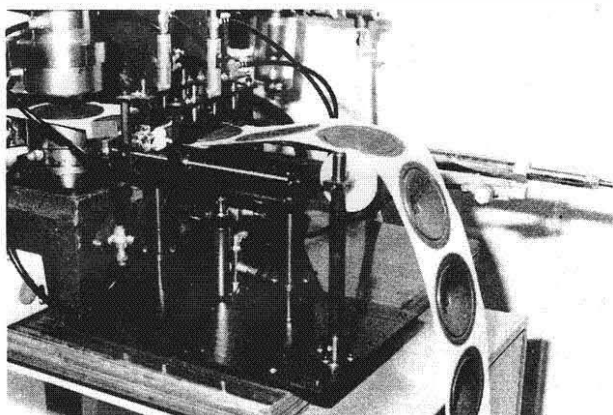


Fig. 14 Continuous mass production apparatus of CFR-olefin diaphragms.

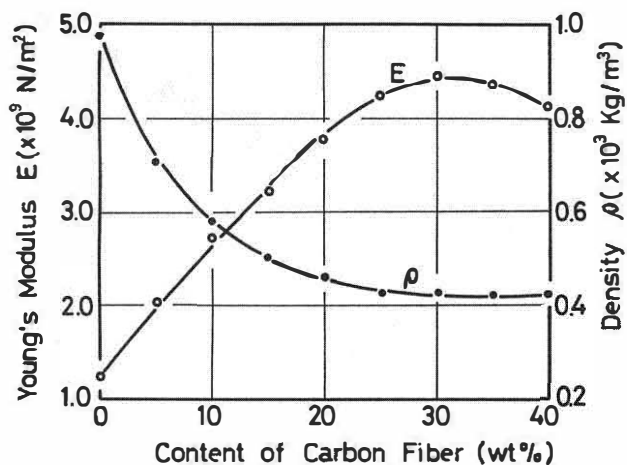
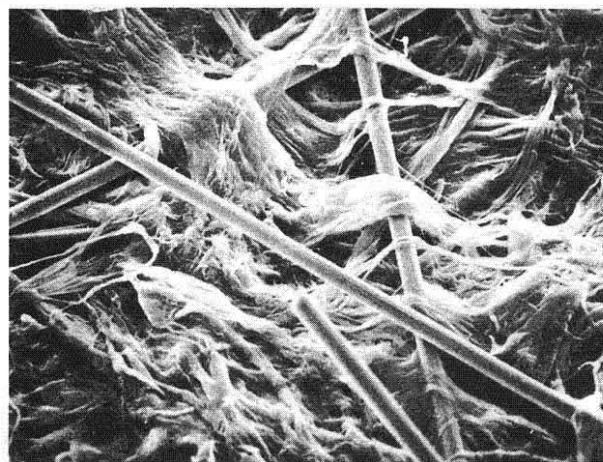
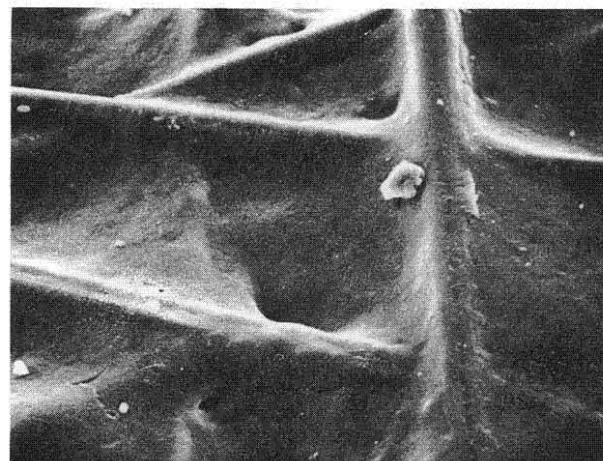


Fig. 16 Relation between Young's modulus and density of CFR-olefin diaphragm, and weight content of carbon fiber



a) Before heat treatment



b) After heat treatment

Fig. 15 Scanning electron micrographs of CFR-olefin sheets before (a), and after heat treatment (b).

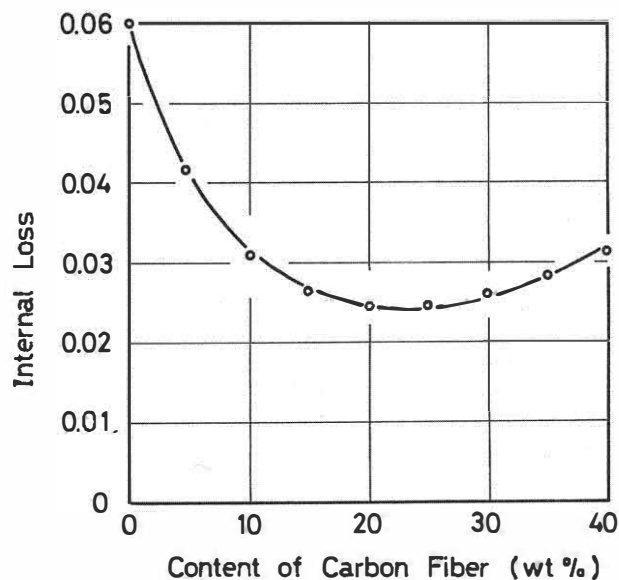


Fig. 17 Relation between internal loss of CFR-olefin diaphragm and weight content of carbon fiber.

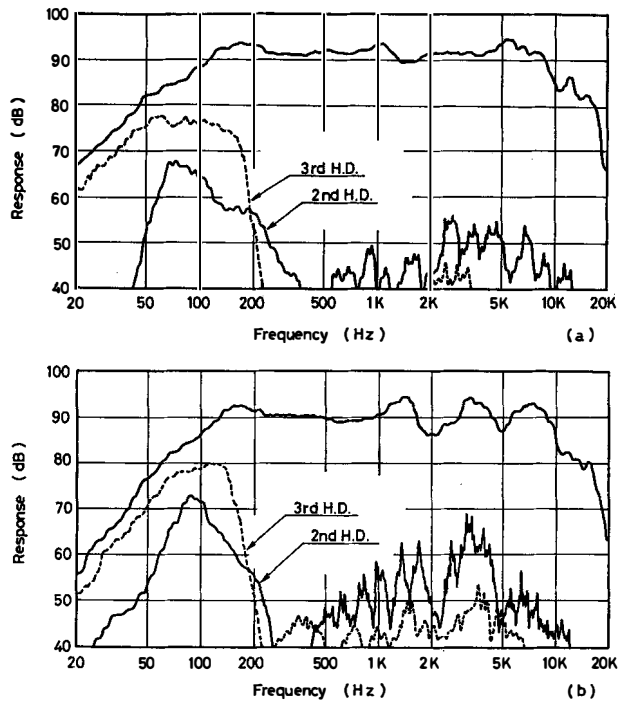


Fig. 18 Comparison of sound pressure level frequency responses of 10cm cone type loudspeakers with CFR-olefin diaphragm and paper cone.

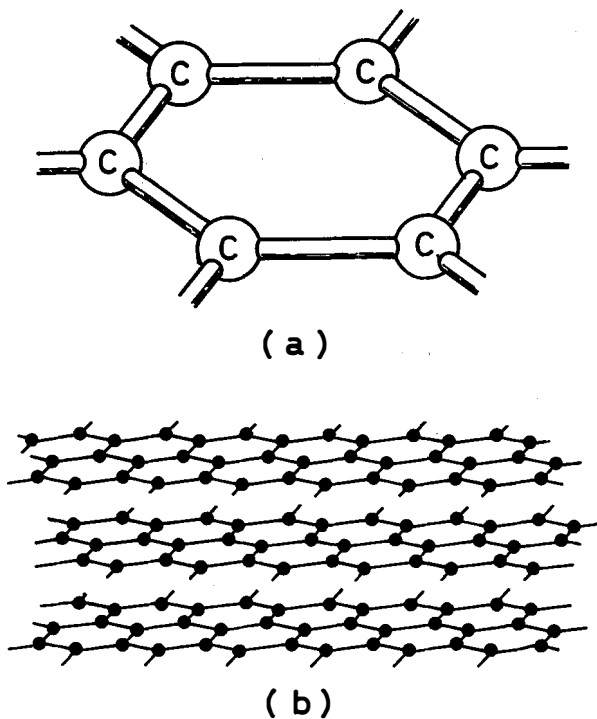


Fig. 19 Schematic models of bonding of carbon atoms (a), and laminar structure of graphite crystal (b).

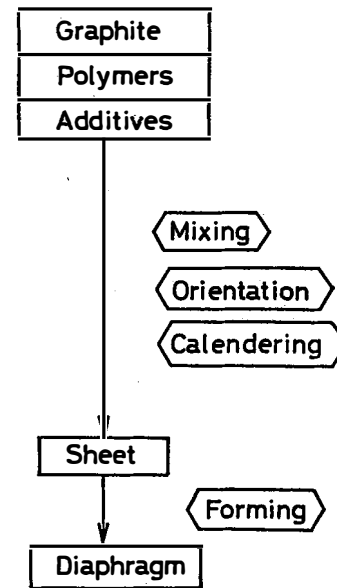


Fig. 20 Flow chart of PG composite diaphragm production.

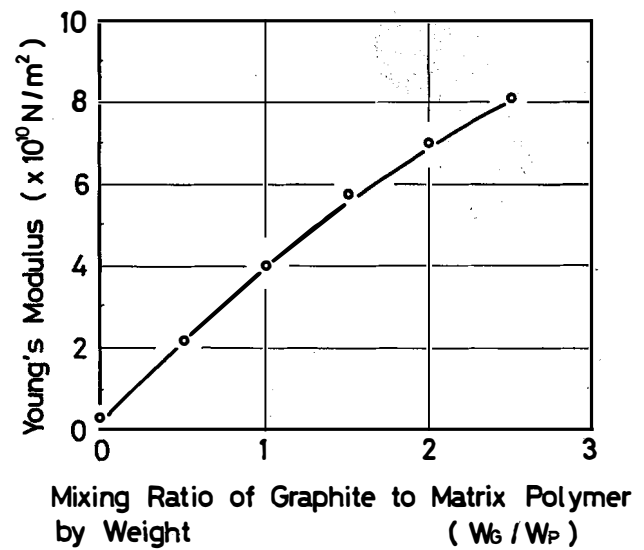


Fig. 21 Relation between Young's modulus of PG composite sheet and mixing ratio of graphite to PVC matrix by weight.

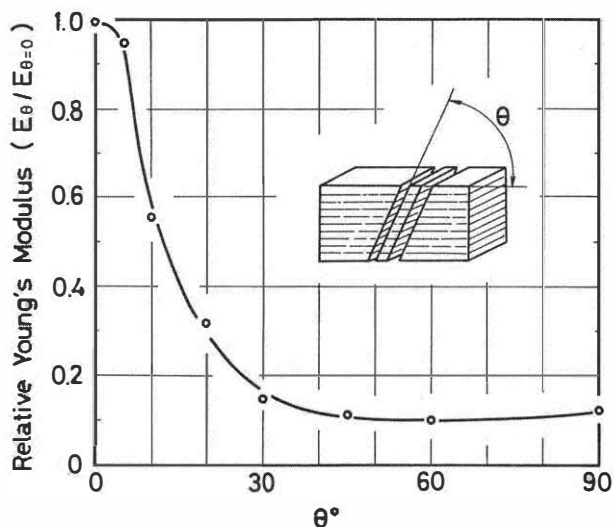


Fig. 22 Variation of Young's modulus by orientation of graphite flakes.

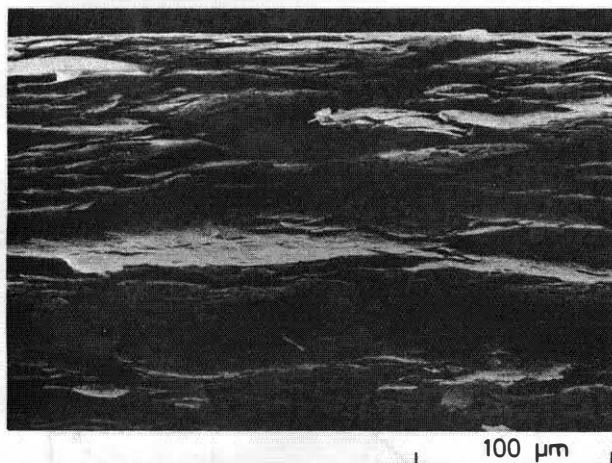


Fig. 23 Scanning electron micrograph of fracture cross section of PG composite sheet.

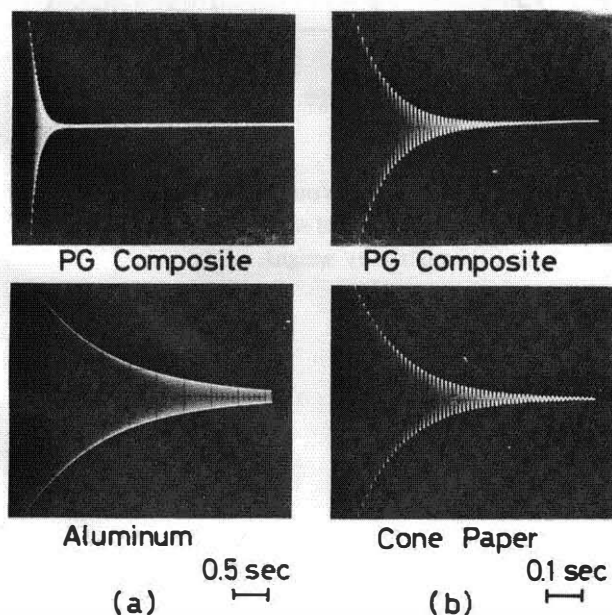


Fig. 24 Comparison of decay patterns of free vibration.
(a) PG composite and aluminum
(b) PG composite and cone paper



Fig. 25 40cm low frequency loudspeaker with PG composite diaphragm.

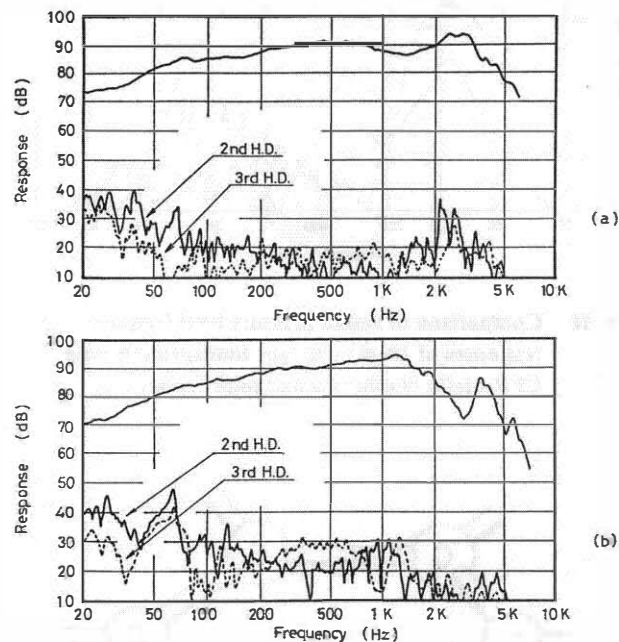


Fig. 26 Comparison of sound pressure level frequency responses of 40cm low frequency loudspeakers with PG composite diaphragm (a), and paper cone (b).

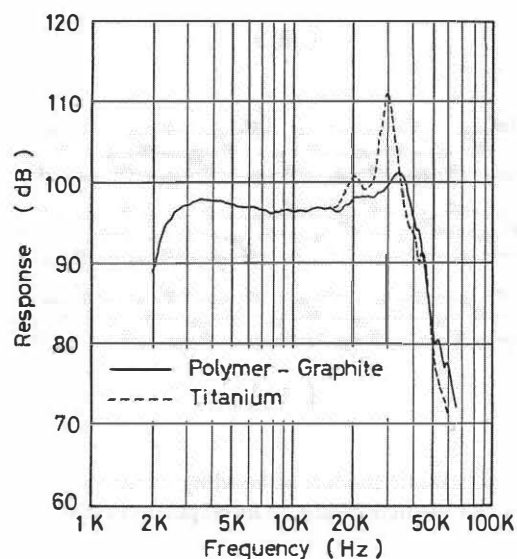


Fig. 27 Comparison of sound pressure level frequency responses of 2.5cm high frequency loudspeakers with PG composite diaphragm (a), and titanium diaphragm (b).

[54] **METHOD OF PRODUCING A CARBON
DIAPHRAGM FOR AN ACOUSTIC
INSTRUMENT**

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[52] U.S. Cl. **423/445; 181/167;**
264/29.1; 264/29.7; 423/448; 423/449

[58] Field of Search **423/445, 448, 449;**
264/29.1, 29.5, 29.6, 29.7; 181/167, 157, 173

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Marmelstein & Kubovcik

[57] **ABSTRACT**

A method of producing a diaphragm of an acoustic instrument having the steps of blending powders of carbon such as graphite, carbon black or the like and a thermoplastic or a thermosetting resin, shaping the resultant blend into a desired form and then carbonizing the shaped blend. As a result, it has become possible to produce a diaphragm of an acoustic instrument, having a light weight, high rigidity and a large ratio of Young's modulus to density.

22 Claims, 2 Drawing Figures

METHOD OF PRODUCING A CARBON DIAPHRAGM FOR AN ACOUSTIC INSTRUMENT

BACKGROUND OF THE INVENTION

The present invention relates to a method of producing a diaphragm of an acoustic instrument, having a low density and a high elasticity. More particularly, the invention is concerned with a method of easily producing the diaphragm of an acoustic instrument, the method including blending and kneading plastic and carbon powders with each other, shaping the blend, and carbonizing the shaped blend by heating.

Generally speaking, the diaphragms of acoustic instruments, particularly the diaphragm of a speaker is required to have light weight, large rigidity and a large ratio E/ρ of Young's modulus E to density ρ , so that it may reproduce the acoustic signal efficiently over a wide range of frequency and at a high fidelity.

For this reason, conventionally, wood pulps, plastics, aluminum, titanium and the like materials have been used as the material of the diaphragm. These conventional materials, however, could not fully meet the above requirements.

Also, it has been proposed and actually carried out to make use of carbon materials. One of these carbon materials is a composite material of carbon fibers and a plastic. This composite material, however, cannot provide sufficient rigidity, when it is formed into a tabular forms of diaphragm, partly because of insufficient binding of carbon fibers attributable to the lubricating nature of the surface of carbon fiber itself, and partly because of the large anisotropy of the carbon fibers.

Under these circumstances, the present inventors have proposed a diaphragm composed of carbonized or graphitized plastic, so as to make the most of the advantages of carbon as the diaphragm material, i.e. light weight, high rigidity and large ratio of Young's modulus E to the density ρ .

It is difficult, however, to carbonize or graphitize the plastic while preserving the shape of the diaphragm. At the same time, a high orientation which would ensure a high elasticity cannot be obtained unless a suitable tension is applied to the diaphragm material. In addition, the diaphragm material inconveniently exhibits a large distortion in the course of carbonization or graphitization, resulting in cracking of the diaphragm.

SUMMARY OF THE INVENTION

It is therefore a major object of the present invention to eliminate the drawbacks of the conventional methods of producing a diaphragm.

More specifically, it is an object of the invention to provide a method of producing a diaphragm of an acoustic instrument, by carbonizing or graphitizing of a plastic, in which the undesirable distortion of the diaphragm material in the course of the carbonizing or graphitizing is conveniently avoided, while preserving the advantages as the material of diaphragm of acoustic instrument, i.e. the light weight, high rigidity and large ratio E/ρ of Young's modulus to density.

To this end, according to the present invention, there is provided a method of producing a diaphragm of an acoustic instrument having the steps of blending and kneading carbon powders and a plastic, shaping the blend into a desired form, and carbonizing the shaped blend.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a block diagram showing the steps of the process in accordance with an embodiment of the invention; and

FIG. 2 is a chart showing the frequency characteristic of the diaphragm produced in accordance with the method of the invention, in comparison with that of a beryllium diaphragm.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to obtain a carbon material having a large Young's modulus and high mechanical strength, for use as the material of a diaphragm of an acoustic instrument, it is necessary to carbonize a raw material having a high carbon content. However, it is difficult to carbonize PVC material shaped into the form of a diaphragm, without being accompanied by distortion of the material, if the PVC is used solely. At the same time, for obtaining a high elasticity, it is necessary to enhance the graphite orientation by imparting a suitable tension to the material during carbonizing.

Since the PVC material shaped into the form of a diaphragm is likely to be distorted during carbonizing, when the PVC material is used solely, it becomes necessary to add solid powders to the PVC material. The solid powder for this purpose is most preferably powdered graphite. The addition of graphite offers the following advantages.

(1) It is possible to prevent shrinkage and distortion which are liable to occur in the preparatory baking and carbonizing.

(2) The graphite powders are orientated during the blending of the PVC and powdered graphite, so that the Young's modulus and mechanical strength are considerably improved.

(3) Carbons of goods crystallinity can be obtained, because the graphite powders constitute a nucleus of the crystals, so that Young's modulus and the mechanical strength after carbonizing are considerably improved.

In general, carbon black and carbon fiber can be used as the material added before carbonization. The carbon black, however, cannot constitute a good nucleus because it has a poor crystallization characteristic. Carbon fiber, when used as the material added before carbonizing, is preferably graphitized. The carbon fiber may constitute a good nucleus when it is cut to a length of about 5 microns or smaller. However, it is extremely difficult to cut the carbon fiber into such short pieces. Even if possible, such fibers cut into short pieces are extremely expensive and impractical.

Hereinafter, practical embodiments of the invention will be described in more detail.

Embodiment 1

FIG. 1 shows the steps of method in accordance with a first embodiment of the invention.

Mixing and Kneading Step

Powders of graphite (scale-like graphite) of diameters ranging between 0.1 and 50 microns are added to vinyl chloride resin. The resin and graphite powders are blended and kneaded by means of a kneader or a roller at a temperature of 130° to 200° C. The rate of addition of graphite powder is 10 to 90% by weight, preferably 40 to 70% by weight. The smaller the grain size of the

graphite becomes, the better result is obtained. Thus, the grain size is preferably between 0.1 and about 5 microns. The mean grain size is preferably below 5 microns.

The blend of the vinyl chloride and powders of graphite is then sent to the subsequent step of shaping.

Shaping Step

The blend obtained is then rolled into a tabular form by means of rolls. Then, the rolled material is shaped into a desired form, e.g. dome-like or conical shape, at a temperature of its softening points, i.e., 70° to 150° C., by means of vacuum, a press, or the like.

Preparatory Baking Step

The shaped body obtained is heated in the air (oxidizing atmosphere). The temperature is raised from 80° C. at a rate of 1° to 20° C. per hour up to a temperature of 250° to 300° C., so as to oxidize the shaped body at least at the surface thereof, thereby to make the surface infusible, so that the shaped body may not be distorted in the next step of carbonizing. This treatment for making the material infusible may include a preparatory step of heating at 50° to 80° C. in ozone for 4 to 5 hours, before heating in the air.

In order to avoid a slightest possibility that the shaped body may be distorted during the heating in this step, the shaped body may be held during heating by a jig made of a metal gauze wire or a punched thin metallic web, or between jigs.

A good result is obtained by a heating for 10 hours or longer.

Carbonizing Step

The shaped body after the preparatory baking is then carbonized by heating at 1000° to 1500° C. for one hour, in a non-oxidizing atmosphere such as nitrogen, argon or the like gas. It is necessary to take a preheating step, before the shaped body is heated up to the above-mentioned carbonizing temperature. The rate of increase of the temperature at early stage has to be controlled. Preferably, the heating is made at a small rate of 1° to 20° C./hour, until the shaped body is heated to 400° C., and, thereafter, at a rate of 10° to 100° C./hour.

This small rate of temperature increase at the early stage ensures a carbide having good property, because the coarsening of the structure, which would reduce the Young's modulus and mechanical strength, is prevented by controlling the rate of temperature increase before the shaped material is heated to 400° C. After the temperature is raised beyond 400° C., the rate of temperature rise may be economically selected, because the undesirable coarsening of the structure is less likely to take place at temperatures beyond 400° C.

At the same time, in order to prevent distortion of the shaped body during carbonizing, it is preferable to mount the shaped body on a jig made of carbon or the like material having a high melting point and the desired shape, or to hold the shaped body between similar jigs, during carbonizing.

The carbonized body is directly used as the diaphragm or, as desired, subjected to processing such as removal of burrs or boring, so as to make a complete diaphragm.

The diaphragm produced from vinyl chloride resin in accordance with the method of the present invention exhibits, a specific modulus of elasticity E_p which is about 5 times as large that of a diaphragm made of

aluminum, but slightly below that of a beryllium diaphragm.

At the same time, the diaphragm produced by the method of the present invention has an internal loss which is about 10 times as large that of the beryllium diaphragm. FIG. 2 shows the frequency characteristic of the diaphragm produced in accordance with the method of the invention as full line curve, in comparison with that of a beryllium diaphragm shown as broken line curve. The diaphragm of the present invention provides a resonance frequency at a high frequency range substantially equivalent to that of the beryllium diaphragm and flat pattern of frequency characteristic, which ensures a good frequency characteristic at a high frequency range and a superior total frequency response characteristic of the diaphragm.

	Young's modulus E Kg/mm ²	Density ϕ g/cm ³	Specific modulus of elasticity $E/\phi \times 10^3 \text{cm}$
Aluminum	7400	2.7	2.8
Beryllium	28000	1.8	15.5
Carbonized blend of PVC & powdered graphite	16000	1.6	10.6

Embodiment 2

A second embodiment of the invention will be described hereinafter. In the mixing and kneading step of this second embodiment, graphite powders of grain sizes of 1 to 100 microns are used as the carbon powders, while vinyl chloride is used as the plastic material. More specifically, the composition of the blend includes 20 parts by weight of graphite powders, 30 parts by weight of vinyl chloride, 10 parts by weight of plasticizer (dioctyl phthalate) and 50 parts by weight of solvent (methyl ethyl ketone), and is well blended and kneaded.

In the shaping step, the shaping of the blend into the desired form, e.g. dome or conical form, is made by means of a mold at a room temperature. Thereafter, the blend is allowed to stand or subjected to heat for drying.

In the preparatory baking step, the shaped body and the mold is put into a furnace and heated gradually up to 300° C. taking 35 hours.

Finally, carbonizing is effected by heating at 1000° C., 1 hour, in a non-oxidizing atmosphere such as argon, nitrogen or the like.

The diaphragm thus produced exhibits an extremely small distortion during carbonizing as compared with that made of only a plastic, i.e. containing no carbon, and has a density of 1.54 g/cm³ and Young's modulus of 16,000 Kg/mm². Consequently, the reproduceable frequency range is widened and the distortion is reduced over the entire frequency range, so as to ensure a superior reproduceability to that of the conventional diaphragm material.

Further, this diaphragm was graphitized by heating for 5 minutes at 2400° C., in an inert atmosphere, together with a graphite mold for preventing distortion. As a result, a diaphragm exhibiting a superior characteristic, having larger density has 1.8 g/cm³ and Young's modulus of 18,000 Kg/mm² was obtained.

Embodiment 3

A third embodiment of the invention will be described hereinafter.

According to this embodiment, the blend material consists of 20 parts by weight of graphite of grain size of 1 to 100 microns, 10 parts by weight of vinyl chloride resin, 1 part by weight of plasticizer (D.O.P.) and 0.2 part by weight of stabilizer (lead stearate). The blending and kneading is done by means of rolls at a temperature of softening point (a temperature which would not cause decomposition i.e. 130° to 200° C.).

In the subsequent shaping step, the blend is rolled into tabular form, as is the case of the first embodiment, so as to improve the graphite orientation, and then is shaped in conical form by means of a vacuum at the same temperature as in the preceding step. Then, the preparatory baking is effected by heating up to 300° C. in air or oxidizing atmosphere, so as to make the shaped body infusible. In the final step of carbonization, a heating is made for 1 hour at 1000° to 1200° C., under a non-oxidizing atmosphere, so as to carbonize the shaped body. A carbonizing heating temperature below 1000° C. cannot provide a sufficiently large Young's modulus, while a temperature exceeding 1200° C. cannot provide any remarkable effect over that provided by the carbonizing temperature of 1200° C. In this embodiment, the above-stated carbonization may be substituted by a graphitization occurring 5 minutes heating at 2000° to 2500° C. The diaphragm thus produced by carbonization has a Young's modulus of 16,000 Kg/mm² and a density of 1.6 g/cm³. On the other hand, the diaphragm produced by graphitization has a Young's modulus of 25,000 Kg/mm² and a density of 1.8 g/cm³.

Embodiment 4

A fourth embodiment of the invention will be described hereinafter. In the blending step, 10 parts by weight of furan resin, 20 parts by weight of graphite and 0.2 part by weight of hardening agent are blended and kneaded by means of a kneader. Thereafter, the blend is shaped at a temperature of 150° C. or so, by means of a mold. In the carbonizing step, the shaped body was heated at 1200° C. for 1 hour, within a non-oxidizing atmosphere. Young's modulus E of 10,000 Kg/mm² and density of 1.7 g/cm³ were obtained.

In this embodiment, it is not necessary to take the step of preparatory baking for making the shaped body infusible, because the plastic used is a thermosetting resin.

The plastic as used in the method of the present invention should have a high carbon content, whether it may be a thermoplastic or thermosetting resin. Thus, in addition to the described vinyl chloride, styrol, silicone and other vinyl resins are advantageously used as the plastic material. Further, it is possible to use, solely or in combination, acryl, phenol, furan, urea, and other resins.

As acryl resin, 10 to 90% by weight of polymethyl methacrylate (PMMA) is blended with 90 to 10% by weight of graphite and kneaded. After kneading, the blend is shaped at a temperature of 140° to 150° C. A preparatory baking and carbonizing are effected under the same condition as in Embodiment 3.

As silicone resin, 10 to 90% by weight of trimethylchlorosilane compound is blended with 90 to 10% by weight of graphite. The blend is shaped by means of a mold having a molding pressure of 70 Kg/cm² at a temperature of 110° to 120° C. for less than 10 minutes.

Carbonizing is effected under the same condition as in Embodiment 3.

As phenol resin, 42 to 45% by weight of phenolformaldehyde resin (novolak) is blended with 42 to 45% by weight of graphite and 10 to 16% by weight of hardening agent (hexamethylenetetramine). The blend is shaped at a temperature of 100° to 110° C. by means of a mold having a molding pressure of 5 to 10 Kg/cm². Carbonizing is effected under the same condition as in Embodiment 3.

As urea resin, about 35% by weight of dimethylol urea and about 35% by weight of monomethylol urea are blended with about 30% by weight of graphite. The blend is shaped by means of a mold having a molding pressure of 100 to 300 Kg/cm² for one minute at a temperature of 130° to 150° C. Carbonizing is effected under the same condition as in Embodiment 3.

As furan resin, 10 to 90 parts by weight of furfuryl alcohol is blended with 90 to 10 parts by weight of graphite. The blend is shaped in a soft condition by adding 1 to 2 parts by weight of sulfonic acid at a temperature of about 30° C., by means of a mold having a molding pressure of 5 to 10 Kg/cm² for 24 hours. Thereafter, the temperature is raised up to 80° C. and it is allowed to stand for 24 to 48 hours. Carbonizing is effected under the same condition as in Embodiment 3.

It is possible to use carbon black as the material of the carbon powder.

The kinds of plasticizer, solvent and so forth are suitably selected in consideration of the kind of the plastic. Also, the condition of heat treatment for carbonizing or graphitizing is suitably adjusted and changed in view of the composition of blend of the plastic, plasticizer and solvent.

As has been described, according to the production method of the present invention, the distortion of the the plastic in the preparatory baking and carbonizing steps can be avoided, and dome or conical diaphragms for acoustic instruments such as speaker, microphone and so forth can be produced with high precision and good yield. In addition, since the powder material used for the production consists of carbon, it is possible to adopt a high heating temperature in the course of the graphitizing, so that the Young's modulus E or the specific modulus of elasticity E/ ρ is considerably increased to ensure a good frequency characteristic of the diaphragm.

What is claimed is:

1. A method of producing a diaphragm of an acoustic instrument comprising the steps of blending and kneading scale-like graphite powder and a thermoplastic resin with each other, rolling the resulting blend into a plate form to orient the graphite, making the plate form infusible by baking the form, and carbonizing the rolled blend, thereby producing a diaphragm which is substantially distortion-free and has a high specific modulus of elasticity.

2. A method as claimed in claim 1, wherein said scale-like graphite powder has a grain size of 0.1 to 100 microns.

3. A method as claimed in claim 1, wherein said scale-like graphite powder has a grain size of 0.1 to 5 microns.

4. A method as claimed in claim 1, wherein said blend includes 10 to 90 parts by weight of graphite and 90 to 10 parts by weight of the resin.

5. A method as claimed in claim 1, wherein said blend preferably includes 40 to 70 parts by weight of graphite and 60 to 30 parts by weight of the resin.

6. A method as claimed in claim 1, wherein said thermoplastic resin is a resin selected from a group consisting of vinyl, silicone, and acryl resins.

7. A method as claimed in claim 6, wherein said vinyl resin is selected from a group consisting of vinyl chloride and styrene.

8. A method as claimed in claim 6, wherein said silicone resin includes trimethylchlorosilane compound.

9. A method as claimed in claim 6, wherein said acryl resin includes polymethyl methacrylate.

10. A method as claimed in claim 1, wherein said blend includes about 1.9 to about 25% by weight of plasticizer.

11. A method as claimed in claim 1, wherein said blend includes about 45 to about 61% by weight of solvent.

12. A method as claimed in claim 1, wherein said blend includes a stabilizer in an amount sufficient to provide the stabilizing effect.

13. A method as claimed in claim 1, wherein said carbonizing step includes a step of heating the plate form at 1000° to 1500° C. for one hour, in a non-oxidizing atmosphere.

14. A method as claimed in claim 13, wherein said baking step comprises raising the temperature in an oxidizing atmosphere at a rate of 1° to 20° C./hour up to 400° C. and at a rate of 10° to 100° C. thereafter.

15. A method as claimed in claim 1 further comprising after said rolling, shaping of said plate form by vacuum, or a press at a temperature of the softening point of the blend.

16. A diaphragm for use in an acoustic instrument, said diaphragm being made by a process comprising blending and kneading scale like graphite powder with a thermoplastic resin, rolling the resulting blend into a plate form, making the plate form infusible by baking the form and carbonizing the rolled blend wherein the graphite scales are oriented and the diaphragm is substantially distortion-free and has a high specific modulus of elasticity.

17. The diaphragm of claim 16 wherein said blend includes 10 to 90 parts by weight of graphite having a particle size of 0.1 to 100 microns and 90 to 10 parts by weight of said thermoplastic resin.

18. A diaphragm of claim 16 wherein said baking step comprises increasing the temperature in an oxidizing atmosphere at a rate of 1° to 20°/hour up to 400° C. and at a rate of 10° to 100° C. thereafter.

19. The diaphragm of claim 17 wherein said blend includes 40-70 parts by weight of graphite having a particle size of 0.1 to 5 microns and 60 to 30 parts by weight of the resin.

20. The diaphragm of claim 16 wherein said thermoplastic resin is selected from the group consisting of vinyl, silicone and acryl resins.

21. The diaphragm of claim 20 wherein said resin is selected from the group consisting of vinyl chloride, styrene, trimethylchlorosilane, and polymethyl methacrylate.

22. The diaphragm of claim 16 wherein said blend further includes about 1.9% to 25% by weight of a plasticizer and a stabilizing amount of a stabilizer.

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FIG. 1

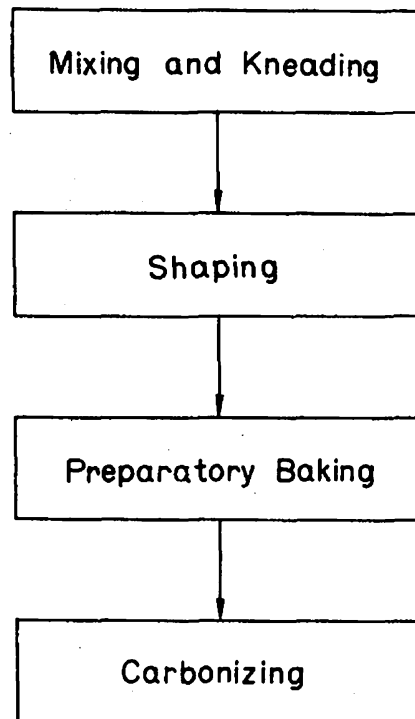
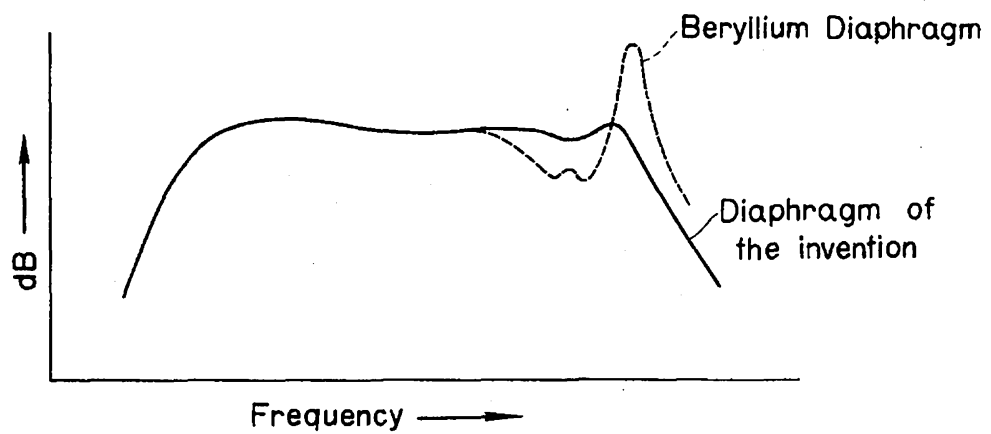


FIG. 2



[54] ARM PIPE FOR RECORD PLAYER
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[21] Appl. No.: 63,531

[22] Filed: Aug. 3, 1979

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Dec. 28, 1978 [JP]	Japan	53-161225

[51] Int. Cl.³ G11B 3/10; B29D 3/02;
D03D 43/00[52] U.S. Cl. 369/158; 138/174;
264/29.1; 264/108; 428/36[58] Field of Search 274/23 R, 1 R; 138/172,
138/174, 177; 428/36, 542; 264/108, 29.1

[56]

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Primary Examiner—William R. Dixon, Jr.

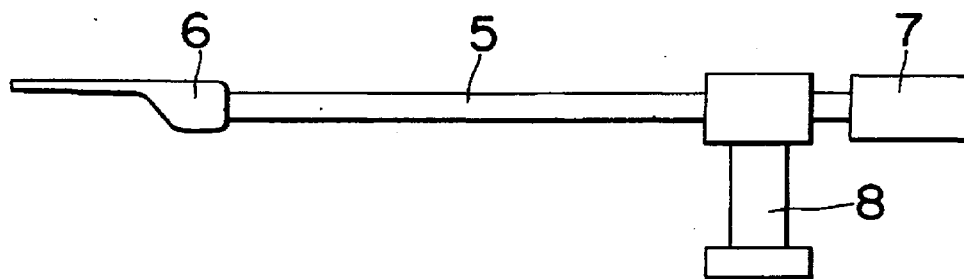
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[57]

ABSTRACT

An arm pipe for a record player tonearm comprises a composite material essentially consisting of a thermoplastic resin and graphite powder. The composite material is prepared by kneading the components, rolled to impart a degree of orientation to the graphite powder particles, which are in the form of flaky graphite and then molded into a pipe, along the surface of which the graphite particles are oriented. Arm pipes wherein the composite material is oxidized at the surface of the pipe and arm pipes wherein the composite material is carbonized or graphitized are also included. A light weight, rigid arm pipe having a high specific modulus of elasticity is obtained through a simple procedure at low cost.

8 Claims, 5 Drawing Figures



ARM PIPE FOR RECORD PLAYER TONEARMS

BACKGROUND OF THE INVENTION

This invention relates to arm pipes for record player tonearms.

The recent trend of tonearms for record players is directed toward a reduction of the mass and an increase of the compliance of a vibration system in order to enhance the trackability of a cartridge.

With the compliance of a cartridge increased, the low range resonance frequency attributable to the cartridge compliance and the equivalent mass of a tone arm (including the cartridge) at the stylus tip is reduced such that noise signals due to warpage and eccentricity of a record may be often picked up. That is, the increased compliance results in a reduced signal-to-noise ratio. It is therefore necessary to adjust low range resonance to an inoffensive level, generally to a range of 10 to 15 hertz while the stylus equivalent mass is kept low.

To reduce the equivalent mass at the stylus tip, in usual practice, tonearm component parts such as arm pipe and head shell may be reduced in weight. Parts having a wall thickness reduced for light weight exhibit a low rigidity which in turn, allows undesirable phenomena such as partial vibration to occur, resulting in deteriorated sound quality. To obtain light weight arm pipes and head shells having a high rigidity, materials are required having a high specific modulus of elasticity.

In prior art arm pipe and head shell manufacture, aluminum and titanium are used because they have a relatively high specific modulus. However, the use of a cartridge with an increased compliance requires the arm pipes and head shells to be made of material having a higher specific modulus than aluminum and titanium.

Arm pipes and head shells made of fibrous carbon are known. Fibrous carbon itself has a sufficiently high specific modulus while it cannot be formed into a part without a binder. Usually, resin is used to bind fibrous carbon. However, the addition of a resin binder to fibrous carbon causes the specific modulus of elasticity to reduce to a level equal to or less than those of aluminum and titanium. Therefore, the fibrous carbon composite material is not satisfactory as the material for arm pipes and head shells.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a high performance arm pipe made of a light weight, rigid composite material having a high specific modulus of elasticity.

According to one aspect of this invention, there is provided an arm pipe for a tonearm of a record player which comprises a composite material of a thermoplastic resin and graphite powder. The material is obtained simply by kneading the components and the graphite powder particles are oriented substantially in parallel with the surface of the pipe.

According to another aspect of this invention, the material in the form of a pipe is oxidized at least at the surface of the pipe. The material may also be carbonized.

To provide the graphite powder particles with a substantial degree of orientation, the kneaded mixture may preferably be rolled into a sheet and the sheet is then formed into a pipe.

BRIEF DESCRIPTION OF THE DRAWING

The invention will now be described in further detail by referring to the accompanying drawings wherein:

FIG. 1 is a partial cross-sectional view of a mixture of graphite particles and a resin matrix;

FIG. 2 is a partial cross-sectional view of a sheet of a composite material wherein graphite particles are oriented in a resin matrix;

FIG. 3 is an axial cross-sectional view of the arm pipe of the invention;

FIG. 4 is a cross-sectional view of the arm pipe taken along the line IV—IV in FIG. 3; and

FIG. 5 is a schematic view of a tonearm system.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The thermoplastic resins used herein include polyvinyl chloride, polyvinylidene chloride, vinyl chloride-acrylonitrile copolymers, vinylidene chloride-acrylonitrile copolymers, vinyl chloride-vinyl acetate copolymers, etc., and mixtures thereof. The resins may be changed into a pitch-like state by dry distillation before it is kneaded with graphite powder according to this invention.

The graphite powder is available from many manufacturers. Flaky graphite powder is most preferable. The graphite powder may preferably have an average particle size of less than 20 microns (inclusive), particularly 0.1 to 5 microns.

The weight ratio of resin to graphite varies from 1:9 to 9:1, preferably 3:7 to 7:3.

An example of this invention is shown below. Polyvinyl chloride (to be abbreviated as "PVC" hereinafter) is used as a typical thermoplastic resin. In a kneader, 30 parts by weight of PVC is blended and kneaded with 70 parts by weight of graphite powder at a temperature of 130°–200° C. The green intimate mixture is further mixed and rolled into a sheet at a similar temperature. This sheet exhibits a Young's modulus E of 6,000 kg/mm² (5.9×10^{10} N/m²) and a density of ρ of 1.8 g/cm³. The specific modulus of elasticity calculated in terms of $\sqrt{E/\rho}$ is 5.7×10^3 m/sec, which value is higher than the specific modulus of titanium of 5.2×10^3 m/sec. The green, but oriented sheet is formed into a pipe though the following description omits this process for the purpose of illustrating measured values.

The rolled sheet is then subjected to presintering or oxidation by gradually heating it in an oxidizing atmosphere to a temperature of 100°–500° C., preferably 250°–300° C. at a rate of 1°–10° C./hour. The oxidized product has a Young's modulus E of 9,000 kg/mm², a density ρ of 1.8 g/cm³ and a specific modulus $\sqrt{E/\rho}$ of 7.0×10^3 m/sec.

The oxidized sheet is further subjected to carbonization or graphitization by heating it in a non-oxidizing atmosphere or in vacuum to a temperature of about 1200° C. or higher at a rate of 10°–20° C./hour. The carbonized sheet exhibits a Young's modulus E of 16,000 kg/mm² and a density ρ of 1.8 g/cm³. The specific modulus of elasticity of 9.33×10^3 m/sec is about 2 times higher than those of aluminum and titanium. Graphitization of the sheet at about 2500° C. increases the Young's modulus 1.5 times to 24,000 kg/mm².

Orientation of graphite powder particles is essential to achieve the above-illustrated desired values. When PVC is kneaded with graphite powder and the resulting green mixture is formed into a desired shape by extru-

sion, for example, without an orientation procedure, the resulting product shows a poor Young's modulus. By way of example, when 30 parts of PVC was kneaded with 70 parts of graphite powder and the mixture was then extrusion molded by means of an extruder into a plate, the plate showed a Young's modulus of about 1,300 kg/mm². This value is less than a quarter of that of the graphite-oriented sheet described above. Further carbonization of this non-oriented plate resulted in a Young's modulus of about 4,000 kg/mm², which value is about 1/6 of that of the graphite-oriented one after carbonization.

Further, it has been found that the internal loss (tan δ) of the composite material according to this invention is higher than those of aluminum and titanium. The higher the internal loss, the less undesirable resonance is liable to occur.

The measurements of various properties show that the composite material of this invention has a relatively light weight, a high rigidity, a high specific modulus of elasticity, and a good internal loss.

As described above, to fabricate an arm pipe without impairing the characteristics of the composite material according to this invention, graphite powder particles must be oriented in the resulting arm pipe. In this respect, extrusion molding which is generally used in prior art arm pipe manufacture is not applicable because graphite particles are not substantially oriented so that molded products are less rigid.

Referring to FIG. 1, a fragmental portion of a kneaded or intimate mixture is shown wherein a resin matrix 1 contains graphite flakes 2 at random. The graphite particles in the form of a flake may be considered as a disc having a high ratio of diameter to thickness. The intimate mixture shows a random distribution of graphite flakes 2 in the resin matrix 1.

The intimate mixture is then rolled into a sheet at elevated temperatures by means of rollers, presses or the like. FIG. 2 shows a rolled sheet 3 wherein graphite flakes 2 are oriented in parallel with the surface of the sheet 3. Rolling is a typical, but non-limiting treatment for imparting a substantial degree of orientation to graphite particles. The thickness of the sheet 3 may suitably be selected in accordance with a desired wall thickness of an arm pipe.

Thereafter, the sheet 3 is rounded into a pipe of a desired diameter under high temperature and pressure conditions as shown in FIGS. 3 and 4. The opposite ends of the sheet may be joined at an interface 4 in any suitable manner as by thermal pressure bonding or by applying an adhesive. A pipe may also be fabricated by wrapping the sheet in the form of an elongated narrow tape around a core in a spiral manner. Alternatively, two sheets may be placed at the opposite sides of a cylindrical core and then press or compression molded at elevated temperatures. The pipe may be fabricated to a given length of arm pipe or a long cylindrical product may be cut to a given length. In either case, graphite particles are oriented in parallel with the surface of the arm pipe as shown in FIGS. 3 and 4. There is obtained a rigid arm pipe.

After the arm pipe 5 shown in FIGS. 3 and 4 is formed, it is subjected to pre-sintering or oxidation by heating it in an oxidizing atmosphere to a temperature of about 250° C. at a rate of 1°-10° C./hour. Further, the arm pipe is subjected to carbonization or graphitization by heating it in a non-oxidizing atmosphere to a temperature of 1200° C. at a rate of 10°-20° C./hour. The

rigidity of the arm pipe is increased by carbonization while the internal loss is reduced in proportion.

The arm pipe 5 is susceptible to deformation during the pre-sintering or oxidation step. Therefore, the arm pipe should be supported in a suitable manner, for instance, by inserting a core (made of material not deformable at a temperature above 250° C.) into the bore of the pipe, or by enclosing the pipe within a support sheath. Since the pipe becomes self-supporting after the oxidation, no support is required during carbonization.

The carbonization temperature may be higher than 1200° C. The arm pipe graphitized at a temperature of 2,500° C. is 1.5 times higher in rigidity than that carbonized at a temperature of 1,200° C.

FIG. 5 shows an entire tonearm system. The arm pipe 5 of this invention has a head shell 6, which may be fabricated of the same material as the arm pipe, and a counter weight 7 mounted at opposite ends, and is supported by an arm support 8.

A sample was prepared by blending and kneading a polyvinyl chloride-polyvinyl acetate copolymer and graphite powder at a weight ratio of 1:2. The resulting intimate mixture was rolled to achieve a substantial degree of orientation of graphite. Measurement was made after rolling, oxidation, and carbonization. The results are tabulated below.

TABLE

	Density ρ (g/cm ³)	Young's modulus E (kg/mm ²)	Specific modulus $\sqrt{E/\rho}$ (m/sec)	loss tan δ
Rolled	1.8	6,000	5.7×10^3	0.05
Oxidized	1.8	9,000	7×10^3	0.02
Carbonized	1.8	16,000	9.33×10^3	0.015
Aluminum	2.7	7,400	5.18×10^3	0.003
Titanium	4.4	12,000	5.22×10^3	0.003

As understood from the foregoing, the orientation of graphite powder particles in the resinous matrix in a direction substantially parallel with the surface provides a light weight arm pipe having a high rigidity, that is, an arm pipe having a low equivalent mass at the stylus tip. Such an arm pipe tends to pick up few noise signals due to warpage and eccentricity of a record and ensures reproduction at an improved S/N ratio when used in combination with a high compliance cartridge. The arm pipe of the invention has an internal loss such that undesirable resonance or partial vibration may not occur. Further, the composite material is readily prepared by kneading relatively inexpensive starting components, orientation is imparted by rolling or other suitable treatments, and the material is formed by a conventional method. These factors contribute to a reduction of cost.

Although the present invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it will, of course, be understood that various changes and modifications may be made in the form, details, and arrangements of the parts without departing from the scope of the invention as set forth in the following claims.

What is claimed is:

1. An arm pipe for a record player tonearm comprising a composite material essentially consisting of 10-90 parts by weight of a thermoplastic resin and 90-10 parts by weight of flaky graphite wherein the composite material is prepared by kneading the components and the graphite flakes are oriented substantially in parallel with the surface of the shell.

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2. An arm pipe according to claim 1, wherein said composite material is oxidized at least at the surface of the pipe.

3. An arm pipe according to claim 1, wherein said composite material is carbonized.

4. An arm pipe according to claim 1, wherein said pipe is fabricated by kneading the components, rolling the kneaded mixture into a sheet to achieve a substantial degree of orientation of the graphite flakes, and then forming the sheet into a hollow cylinder.

5. An arm pipe according to any one of claims 1 to 3, wherein said thermoplastic resin is selected from the group consisting of polyvinyl chloride, polyvinylidene

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chloride, vinyl chloride-acrylonitrile copolymers, vinylidene chloride-acrylonitrile copolymers, vinyl chloride-vinyl acetate copolymers, and mixtures thereof.

6. An arm pipe according to any one of claims 1 to 3, wherein said graphite flakes have a particle size of 0.1 to 20 microns.

7. An arm pipe according to claim 6, wherein said graphite flakes have a particle size of 0.1 to 5 microns.

8. An arm pipe according to claim 1, wherein said composite material includes 30 to 70 parts by weight of said thermoplastic resin and 70 to 30 parts by weight of said flaky graphite.

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FIG. 1

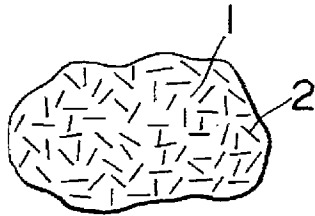


FIG. 2

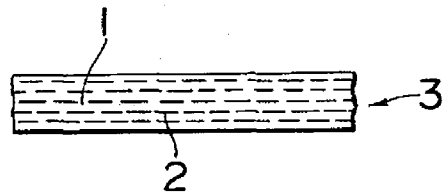


FIG. 3

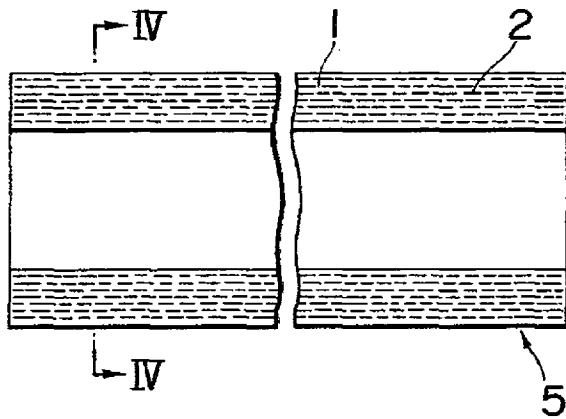


FIG. 4

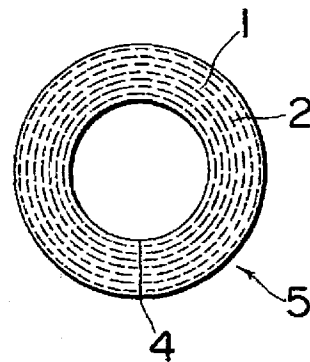
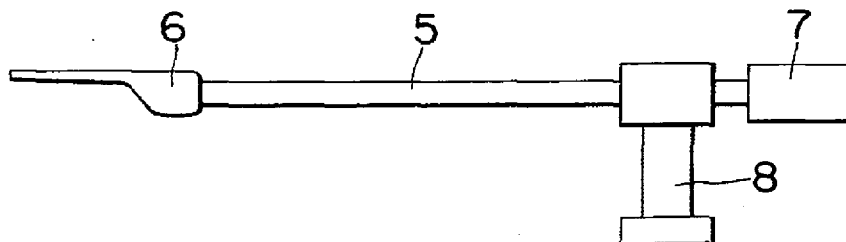


FIG. 5



[54] VIBRATORY ELEMENTS FOR AUDIO EQUIPMENT

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[21] Appl. No.: 241,554

[22] Filed: Mar. 9, 1981

[30] Foreign Application Priority Data

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 Mar. 31, 1980 [JP] Japan 55-40271

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[52] U.S. Cl. 181/167; 428/338; 428/408; 524/496

[58] Field of Search 428/402, 403, 404, 408, 428/338, 522; 260/42, 49; 181/167

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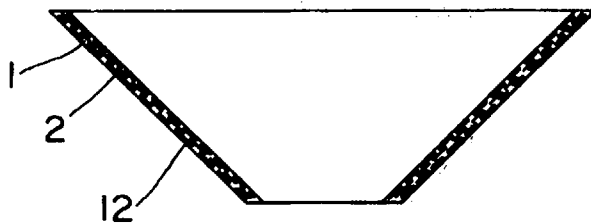
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Primary Examiner—William J. Van Balen

[57] ABSTRACT

Vibratory elements for use in audio equipment are fabricated from a kneaded mixture comprising post-chlorinated polyvinyl chloride and flaky graphite powder. The kneaded mixture is rolled into a sheet in which graphite flakes are oriented parallel to the surface and the sheet is then formed into a desired shape, for example, a dome- or cone-shaped diaphragm and a cantilever, as by vacuum forming, air-pressure forming or press molding. The mixture may further include polymethyl methacrylate and/or rubber-like material. The elements are characterized by improved temperature resistance.

15 Claims, 19 Drawing Figures



VIBRATORY ELEMENTS FOR AUDIO EQUIPMENT

BACKGROUND OF THE INVENTION

This invention relates to elements for use in audio equipment, and particularly to acoustic vibratory elements such as diaphragms for speakers and microphones and cartridge cantilevers for record players, the elements being lightweight, highly stiff and highly elastic and having a sufficient internal loss and an improved temperature resistance.

In general, acoustic vibratory elements such as acoustic diaphragms and cantilevers are required to have low density high stiffness, high elasticity, and sufficient internal loss. Low density, high stiffness and high elasticity are necessary to provide efficient reproduction up to a high frequency range without causing partial vibration while sufficient internal loss is effective for preventing sound pressure from rapidly rising at about resonance frequencies in the high range as well as improving damping characteristics. Acoustic vibratory elements are known which are formed from lightweight, highly elastic materials, for example such as aluminum, titanium and beryllium, and composite materials such as carbon fiber reinforced plastics (CFRP). None of these known materials are free of the problem of poor internal loss. Acoustic diaphragms with sufficient internal loss are also known which are formed from paper, synthetic resins or composite materials thereof. Though these materials have sufficient internal loss, they show a low modulus of elasticity and hence, a low specific modulus (ratio of modulus of elasticity E to density ρ , simply referred to as " E/ρ "). There is need for material which has not only a low density and high elasticity, but also sufficient internal loss.

Recently, the inventors proposed in U.S. Ser. No. 147,866 (filed May 8, 1980) cantilevers and diaphragms which are characterized by low density, high elasticity and high internal loss, the cantilevers and diaphragms being formed from a kneaded mixture comprising polyvinyl chloride, polyvinylidene chloride and flaky graphite powder. The proposed material has improved physical properties which are not found in prior art materials. In various application of the previously proposed material, the inventors encountered a problem that it is insufficient in temperature resistance. Elements made of this material tend to be deformed particularly when used in automobile audio sets which may be exposed to the summer sun or possibly used in the tropics.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an improved acoustic vibratory element which has satisfactory temperature resistance as well as excellent qualities of low density, high elasticity and sufficient internal loss.

According to a first aspect of the present invention, there is provided an acoustic vibratory element fabricated from a kneaded mixture comprising post-chlorinated polyvinyl chloride and flaky graphite powder, the graphite flakes being oriented substantially parallel to the surface of the element.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects, features and advantages of the present invention will be more fully understood

from the following description taken in connection with the accompanying drawings in which:

FIG. 1a is a cross-sectional view of a kneaded mass of graphite flakes in a resin matrix;

FIG. 1b is a cross-sectional view of a rolled sheet in which graphite flakes are oriented parallel to the surface according to the present invention;

FIG. 2 is a perspective view of a laminate having four rolled sheets placed one on top of the other;

FIG. 3 is a cross-sectional view of an embodiment of the cone-shaped diaphragm according to the present invention;

FIGS. 4a and 4b are radial and axial cross-sectional views of a cylindrical member formed from the rolled sheet, respectively.

FIG. 5 is an axial cross-sectional view of a cantilever prepared from the cylindrical member shown in FIGS. 4a and 4b;

FIGS. 6a, 6b and 6c illustrate successive steps of molding the kneaded mixture into a desired article;

FIGS. 7a, 7b and 7c are perspective views of a speaker enclosure, a record player base and a radio/cassette player casing, respectively;

FIG. 8 is an exploded view of a speaker enclosure; and

FIGS. 9a, 9b, 9c, 9d and 9e are perspective views of a speaker frame, a horn, an acoustic lens, an acoustic equalizer and a grille, respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The acoustic vibratory element according to the present invention is fabricated from a kneaded mixture mainly containing post-chlorinated polyvinyl chloride and flaky graphite powder. The resin component may be post-chlorinated polyvinyl chloride alone or in admixture with polymethyl methacrylate (PMMA).

The post-chlorinated polyvinyl chloride used herein may be prepared by chlorinated polyvinyl chloride (PVC) as disclosed in U.S. Pat. No. 2,996,489 which is incorporated herein by reference. Such post-chlorinated PVC has a softening point which is higher by 20 degrees Centigrade or more than the softening point of 80° C. of normal PVC.

Preferred examples of polymethyl methacrylate are those having a softening point which is higher by about 10° C. than normal PVC.

Further, a rubber-like material may also be added to the post-chlorinated PVC. It is also contemplated in the present invention to add both a rubber-like material and polymethyl methacrylate to the post-chlorinated PVC. Examples of the rubber-like material are acrylonitrile-butadiene rubber (NBR), butyl rubber (IIR), styrene-butadiene rubber (SBR), etc. It is to be understood that the rubber-like materials contribute to a further improvement in internal loss.

In general, the modulus of elasticity of a resin gradually decreases as the surrounding temperature is raised. The temperature at which modulus of elasticity decreases to one-half of the original value at room temperature is referred to as half-modulus temperature in this specification. When the half-modulus temperatures of resins of interest are compared, the half-modulus temperature of post-chlorinated PVC is higher by about 10-20 degrees Centigrade than that of normal PVC, and PMMA is higher by 10 degrees Centigrade than the latter. Accordingly, molding materials comprising flaky graphite powder, post-chlorinated PVC and op-

tionally, PMMA have a higher half-modulus temperature and hence, improved temperature resistance as compared with the previous PVC-based molding materials.

The flaky graphite powder contributes to an improvement in modulus of elasticity, which cannot be expected in the case of resin components per se. The modulus of elasticity is substantially increased when graphite flakes are oriented in one direction, preferably parallel to the surface of a molded product. Graphite flakes have a thin disc- or platelet-form and preferably have an average particle size of about 0.1 to about 20 microns, particularly about 0.1 to about 5 microns. An improvement in modulus of elasticity attributable to graphite flakes are satisfactory moldability can be expected and moldings are free of embrittlement when about 10 to 90 parts by weight of graphite powder is combined with 90 to 10 parts by weight of the resin component. An outstanding improvement is achieved when about 50 to 75 parts by weight of graphite powder is combined with about 50 to 25 parts by weight of the resin component.

PMMA is widely used with post-chlorinated PVC as its processing aid and the amount of PMMA to be added may be varied in the range of 1-15%, preferably 5-10% by weight of the post-chlorinated PVC, depending on the shape and properties of an intended product. The rubber-like material may be added in an amount of about 2 to 50 parts per 100 parts by weight of the resin component. The addition of about 10 pph of the rubber-like material will result in a 20% reduction of modulus of elasticity while internal loss is increased about 1.5 to 2.0 times.

The present invention will be more fully understood by referring to the preferred embodiments in conjunction with the drawing.

Acoustic vibratory elements may be fabricated by first mixing flaky graphite powder with a resin component which may be post-chlorinated polyvinyl chloride alone or its admixture with polymethyl methacrylate and an optional rubber-like material. Also, a plasticizer and/or stabilizer may optionally be added. The thus obtained mixture is fully kneaded by means of a conventional kneader or roll mill while heating to a temperature of 130°-180° C. at which the resins will soften or melt. The kneaded mass is designated at 3 in FIG. 1a as containing graphite flakes 2 in a resin matrix 1. As seen from FIG. 1a, graphite flakes 2 are randomly distributed throughout the resin matrix 1.

The kneaded material 3 is then repeatedly rolled by means of a roll mill into a sheet 4 as shown in FIG. 1b. The rolling of the kneaded material causes graphite flakes 2 to be oriented parallel to the surface of the sheet 4. As a result of graphite orientation, the modulus of elasticity of the rolled sheet is increased two or three times over kneaded materials containing randomly distributed graphite flakes.

One sheet 4 may be fabricated into an acoustic vibratory element of a desired shape by any suitable method including vacuum forming, air-pressure forming or press molding while heating to about the softening temperature of the resin. If desired, two or more sheets 4

may be placed one on top of the other to form a laminate having a desired thickness. FIG. 2 illustrates such a laminate 11 having four sheets 4. Heat bonding or adhesive application may be effected to bond the adjoining sheets.

In fabricating a speaker diaphragm 12 as shown in FIG. 3, the sheet 4 or the laminate 11 of some sheets laminated to a desired thickness in press molded between upper and lower mold halves at temperatures of 100°-200° C. The resulting diaphragm 12 exhibits a high stiffness and a high modulus of elasticity as graphite flakes 2 are oriented parallel to the surface as shown in FIG. 3. Although the diaphragm is of cone shape in this example, it may be of dome shape.

A cantilever may be fabricated by rounding the single sheet 4 or the laminate 11 of some sheets into a cylinder as shown in FIGS. 4a and 4b while heating to temperatures of 150°-200° C. The abutting edges of the rounded sheet are heat bonded under pressure or bonded with an adhesive at an interface 5. The thus integrated cylindrical member may be deformed into a cantilever 13 as shown in FIG. 5 using suitable deforming means.

Examples of the present invention are described below.

Parts by weight	
Example 1	
Post-chlorinated PVC	100
Flaky graphite powder	200
Lead stearate (stabilizer)	5
DOP* (plasticizer)	10
* dioctyl phthalate	
Example 2	
Post-chlorinated PVC	100
Polymethyl methacrylate	5
Flaky graphite powder	150
Lead stearate	2
DOP	10
Example 3	
Post-chlorinated PVC	100
IIR	10
Flaky graphite powder	200
Lead stearate	5
DOP	10
Example 4	
Post-chlorinated PVC	100
Polymethyl methacrylate	5
IIR	10
Flaky graphite powder	150
Lead stearate	2
DOP	10
Control	
Polyvinyl chloride	100
Flaky graphite powder	200
Lead stearate	5
DOP	10

In the each Example, powder ingredients were fully kneaded in a kneader at a temperature of 150°-160° C. using the above-mentioned formulation. A portion of the thus kneaded material was rolled several times by means of a roll mill, obtaining a sheet in which graphite flakes were oriented parallel to the surface. Samples of the kneaded materials and rolled sheets were determined for their physical properties. The results are shown in the following Table.

TABLE

Example	Graphite distribution	Modulus of elasticity E ($\times 10^{10}$ N/m ²)	Density ρ ($\times 10^3$ kg/m ³)	Internal loss tan δ	Half-modulus temperature* (°C.)
1	random	3.0	1.9	0.015	75
1	oriented	8.0	1.9	0.015	75

TABLE-continued

Example	Graphite distribution	Modulus of elasticity $E (\times 10^{10} \text{N/m}^2)$	Density $\rho (\times 10^3 \text{kg/m}^3)$	Internal loss $\tan \delta$	Half-modulus temperature* (°C.)
2	random	2.0	1.8	0.02	75
2	oriented	4.5	1.8	0.02	75
3	random	2.5	1.9	0.03	75
3	oriented	6.5	1.9	0.03	75
4	random	1.5	1.8	0.04	75
4	oriented	3.5	1.8	0.04	75
Control	random	2.2	1.8	0.03	55
Control	oriented	6.0	1.8	0.03	55
Aluminum		7.1	2.7	0.003	—
Kraft paper		0.2	0.6	0.05	—

*Temperature at which modulus of elasticity is reduced to one-half of the initial value when the temperature is raised from room temperature.

A sheet having a thickness of 100 microns obtained by rolling in each Example is vacuum formed at 100° C. into a cone-shaped diaphragm as shown in FIG. 3.

In addition, each sheet is heated to 100° C. before it is rounded on a cylindrical core. The abutting edges of the rounded sheet are heat bonded and the core is then withdrawn. The resulting cylindrical member is de-

formed into a cantilever shape as shown in FIG. 5. The thus fabricated diaphragms and cantilevers exhibit a high modulus of elasticity and a high specific modulus as graphite flakes are oriented parallel to the surface. As seen from the Table, they show a high specific modulus E_p exceeding the specific modulus of metals such as aluminum and a large internal loss approximating the internal loss of paper. Due to these improved properties, the diaphragms of the present invention exhibit more flat frequency response over a wide frequency range without inducing partial vibration. In addition, the temperature resistance of the diaphragms according to the present invention is improved by about 20 degrees Centigrade over the previously proposed material as proved by a heat distortion temperature of above 120° C.

It is to be noted that the kneaded mixture 3 of the resin matrix 1 having graphite flakes 2 randomly distributed therein as shown in FIG. 1a is ready for use in molding various articles which need not necessarily have a substantially increased modulus of elasticity. Such articles are casings for acoustic equipment, for example, speaker enclosures, record player bases and portable radio/cassette player casings. Other examples are non-vibratory elements for speaker systems, for instance, speaker frames, horns, equalizers, acoustic lens, and grilles. These articles may be molded directly from the kneaded mixture 3 by any suitable molding techniques including compression molding, injection molding and press molding. A process of compression molding, for example, is illustrated in FIGS. 6a-6c. Lower and upper mold halves 21 and 22 define a cavity having a configuration corresponding to the shape of a desired article, when mated together. A metered amount of the kneaded mixture material 3 is placed on the cavity-defining surface of the lower mold half 21 as shown in FIG. 6a, and then the upper mold half 22 is moved downward to compress the material while heating, allowing the material to flow throughout the cavity. Thereafter, the mold halves 21 and 22 are cooled and separated. A molded article 23 is then removed.

The molded article 23 may take the form of a speaker enclosure 24, a record player base 25, and a radio-cas-

sette player casing 26 shown in FIGS. 7a, 7b, and 7c, respectively.

Although the kneaded material containing randomly distributed graphite flakes or the article 23 directly molded therefrom has a modulus of elasticity which is about one-half or one third of that of a material of the same composition, but having graphite flakes oriented. However, the former and the latter are equal in internal loss. Therefore, acoustic equipment casings molded from the kneaded material are satisfactory because only improved vibration damping characteristics are required for such casings.

Of course, the sheet 4 obtained from the kneaded material by rolling and having graphite flakes 2 oriented may be used to fabricate casings. Usually, a plurality of sheets are placed one on top of the other to form the laminate 11 as shown in FIG. 2. For example, a speaker enclosure may be fabricated by assembling a front panel 31a, a top panel 31b, side panels 31c and a bottom panel 31d as shown in FIG. 8. The assembly may be completed by heat bonding or adhesive bonding.

A record player base may be fabricated by superposing a number of sheets 4 to a required thickness. The laminate 11 is then provided with openings (not shown) for receiving a turntable assembly and a tone-arm base.

It will be understood that the article 23 may be either molded directly from the kneaded material or assembled from some components or rolled sheets. For example, a one-piece integral enclosure 24 shown in FIG. 7a can be easily molded directly from the kneaded material whereas the enclosure assembled from panels 31 of rolled sheets as shown in FIG. 8 is rigid than the former.

FIGS. 9a to 9e illustrate a speaker frame, a horn, an acoustic lens, an acoustic equalizer, and a grille which are typical examples of articles molded using the compression molding technique as shown in FIGS. 6a to 6c. Such an article may be either a one-piece article molded from the kneaded material or an article assembled from two or more shaped components. As the kneaded material has sufficient internal loss, these speaker elements molded therefrom are substantially free of resonance and exhibit sufficient vibration damping characteristics.

What we claim:

1. An acoustic vibratory element fabricated from a kneaded mixture comprising post-chlorinated polyvinyl chloride and flaky graphite powder, the graphite flakes being oriented substantially parallel to the surface of the element.

2. An acoustic vibratory element according to claim 1 wherein the kneaded mixture further contains polymethyl methacrylate.

3. An acoustic vibratory element according to claim 1 wherein the kneaded mixture further contains a rubber-like material.

4. An acoustic vibratory element according to claim 1 wherein the kneaded material further contains polymethyl methacrylate and a rubber-like material.

5. An acoustic vibratory element according to claim 3 or 4 wherein said rubber-like material is selected from the group consisting of acrylonitrile-butadiene rubber, butyl rubber and styrene-butadiene rubber.

6. An acoustic vibratory element according to claim 1 wherein said kneaded mixture contains 90 to 10% by weight of post-chlorinated polyvinyl chloride and 10 to 90% by weight of flaky graphite powder.

7. An acoustic vibratory element according to claim 6 wherein said kneaded mixture contains 50 to 25% by weight of post-chlorinated polyvinyl chloride and 50 to 75% by weight of flaky graphite powder.

8. An acoustic vibratory element according to claim 6 wherein the mixture further contains 1-15% by weight of polymethyl methacrylate and/or 2-50% by

weight of a rubber-like material based on the weight of the post-chlorinated polyvinyl chloride.

9. An acoustic vibratory element according to any one of claims 1 to 8 wherein the graphite flakes have a particle size of 0.1 to about 20 microns.

10. An acoustic vibratory element according to claim 9 wherein the graphite flakes have a particle size of 0.1 to about 5 microns.

11. An acoustic vibratory element according to claim 1 wherein the element is fabricated by rolling the kneaded mixture into a sheet and then forming the sheet into a desired shape by way of vacuum forming, air-pressure forming or press molding.

12. An acoustic vibratory element according to any one of claim 1 to 11 wherein said element is a diaphragm.

13. An acoustic vibratory element according to claim 12 wherein said element is a cone-shaped diaphragm.

14. An acoustic vibratory element according to claim 12 wherein said element is a dome-shaped diaphragm.

15. An acoustic vibratory element according to any one of claims 1 to 11 wherein said element is a cantilever.

* * * * *

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FIG. 1a

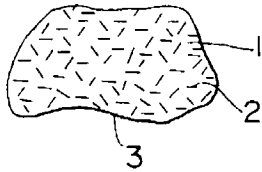


FIG. 1b

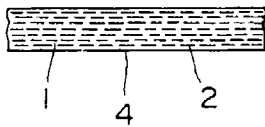


FIG. 2

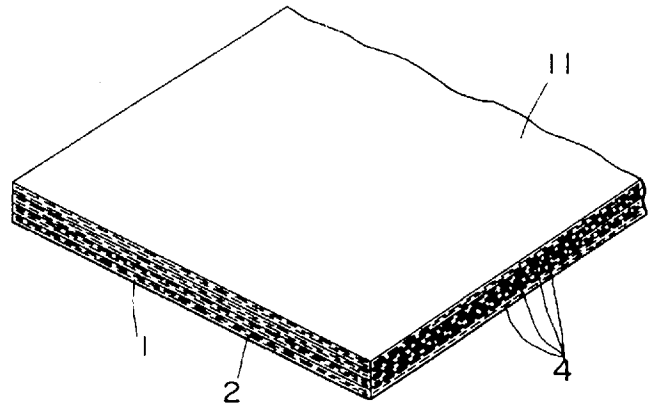


FIG. 4a

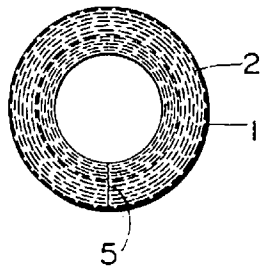


FIG. 3

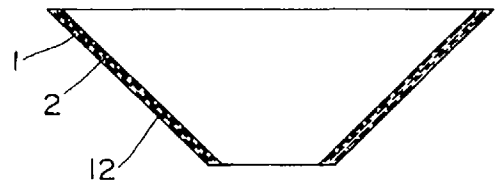


FIG. 4b

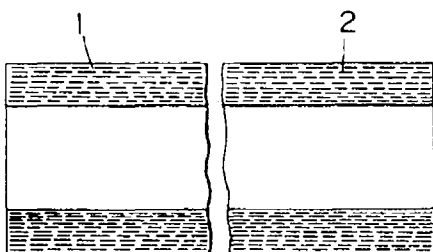


FIG. 5

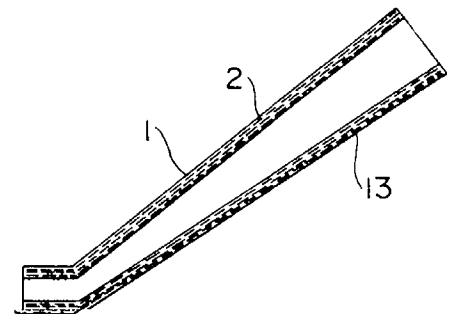


FIG. 6a

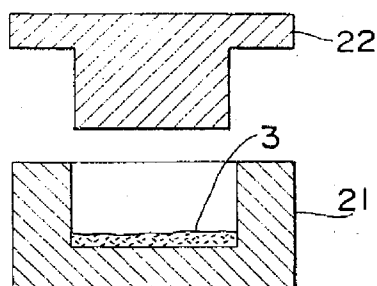


FIG. 6b

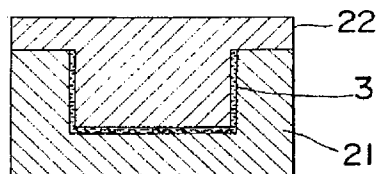


FIG. 6c

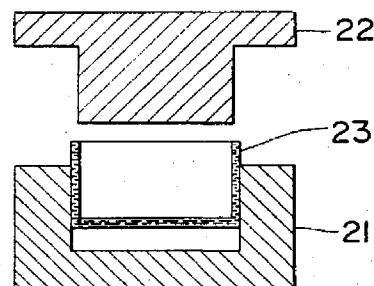


FIG. 7a

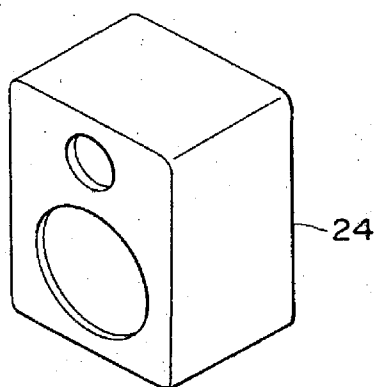


FIG. 7b

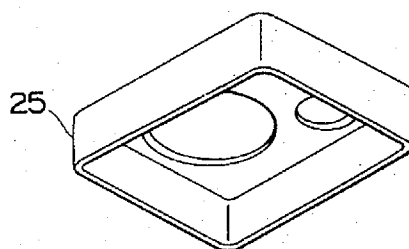


FIG. 7c

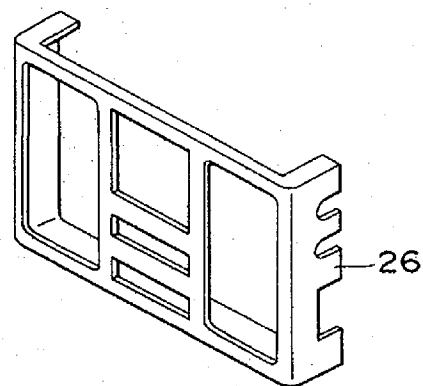


FIG. 8

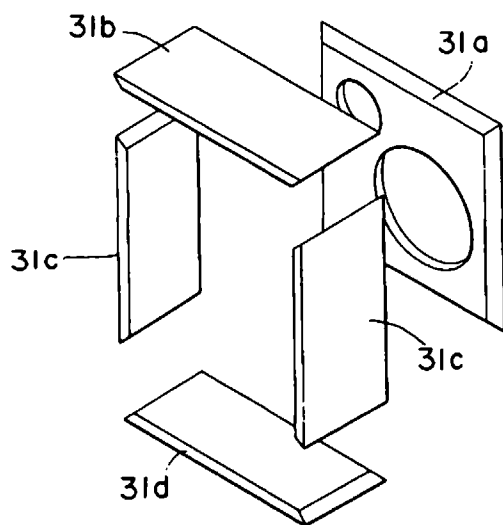


FIG. 9a

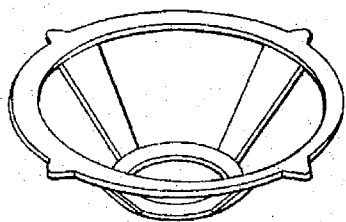


FIG. 9b

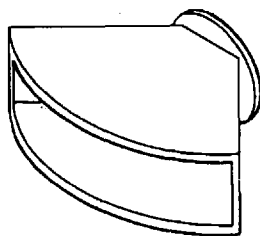


FIG. 9c

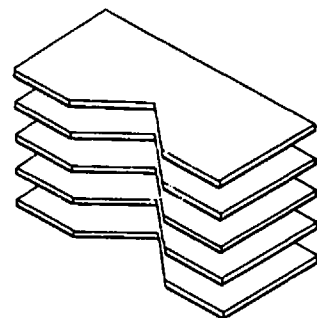


FIG. 9d

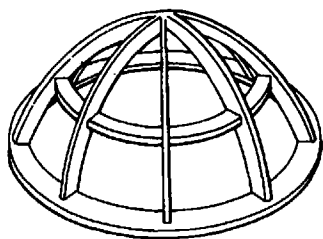
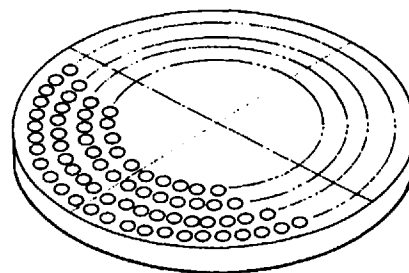


FIG. 9e



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2,996,489

RESIN COMPOSITIONS OF IMPROVED TOLERANCE FOR HIGH TEMPERATURES AND PROCESS OF PRODUCING SAME

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No Drawing. Filed Jan. 8, 1958, Ser. No. 707,672
10 Claims. (Cl. 260—92.8)

The present invention relates generally to vinyl compositions having increased high temperature tolerance including good heat resistance and materially increased softening or flow points. More specifically, the invention relates to a rigid type of vinyl resin having materially improved resistance to solvents, as well as being useful at higher temperatures, and to a process of producing same.

Vinyl chloride resins have been made in both the hard, rigid unplasticized condition and in the soft, flexible plasticized form. Both types suffer from the principal disadvantage of being unusable at moderately elevated service temperatures, the plasticized resins being unusable at temperatures exceeding about 75° C. Some of the resins sag badly while others decompose badly at even moderately elevated temperatures. Polyvinyl chloride, in its unplasticized condition, is a stable, strong, rigid material that has an added advantage of not supporting combustion. However, this rigid material usually is not employed in structural applications at temperatures exceeding about 60 or 70° C. Polyvinylidene chloride is somewhat similar and, in addition, has a very low second order transition temperature of about -20° C. and is less stable than polyvinyl chloride. Copolymers of these two monomers also have quite low softening points and poor stabilities. Blends of unplasticized polyvinyl chloride with one or more solid plasticizers, or resinous "processing aids," such as a styrene-acrylonitrile copolymer, are more easily processed but are not sufficiently stable and soften at lower temperatures than is desirable for many applications.

A growing use for rigid and semi-rigid compositions of the type described is in the form of extruded pipe, tubing and cable jacketing. However, because of low softening or "sag" temperatures, polyvinyl chloride pipe has been utilized principally where corrosion resistance, weather resistance, light resistance, flame resistance, etc. render other rigid plastics unusable. There is a need, therefore, for a composition having all the above-mentioned excellent properties of unplasticized polyvinyl chloride and, in addition, having increased tolerance for high temperature including outstanding resistance to decomposition by heat, greater dimensional stability and materially increased softening temperatures.

In the field of thermoplastic, structural dielectrics polystyrene and polyethylene have been dominant. Polystyrene suffers from heat distortion at moderately low temperatures and also from high flammability. Polyethylene also will burn quite rapidly. With most common plastic dielectric materials the loss factor increases with frequency in electronic applications. Since the tendency for the electronic industry is to push ever higher in frequency and service temperatures, it is becoming increasingly apparent that better plastic dielectrics are required.

Another objective of this invention is to provide an inexpensive method of making the plastic materials of this invention, such as are described herein, from cheap and readily available materials.

These and other objectives are achieved, according to this invention, in a high molecular weight chlorinated polyvinyl chloride resin having a structure in which at

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least 75%, more preferably at least 95%, and most preferably essentially all (i.e. at least 97-98%), of the chlorinated vinyl chloride units are 1,2-dichloroethylene units. Such products are thus distinguished over prior art chlorinated polyvinyl chloride resins which contain a significantly higher proportion (i.e. greater than 10%) of the chlorinated vinyl chloride units as the undesirable 1,1-dichloroethylene units. In addition, the products of this invention are distinguished over known polymers and chlorinated polymers of 1,2-dichloroethylene by the materially higher molecular weight and stabilities of the former compared to the latter. The products of this invention have intrinsic viscosities of at least 0.90, more preferably of at least 1.0. Prior polymers of 1,2-dichloroethylene prepared by polymerization of 1,2-dichloroethylene monomer are very low in molecular weight because of the well-known chain transfer characteristics of the monomer. As to stabilities, the products of this invention are uniformly characterized by heat stabilities greater than those of the unchlorinated resins from which they are derived. To be "stable," according to this invention, the stabilizer-free chlorinated resin must be able to withstand heating (that is, not turn black or generate bubbles) in air for at least 10 minutes at 375° F. A good quality polyvinyl chloride will turn black, generate bubbles, and otherwise lose its integrity in 5 minutes or less under the same conditions.

Such products are further distinguished over prior known chlorinated resins by materially-reduced solubilities in common solvents, especially in those solvents utilized in varnishes and lacquers, and by higher softening temperatures, as compared to prior resins of comparable chlorine content. These latter properties, together with their higher molecular weight and their very materially improved resistance to heat, are characteristic of the products of this invention, irrespective of the extent to which the chlorination process has been carried.

The chlorinated products of this invention may be plasticized in much the same manner as any other vinyl chloride polymers, although the usual polyvinyl chloride plasticizers are somewhat less effective in the chlorinated resins. It is surprising, however, that the aforementioned improved properties of the chlorinated products are maintained to such a large degree, upon being combined with plasticizers of all types. Fillers, stabilizers, plasticizers, extenders, coloring dyes and pigments, mold-release agents, lubricants and other conventional additives also can be employed in the usual way.

General purpose types of commercially-available polyvinyl chloride have specific viscosities of 0.50 to 0.54, contain about 56.7% by weight chlorine, have a density of about 1.40 gms./cc., and have a second-order transition temperature of between about 75° to about 80° C. When, by the process of this invention, the density of the lightly-chlorinated polyvinyl chloride resin has been increased slightly, up to a maximum of about 1.42, a lightly-chlorinated product is obtained having an improved stability to heat and light and a second order transition temperature usually above about 80° C. While the reason for the improvement in properties is obscure, it may be that chlorination converts the small amount of unstable groupings (usually found in commercial-grade resins) to a more stable chlorinated form. For example, there is evidence that the commercial polyvinyl chlorides contain a small proportion of unsaturation which the chlorine may saturate. Only about 0.1 to 0.2% by weight of added chlorine will do this. Up to about 1% by weight of chlorine has this same effect. Products of this type are improved forms of polyvinyl chloride resins suitable in the usual polyvinyl chloride applications.

When, however, the chlorination is continued to the density range of about 1.43 to about 1.48, the product

changes even more profoundly. Most surprisingly, these materials process more easily, without plasticizer, than the original resin, and at about the same processing temperatures. Also, the second order transition temperature increases rapidly to a value in the range of 80° to 90° C. and the product has a dipole peak (peak in the curve of a plot of loss factor vs. temperature at 1000 cycles) in the range of 105° to 115° C. Also the resistance of the chlorinated polymer to heat is considerably improved as shown by stabilizer-free samples withstanding heating in air for 10 to 20 minutes or more at 375° F. Such improvement in heat stability is additive and synergistic with the action of conventional stabilizers. Resinous processing aids or other lubricants do not seem to be required for the formation of smooth milled sheets, although these latter materials may be utilized, if desired. Upon milling, the chlorinated resin forms a smooth sheet and clings to one of the rolls of a two-roll plastic mill at temperatures between 300° and 350° F. without breaking into the loose, lacy appearance characteristic of plasticizer-free polyvinyl chloride. Because of their improved processability this class of materials avoids the sensitivity to chemical attack introduced upon the addition of processing aids to unchlorinated polyvinyl chloride in rigid formulations.

Further increase in density in the range of from about 1.50 to about 1.54 produces resinous materials which are exceptionally hard, stiff and tough, yet which can be processed in conventional plastics processing equipment capable of being heated to 350° F. Chlorinated polyvinyl chlorides of this type exhibit a second order transition temperature of at least 110° C. and, even when suitably lubricated and stabilized, have a softening point at least 20° C. higher than similar formulations of the original polyvinyl chloride. The "dipole peak" of this type of material occurs at a temperature above about 120° C. and the loss factor at this "peak" temperature is below about 0.90 and below 0.09 at room temperature, these properties indicating utility as a cable and wire insulation. Because of the very materially increased processing temperatures required, this material, to be considered "stable," must withstand heating in air for at least 20 minutes at 400° F. when suitably stabilized. Materials in this density range are quite tough as indicated by Izod impact values of at least 0.6 lb. per inch of notch, usually between about 0.6 to about 0.8 lb. per inch of notch, without the addition of fillers and reinforcing materials.

When the chlorination reaction has progressed to a density of above about 1.58, and particularly in the range of above about 1.58 to about 1.65, the product has a second order transition temperature of at least about 130° C. For processing, these materials require stock temperatures above about 400° F. yet are easily molded or pressed to form clear sheets in as little as 1 minute to 400° F. under pressures of 5,000–10,000 lbs. per square inch. Such a material has a loss factor at 1,000 cycles (at room temperature) less than about 0.05. Most unusually, the loss factor of these materials at room temperature decreases with increasing frequency in the range at least up to 100 mc. The dipole peak of such a material usually occurs at a temperature not less than about 150° C. Thus, the materials of this class approach polystyrene in dielectric properties and, in addition, they can be used at higher temperatures, they will not support combustion, and they are considerably tougher than polystyrene. When suitably compounded these materials form a most novel material for application as a low-loss, heat- and combustion-resistant wire and cable insulation. Without plasticizer and/or lubricants, these same materials form a class of high-melting, heat-resistant, low-loss structural dielectrics. Materials of this class also can be solvent-spun to form superior filaments and fiber useful in chemical filter pads.

Still further increases in density produce what is essentially high molecular weight poly-1,2-dichloroethylene

having a density of 1.69 to 1.71 (theoretically 1.70). Such a material is most difficult to process by ordinary techniques although the special techniques and equipment developed for the high-softening poly-fluoroethylene resins can be employed. Poly-1,2-chloroethylene can be powder-sintered at 400–525° F. to form products of exceptional heat resistance and very good dielectric properties. These materials have second order transition temperatures in the range of 170–180° C. or more and heat resistance values of 20 minutes or more at 375° F. (unstabilized).

For general use by persons not particularly skilled in handling such high-softening materials, chlorinated products above about 1.48 in density require a stabilizer to prevent degradation while working-in of added ingredients. In general, from about 1 to about 10% by weight of a stabilizer will enable one to mix in other added ingredients without careful precautions being observed. Many of the known organic or metal-organic stabilizers have lubricating action so that a stabilized composition would more readily coalesce into a sheet on a plastic mill, or to a well-fused solid in an extruder or Banbury mixer. Dibutyl tin dilaurate, barium and cadmium stearates, tin-maleate types, epoxy-type esters and polymers, and the like, have this action. Solids such as basic lead carbonate can also be added to contribute ready-processability to the finished resin. Stabilized resins of this type are of markedly greater commercial utility than the raw resin. As pointed out above, products of this type are unique in having a softening point at least 20° C. higher than unplasticized polyvinyl chloride and by a heat-stability in air of at least 10 minutes at 400° F.

As indicated above, all the described materials are characterized by molecular weight and a structure in which the ratio of 1,2-dichloroethylene units to 1,1-dichloroethylene units is very high. Products of this type are characterized by the absence in their structure of destabilizing groups and by intrinsic viscosities as high or higher than those of the corresponding original resin.

Products answering these descriptions are made by a unique photochemically-induced chlorination of macrogranular particles of a high quality, high molecular weight polyvinyl chloride resin at temperatures below about 65° C. while suspended in an essentially inert liquid medium having at most a mild swelling action on the polymer and while maintaining an excess of dissolved chlorine, especially in those portions of the reaction mixtures most strongly exposed to photochemical activation. It has been found, contrary to accepted beliefs, that the chlorination reaction is very rapid and that the principal limiting factor is the concentration of dissolved chlorine at the locus or site of the reaction. It has been found that two factors are largely determinative of the rate of the reaction, namely, (1) the dissolved chlorine content and (2) the level of photochemical activation. In fact, it has been found that quite moderate levels of photochemical activation can easily outstrip the ability to dissolve chlorine in the mixture.

Prior art processes for chlorinating polyvinyl chloride have been operated, unknowingly, under conditions of acute chlorine-starvation. Consequently, reaction times of 10, 20 and even up to 100 hours at temperatures of 75 to 100° C. have been reported. The literature is seemingly preoccupied with the improvement of the solubility of the product. Prior known forms of chlorinated polyvinyl chloride are notorious for their instability and hence have no known use outside of the coating resin and fiber fields. While there have been reports of moderately increased softening points and lowered solubilities of certain products, these have been indicated as undesirable. Analysis of some of these prior art products has shown them to be highly degraded.

In contrast, the products of this invention are free of degradation and have extraordinary heat stabilities hitherto

to unknown among vinyl chloride polymers. Upon examination such products are found to have a remarkable combination of properties as an insoluble, solid, rigid structural and dielectric material taking them completely outside the usual fields of application of prior chlorinated polyvinyl chlorides. The more dense of these products are somewhat crystalline and form superior films and filaments. Analysis of pyrolysis gases evolved by these products indicates clearly the substantial absence of the 1,1-dichloroethylene structure (i.e. 2-7% or less).

These desirable products result when the photochemically-activated reaction is carried out at temperatures not higher than about 65° C. in the presence of an excess of dissolved chlorine. Moderately lower levels of photochemical activation assist in maintaining an excess of dissolved chlorine by materially reducing the rate of photochemical attack on the polymer.

In more preferred embodiments of the process, still other means are employed to facilitate the delivery of dissolved chlorine to the site of reaction. One such means is the employment of a porous polymer to speed the diffusion of chlorine to the interior of the particle. Another is the use of a small amount of a volatile chloromethylene swelling or wetting agent to open the polymer particles to diffusion of chlorine.

It has also been found undesirable to allow the dissolved chlorine concentration to fall to dangerous levels at any time that the polymer is exposed to chlorine in the presence of actinic activation. For example, if chlorine gas flow and illumination are commenced simultaneously it seems that a small amount of 1,1-dichloroethylene structure is formed early in the reaction and virtually none after equilibrium chlorine saturation values have been achieved. For these reasons it is believed to be better to presaturate the reaction mixture with chlorine before exposure to illumination. Likewise, it also appears better to allow some time for the polymer to combine with the swelling agent and for swelling to occur before adding chlorine and supplying illumination. By these means the formation of 1,1-dichloroethylene structure is minimized. Infra-red analyses of the structure of polymers made in this fashion indicate the substantial absence of the undesirable structural isomer.

For greatly increased stability in the product it is necessary to employ, as the swelling agent, a hydro-chloromethylene compound, that is, a chlorinated hydrocarbon containing at least one chlorine atom, at least one hydrogen atom and only one carbon atom. Such materials include monochloro methane; dichloro methane, and trichloro methane (chloroform). The hydro-chloromethylenes are greatly preferred over other chlorinated hydrocarbons because they react but slowly with chlorine and the final product of such reaction is carbon tetrachloride, an innocuous material easily-removed from the final polymer. Chlorinated ethylene and ethane derivatives, and other chlorinated higher alkyl hydrocarbons are readily converted to high-boiling poly-chloro derivatives very difficult to remove from the polymer. Some of the chloroethylene and chloro-ethane derivatives seem to inhibit the chlorination reaction.

For the production of chlorinated polyvinyl chloride resins of maximum stability and maximum softening temperature (for a given proportion of added chlorine), it is necessary to employ chloroform as the swelling-wetting agent. Chloroform is by far the most effective and it is unique in that it seems to produce the most stable resins and, further, seems to have a much more pronounced directive effect on the chlorination reaction. Chloroform seems to be a necessary ingredient when it is desired to produce a polymer in which substantially all the chlorinated vinyl chloride units are 1,2-dichloroethylene units. Further, chloroform seems to be a mild catalyst producing the fastest reactions. The mechanism by which chloroform functions is not understood. It is believed, however, that chloroform functions as a "free-radical ac-

ceptor" or "hydrogen-donor" acting to decrease the number of excess polymer radicals in localized areas of low chlorine concentration. By donating a hydrogen atom or a trichloromethylene group, chloroform satisfies the excess of polymer radicals induced by irradiation before they can disproportionate to 1,1-dichloroethylene groups, or form double bonds, or serve as loci for chain scission. Products made with chloroform have intrinsic viscosities as high or higher than the original polyvinyl chloride resin. Further, since the chlorinated products are completely soluble in hot tetrahydrofurane, hot cyclohexanone, or hot chlorobenzene, chlorination and the consequent gain in molecular weight (and in intrinsic viscosity) is not due to cross-linking.

In the process of this invention, the starting material must be a polyvinyl chloride resin having three essential characteristics, namely, (1) a high molecular weight; (2) a macro-granular form; and (3) purity and freedom from contamination and degradation. The molecular weight of polyvinyl chloride usually is expressed in terms of "specific viscosity," as defined below. Thus, to be usable in the process of this invention, polyvinyl chloride must have a minimum specific viscosity of at least as high as 0.40, more preferably at least about 0.45, and most preferably above about 0.50.

As used herein the terms "specific viscosity" and "intrinsic viscosity" are calculated values derived from viscosity measurements. Solutions for viscometric study are prepared by dissolving 0.35 gram of the chlorinated resin in 25 ml. of tetrahydrofurane while mildly heating and agitating on a solution roller. The solutions are then filtered into an appropriate Ubbelohde viscometer, previously calibrated for the pure solvent. The flow times in seconds for the solutions are determined at four different dilutions to obtain flow data at a number of concentrations. A portion of the original filtered solution is dried to constant weight at 130° C. to obtain a true concentration value. The ratio of the flow time to the flow time of the pure solvent is a value known as the "reduced viscosity." When the number (1) is subtracted from "reduced viscosity," one obtains the value known as the "specific viscosity." When the "specific viscosity" is divided by the concentration and the values obtained plotted against concentration, the extrapolation of the resulting straight line to zero concentration gives one the value known as "intrinsic viscosity."

The "macro-granular" form of polyvinyl chloride resin is required to obtain the low slurry viscosity necessary for efficient agitation and to obtain low viscosity at high solids levels. It is necessary to vigorously agitate the chlorinating medium in order to facilitate chlorine solution and distribute the dissolved chlorine to each of the suspended resin particles. As used herein, the term "macro-granular" means a granular resin in which essentially all of the particles are above about 10 microns, more preferably a preponderant proportion above about 50 microns, in diameter. The coarsely-granular "general-purpose" grades of polymer containing particles up to 200 microns or more in diameter are perfectly satisfactory.

The proportion of such a resin in the slurry-like reaction mixture may vary quite widely up to a concentration of about 35-40% by weight. No real lower limit on slurry solids content exists, although practical economic considerations require a minimum of not less than about 5-10%. High solids levels are possible with macro-granular resins whereas extremely fine resins exhibit prohibitively high viscosities at 10% solids or less. The present process has the inherent advantage of high output for a given reactor unit volume.

The starting resin is strongly preferred to be somewhat porous in nature. It has been found that porous polymers increase the "chlorination efficiency" which is the ability of the reaction medium to induce a 1,2-dichloroethylene structure in the product. The use of a porous polymer so greatly facilitates the diffusion of

chlorine as to permit the production of the highly stable 1,2-dichloroethylene type polymers under a wider range of operating conditions. Solid, nonporous polymers must be more highly swollen and require higher dissolved chlorine concentrations to produce acceptable products. For these reasons polyvinyl chloride resins containing from about 5 to about 50% by volume of pore space are strongly preferred.

By the term "polyvinyl chloride resin" is meant any thermoplastic polymer produced from a monomeric mixture containing not less than about 95% by weight of vinyl chloride. Thus, copolymers of vinyl chloride with minor amounts of 1-monoolefinic or vinyl-type (i.e. containing a single $\text{CH}_2=\text{C}<$ grouping per molecule) comonomers can be utilized. Illustrative co-monomers are vinylidene chloride, vinyl acetate, methyl acrylate, styrene, acrylonitrile, methyl methacrylate, ethylene, propylene and others. Polyvinylchloride (i.e. the homopolymer) is greatly preferred. When copolymers are employed they must have a molecular weight at least equivalent to those given above for polyvinyl chloride.

According to the process of this invention, the polyvinyl chloride resin starting material is suspended in an inert liquid medium having a boiling point not over about 100° C. at atmospheric pressure and at most only a mild swelling action on the starting resin and on the chlorinated products. Such medium should have relatively little ability to react with chlorine or the resin and should be readily removed from the final product. Relatively few materials have these qualifications. Most hydrocarbons and chlorinated hydrocarbons are too readily chlorinated and are too high boiling for easy removal from the product. One satisfactory diluent medium is carbon tetrachloride and mixtures of carbon tetrachloride with from about 5 to about 15% by vol. of a hydrochloromethylene of the class defined. Such a medium is satisfactory for operation up to a density not above about 1.55 because the increased solubility of polymers having densities in the range 1.55 to 1.58 cause thickening or gelling of the reaction mixture and absorption of chlorine becomes very slow. More satisfactory are water and aqueous hydrochloric acid solutions, preferably containing from about 5 to about 25% by volume of a swelling agent such as carbon tetrachloride or, more preferably a hydrochloromethylene and most preferably chloroform. Water and aqueous hydrohalogen acid mediums are relatively more fluid than organic substances, have generally higher chlorine absorbing capacities, and have substantially no solvent effect on the polymer in either its original or any of its chlorinated forms. Aqueous media, however, are deficient in wetting and swelling tendencies so it is preferred to admix therewith a small proportion (see above) of a hydro-chloromethylene, preferably chloroform.

As indicated above, the reaction mixture must be maintained at a temperature below about 65° C. in order to obtain stable products. The products made at 55° C. are superior to those made at 65° C. and those made at 45° and 35° C. appear to be better than those made at 55° C. Temperatures as low as 0° C. can be employed, if desired although temperatures of from about 15 to about 55° C. are preferred. The chlorination rate appears to be less dependent on temperature in the range of from 25° to 65° C. than it does on illumination level. Due to the only mildly exothermic character of the reaction, no difficulties in temperature control are encountered even with the fastest reactions complete in 0.1 to 1 hour.

In general, it is preferred to carry out the reaction while taking precautions to exclude significant amounts of oxygen. This may be done by pre-heating to drive off dissolved oxygen or by purging with an inert gas such as hydrogen chloride or nitrogen. The presence of hydrogen chloride or other hydrohalogen acid is sometimes advantageous because of the density change induced in the diluent medium. Some polyvinyl chloride resins are too dense and are difficult to suspend. Others, and par-

ticularly the porous polymers have a tendency to float. Hydrogen chloride, under some circumstances, tends to cause the porous polymers to sink.

The chlorination reaction has been found to be very, very slow, or to proceed not at all, in the total absence of light. However, the source of actinic radiation for photochemical activation does not appear to be critical. In transparent glass laboratory equipment, the ambient room illumination level supplied by a high level fluorescent lighting system has been found sufficient to induce reaction. Better control of illumination level is afforded by employing sources of artificial light in close proximity to the reaction medium. Ordinary incandescent lamps have proven satisfactory although less sensible heat for a given level activation will be realized from mercury vapor or arc lamps. Neon glow tubes, fluorescent tubes, carbon arcs, and sodium vapor lamps may also be employed.

As indicated above, the level of illumination, or rather the level of activation derived therefrom, should be controlled or adjusted so as to stay within the chlorine-dissolving capacity of the medium in the particular apparatus employed. The destabilizing effects of excess illumination can be minimized both by insuring a high absorbed chlorine content and by limiting the time of exposure of the slurry thereto and removing the slurry from exposure to illumination before the dissolved chlorine supply is exhausted. The latter procedure can be carried out by suspending a light source concentrically within a throat structure enclosed in a concentric baffle, the whole being suspended in a reaction vessel together with an agitator adapted to draw reaction mixture from the body of liquid and pass it through the throat over the light source and then back into the body of liquid again. The entire baffling structure can be shielded to prevent light reaching the body of slurry in the vessel. A chlorine disperser tube or device can be located near the vortex of the agitator so that the liquid passing through the throat area will be rich in dissolved chlorine content. By-product hydrochloric acid gas can be separated from the liquid at the top of the main body of liquid. These operations can also be carried out by arranging a plurality of vessels, or a plurality of zones within a single vessel, to carry out successive steps of chlorine saturation and illumination. In more simple forms of apparatus, the light source can be turned off intermittently according to a timed sequence to provide intervals during which the chlorine level is allowed to build back up. In most cases the chlorine flow rate can be adjusted by visual observation of the color of the slurry.

It is possible to be easily misled by mere observation of chlorine gas in the gas discharge or vent line. High rates of chlorine flow will simply blow raw chlorine through the charge without appreciable increase in dissolved chlorine content. High-shear agitation will insure chlorine absorption. Actual visual observation of the color of the liquid is best, the appearance of the characteristic greenish-yellow color of dissolved chlorine being the most reliable indication of excess dissolved chlorine. In a suitable instance, the reaction vessel can be pressurized to increase the chlorine-absorbing capacity of the liquid. Whenever the illumination level and/or the time of exposure thereto is increased it is also necessary to increase the chlorine feed rate to guard against chlorine-starvation. However, since the ability in any given instance to dissolve chlorine is limited by apparatus, temperature and time, it is more practical to operate with either or both reduced activation levels and/or controlled exposure times in order to stay within the available chlorine supply. Even under the latter conditions reaction to densities above 1.60 in a half hour or less are easily obtained.

Following the completion of the chlorination step, the polymer slurry is simply filtered or centrifuged to free it of the liquid phase and the filter cake is neutralized

by the addition of water-soluble alkali such as sodium, ammonium or potassium hydroxides, carbonates, phosphates, etc. The neutralized polymer is then washed with pure water to neutrality to remove residual electrolyte. Drying of the washed cake can be carried out in air or vacuum ovens, by suspension dryers, and the like employing temperatures, preferably below about 75° C. The water-wetted filter cake can be washed with alcohol or acetone to displace the absorbed water and then the alcohol- or acetone-wetted polymer dried in a vacuum oven at very moderate temperatures of about 50° C. Where it is desired to recover the hydrochloromethylene and its chlorinated products, the reaction slurry can be steam distilled and then worked up as described above.

The invention will now be more fully described with respect to several illustrative examples.

Example 1

In this example, a high quality, commercial grade of high molecular weight polyvinyl chloride ("Geon 101 EP," an easy-processing, general purpose type of resin made by the B. F. Goodrich Chemical Company, Cleveland, Ohio, having a specific viscosity of about 0.54) is chlorinated by a preferred procedure in an aqueous hydrochloric acid solution containing about 10% by volume of chloroform. The above-mentioned polymer is a fairly coarse, granular resin which passes a 42 mesh screen and which is retained 100% by a 200 mesh screen. The preponderance of the particles appear to be larger than 25 microns in diameter and they are porous. By actual measurement the pore space is from about 15 to about 20% by volume. Total surface area determinations, by the nitrogen absorption method, indicate that this resin has a total particle surface area about equivalent to a polyvinyl chloride resin having particles only 1 to 3 microns in diameter.

In this example, a mixture of 800 grams of "Geon 101 EP," 1600 ml. of concentrated (37%) hydrochloric acid, 1375 ml. of water, and 300 ml. of chloroform are charged to a 5-liter "creased," clear glass flask fitted with a stirrer, condenser, Dry-Ice trap, and a gas dip tube. The flask is arranged to be illuminated by a 100 watt mercury arc lamp positioned in close contact with the flask. A rotameter is provided in a chlorine supply line connected to the gas dip tube. The flask also is provided with a water bath and an air jet for cooling to make possible control of reaction temperature at about 55° C. The stirrer is rapidly rotated while the flow of chlorine gas is started at a rate equal to about 210 ml./min. at a rotameter reading of about 5.0. The mercury lamp is turned on after the chlorine flow has commenced. After about 1 hour of reaction a 500 ml. sample of the slurry is withdrawn, filtered, the filter cake digested 30 minutes in 5% NaHCO₃ solution and filtered again, the cake washed with water to neutrality, then flushed with alcohol on the filter and finally dried at 50° C. in vacuum oven to a constant weight. This product, identified as Sample "A," is a white, granular resin very similar in appearance to the original "Geon 101 EP."

The chlorine flow rate is maintained at rotameter reading of 5.0 or a level of about 210 ml./min. for a total of over five hours, with a 500 ml. sample of slurry being taken after 3 hours and another after 5 hours. These are, respectively, Sample "B" and Sample "C." These are worked up immediately by the procedure used with Sample "A." After 5 hours and twenty minutes the chlorine flow rate is raised to a rotameter reading of 11.0, or more than double the original rate. This higher rate is maintained for one hour and 10 minutes (i.e., total time 5.5 hours) after which the reaction is terminated and the remainder of the charge worked up as before to yield sample "D."

The product in each case is a free-flowing granular, white powder much resembling the original polyvinyl chloride in appearance. The dried, raw resin samples

are tested for density, percent chlorine, and dynamic extrusion properties, the latter being a test wherein a "consolidation" temperature and a "flow" temperature are determined. In the latter test, a sample of resin is placed in a temperature-controlled plunger cavity mold having an orifice in the bottom and a standard pressure is applied by means of the plunger. The cavity is then gradually heated up until (1) the powder coalesces or consolidates to a solid mass (the temperature at which this occurs is the "consolidation" temperature) and (2) until the consolidated mass begins to flow out of the orifice (the temperature at which this occurs is the "flow" temperature). The "consolidation" temperature is a value usually about 15° C. above what is more commonly known as a "second-order transition temperature." The remaining tests are carried out on discs molded in a 1 in. plunger mold for one minute at 10,000 lbs./sq. in. and 170° C. The data are as follows:

Sample No.	Reaction Time, hrs.	Percent Wt. Chlorine	Density at 25° C.	Consolidation Temp., ° C.	Flow Temp., ° C.	Calculated Percent Conversion ¹
A-----	1	58.98	1.438	100	150	11
B-----	3	60.38	1.457	107	151	19
C-----	5	62.36	1.493	117	153	32
D-----	6.5	-----	1.532	137	170	60
"Geon 101 EP"-----	-----	56.70	1.400	96	152	-----

¹ Proportion of vinyl chloride units chlorinated.

Samples "B" through "D" are milled on a two-roll plastic mill capable of roll temperatures up to 500° F. or higher. The resins of Samples "A" through "D" band very well on the mill, quite unlike unplasticized polyvinyl chloride which does not "band" or adhere to one roll and forms a loose sheet of "lacy" appearance. During milling of each sample, 3 parts by wt. per 100 parts by weight of resin (phr.) of "Ferro 1827X," a mixed barium/cadmium organic acid salt, and 0.5 phr. of "Ferro 904," an epoxy resin "booster" stabilizer (both made by Ferro Corporation, Cleveland, Ohio) are worked in. The stabilized mixture is then sheeted off and portions of the sheets subjected to heat at 400° F. in air to estimate their heat stability. The data below list the mill roll temperature, the batch temperature (temperature of the resin sheet during milling) and the heat stability observations.

Sample No.	Mill Temp., ° F.	Batch Temp., ° F.	Heat Stability at 400° F.
"Geon 101 EP"-----	340	340	Failure in less than 5 min.
B-----	395	390	Tan color at 20 min.
C-----	390	400	Tan color at 20 min.
D-----	397	410	Tan color at 30 min.

Other portions of the milled sheets are tested for tensile strength, ASTM "Sag" temperature, dynamic extrusion properties, "dipole peak" temperature, and loss factor (at the dipole peak).

Sample No.	Tensile lbs./sq. in.	Consolidation Temp., ° C.	Flow Temp., ° C.	A.S.T.M. Sag, ° C.	Dipole Peak, ° C.	Loss Factor Max.
"Geon 101 EP"-----	-----	89	140	69	104	1.40
B-----	8,800	106	146	86	120	1.22
C-----	9,340	117	151	95	131	0.90
D-----	9,870	135	166	107	144	0.53

The above data show clearly the improvement in properties with increasing chlorination. It further should be noted that the dynamic extrusion properties determined on the milled sheets do not differ appreciably from the corresponding values on the raw resin. Any differences

noted are due to removal of residual solvent and/or the slight lubricating and plasticizing action of the stabilizers added. Clearly, the polymer was not degraded even after processing at roughly 50° F. higher than is normal for polyvinyl chloride. Further, note that the heat stability values reported are on the milled sheets. In other words each of the heat stability values should be increased by the amount of milling time at 390°–410° F. Truly, these products are amazingly stable; more stable than any previous known vinyl chloride polymer.

It should also be noted that sample "D" shows a relatively larger increase in chlorine content, density, stability, and dynamic extrusion properties than would be expected for the additional 1.5 hours of reaction time near the end of the reaction period. Such an increase must be due to the increased flow rate during the last stage. Because of this, the next examples are carried out employing successively higher flow rates throughout the reaction period.

Example 2

The procedure of the foregoing example is repeated employing an identical charge and identical conditions except for two changes adapted to increase the rate of chlorine absorption and diffusion namely, (1) a chlorine flow rate of 625 ml./min. and (2) water is added to maintain an adequate liquid level in the pot after sampling. In this case intrinsic viscosity measurements are made on the resins as a check on degradation. The data are as follows:

Sample No.	Reaction Time, Hrs.	Percent Wt. Chlorine	Density at 25° C.	Consolidation Temp., ° C.	Flow Temp., ° C.	I.V.	Percent Conv.
A-----	2.0	61.2	1.462	112	150	1.16	24
B-----	3.5	63.60	1.525	130	163	1.26	45
C-----	5.75	68.1	1.592	170	202	1.20	69
D-----	8.25	70.7	1.637	194	235	1.42	82
E-----	10.50	71.9	1.652	187	245	1.30	88
F-----	14.5	72.5	1.678	165	220	1.00	95
"Geon 101 EP"		56.7	1.400	95	154	1.18	0

Several observations can be made based on the comparison of the above values with those of Example 1. One is that the reaction rate in Example 2 is very nearly double that of Example 1, indicating that maximum chlorine flow rates and chlorine absorption has not yet been achieved. The next succeeding example will demonstrate the use of a still higher flow rate. Samples E and F show decreasing consolidation temperature and intrinsic viscosity values with increasing time of reaction. It is believed that the chloroform content of the reaction became exhausted. Succeeding examples will demonstrate that the latter may have occurred.

The samples A through D of Example 2 are subjected to milling and stabilization by a procedure similar to that of Example 1. The data are as follows:

Sample No.	Batch Temp., ° F.	Mill Temp., ° F.	Consolidation Temp., ° C.	Flow Temp., ° C.	Dipole Peak, ° C.	Loss Factor Max.
A-----	365	365	111	146	126	1.15
B-----	370	370	127	162	141	0.69
C-----		380	161	201	187	0.25
D-----		425	195	231	200	

Samples "C," "D," "E" and "F" did not fuse at the mill temperatures of (425° F.) available in the equipment used. Again the resins show no signs of decomposition at temperatures as high as 425° F. indicating that their heat stability is equal to or greater than those of the resins of Example 1. Sample "F" is essentially poly-1,2-dichloroethylene.

Samples "A" through "F" are analyzed by means of the infra-red spectrometer to determine the proportion of

1,1-dichloroethylene units and the proportion of 1,2-dichloroethylene units in the resins. The concentration of vinyl chloride units is calculated from the chlorine analysis values assuming only one chlorine atom adds to a single vinyl chloride unit. The ratio of 1,1-dichloroethylene units to vinyl chloride units is determined from the ratio of infra-red absorption intensity at 9.50 microns to that at 7.47 microns. Analyzed (known) copolymers of vinyl chloride and vinylidene chloride are used to construct a calibration curve for determination of the above ratio. The concentration of 1,2-dichloroethylene units can be determined by difference, assuming that all chlorinated vinyl chloride units not determined to be 1,1-dichloro are 1,2-dichloro in nature. Study of this method indicates that the 1,2-dichloro structure does not interfere with absorption by the 1,1-dichloro and vinyl chloride units. The results are as follows:

Sample No.	Density at 25° C.	Percent Wt. of Chlorine	Percent Vinyl Chloride Units converted to 1,1-dichloroethylene Units	Consolidation Temperature, ° C.	I.V.
A-----	1.462	61.2	4.6	112	1.16
B-----	1.525	63.6	7.3	130	1.26
C-----	1.592	68.1	7.1	170	1.20
D-----	1.637	70.7	3.5	194	1.42
E-----	1.652	71.9	2.6	187	1.30
F-----	1.678	72.5	5.8	165	1.18

The infra-red analysis and intrinsic viscosity values tend to confirm that the good heat distortion or "sag" properties of the products of this invention are largely due to lack of degradation and their high 1,2-dichloroethylene content. However, similar analyses of other chlorinated polyvinyl chlorides indicate that it is possible to have comparable chlorine contents and varying heat stability. It is believed that unstable forms of chlorinated polyvinyl chloride may contain proportions of unstable groupings too small to be detected by infra-red absorption but which severely limit the stability of the resin.

Example 3

In neither of the preceding experiments had excess chlorine gas been noted at the condenser exit initially, indicating essentially complete utilization of the chlorine. As a result, in the present experiment the chlorine gas flow rate is double that of Example 2 or 1375 ml./min. In this experiment the charge, equipment and procedure are the same as in the preceding experiments with the exception that the charge is placed in the flask and heat and the chlorine flow, at a low rate, are turned on first and then, a half an hour later when the slurry is up to temperature, the 100 watt mercury arc lamp (A4-H100 type) is turned on. A small amount of chlorine gas is visible at the condenser outlet at this high rate of flow. The data are as follows:

Sample No.	Reaction Time, Hrs.	Percent Wt. Chlorine	Density at 25° C.	Consolidation Temp., ° C.	Flow Temp., ° C.	I.V.	Percent Conv.
A-----	2	65.9	1.561	140	169	1.18	58
B-----	4	70.58	1.632	183	220	1.15	71
C-----	6	71.75	1.652	185	230	1.20	81
D-----	7.5	71.93	1.662	186	234	1.24	91
"Geon 101 EP"		56.7	1.400	96	152	1.18	

It is readily apparent that another marked increase in reaction rate is achieved by the use of this extremely high chlorine flow rate. Further, it should be noted that throughout the reaction the intrinsic viscosity is as high or higher than that of the starting resin.

Samples "A" and "B" of Example 3 are subjected to

infra-red analysis according to the procedure of the preceding example. The tests indicate that in Sample "A," only 7.8% of the chlorinated vinyl chloride units were converted to the 1,1-dichloroethylene structure and in the case of Sample "B," only 5.4%. The outstanding stability of Sample "A" indicates a further improvement derived from a larger excess of dissolved chlorine. Samples "C" and "D" of Example 3 are molded at 425 to 500° F. under pressures of 5,000 to 10,000 lbs./sq. in. to form molded articles of exceptionally good dielectric properties.

Example 4

In this example, polyvinyl chloride is chlorinated without a swelling agent. The charge of materials employed consists of 600 grams of "Geon 101 EP," 1200 ml. of concentrated hydrochloric acid and 1030 ml. of water. The equipment and procedure are otherwise the same as that employed in the previous examples. Chlorine gas is passed into the fluid, rapidly-agitated slurry at a rate of 640 ml./min. and the mercury arc lamp is turned on while controlling the temperature at about 55° C. At first, no excess chlorine gas appears in the condenser indicating that even at this moderately high flow rate the resin is taking up the chlorine as fast as it dissolves in the medium. After about 20 minutes a small amount of chlorine gas can be detected at the condenser exit. After a total of seven hours' time the reaction is terminated. The data are as follows:

Sample No.	Reaction Time, Hrs.	Percent Wt. Chlorine	Density at 25° C.	Consolidation Temp., ° C.	Flow Temp., ° C.	I.V.
A-----	2	63.1	1.511	116	151	1.09
B-----	4	66.45	1.569	137	166	1.00
C-----	6	68.4	1.600	147	175	0.96
D-----	7	68.7	1.614	149	177	-----
"Geon 101 EP"-----	-----	56.7	1.400	96	151	1.18

The above data indicate that the porous nature of the polymer permitted a fairly rapid uptake of chlorine even in the absence of a swelling agent. However, the product quality is not as good as those of the preceding examples, as is evidenced by the lower I.V. values above, and the physical properties of milled stocks listed below:

Sample No.	Density at 25° C.	A.S.T.M. Sag., ° C.	Consolidation Temp., ° C.	Flow Temp., ° C.	Dipole Peak, ° C.	Loss Factor, Max.	Heat Stability, 400° F.
A-----	1.51	89	112	150	126	0.70	dark tan, 10 min.
B-----	1.57	103.5	135	163	160	0.34	black, 20 min.
C-----	1.60	106	139	176	-----	-----	burnt black on molding.

The heat stability of the resins made without a swelling agent is low for resins of these density values. For example, compare Sample "C" above with Sample "C" of Example 2. The consolidation temperatures also are very low. It is concluded that a swelling agent is required for the production of an acceptable product. The infra-red analysis shows a higher proportion of 1,1-dichloroethylene (i.e. over 10%) content for Samples "A"-"D," above. The next example is carried out with carbon tetrachloride as a substitute for the chloroform of the previous examples to determine (1) if another swelling agent can equal the performance of chloroform and (2) whether chloroform is unique.

Example 5

A mixture of 600 grams of "Geon 101 EP," 1630 ml. of water, 1200 ml. of 37% hydrochloric acid, and 230 ml. of carbon tetrachloride are employed in a chlorination carried out by the procedure of the foregoing exam-

ples at 45° C. utilizing a chlorine flow rate of 925 ml./min. for 118 minutes when Sample "A" is taken. Then the flow rate is increased to about 1350 ml./min. for an additional 70 minutes (188 minutes total) when Sample "B" is taken. After a total of 270 minutes the remainder of reaction mixture is worked up as Sample "C." The dried resins are white, finely granular and have the following properties:

Sample No.	Density at 25° C.	Reaction Time, Minutes	A.S.T.M. "Sag" D648	Consolidation Temp., ° C.	Flow Temp., ° C.
A-----	1.522	118	97.5	128	168
B-----	1.608	188	130.5	163	194
C-----	1.636	270	-----	170	205

When these samples are pressed for one minute at 400° F., smooth discs are obtained which are much darker than other resins of this invention of comparable density. However, the discolored discs do not change appreciably when heated in air for as much as 20 minutes at 375° F. It should be noted that Sample "C," above, compares unfavorably with Sample "B" of Example 3 as regards consolidation and flow temperatures. It is clear that chloroform produces materials of better color, higher softening, and of better stability than does carbon tetrachloride and, therefore, is unique as a swelling-protective agent.

Example 6

In this example, three chlorination reactions are conducted, one at 35° C.; one at 45° C.; and one at 55° C. The object is to illustrate the effect of temperature on the course of the reaction. The reaction mixture in each case is made up of 600 grams of "Geon 101 EP," 1200 ml. of concentrated hydrochloric acid, 1030 ml. of water, and 230 ml. of chloroform. Illumination is supplied by the same 100 watt mercury arc lamp used in the preceding examples. In each case the reaction mixture is heated to reaction temperature while passing nitrogen through the flask. When reaction temperature is reached the nitrogen flow is cut off and chlorine gas bubbled into the slurry at approximately 640 ml./min. while rapidly agitating the mix. At this chlorine flow rate, excess chlorine is noted leaving the condenser in both the 35° and

55° C. reactions but not in the case of the 45° C. experiment. It is not known whether there is an optimum for chlorine absorption, although it is possible that at 35° C. the diffusional process may be slower and at 55° C. the actual solubility of chlorine may be lower than at 35° to 45° C.

Approximately 25 to 30 minutes after commencement of chlorine feed the mercury lamp is turned on. Samples of slurry are withdrawn at intervals and worked up by a procedure slightly different from that of the preceding examples. The slurry sample is first subjected to steam stripping for 25 to 30 minutes in a distillation flask to recover and measure residual swelling agent. After steam stripping the slurry is filtered, washed with water, then with 5% NaHCO₃ solution, again with water and finally with ethanol. The ethanol wetted filter cake is dried in a vacuum oven at 50-60° C. In the 55° C. experiment only, the condensate from the steam stripping operation is separated into layers and the lower chloro-

form/carbon tetrachloride layer washed with water, 5% NaHCO₃ solution, twice with water again, and finally dried over anhydrous MgSO₄. The refractive index is then determined to estimate the proportion of chloroform in the dried liquid. The amount of chloroform consumed (assuming the remainder is converted to carbon tetrachloride) is then calculated on the basis of ml./hr./100 grams of polyvinyl chloride in the original charge. The data are as follows:

Sample No.	Reaction Temp., ° C.	Reaction Time, hrs.	Percent/Wt. Chlorine	Density at 25° C.	Consol. Temp.	Flow Temp.	CHCl ₃ ml./hr./100 g.	Percent Conv.
A.....	55	2.0	61.45	1.496	118	155	9.0	37
B.....	55	4.0	65.24	1.578	145	176	4.0	66
C.....	55	6.0	67.70	1.643	165	209	6.0	83
D.....	45	2.0	63.24	1.511	125	158	-----	-----
E.....	45	4.0	67.43	1.578	135	186	-----	-----
F.....	45	6.0	70.25	1.621	187	230	-----	-----
G.....	45	7.0	71.48	1.637	192	240	-----	-----
H.....	35	2.0	61.86	1.500	124	158	-----	37
I.....	35	4.0	67.02	1.575	160	187	-----	62
J.....	35	6.0	69.59	1.619	180	215	-----	74
K.....	35	7.0	69.73	1.629	181	214	-----	81

While the above data shows relatively little temperature dependence, the resins made at the lower temperatures are better than those made at 55° C. When Samples A and B (55° C.) and Samples H and I (35° C.) are milled with 3 phr. of "Ferro 1827X" stabilizer and then tested for heat stability, the following data are obtained:

Sample No.	Density at 25° C.	Mill Temp., ° F.	Batch Temp., ° F.	Dipole Peak, ° C.	Loss Factor, Max.	A.S.T.M. Sag., ° C.	Tensile Strength, lbs./sq. in.
A.....	1.496	390	405	129	0.91	93	9,300
B.....	1.578	430	460	147	0.34	118	11,090
H.....	1.500	390	405	132	0.82	92.5	9,270
I.....	1.575	405	422	171	0.28	128	10,840

These data show Sample "I" (made at 35° C.) is much higher in softening point than is its counterpart, Sample "B," made at 55° C. Heat stability of Sample H and I also is somewhat better (black in 45-60 minutes for "H" and "I" as against 20-30 minutes for "A" and "B"). When the experiment above is repeated at 65° C. there are obtained resins of slightly poorer stability than that of any of the above resins, although the 65° C. material is still much more stable than the original polyvinyl chloride.

Referring back to the data concerning the consumption of chloroform, it is readily apparent that the degradation sometimes incurred in the later stages of the reaction can be due, at least in part, to depletion of the chloroform supply. In this example, the average consumption seemed to be about 6 ml./hr./100 grams of polyvinyl chloride. This means that the chloroform supply may have been very nearly exhausted after about 6 hours of reaction. Carbon tetrachloride obtained as a by-product of the chlorination of chloroform seems to be fairly effective as a swelling agent but deficient as a protective "radical acceptor" or "hydrogen donor."

Example 7

In this example, three different polyvinyl chloride resins are chlorinated under essentially identical conditions to elucidate (1) the effect of a porous polymer against that of a closely similar polymer having no porosity and (2) to chlorinate two resins of widely differing molecular weights. The resins utilized are (1) "Geon 101 EP," the porous polyvinyl chloride utilized in the previous ex-

amples; (2) "Geon 101," a polyvinyl chloride closely similar to (1) but having no porosity (i.e. a general purpose grade of coarsely granular polyvinyl chloride having a specific viscosity of about 0.54 and composed of particles ranging from about 50 to about 200 microns); and (3) "Geon 100×6," a coarsely granular form of polyvinyl

chloride having a particle size similar to resin (2), a porosity similar to resin (1), and a very materially higher molecular weight as shown by a specific viscosity of 0.85. The charge consists, in each case, of 600 grams of resin, 1600 ml. of water, 1200 ml. of concentrated hydrochloric acid, and 230 ml. of chloroform. Illumination is supplied by the 100 watt A4-H100 mercury arc lamp utilized in the previous examples. The reaction is started up by passing nitrogen gas through the flask during the heat up to 55° C. and then cutting off the nitrogen and turning on the chlorine and the lamp. A fritted glass filter stick is attached to the dip tube to assist in dispersing the chlorine gas. Chlorine flow is adjusted to about 800-850 ml./min. in the case of the "Geon 101 EP" and "Geon 100×6" experiments while in the experiment "Geon 101" the flow rate is 1200-1300 ml./min. under a slight positive pressure of about 11 inches of H₂SO₄ solution. Slurry samples are withdrawn at intervals and are worked up as in the previous examples. As a means of improving chlorine absorption, water and/or chloroform are added to maintain rapid agitation and adequate liquid level. Chloroform is added in an attempt to replace the chloroform consumed. The data are as follows:

Sample No.	Reaction Time, hrs.	Chlorine Flow, cc./min.	Percent/Wt. Chlorine	Density at 25° C.	Consol. Temp., ° C.	Flow Temp., ° C.	Resin Employed
A.....	2.25	850	68.84	1.599	157	189	"Geon 101 EP."
B.....	4.00	950	71.77	1.652	180	214	Do.
C.....	5.2	850	72.94	1.680	180	225	Do.
D.....	0.5	1400	60.12	1.482	100	150	"Geon 101."
E.....	1.0	1400	63.01	1.508	114	156	Do.
F.....	2.5	1400	68.70	1.622	160	197	Do.
G.....	2.0	640	-----	1.604	120	161	"Geon 100×6."
H.....	3.0	640	-----	1.636	128	166	Do.
I.....	4.1	640	-----	1.675	147	181	Do.

It will be noted that the non-porous "Geon 101" does not yield a reaction rate as fast as that of its porous counterpart "Geon 101 EP." However, the "chlorination efficiency" is seen to be lower when one takes into account the higher chlorine flow rates utilized in the preparation of Samples "D" and "F." The higher molecular weight "Geon 100X6" chlorinates fairly well. While all the products are of acceptable stability, those made from the porous polymers are definitely superior. During milling, no significant differences in behavior are observed indicating molecular weight in the specific viscosity range 0.54 to 0.85 is not an important factor. The above data, however, clearly indicates that a porous polymer produces much better products in a much shorter reaction time, and should be strongly preferred.

Example 8

In this example, polyvinyl chloride is chlorinated to a moderate density while suspended in a carbon tetrachloride/chloroform medium. The reaction charge consists of 800 grams of the above-described "Geon 101 EP" resin, 2700 ml. of carbon tetrachloride, and 300 ml. of chloroform. No artificial source of illumination is employed in this example. However, the reaction is carried out in a clear glass flask fully exposed to the ambient illumination supplied by a modern, high-level fluorescent lamp installation delivering an average of about 65 foot candles. The slurry is stirred rapidly while dry hydrogen chloride is bubbled through it for about 30 minutes. Then the hydrogen chloride flow is cut off and dry chlorine gas is bubbled through the slurry at a rate of about 300 ml./min., a rate sufficient to cause chlorine to appear at the condenser exit. The temperature of the slurry is maintained in the range of 45 to 50° C. by heating and cooling, as necessary. After a period of 3 hours a 500 ml. sample (Sample A) of slurry is withdrawn and stored in a brown glass bottle. Chlorination is continued in the same fashion with samples being withdrawn at 6½ hours (Sample B); 10 hours (Sample C); 14 hours (Sample D); and the reaction is terminated at 18 hours (Sample E).

The above samples are worked up by a procedure comprising the steps: (1) mix slurry sample with equal volume of ethanol to insure precipitation of small amounts of soluble polymer, if any; (2) grind alcohol/carbon tetrachloride/chloroform/polymer mixture in a Waring Blender for 5 minutes and let stand 30 minutes before filtering; (3) filter; (4) soak filter cake for one-half hour in 5% aqueous NaHCO₃ solution to neutralize; (5) filter; (6) wash filter cake with distilled water until neutral; (7) flush filter cake with ethanol to remove water; and (8) dry the alcohol-wetted filter cake to constant weight at 50° C. in a vacuum oven.

The product in each sample is a granular, white polymer very closely resembling the original polyvinyl chloride in appearance. The dried samples are analyzed for chlorine content, density, consolidation temperature and flow temperature. The data are as follows:

Sample No.	A	B	C	D	E	"Geon 101 EP"
Percent/Wt. Chlorine	58.53	63.26	67.30	68.9	69.54	56.7
Density at 25° C.	1.440	1.516	1.583	1.607	1.626	1.407
Consolidation Temp. (° C.)	103	128	158	165	165	97
Flow Temp. (° C.)	153	160	190	203	204	146
Reaction Time, hrs.	3	6.5	10	14	18	

The above data indicate that chlorinated polymers are obtained which compare quite favorably with products of similar density (1.40-1.58) made in aqueous systems. However, Samples "D" and "E" above are very definitely inferior to samples of comparable density made in the water/chloroform medium. These observations coincide with visual observations made during the reaction that between Samples "C" and "D" the medium became thick indicating an increasing proportion of the resin is passing

into solution and interfering with chlorine absorption and also with chlorine dispersion through reduction of agitation.

These same samples are submitted to extensive testing and structure analysis including X-ray diffraction (Sample D); pyrolysis and analysis of the gases produced by the mass spectrometer; infra-red spectrum; and dielectric testing for dielectric constant at 1000 cycles at room temperature, maximum loss factor, and dipole peak temperature.

The X-ray diffraction pattern of Sample D differs radically from that of a vinyl chloride/vinylidene chloride copolymer of comparable (60% vinylidene chloride) dichloroethylene content. It is obvious from this that the chlorine did not enter the polymer as the 1,1-dichloroethylene structure. The infra-red spectrum likewise differs radically in the absorption intensity at 9.50 and 7.47 microns. Sample "D," according to infra-red, indicated that about 96.5% of the chlorinated vinyl chloride units are 1,2-dichloroethylene and only about 3.5% are 1,1-dichloroethylene. This is an interesting result, showing that high 1,2-dichloro structure is not solely responsible for high stability and high softening point. Obviously, other structures and/or lowered molecular weight may have contributed to the lowered consolidation and flow temperatures in Samples D and E.

Sample "D" pyrolyzes at 700° C. to form only (1) a black mass of solid carbon, (2) hydrogen gas, and (3) hydrogen chloride gas. Polyvinyl chloride, however, pyrolyzes under the same conditions to form the black carbon, hydrogen gas, hydrogen chloride gas, and, in addition, hydrocarbons including specifically benzene, toluene and xylene. Pyrolysis of chlorinated polyvinyl chlorides of density lower than Sample "D" produces reduced proportions of the aromatic hydrocarbons and shows that as the density increases the proportion of hydrocarbon diminishes. Vinyl chloride/vinylidene chloride copolymers pyrolyze to yield black carbon residue, hydrogen, hydrogen chloride, and chlorinated hydrocarbons, chiefly chlorobenzene. These data indicate that the chlorine added in Sample "D" is present primarily in chloromethylene units rather than as dichloromethylene units.

The dielectric properties of the samples of Example 8 are highly interesting. Dipole peak temperatures (peak in curve of loss factor at 1000 cycles vs. temperature) are as follows:

Resin	I.V.	Dipole Peak, ° C.	Loss Factor, Max.
"Geon 101 EP".....	1.13	108	1.3
Sample B.....	1.18	136	0.9
Sample C.....	1.21		
Sample D.....	1.21	165	0.3
Sample E.....	1.18	172	0.2
	1.08	178	0.17

It is seen that the loss factor of Samples B through E is a materially reduced value and that progressive chlorination reduces it to a very low value. The loss factor at room temperature of Samples D and E is less than 0.1. Notice also that the dipole peak in each curve is shifted to very materially higher temperatures as the extent of chlorination is increased. During these tests it was also found that with increasing frequency the loss factor diminishes, in the range up to about 100 mc. Samples C through E are exceptionally good dielectric materials.

The intrinsic viscosity measurements reported above indicate that degradation may have begun in Sample E. This reduction in molecular weight is believed due to lowered dissolved chlorine content and unduly extended reaction time. A further interesting observation is that all of the samples are more stable to heat than "Geon 101 EP," although Sample D is much more stable than Sample E. In this example, it is clearly shown that low-

ered chlorine flow rates can be employed to produce excellent products if the illumination or activation level is correspondingly reduced. The level of illumination in Example 8 is a mere fraction of that existing when the mercury arc lamp is employed. Thus, the 300 ml./min. chlorine flow rate furnished an adequate dissolved chlorine content, at least in the early stages before thickening of the slurry occurred.

Example 9

In this example, 600 grams of "Geon 101 EP," 1300

The above compositions handled well on the two-roll plastic mill, forming smooth sheets of excellent color and quality. Those of density from 1.490 to 1.545 also are easily extruded to form smooth-surfaced extrudates of excellent appearance. These formulations have at least 10° C. higher softening points than that of the polyvinyl chloride control.

Similar formulations are prepared according to the above general recipes except for the use of various plasticizers in varying amounts. The compositions are subjected to physical testing, the results being as follows:

Composition No.	Plasticizer	phr.	Tensile, lbs./sq. in.	Elastic limit, lbs./sq. in.	100% mod.	Ult. Elong., percent	ASTM Brittle Temp., ° C.
Geon 101 (Control)	Diethyl phthalate	30	4,869	1,640	3,281	255	-15
D.O.	do	50	3,087	472	1,405	315	-25
D.O.	do	70	2,607	306	709	408	-40
Chlorinated Polyvinyl Chloride (D-1.590).	do	80	5,263	5,263		5	-5
D.O.	do	50	4,037	868	2,912	157	-20
D.O.	do	70	2,120	2,120	695	237	-25
D.O.	Diethyl sebacate	47	2,087	282	1,886	117	-35
D.O.	Paraplex G-50 ¹	50	4,151	113		67	0
D.O.	do	60	3,847	1,103		63	-5
D.O.	Tricresyl phosphate	60	4,350	844	2,723	158	0
D.O.	Santizer 141 ²	50	2,399	2,237	1,445	172	-25
D.O.	Hycar 1312 ³	51	4,729	3,164		45	

¹ Commercially available epoxidized polymeric esters, Rohm and Haas.

² Made by Monsanto Chemical Co.

³ A low molecular weight, semi-liquid copolymer of 87% by wt. of butadiene and 13% of acrylonitrile, made by B. F. Goodrich Chemical Co.

ml. of water, 1,100 ml. of concentrated hydrochloric acid, and 230 ml. of chloroform are combined in a flask illuminated with two 100 watt mercury arc lamps, one on each side of the flask, and with two chlorine dip tubes, one on each side of the agitator. Total chlorine flow is maintained at about 2,600 ml./min. of chlorine while maintaining a temperature of 55-60° C. Samples are removed at short intervals in order to follow the course of the reaction. The data are as follows:

Sample No.	A	B	C	D	E	F
Time-minutes	5	10	26	35	42	48
Density at 25° C., Calculated	1.418	1.435	1.479	1.511	1.540	1.558
Conversion, Percent	4	11	27	40	50	56
Consolidation Temp., ° C.	96	100	112	123	130	135
Flow Temp., ° C.	147	145	147	157	162	165

Thus, in only 35 minutes, a density of 1.511 is obtained. With both lowered chlorine flow and lowered illumination, from 2 to 4 hours are usually required to reach the same density. This experiment shows (1) that when the dissolved chlorine and the activation level are kept in balance, very good products are obtained in a very short time and (2) that reaction rate is primarily determined by the dissolved chlorine level at the site of reaction.

Example 10

In this experiment several chlorinated polyvinyl chlorides made in the preferred water/chloroform system are compounded, on an equivalent volume basis, in a conventional polyvinyl chloride recipe containing plasticizers, stabilizers and fillers. The data appear below including, for purposes of comparison, a polyvinyl chloride control.

Several of the above compositions are equal to or superior to the polyvinyl chloride control in all properties. The data tend to indicate the plasticizers are, in general, slightly less effective in the chlorinated resin. Further work along these lines shows that the chlorinated polyvinyl chloride have stress-strain properties differing from the original polyvinyl chloride when compared in equivalent recipes. The former show a Hookean behavior up to a yield point followed by continued extension to break. The latter more closely resembles rubbers.

Example 11

In this experiment polyvinyl chloride is very lightly chlorinated by slurring 5 grams of "Geon 101 EP" in 50 ml. of water in a clear glass flask, bubbling chlorine gas into the slurry for several minutes while exposed to the ambient illumination level furnished by a high-level fluorescent tube lighting system delivering an average of about 65 foot candles, and then placing the flask in an ultrasonic sound generator for several minutes. The slurry is then worked up as in the preceding examples and the resulting dry powder tested for gravity and rate of HCl liberation (a measure of heat stability). The product has a density of 1.40 gms./cc. showing that the density increase, if any, was within the limits of accuracy of the gravity determination. The HCl-liberation test is carried out by heating the dry powder at 180° C. while passing dry nitrogen through it. The nitrogen is then passed into a water-filled HCl-absorber. Titration of a portion of the absorber liquid reveals the amount of HCl liberated. A sample of untreated "Geon 101 EP" is tested in a similar fashion as a control. The lightly chlorinated resin of this example liberates only 0.085 millimole of HCl/grm. of polymer in 8,000 seconds as compared to 0.160 millimole for the control. It is clear that the addi-

Material	Geon 101 EP parts/wt.	Cl-pvc 1.490	Cl-pvc D=1.522	Cl-pvc D=1.545	Cl-pvc D=1.590
Polymer	100	106	108	110	113
Diethyl phthalate	42	42	42	42	42
Basic lead carbonate	10	10	10	10	10
Clay	7	7	7	7	7
Mill Temp., ° C.	290	300	300	315	335
Handling ease	OK	OK	OK	OK	OK

tion of even a very small amount of chlorine doubles the stability of polyvinyl chloride.

We claim:

1. A process for preparing a chlorinated polyvinyl chloride resin having a density at 25° C. in the range of 1.43 to 1.65 and characterized in that the resin, without added stabilizers, possesses a heat stability such that a pressed film thereof does not turn black when exposed for 10 minutes to air at a temperature of 375° F., said process comprising the steps of (1) preparing a suspension of a minor proportion of a solid polyvinyl chloride resin in a major proportion of a liquid aqueous medium, the polyvinyl chloride resin being (a) in macro-granular form having substantially all its particles above 10 microns in diameter (b) porous to the extent that its particles contain between about 5 and 50% by volume of pore space and (c) of high molecular weight such that it possesses a specific viscosity of at least 0.4, said suspension containing about 5 to 25% by volume based on the aqueous medium of a chlorohydrocarbon selected from the class consisting of monochloro methane, dichloromethane and chloroform, which functions as a swelling agent for the suspended polyvinyl chloride resin, (2) passing chlorine gas into said suspension, while said suspension is maintained under conditions of rapid agitation, a temperature no greater than about 65° C. and in the substantial absence of oxygen, substantially to saturate the aqueous phase of said suspension with chlorine (3) photo-illuminating said suspension, with chlorine dissolved in the aqueous phase thereof, and while maintaining said conditions, to induce chlorination reaction between the dissolved chlorine and the suspended, swollen, porous, macro-granular polyvinyl chloride resin and passing more chlorine gas into said suspension so that there is always present an excess of dissolved chlorine over that momentarily reacting with the suspended polyvinyl chloride resin (4) terminating the chlorination reaction when the desired amount of chlorine has reacted by extinguishing the photo-illumination and (5) separating

from said suspension the solid macro-granular product of said chlorination reaction and neutralizing said product, whereby to obtain the desired chlorinated polyvinyl chloride resin.

2. The process of claim 1 wherein the polyvinyl chloride resin is polyvinyl chloride of a specific viscosity above about 0.5.

3. The process of claim 2 wherein the chloro-hydrocarbon is chloroform.

4. The process of claim 3 wherein the temperature during the chlorination reaction is about 35 to 45° C.

5. The process of claim 3 wherein the liquid aqueous medium is water.

6. The process of claim 3 wherein the suspension contains from 5 to 15% by volume of chloroform.

7. The process of claim 3 wherein the liquid aqueous medium is dilute hydrochloric acid.

8. A composition of matter comprising a chlorinated polyvinyl chloride resin having a density at 25° C. in the range of 1.43 to 1.65, characterized in that said resin, without added stabilizer, possesses a heat stability such that a pressed film thereof does not turn black when exposed for 10 minutes to air at a temperature of 375° C., said resin being prepared by the process of claim 1.

9. The composition of claim 8 wherein the resin is chlorinated polyvinyl chloride of density in the range of 1.43 to 1.65.

10. The composition of claim 9 wherein the density is about 1.55 to 1.58.

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[54] DIAPHRAGMS FOR ACOUSTIC
INSTRUMENTS AND METHOD OF
PRODUCING THE SAME

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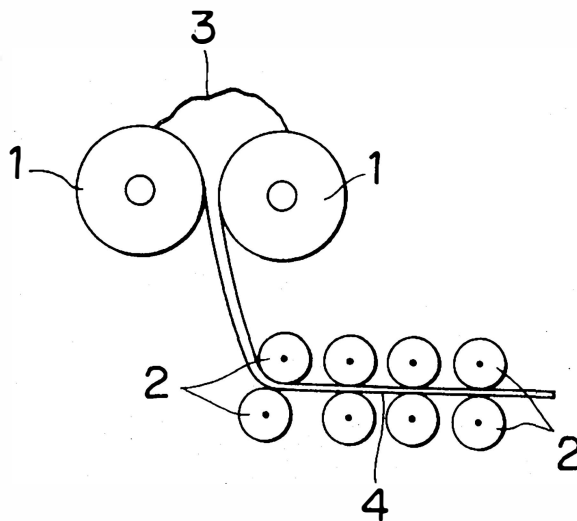
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[57]

ABSTRACT

A diaphragm for acoustic instruments such as speakers is produced by blending and kneading a thermoplastic resin such as polyvinyl chloride resin with graphite powder, rolling the blend into a sheet until graphite particles are oriented, and forming the sheet into a desired diaphragm shape. The diaphragm of the composite material containing graphite particles oriented shows an improved combination of density, elasticity and internal loss.

13 Claims, 2 Drawing Figures



DIAPHRAGMS FOR ACOUSTIC INSTRUMENTS AND METHOD OF PRODUCING THE SAME

BACKGROUND OF THE INVENTION

This invention relates to diaphragms for use in acoustic instruments. More particularly, this invention relates to a diaphragm comprising a shaped body of a composite material consisting essentially of a thermoplastic resin such as polyvinyl chloride resin and graphite powder, and a method of producing the same.

Diaphragms for acoustic instruments, particularly diaphragms for speakers and microphones are required to have light weight, high rigidity and a high specific modulus of elasticity E/ρ , wherein E is Young's modulus and ρ is the density, so that the diaphragms may efficiently reproduce acoustic signals over a wide frequency range with a high fidelity.

For this reason, wood pulp, plastics, aluminum, titanium and other materials have previously been used to form diaphragms. These materials, however, do not fully meet the above-mentioned requirements.

Synthetic resins have also been used in the manufacture of diaphragms. Examples include composite materials of carbon fiber and a synthetic resin. These composite materials, however, cannot provide sufficient rigidity when molded into a diaphragm shape partly because of insufficient integration of the resin attributable to the lubricating nature of the carbon fiber surface.

Boron, beryllium and carbon are known as having a high specific modulus. These materials have poor processing characteristics, which increase costs for molding them into diaphragms.

SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide a diaphragm for acoustic instruments which comprises a composite material capable of being readily worked into a desired form as well as satisfying the requirements for diaphragms including light weight, high rigidity, high specific modulus and good internal loss.

It is another object of this invention to provide a method for producing a diaphragm for acoustic instruments from a composite material at low cost.

According to one aspect of this invention, a diaphragm for use in an acoustic instrument comprises a body formed of a composite material consisting essentially of a thermoplastic resin and graphite powder. Graphite powder particles should be substantially oriented in the body.

According to another aspect of this invention, a diaphragm is produced by blending and kneading a thermoplastic resin with graphite powder having a particle size of 0.1–50 microns, particularly 0.1–0.5 microns. The blend is rolled into a sheet which is then formed into a desired shape.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described in further detail by referring to the accompanying drawings wherein:

FIG. 1 is a schematic view showing an arrangement used for carrying out the present method; and

FIG. 2 is a graph showing Young's modulus for various composite materials relative to the graphite blending ratio.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Considering that carbon has light weight, high rigidity, and a high specific modulus of elasticity E/ρ , the inventors proposed a diaphragm comprising a formed body of a carbonized or graphitized composite material consisting of an organic substance and carbon powder, typically graphite powder (Copending Japanese Patent Application No. 52-154315 filed Dec. 23, 1977).

Carbonization or graphitization is used because diaphragms show a low specific modulus when they are molded from a blend of organic substances and graphite powder by compression forming or injection molding. By way of illustration, polyvinyl chloride was blended and kneaded with graphite powder at a varying blending ratio and the blends were compression formed into sheets having a thickness of 0.8 mm. The Young's modulus of these sheets was measured. The obtained values are plotted in relation to the blending ratio to give curve a in FIG. 2, wherein the Young's modulus is on the abscissa and the amount of graphite powder blended in the composite material (expressed in terms of percent by weight of the total composite material) is on the ordinate. Curve a shows that a maximum Young's modulus of about 3,000 kg/mm² is obtained when a blend of polyvinyl chloride and graphite is molded into a sheet without orientation. Curve b corresponds to the Young's modulus of similar sheets after being subjected to carbonization at 1,200° C. In this case, the maximum modulus reaches about 6,000 kg/mm². This increased Young's modulus corresponds to a specific modulus of elasticity of 5.7×10^3 m/sec which is higher than that of aluminum, but is still insufficient although various acoustic characteristics of the carbonized material are equal to or slightly superior to those of the prior art materials.

The inventors have found that orientation of graphite particles in a composite material of graphite and a thermoplastic resin improves the physical properties, particularly Young's modulus of the material.

The thermoplastic resin used herein is selected from the group consisting of polyvinyl chloride resins including polyvinyl chloride homopolymers and copolymers such as vinyl chloride-acrylonitrile and vinyl chloride-vinyl acetate copolymers; polyvinylidene chloride resins including polyvinylidene chloride homopolymers and copolymers such as vinylidene chloride-acrylonitrile copolymers; polycarbonate resins; and mixtures thereof. The amount of graphite powder to be added is 10–90 % by weight, preferably 30–80 % by weight of the total blend. Better results are obtained with a smaller size of graphite particles. The particle size of graphite is between 0.1 and about 50 microns, preferably between 0.1 and 5 microns.

FIG. 1 schematically shows a process of producing a diaphragm according to this invention. The illustrated arrangement includes a mixing mill 1 and a series of rollers 2. A thermoplastic resin, for example, a polyvinyl chloride resin is blended with graphite powder at a blending ratio of 1:2 (weight ratio) and the blend 3 is thoroughly kneaded by means of the mixing mill 1. During this kneading, the blend is heated to an elevated temperature above the softening point of the polyvinyl chloride resin, preferably to a temperature of 120°–250° C.

The kneaded material 3 is then rolled by means of the rollers 2 into a sheet 4 having a uniform thickness. Roll-

ing is also performed at a temperature above the softening point of the resin, preferably at a temperature of 120°–250° C. By rolling the kneaded material into a sheet, graphite particles are oriented in parallel with the surface of the sheet. As a result, the longitudinal modulus of the sheet 4 is improved.

For the purpose of mixing and kneading the components, a mill followed by rollers is used in the illustrated embodiment. The same purpose can be achieved by extrusion molding. In this case, the resin and graphite are introduced into an extruder at an elevated temperature which serves to mix and knead the components. An extrudate is yielded from the extruder and then rolled into a sheet to orient the graphite particles.

For the purpose of imparting a substantial degree of orientation to graphite particles as well as forming the kneaded material into a sheet, rolling is contemplated in this invention. Rolling may advantageously be repeated because repeated rolling can further enhance the orientation of graphite particles in parallel with the surface of the sheet. The thickness of the rolled sheet depends on the final requirements such as the thickness, size and configuration of an intended diaphragm.

The sheet in which graphite particles are oriented is then formed into a dome or cone shape suitable for use as a diaphragm. Vacuum forming, thermal compression or pressure forming and other conventional methods may be employed for this purpose.

The rolled sheet shows a high longitudinal modulus since graphite particles are oriented in parallel with the surface of the sheet to a considerable extent. Rigid diaphragms may be prepared from such sheets.

The Young's modulus of rolled sheets having a varying graphite content is plotted as curve A in FIG. 2, which proves a doubled or more improvement in Young's modulus as compared with curve a of non-oriented sheets.

When the rolled sheets are further carbonized at a temperature of 500°–1200° C. or graphitized at a temperature of 2,000°–3,000° C., the Young's modulus is further increased as shown by curve B. However, the internal loss of the sheets is reduced.

The inventors have found that diaphragms prepared from oriented sheets are equal to or superior to those of carbonized or graphitized sheets from a point of view of commercial diaphragm production. First, the Young's modulus of oriented sheets reaches about 7,000–8,000 kg/mm² and hence, the specific modulus of elasticity is satisfactorily high. The internal loss expressed by tan δ typically approximates to 0.05 so that the undesired resonance peak may be suppressed. In the case of carbonized or graphitized sheets, the Young's modulus is increased to an extremely high level reaching about 15,000 kg/mm² whereas the internal loss is reduced to about 0.015. When a combination of Young's modulus and internal loss is considered, the oriented sheets are comparable to the carbonized or graphitized sheets.

Secondly, the method of producing a graphite oriented sheet is very simple because it only requires kneading and rolling. On the other hand, the carbonizing or graphitizing method is time consuming and expensive because the temperature must be increased to 1000°–2000° C. or more at a rate of 1°–20° C./hour and sometimes a pretreatment is also required.

A sample was prepared by blending and kneading polyvinyl chloride-polyvinyl acetate copolymer with graphite powder at a ratio of 3:7. The resulting intimate mixture was rolled into a sheet to achieve a substantial

degree of orientation of graphite. The Young's modulus, density and internal loss of the rolled sheet were measured. For comparison, the sheet was then subjected to oxidation by heating it in an oxidizing atmosphere to about 250° C. at a rate of 1°–10° C./hour and thereafter subjected to carbonization by heating it in a non-oxidizing atmosphere to 1200° C. at a rate of 10°–20° C./hour. The Young's modulus, density and internal loss of the carbonized sheet were measured. The results are shown in the following Table.

TABLE

	Density	Young's modulus	Specific modulus	Internal loss
	ρ (g/cm ³)	E (kg/mm ²)	$\sqrt{E/\rho}$ (m/sec)	$\tan \delta$
Rolled sheet	1.8	8,000	6.60×10^3	0.05
Carbonized sheet	1.8	16,000	9.33×10^3	0.015
Aluminum	2.7	7,400	5.18×10^3	0.003
Titanium	4.4	12,000	5.17×10^3	0.003
Beryllium	1.8	28,000	12.35×10^3	0.003

In the Table, the physical properties of aluminum, titanium and beryllium are also involved. For specific modulus, the rolled or oriented sheet is superior to aluminum and titanium, but inferior to the carbonized sheet and beryllium. The internal loss of the rolled sheet is the highest of the other materials. Therefore the rolled sheet affords a desirable combination of specific modulus and internal loss required for acoustic diaphragms. Further, diaphragm manufacturing cost is minimized with the use of the rolled sheet of the composite material because the manufacturing process is very simple.

It has also been found that the diaphragm according to this invention shows an improved frequency response, particularly in a high frequency range. The frequency response to the present diaphragm is substantially equivalent to that of the beryllium diaphragm in the low and mid ranges and flatter in the high range.

What is claimed is:

1. An acoustic diaphragm formed of a homogeneous composite material consisting essentially of a thermoplastic resin selected from the group consisting of polyvinyl chloride, polyvinylidene chloride, polycarbonate resins and mixtures thereof; and graphite powder having a particle size of 0.1 to 50 microns being substantially parallel oriented in said diaphragm.

2. An acoustic diaphragm formed of a homogeneous composite material consisting essentially of a thermoplastic resin and graphite powder particles, the graphite powder particles being substantially parallel oriented in said diaphragm.

3. A diaphragm of claim 2 wherein said thermoplastic resin is selected from the group consisting of polyvinyl chloride, polyvinylidene chloride, polycarbonate resins and mixtures thereof.

4. A diaphragm of claim 3 wherein said thermoplastic resin is a vinyl chloride-vinyl acetate copolymer.

5. A diaphragm of claim 2 wherein the graphite has a particle size of 0.1 to 50 microns.

6. A diaphragm of claim 5 wherein the graphite has a particle size of 0.1 to 5 microns.

7. A diaphragm of claim 2 wherein said composite material includes 10 to 90 parts by weight of graphite powder and 90 to 10 parts by weight of the thermoplastic resin.

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8. A diaphragm of claim 7 wherein said composite material includes 30 to 80 parts by weight of graphite powder and 70 to 20 parts by weight of the thermoplastic resin.

9. A diaphragm of claim 2 wherein said formed body is of a cone configuration.

10. A diaphragm of claim 2 wherein said formed body is of a dome configuration.

11. A diaphragm of claim 2, formed from a rolled composite sheet having a Young's modulus of about 7,000 to 8,000 kg/mm² and an internal loss of about 0.05.

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12. A diaphragm of claim 2, formed from a rolled carbonized composite sheet having a Young's modulus of about 15,000 to 16,000 kg/mm² and an internal loss of about 0.015.

13. An acoustic diaphragm formed of a homogeneous composite material consisting essentially of a thermoplastic resin and graphite powder particles, the graphite powder particles being substantially parallel oriented in said diaphragm, and wherein said composite material has a Young's modulus of about 7000 to 16000 kg/mm² and an internal loss of about 0.05 to 0.015.

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FIG. 1

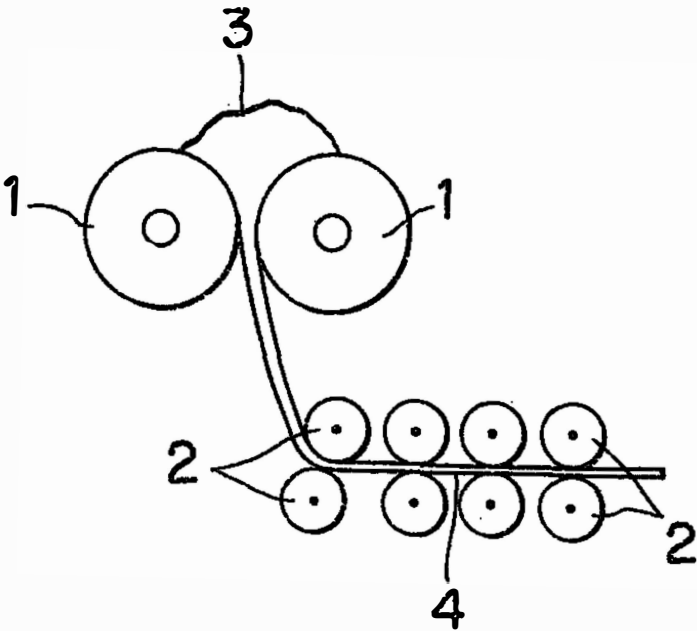
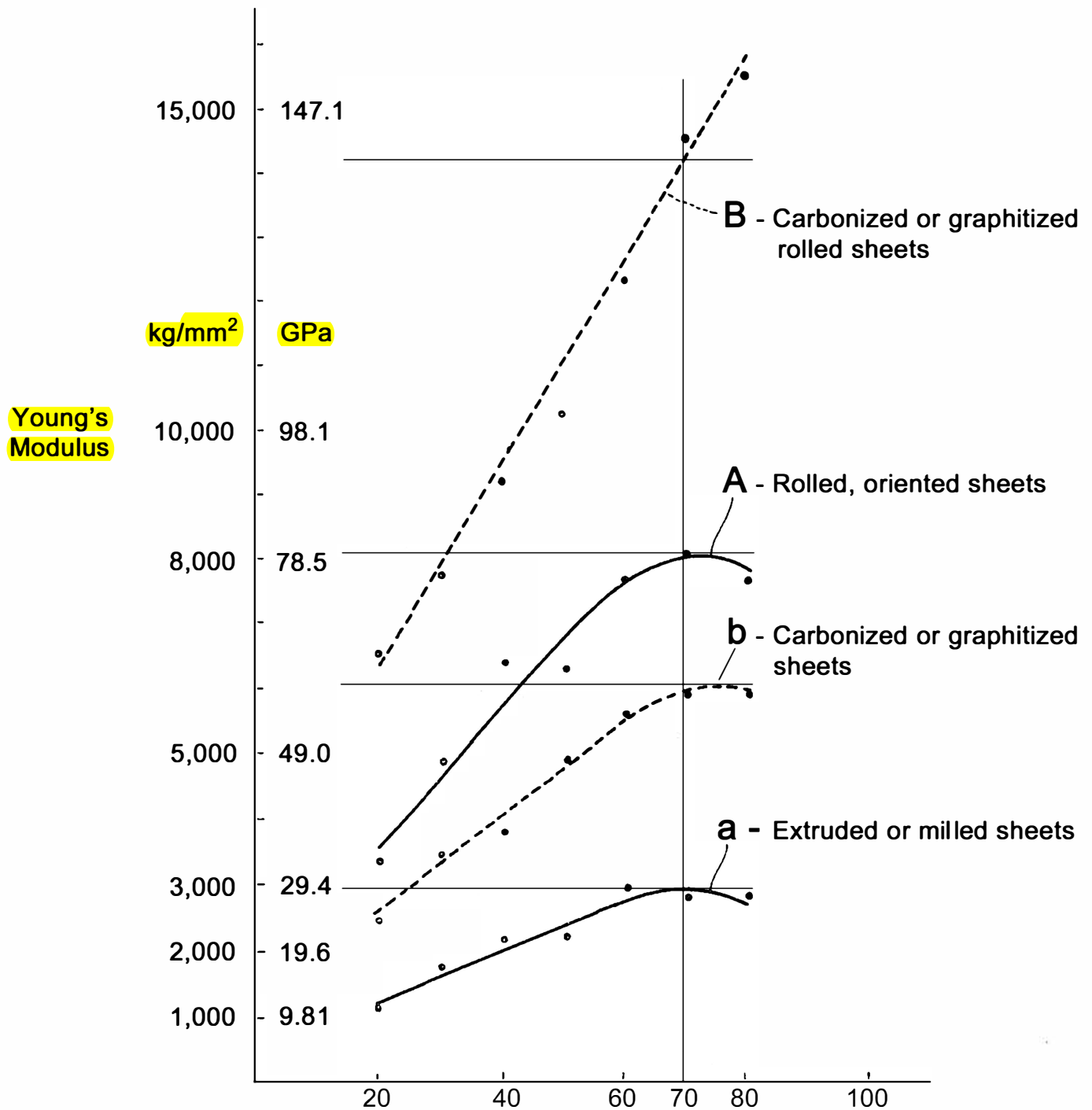


FIG. 2



Percent of Graphite Blended (wt%)

ρ - Graphite crystal = 2.27gm/cm³ = 30.8cc/100gm

ρ - PVCs \approx 1.4gm/cm³ = 21.4cc/100gm

[54] **DIAPHRAGM FOR ACOUSTIC INSTRUMENTS AND METHOD OF MANUFACTURING THE SAME**

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[52] U.S. Cl. **181/170; 428/408**

[58] Field of Search 181/157, 166, 167, 170,
181/174, 180, DIG. 1, 144-156; 428/408, 402,
403, 367, 116; 179/181 F, 115.5 R; 260/42.17

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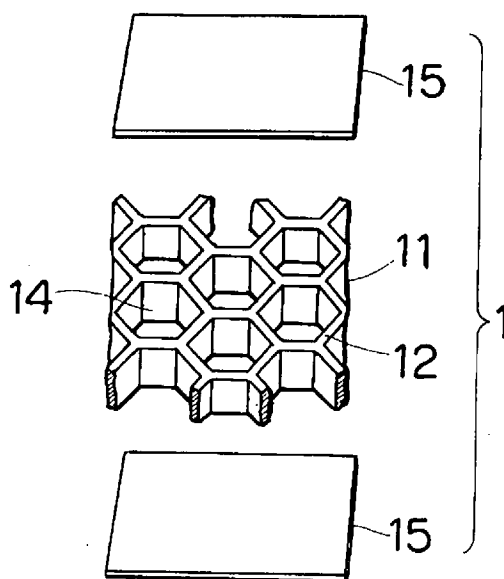
Primary Examiner—Benjamin R. Fuller
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Marmelstein & Kubovcik

[57] **ABSTRACT**

A honeycomb shaped diaphragm for use in acoustic instruments such as speakers is manufactured by kneading a mixture of flaky graphite powder and thermoplastic resin, preferably polyvinyl chloride, rolling the mixture into a plate, forming honeycomb recesses in the plate, and mating two recessed plates with each other so that the corresponding recesses form closed cavities.

The formed plate may be carbonized before assembly. The resultant diaphragm shows a high Young's modulus, a low apparent density and a remarkably high specific modulus of elasticity ensuring improved acoustic characteristics.

15 Claims, 6 Drawing Figures



DIAPHRAGM FOR ACOUSTIC INSTRUMENTS AND METHOD OF MANUFACTURING THE SAME

BACKGROUND OF THE INVENTION

This invention relates to a diaphragm for use in acoustic instruments such as speakers and microphones. This invention also pertains to a method of manufacturing an acoustic diaphragm.

To improve the performance of acoustic diaphragms, attempts have been made to reduce the density and increase the Young's modulus for materials from which diaphragms are made. One example is a honeycomb structure having a honeycomb core sandwiched between skins. The advantages of the honeycomb structure are light weight and rigidity. In the prior art, aluminum or fibrous carbon in a resinous matrix is used for the skin and aluminum is often used for the honeycomb core. Since these structures have a relatively large mass, and particularly a low specific modulus of elasticity E/ρ (E is Young's modulus and ρ is density) in the case of resin-bonded carbon fiber, the acoustic characteristics of the resulting diaphragms are not satisfactory. Furthermore, it is actually very difficult to form a honeycomb core from aluminum without a special complicated technique. This increases the cost of aluminum honeycomb diaphragms.

SUMMARY OF THE INVENTION

It is a primary object of this invention to provide a diaphragm for use in acoustic instruments which has improved acoustic characteristics.

Another object of this invention is to provide a method of manufacturing an acoustic diaphragm in a simple manner at low cost.

A diaphragm for use in an acoustic instrument according to this invention comprises a body of a kneaded mixture of flaky graphite powder and thermoplastic resin. The terminology "flaky graphite powder" is utilized in the present specification to mean a flaky graphite in powder form. The body includes a plurality of closed interior cavities therein. The cavities contain air and are partitioned by a rib which preferably extends transverse to the surface of the body, preferably in the form of a plate.

The flaky graphite powder has a diameter of 0.1 to 100 microns, preferably a diameter of 0.1 to 5 microns. The mixture includes 10 to 90 parts by weight of flaky graphite powder and 90 to 10 parts by weight of the resin. The preferred mixture includes 30 to 70 parts by weight of flaky graphite powder and 70 to 30 parts by weight of the resin. Smaller amounts of graphite are insufficient to improve Young's modulus while larger amounts result in fragile products. The flaky graphite powder is blended with the thermoplastic resin in a suitable ratio within the above range and the mixture is thoroughly kneaded by means of any suitable well-known kneader. Preferably, kneading is carried out at the softening point of the resin used. The resulting mixture is ready for use to mold a diaphragm element. Preferably, the mixture is rolled into a plate so as to orient the graphite flakes in parallel with the surface of the plate since the orientation of flakes in the resin matrix can increase the Young's modulus of the resulting plate.

The thermoplastic resins which can be used in this invention include polyvinyl chloride, polyvinylidene

chloride, vinyl chloride-acrylonitrile copolymers, vinylidene chloride-acrylonitrile copolymers, vinyl chloride-vinyl acetate copolymers, and mixtures thereof.

The mixture according to this invention may further contain effective amounts of a plasticizer and a stabilizer.

BRIEF DESCRIPTION OF THE DRAWING

The above and other objects and advantages of the invention will become apparent from the following discussion of the accompanying drawings, wherein

FIG. 1 is an exploded perspective view of a first embodiment of a diaphragm according to this invention;

FIG. 2 is a plan view showing a core used in another embodiment of a diaphragm according to this invention; and

FIGS. 3a to 3d are views of elements in various steps of diaphragm preparation according to this invention,

FIG. 3a being a cross section of a starting plate,

FIG. 3b being a plan view of a molded half,

FIG. 3c being a cross section of the molded half viewed along line C—C of FIG. 3b, and

FIG. 3d being a cross section of a diaphragm completed by mating two molded halves.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 1, there is shown a honeycomb structured acoustic diaphragm according to a first embodiment of this invention. The structure itself is known in the art. The diaphragm designated by numeral 1 comprises a honeycomb core 11 having open hexagonal cavities 14 partitioned by a rib 12. The core 11 is sandwiched by two skins 15 and 15.

According to this invention, the honeycomb core 11 is prepared by blending flaky graphite powder with polyvinyl chloride (to be referred to as "PVC", hereinafter) and molding the blend by any conventional process such as press molding, injection molding and compression molding. In a preferred embodiment, 20 parts by weight of flaky graphite powder is blended and kneaded with 10 parts by weight of PVC and the resulting blend is compression molded into a honeycomb structure. Compression molding permits graphite flakes to be oriented in the resin, imparting high rigidity to the resulting core 11. In the most preferred embodiment, the blend is rolled into a sheet, such rolled sheets are laminated and hot pressed into a laminate plate, and the plate is punched to form a honeycomb core. After molding, the honeycomb core may be pre-sintered by heating it at a temperature of 250° C. in an oxidizing atmosphere. The core may then be carbonized by heating it to a temperature of 1,200° C. in a non-oxidizing atmosphere. The carbonized core has a Young's modulus of 6,000–8,000 kg/mm² and a density of about 1.7 g/cm³. The ratio of Young's modulus to density or specific modulus of elasticity of the carbonized core is about 1.5 times higher than aluminum.

The skin 15 is prepared by rolling the same blend as prepared for the core 11 into a flat plate. Extrusion molding or other molding methods may be employed to prepare a flat plate. However, the plates prepared by extrusion molding the blend of flaky graphite powder and PVC show a somewhat reduced Young's modulus since graphite flakes are not oriented in the resin. Rolling can orient graphite flakes in the plate and thus in-

crease the Young's modulus. Therefore, rolling is the best method for preparing a flat plate for the skin 15.

For example, 20 parts by weight of flaky graphite powder is thoroughly kneaded with 10 parts by weight of PVC and the resulting blend is rolled into a plate which shows a Young's modulus of 6,000 kg/mm², a density of 1.8 g/cm³, a specific modulus of 3.3×10^9 mm, and an internal loss (tan δ) of 0.05. This means that the rolled plate is about 1.3 times higher in specific modulus than aluminum which has a Young's modulus of 7,000 kg/mm², a density of 2.7 g/cm³, and a specific modulus of 2.6×10^9 mm. A higher specific modulus indicates that sound is transmitted through the plate at a higher speed and piston motion is available up to a higher frequency range. The internal loss of the plate which is larger by one order than the internal loss of aluminum of 0.003 results in a flatter frequency response.

The Young's modulus of a plate of the above-formulated mixture may be significantly increased by carbonization. To this end, the plate is first pre-sintered and made infusible, for example, by heating it to a temperature of 100° to 500° C. at a rate of 1°–20° C. per hour in an oxidizing atmosphere, preferably in air. Then the plate is heated to a temperature of 500° to 1500° C., preferably 1000° to 1500° C. at a rate of 1°–20° C. per hour, preferably 10°–20° C. per hour in an inert atmosphere to achieve carbonization or graphitization. The carbonized plate of this example has a Young's modulus of 16,000 kg/mm², a density of 1.7 g/cm³, a specific modulus of 9.4×10^9 mm, and an internal loss (tan δ) of 0.009. This shows a significant increase in specific modulus with a reduction in internal loss.

The core 11 is sandwiched and sealed between the skins 15 and 15 via adhesive interfaces (not shown), obtaining a honeycomb assembly ready for use as an acoustic diaphragm. The openings 14 are closed by skins 15 in the assembly.

FIG. 2 shows another core 11 having a pattern of concentric circles and radial arms. The core 11 comprises concentric annular ribs 12 and radially extending arms or ribs 13 which cooperate to form open cavities 14. Such cores may be press molded, injection molded, or compression molded from a blend according to this invention. A mold may be prepared by cutting concentric annular channels by means of a lathe and by milling radial channels in a mold member.

A third embodiment of the diaphragm of this invention is shown in FIGS. 3a to 3d. This embodiment has a honeycomb structures similar to that of FIG. 1, but comprises different elements. FIG. 3a shows a flat plate 20 which is prepared by rolling a blend of flaky graphite powder and a resin as in the foregoing embodiments. Graphite flakes 19 are shown as being oriented in parallel with the surface of the plate 20. Simply blending flaky graphite with the resin cannot orient graphite flakes. Rolling is carried out as in the first embodiment shown in FIG. 1 to provide orientation of graphite flakes, thereby improving the specific modulus of the plate. The plate 21 is relatively thick so that recesses 23 having a given depth may be formed on a skin portion 25 having a given thickness in the subsequent molding step. The plate 20 may be either a single plate or an integrated multi-layer plate. In the latter case a plurality of thin sheets may be placed one on another and then hot pressed to form an integrated multi-layer plate having a given thickness.

In the next step, the plate 20 is heat pressed between an upper mold having hexagonal projections in a honeycomb pattern and a lower mold having a flat surface, obtaining a honeycomb half 21 as shown in FIGS. 3b and 3c. The honeycomb half 21 has a rib 22 defining hexagonal open recesses 23 on a skin portion 25. During press molding, part of the surface layer of the plate 20 is moved aside to form a portion of the rib 22. The remaining portion maintains orientation of graphite flakes although pressed denser particularly at areas underlying the recesses. No reduction of Young's modulus occurs in the skin portion 25 which will form a skin of a diaphragm after assembly.

The honeycomb half 21 may or may not be heat treated before it is assembled in the next step. If desired, the honeycomb half 21 is pre-sintered by heating to 250° C. in air and then carbonized by heating to 1,200° C. in a non-oxidizing atmosphere. The carbonization increases the Young's modulus significantly as described in the foregoing.

Two honeycomb halves shown in FIGS. 3a and 3c are then mated into a honeycomb assembly 1 shown in FIG. 3d by abutting the top surfaces of the ribs 22 with each other via an adhesive interface 26. The honeycomb assembly 1 consisting of two halves 21 joined at the interface 26 includes a plurality of cavities 24 which are partitioned by the rib 22 and closed by the skin portion 25.

The first embodiment shown in FIG. 1 uses one core and two skins and requires two adhesive applications to attach two skins to either surface of the core. The third embodiment shown in FIG. 3 requires one application of adhesive and one mold, contributing to a reduction of working time and fabrication steps. Accordingly, the third embodiment is more advantageous than the first embodiment.

The essential requirement for acoustic diaphragms is a reduction of weight for improving acoustic characteristics. This means that the weight of an adhesive is an important factor. As the area of an adhesive interface increases, the amount of adhesive applied increases and the risk of non-uniform application will increase. Non-uniform adhesion will deteriorate acoustic characteristics. The first embodiment includes two adhesive interfaces while the third embodiment includes one adhesive interface. The latter case is more advantageous in this respect too. It is to be noted that an adhesive is not necessary when elements to be bonded are not carbonized. Non-carbonized elements can be hot pressed into an assembly.

In the foregoing embodiment, the diaphragm includes cavities of a hexagonal form or a ring segment form. However, cavity form is not limited thereto and may be of a triangular or rectangular form, for example.

Also, the rib is not limited to a honeycomb pattern. The rib may take a pattern as shown in FIG. 2 or a triangular or rectangular pattern. The pattern may be varied insofar as the rib of one half mates with that of the other half in the case of embodiments as shown in FIG. 3.

Further, the foregoing embodiments all relate to flat diaphragms. The diaphragm may also be of a cone or dome shape. Those skilled in the art will select a suitable mold depending on the desired shape and the molding method employed. For example, a cone-shaped diaphragm may be readily obtained by re-forming a plate-shaped diaphragm prepared as above into a cone shape.

This invention will be more fully understood with reference to the following Examples.

EXAMPLE 1

Ingredient	Parts by weight
Polyvinyl chloride	10
Graphite	20
Stabilizer (lead stearate)	0.3
Plasticizer (BBPG)	1.0

These ingredients all in the form of powder were kneaded at a temperature of 150° C. and then rolled into a sheet having a thickness of 1.0 mm. Three sheets were placed one on the other and hot pressed to form an integrated laminate plate. The laminate plate was punched by means of a press having a honeycomb configuration at a temperature of 100° C. to form a honeycomb core similar to the core 11 shown in FIG. 1.

The honeycomb core was sandwiched between two sheets as rolled above (each having a thickness of 1.0 mm) and then hot pressed to complete the assembly which had a final thickness of 5.0 mm.

EXAMPLE 2

A sheet having a thickness of 1.0 mm as rolled in Example 1 was subjected to carbonization. The sheet was first pre-sintered and oxidized by heating it to a temperature of 250° C. at a rate of 1°-10° C./hour in an oxidizing atmosphere, and then carbonized by heating it to a temperature of 1000° C. at a rate of 10°-20° C./hour in an inert atmosphere.

Two carbonized sheets were attached to either surface of a honeycomb core as punched in Example 1 by applying an adhesive to the interface therebetween.

EXAMPLE 3

Two sheets as rolled in Example 1 were hot pressed to form an integrated laminate plate. The laminate plate was pressed by means of a honeycomb pattern press to form a honeycomb half similar to the half 21 shown in FIGS. 3b and 3c. Two halves were mated and hot pressed into honeycomb assembly as shown in FIG. 3d.

EXAMPLE 4

A honeycomb half as pressed in Example 3 was carbonized in the same manner as described in Example 2. Two carbonized halves were bonded using an adhesive, obtaining a honeycomb assembly.

As described in the foregoing, the acoustic diaphragm of this invention is made of a kneaded mixture of flaky graphite powder and a thermoplastic resin and has a structure including a plurality of closed interior cavities partitioned by an interior rib. The cavities contain air and are defined by the rigid rib. The mixture of graphite and a thermoplastic resin is not only readily rolled into a sheet, but also readily molded by press molding, injection molding, compression molding or the like. Accordingly, the diaphragm of this invention can be easily manufactured with a relatively small number of steps. The diaphragm has high rigidity due to the internal rib, a low apparent density due to the air-containing interior cavities, and a high specific modulus of elasticity E/ρ due to an increase of Young's modulus and a reduction of density attributed to the presence of flaky graphite powder.

When employed in speakers, the diaphragms according to this invention have an extended reproduction range and improved acoustic characteristics including distortion and transient response.

What is claimed is:

1. A diaphragm for use in an acoustic instrument comprising a body of a kneaded mixture consisting essentially of 10-90 parts by weight of flaky graphite powder and 90-10 parts by weight of a thermoplastic resin, said body including a plurality of closed interior cavities partitioned by an interior rib.

2. A diaphragm according to claim 1 wherein said flaky graphite powder are oriented in the resin in parallel with the surface of the body at least at the surface portion thereof.

3. A diaphragm according to claim 1 or 2 wherein said rib defining the cavities has a honeycomb pattern.

4. A diaphragm according to claim 1 or 2 wherein said rib defining the cavities has a pattern of concentric circles linked with radial arms.

5. A diaphragm according to claim 3 wherein said kneaded mixture of flaky graphite powder and a thermoplastic resin is carbonized.

6. A diaphragm according to claim 4 wherein said body is a plate having a flat surface.

7. A diaphragm for use in an acoustic instrument comprising two flat plates, and a rib member having two parallel main surfaces and provided with a plurality of openings transverse to the main surfaces, said rib member being sandwiched and sealed between said plates with the main surface abutting the inner surface of the plate so that said openings are closed by the plates, said plates and rib member being made of a kneaded mixture consisting essentially of flaky graphite powder and a thermoplastic resin.

8. A diaphragm for use in an acoustic instrument comprising two segments each made of a kneaded mixture consisting essentially of flaky graphite powder and a thermoplastic resin, having two flat main surfaces and provided at one main surface with a plurality of recesses, said segments mating with each other at their one main surfaces so that the corresponding recesses form closed cavities.

9. A diaphragm according to any one of claims 1, 2, 7 or 8 wherein said flaky graphite powder has a diameter of 0.1 to 100 microns.

10. A diaphragm according to claim 9 wherein said flaky graphite powder has a diameter of 0.1 to 5 microns.

11. A diaphragm according to claim 1 wherein said mixture includes 30-70 parts by weight of graphite and 70-30 parts by weight of the resin.

12. A diaphragm according to any one of claims 1, 2, 7 or 8 wherein said thermoplastic resin is selected from the group consisting of polyvinyl chloride, polyvinylidene chloride, vinyl chloride-acrylonitrile copolymers, vinylidene chloride-acrylonitrile copolymers, vinyl chloride-vinyl acetate copolymers, and mixtures thereof.

13. A diaphragm according to claim 12 wherein said thermoplastic resin is polyvinyl chloride.

14. A diaphragm according to claim 4 wherein said kneaded mixture of flaky graphite powder and a thermoplastic resin is carbonized.

15. A diaphragm according to claim 14 wherein said body is a plate having a flat surface.

* * * * *

FIG. 1

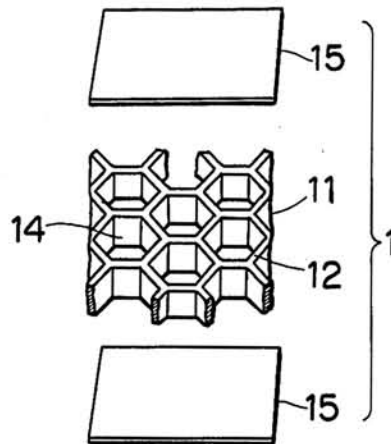


FIG. 2

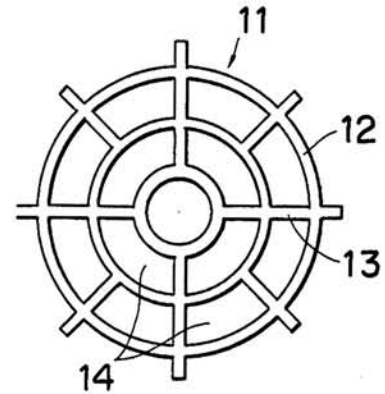


FIG. 3a

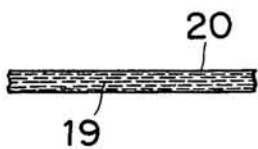


FIG. 3b

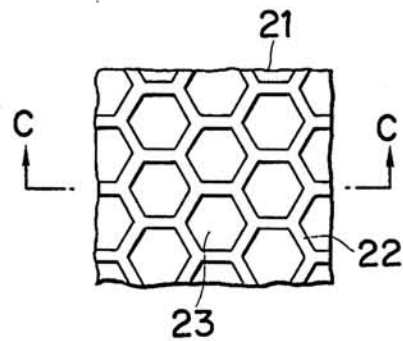


FIG. 3c

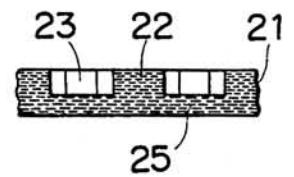
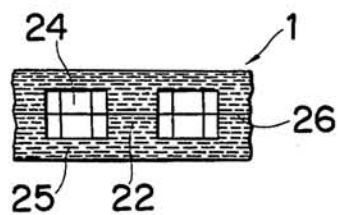


FIG. 3d



[54] **VIBRATORY ELEMENTS FOR AUDIO EQUIPMENT**

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Mar. 31, 1980 [JP]	Japan	55-40269

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[52] U.S. Cl. **428/36; 428/338; 428/408; 524/431**

[58] Field of Search **428/402, 404, 408, 338, 428/523, 36; 260/42, 46; 369/158, 244, 247, 256; 524/431**

[56]

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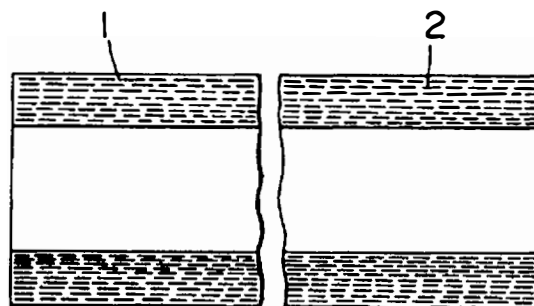
Primary Examiner—William J. Van Balen

[57]

ABSTRACT

Vibratory elements for use in audio equipment are fabricated from a kneaded mixture comprising polypropylene and flaky graphite powder. The kneaded mixture is rolled into a sheet in which graphite flakes are oriented parallel to the surface, and the sheet is then formed into a desired shape, for example, a dome- or cone-shaped diaphragm and a cantilever, as by vacuum forming, air-pressure forming or press molding. The mixture may further include polymethyl methacrylate and/or rubber-like material. The elements are characterized by improved temperature resistance.

12 Claims, 19 Drawing Figures



VIBRATORY ELEMENTS FOR AUDIO EQUIPMENT

BACKGROUND OF THE INVENTION

This invention relates to elements for use in audio equipment, and particularly to acoustic vibratory elements such as diaphragms for speakers and microphones and cartridge cantilevers for record players, the elements being lightweight, highly stiff and highly elastic and having a sufficient internal loss (damping) and an improved temperature resistance.

In general, acoustic vibratory elements such as acoustic diaphragms and cantilevers are required to have low density, high stiffness, high elasticity, and sufficient internal loss. Low density, high stiffness and high elasticity are necessary to provide efficient reproduction up to a high frequency range without causing partial vibration while sufficient internal loss (damping) is effective for preventing sound pressure from rapidly rising at about resonance frequencies in the high range as well as improving damping characteristics. Acoustic vibratory elements are known which are formed from lightweight, highly elastic materials, for example, metals such as aluminum, titanium and beryllium, and composite materials such as carbon fiber reinforced plastics (CFRP). None of these known materials are free of the problem of poor internal loss. Acoustic diaphragms with sufficient internal loss are also known which are formed from paper, synthetic resins or composite materials thereof. Though these materials have sufficient internal loss, they show a low modulus of elasticity and hence, a low specific modulus (ratio of modulus of elasticity E to density ρ , simply referred to as " E/ρ "). There is a need for material which has not only a low density and high elasticity, but also sufficient internal loss.

Recently, the inventors proposed in U.S. Ser. No. 147,866 (filed May 8, 1980) cantilevers and diaphragms which are characterized by low density, high elasticity and high internal loss, the cantilevers and diaphragms being formed from a kneaded mixture comprising polyvinyl chloride, polyvinylidene chloride and flaky graphite powder. The proposed material has improved physical properties which are not found in prior art materials. In various application of the previously proposed material, the inventors encountered a problem that it is insufficient in temperature resistance. Elements made of this material tend to be deformed particularly when used in automobile audio sets which may be exposed to the summer sun or possibly used in the tropics.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an improved acoustic vibratory element which has satisfactory temperature resistance as well as excellent qualities of low density, high elasticity and sufficient internal loss.

According to a first aspect of the present invention, there is provided an acoustic vibratory element fabricated from a kneaded mixture comprising polypropylene and flaky graphite powder, the graphite flakes being oriented substantially parallel to the surface of the element.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects, features and advantages of the present invention will be more fully understood

from the following description taken in connection with the accompanying drawings in which:

FIG. 1a is a cross-sectional view of a kneaded mass of graphite flakes in a resin matrix;

FIG. 1b is a cross-sectional view of a rolled sheet in which graphite flakes are oriented parallel to the surface according to the present invention;

FIG. 2 is a perspective view of a laminate having four rolled sheets placed one on top of the other;

FIG. 3 is a cross-sectional view of an embodiment of the cone-shaped diaphragm according to the present invention;

FIGS. 4a and 4b are radial and axial cross-sectional views of a cylindrical member formed from the rolled sheet, respectively;

FIG. 5 is an axial cross-sectional view of a cantilever prepared from the cylindrical member shown in FIGS. 4a and 4b;

FIGS. 6a, 6b and 6c illustrate successive steps of molding the kneaded mixture into a desired article;

FIGS. 7a, 7b and 7c are perspective views of a speaker enclosure, a record player base and a radio/cassette player casing, respectively;

FIG. 8 is an exploded view of a speaker enclosure; and

FIGS. 9a, 9b, 9c, 9d and 9e are perspective views of a speaker frame, a horn, an acoustic lens, an acoustic equalizer and a grille, respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The acoustic vibratory element according to the present invention is fabricated from a kneaded mixture mainly containing polypropylene and flaky graphite powder. The resin component may be polypropylene alone or in admixture with polymethyl methacrylate (PMMA).

Polypropylene which can be used herein may be propylene homopolymers and block and random copolymers of propylene with ethylene or any other comonomers. These propylene polymers may be prepared by and of well-known methods and are commercially available.

Preferred examples of polymethyl methacrylate are those having a softening point above 90° C.

Further, a rubber-like material may also be added to the polypropylene. It is also contemplated in the present invention to add both a rubber-like material and polymethyl methacrylate to the polypropylene. Examples of the rubber-like material are acrylonitrilebutadiene rubber (NBR), butyl rubber (IIR), styrenebutadiene rubber (SBR), etc. It is to be understood that the rubber-like materials contribute to a further improvement in internal loss.

In general, the modulus of elasticity of a resin gradually decreases as the surrounding temperature is raised. The temperature at which the modulus of elasticity decreases to one-half of the original value at room temperature is referred to as "half-modulus temperature" in this specification. When the half-modulus temperatures of resins of interest are compared, the half-modulus temperature of polypropylene is higher by about 25 degrees Centigrade than that of ordinary PVC, and PMMA is higher by 10 degrees Centigrade than the latter. Accordingly, molding materials comprising flaky graphite powder, polypropylene and optionally, PMMA have a higher half-modulus temperature and

hence, improved temperature resistance as compared with our previous PVC-based molding materials.

The flaky graphite powder contributes to an improvement in modulus of elasticity, which cannot be expected in the case of resin components per se. The modulus of elasticity is substantially increased when graphite flakes are oriented in one direction, preferably parallel to the surface of a molded product. Graphite flakes have a thin disc- or platelet-form and preferably have an average particle size of about 0.1 to about 20 microns, particularly about 0.1 to about 5 microns. An improvement in modulus of elasticity attributable to graphite flakes and satisfactory moldability can be expected and moldings are free of embrittlement when about 10 to 90 parts by weight of graphite powder is combined with 90 to 10 parts by weight of the resin component. An outstanding improvement is achieved when about 50 to 75 parts by weight of graphite powder is combined with about 50 to 25 parts by weight of the resin component.

PMMA is widely used with polypropylene as its processing aid and the amount of PMMA to be added may be varied in the range of 1-30%, preferably 10-25% by weight of the polypropylene, depending on the shape and properties of the intended product. The rubber-like material may be added in an amount of about 2 to 50 parts per 100 parts by weight of the resin component. The addition of about 10 pph of the rubber-like material will result in a 20% reduction of modulus of elasticity while internal loss is increased about 1.5 to 2.0 times.

The present invention will be more fully understood by referring to the preferred embodiments in conjunction with the drawing.

Acoustic vibratory elements may be fabricated by first mixing flaky graphite powder with the resin component which may be polypropylene alone or its admixture with polymethyl methacrylate and an optional rubber-like material. Also, a plasticizer and/or stabilizer may optionally be added. The thus obtained mixture is fully kneaded by means of a conventional kneader or roll mill while heating to a temperature of 190°-210° C. at which the resins will soften or melt. The kneaded mass is designated at 3 in FIG. 1a as containing graphite flakes 2 in a resin matrix 1. As seen from FIG. 1a, graphite flakes 2 are randomly distributed throughout the resin matrix 1.

The kneaded material 3 is then repeatedly rolled by means of a roll mill into a sheet 4 as shown in FIG. 1b. The rolling of the kneaded material causes the graphite flakes 2 to be oriented parallel to the surface of the sheet 4. As a result of graphite orientation, the modulus of elasticity of the rolled sheet is increased two to three times over kneaded materials containing randomly distributed graphite flakes.

One sheet 4 may be fabricated into an acoustic vibratory element of a desired shape by any suitable method including vacuum forming, air-pressure forming or press molding while heating to about the softening temperature of the resin. If desired, two or more sheets 4

may be placed one on top of the other to form a laminate having a desired thickness. FIG. 2 illustrates such a laminate 11 having four sheets 4. Heat bonding or adhesive application may be effected to bond the adjoining sheets.

In fabricating a speaker diaphragm 12 as shown in FIG. 3, the sheet 4 or the laminate 11 of some sheets laminated to a desired thickness is press molded between upper and lower mold halves at about the softening temperature.

The resulting diaphragm 12 exhibits a high stiffness and a high modulus of elasticity as graphite flakes 2 are oriented parallel to the surface as shown in FIG. 3. Although the diaphragm is of cone shape in this example, it may be of dome shape.

A cantilever may be fabricated by rounding the single sheet 4 or the laminate 11 of several sheets into a cylinder as shown in FIGS. 4a and 4b while heating to about the softening temperature. The abutting edges of the rounded sheet are heat bonded under pressure or bonded with an adhesive at an interface 5. The thus integrated cylindrical member may be deformed into a cantilever 13 as shown in FIG. 5 using suitable deforming means at about the softening temperature.

Examples of the present invention are described below.

	Parts by weight
Example 1	
Polypropylene	100
Flaky graphite powder	200
Example 2	
Polypropylene	100
Flaky graphite powder	300
Example 3	
Polypropylene	80
Polymethyl methacrylate	20
Flaky graphite powder	250
Example 4	
Polypropylene	100
IIR (Butyl Rubber)	10
Flaky graphite powder	200
Example 5	
Polypropylene	80
Polymethyl methacrylate	20
IIR (Butyl Rubber)	10
Flaky graphite powder	250
Control	
Polyvinyl chloride	100
Flaky graphite powder	200
Lead stearate (stabilizer)	5
Diocetyl phthalate (plasticizer)	10

In each Example, powder ingredients were fully kneaded in a kneader at a temperature of 190°-210° C. using the above-mentioned formulation. A portion of the thus kneaded material was rolled several times by means of a twin-roll mill, obtaining a sheet in which graphite flakes were oriented parallel to the surface. Samples of the kneaded materials and rolled sheets were determined for their physical properties. The results are shown in the following Table.

TABLE

Example	Graphite distribution	Modulus of elasticity E ($\times 10^{10}$ N/m ²)	Density ρ ($\times 10^3$ kg/m ³)	Internal loss tan δ	Half-modulus temperature* (°C.)
1	random	1.6	1.47	0.05	80
1	oriented	3.2	1.47	0.05	80
2	random	2.5	1.60	0.04	80
2	oriented	4.3	1.60	0.04	80

TABLE-continued

Example	Graphite distribution	Modulus of elasticity $E (\times 10^{10} \text{N/m}^2)$	Density $\rho (\times 10^3 \text{kg/m}^3)$	Internal loss $\tan \delta$	Half-modulus temperature* (°C.)
3	random	2.0	1.55	0.04	80
3	oriented	3.8	1.55	0.04	80
4	random	1.25	1.45	0.07	80
4	oriented	2.50	1.45	0.07	80
5	random	1.5	1.52	0.06	80
5	oriented	3.0	1.52	0.06	80
Control	random	2.2	1.8	0.03	55
Control	oriented	6.0	1.8	0.03	55
Aluminum		7.1	2.7	0.003	—
Kraft paper		0.2	0.6	0.05	—

*Temperature at which modulus of elasticity is reduced to one-half of the initial value when the temperature is raised from room temperature.

A sheet having a thickness of 100 microns obtained by rolling in each Example is vacuum formed at 100° C. into a cone-shaped diaphragm as shown in FIG. 3.

In addition, each sheet is heated to 100° C. before it is rounded on a cylindrical core. The abutting edges of the rounded sheet are heat bonded and the core is then withdrawn. The resulting cylindrical member is deformed into a cantilever shape as shown in FIG. 5.

The thus fabricated diaphragms and cantilevers exhibit a high modulus of elasticity and a high specific modulus as graphite flakes are oriented parallel to the surface. As seen from the Table, they show a high specific modulus E/ρ exceeding the specific modulus of metals such as aluminum and a large internal loss approximating the internal loss of paper. Due to these improved properties, the diaphragms of the present invention exhibit more flat frequency response over a wide frequency range without inducing partial vibration. In addition, the temperature resistance of the diaphragms according to the present invention is improved by about 20 degrees Centigrade over the previously proposed material as proved by a heat distortion temperature of above 120° C.

It is to be noted that the kneaded mixture 3 of the resin matrix 1 having graphite flakes 2 randomly distributed therein as shown in FIG. 1a is ready for use in molding various articles which need not necessarily have a substantially increased modulus of elasticity. Such articles are casings for acoustic equipment, for example, speaker enclosures, record player bases and portable radio/cassette player casings. Other examples are nonvibratory elements for speaker systems, for instance, speaker frames, horns, equalizers, acoustic lens, and grilles. These articles may be molded directly from the kneaded mixture 3 by any suitable molding techniques including compression molding, injection molding and press molding. A process of compression molding, for example, is illustrated in FIGS. 6a-6c. Lower and upper mold halves 21 and 22 define a cavity having a configuration corresponding to the shape of a desired article, when mated together. A metered amount of the kneaded mixture material 3 is placed on the cavity-defining surface of the lower mold half 21 as shown in FIG. 6a, and then the upper mold half 22 is moved downward to compress the material while heating, allowing the material to flow throughout the cavity. Thereafter, the mold halves 21 and 22 are cooled and separated. A molded article 23 is then removed.

The molded article 23 may take the form of a speaker enclosure 24, a record player base 25, and a radio-cassette player casing 26 shown in FIGS. 7a, 7b, and 7c, respectively.

The kneaded material containing randomly distributed graphite flakes or the article 23 directly molded therefrom has a modulus of elasticity which is about one-half or one third of that of a material of the same composition, but having graphite flakes oriented. However, the former and the latter are equal in internal loss. Therefore, acoustic equipment casings molded from the kneaded material are satisfactory because in such uses only improved vibration damping characteristics are required for such casings.

Of course, the sheet 4 obtained from the kneaded material by rolling and having graphite flakes 2 oriented may be used to fabricate casings. Usually, a plurality of sheets are placed one on top of the other to form the laminate 11 as shown in FIG. 2. For example, a speaker enclosure may be fabricated by assembling a front panel 31a, a top panel 31b, side panels 31c and a bottom panel 31d as shown in FIG. 8. The assembly may be completed by heat bonding or adhesive bonding.

A record player base may be fabricated by superposing a number of sheets 4 to a required thickness. The laminate 11 is then provided with openings (not shown) for receiving a turntable assembly and a tone-arm base.

It will be understood that the article 23 may be either molded directly from the kneaded material or assembled from some components of rolled sheets. For example, a one-piece integral enclosure 24 shown in FIG. 7a can be easily molded directly from the kneaded material whereas the enclosure assembled from panels 31 of rolled sheets as shown in FIG. 8 is rigidier than the former.

FIGS. 9a to 9e illustrate a speaker frame, a horn, an acoustic lens, an acoustic equalizer, and a grille which are typical examples of articles molded using the compression molding technique as shown in FIGS. 6a to 6c. Such an article may be either a one-piece article molded from the kneaded material or an article assembled from two or more shaped components. As the kneaded material has sufficient internal loss, these speaker elements molded therefrom are substantially free of resonance and exhibit sufficient vibration damping characteristics.

What we claim:

1. An acoustic vibratory element fabricated from a kneaded mixture comprising polypropylene, polymethyl methacrylate and flaky graphite powder, the graphite flakes being oriented substantially parallel to the surface of the element.

2. The acoustic vibratory element according to claim 1 wherein the kneaded and oriented mixture further contains a rubber-like material.

3. The acoustic vibratory element according to claim 2 wherein said rubber-like material is selected from the

group consisting of acrylonitrile-butadiene rubber, butyl rubber and styrene-butadiene rubber.

4. An acoustic vibratory element according to claim 1 wherein the kneaded and oriented mixture contains 90 to 10% by weight of polypropylene and 10 to 90% by weight of flaky graphite powder and based on the weight of the polypropylene 1-30% by weight of polymethyl methacrylate and 2-50% by weight of a rubber-like material.

5. The acoustic vibratory element according to claim 4 wherein said kneaded and oriented mixture contains 50 to 25% by weight of polypropylene and 50 to 75% by weight of flaky graphite powder.

6. The acoustic vibratory element according to any one of claims 1, 2, 3, 5 or 4 wherein the oriented graphite flakes have a particle size of 0.1 to about 20 microns.

7. The acoustic vibratory element according to claim 6 wherein the oriented graphite flakes have a particle size of 0.1 to about 5 microns.

8. The acoustic vibratory element according to claim 1 wherein the element is fabricated by rolling the kneaded mixture into a sheet and then forming the sheet into a desired shape by way of vacuum forming, air-pressure forming or press molding.

9. The acoustic vibratory element according to claim 1 wherein said element is a diaphragm.

10. The acoustic vibratory element according to claim 9 wherein said element is a cone-shaped diaphragm.

11. The acoustic vibratory element according to claim 9 wherein said element is a dome-shaped diaphragm.

12. The acoustic vibratory element according to claim 1 wherein said element is a cantilever.

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FIG. 1a

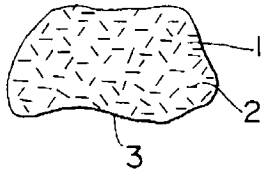


FIG. 1b

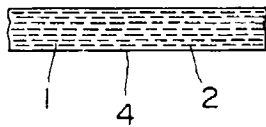


FIG. 2

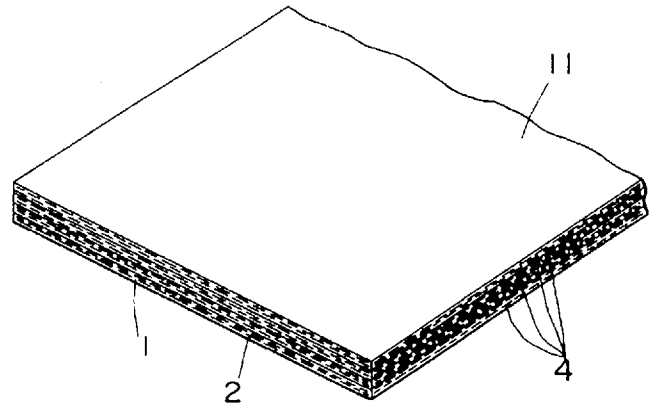


FIG. 4a

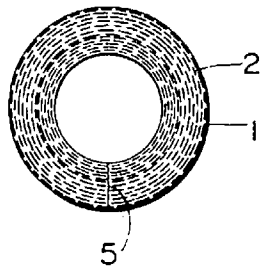


FIG. 3

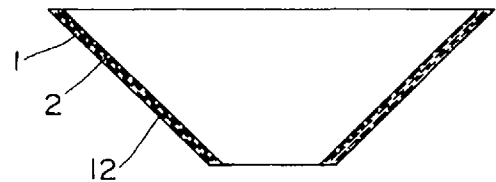


FIG. 4b

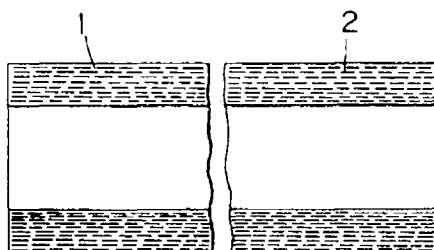


FIG. 5

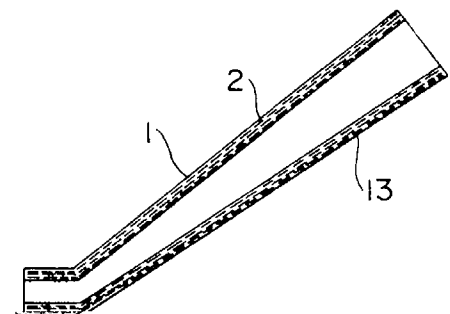


FIG. 6a

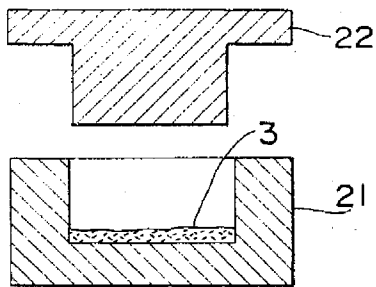


FIG. 6b

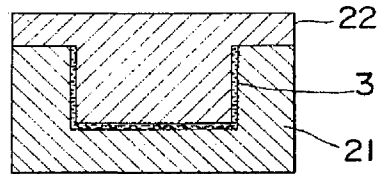


FIG. 6c

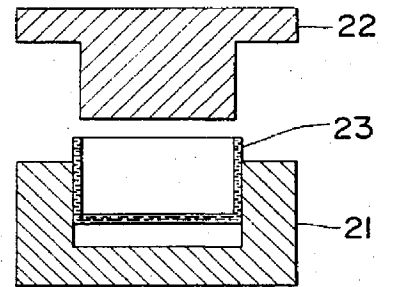


FIG. 7a

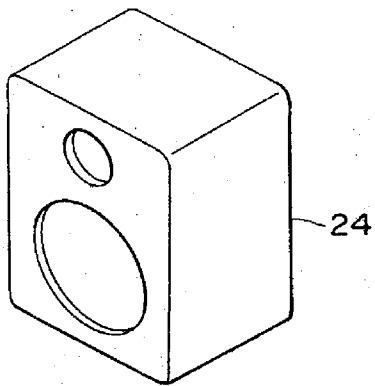


FIG. 7b

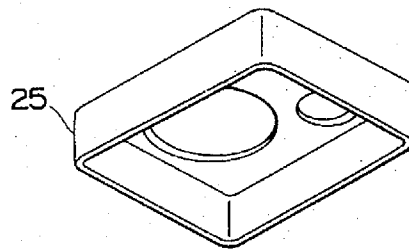


FIG. 7c

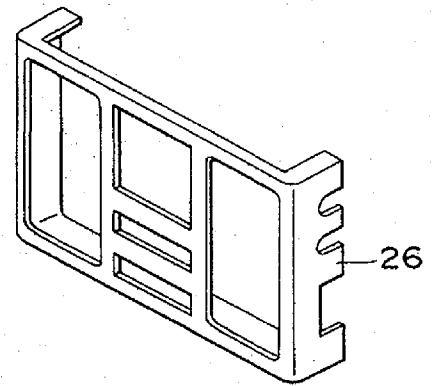


FIG. 8

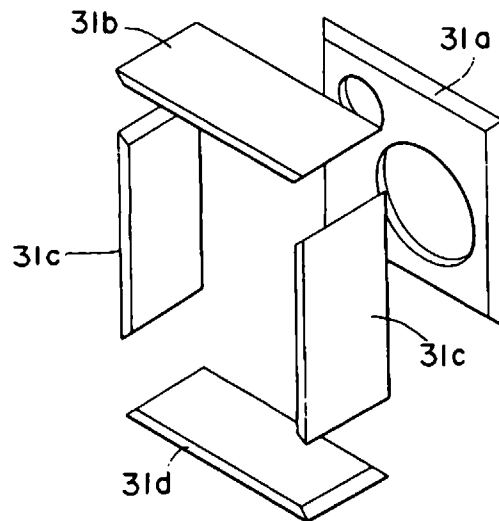


FIG. 9a

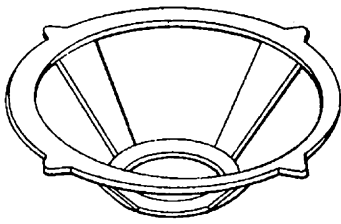


FIG. 9b

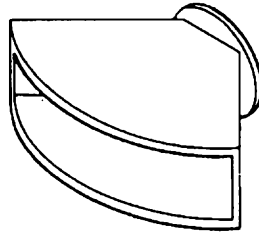


FIG. 9c

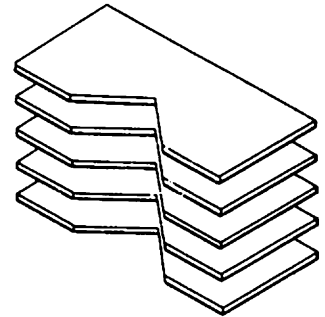


FIG. 9d

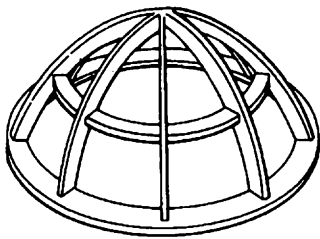
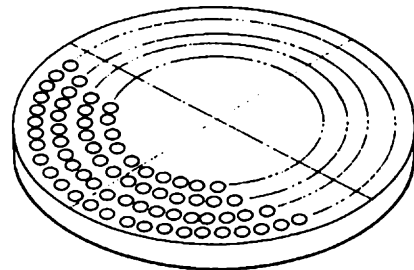


FIG. 9e



[54] TONE-ARM ELEMENTS

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[73] Assignee: Pioneer Electronic Corporation, Tokyo, Japan

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[22] Filed: Mar. 18, 1981

[30] Foreign Application Priority Data

Mar. 31, 1980 [JP] Japan 55-40266

[51] Int. Cl.³ B32B 5/00; B32B 9/00

[52] U.S. Cl. 428/338; 428/408; 524/431

[58] Field of Search 428/402, 404, 408, 338, 428/523; 260/42, 46; 369/158, 244, 247, 256; 524/431

[56]

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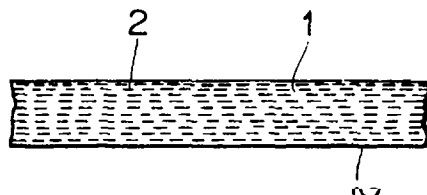
Primary Examiner—William J. Van Balen

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ABSTRACT

Elements for a tone-arm system such as arm pipes, head shells, cartridge bodies, and arm bases are fabricated from a kneaded mixture comprising polypropylene and flaky graphite powder. The mixture may further include polymethyl methacrylate and/or rubber-like material. Graphite flakes are preferably oriented parallel to the surface of the element. The elements show improved temperature resistance.

10 Claims, 16 Drawing Figures



TONE-ARM ELEMENTS

BACKGROUND OF THE INVENTION

This invention relates to tone-arm elements, and more particularly, to those elements constituting the non-vibration system of a tone-arm for a record player, such as tone-arm pipes, cartridge bodies, head shells, arm bases and the like.

To enhance the trackability of a cartridge, it is desirable to reduce the mass of a cartridge-supporting or non-vibration system while obtaining an increased internal loss to prevent partial vibration. The mass of a tone-arm system may be reduced simply by making an arm pipe, a head shell and other tone-arm elements lighter. However, if wall thickness is reduced for this purpose, a correspondingly reduced stiffness tends to cause unwanted partial vibration, debasing the sound quality reproduced through such a tone-arm system. There is a need for arm pipes, head shells and cartridge bodies formed from a light-weight material which has a high stiffness or high modulus of elasticity as well as a sufficient internal loss.

Those arm pipes and head shells formed from a conventional metallic material such as aluminum, titanium, beryllium, etc. are not satisfactory due to poor internal loss (damping) though they have a high modulus of elasticity. Also known are arm pipes and head shells formed from fibrous carbon materials which are physically excellent as they have a high specific modulus of elasticity and a relatively large internal loss. However, carbon fibers must be compounded with a synthetic resin before arm pipes or head shells can be molded therefrom. Such composite carbon fiber-resin materials show a reduced specific modulus of elasticity.

Recently, the inventors proposed arm pipes and head shells molded from a kneaded mixture of polyvinyl chloride and flaky graphite powder and having advantages of light weight, high elasticity and high internal loss as disclosed in U.S. Ser. No. 147,866 (filed May 8, 1980). The proposed tone-arm elements have improved properties which are not found in prior art materials or elements. In various applications of the previously proposed material, the inventors encountered a problem that these elements are still insufficient in heat resistance. These elements tend to be deformed particularly when exposed to the sun in summer or used in the tropics.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an improved tone-arm element which is satisfactory in temperature resistance as well as having excellent qualities of light weight, high elasticity and sufficient internal loss.

According to a first aspect of the present invention, there is provided a tone-arm element fabricated from a kneaded mixture mainly containing polypropylene and flaky graphite powder.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects, features and advantages of the present invention will be more fully understood from the following description taken in connection with the accompanying drawing in which:

FIG. 1 is a cross-sectional view of a kneaded mass of graphite flakes in a resin matrix from which a tone-arm element is fabricated according to the present invention;

FIGS. 2a, 2b and 2c illustrate successive steps of molding a tone-arm element;

FIGS. 3a, 3b and 3c are perspective views of a head shell, a cartridge body and an arm base embodying the tone-arm element of the present invention;

FIG. 4 is a cross-sectional view of a rolled sheet in which graphite flakes are oriented parallel to the surface according to a preferred embodiment of the present invention;

FIGS. 5a and 5b are transverse and longitudinal cross-sections of the head shell shown in FIG. 3a, graphite flakes being oriented;

FIG. 6 illustrates one embodiment of the arm pipe fabricating process in which a strip of rolled molding material is wound on a core;

FIG. 7 illustrates another embodiment of the arm pipe fabricating process in which a core is sandwiched between two sheets;

FIG. 8 is a cross-sectional view of a mold in which an arm pipe is being press molded;

FIG. 9 is a perspective, partially cut-away, view of the arm pipe; and

FIGS. 10a and 10b are transverse and axial cross-sections of the arm pipe shown in FIG. 9.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The tone-arm element according to the present invention is fabricated from a kneaded mixture mainly containing polypropylene and flaky graphite powder. The resin component may be polypropylene alone or in admixture with polymethyl methacrylate (PMMA).

Polypropylene which can be used herein may be propylene homopolymers and block and random copolymers of propylene with ethylene or any other comonomers. These propylene polymers may be prepared by any of well-known methods and are commercially available.

Preferred examples of polymethyl methacrylate are those having a softening point above 90° C.

Further, a rubber-like material may also be added to the polypropylene. It is also contemplated in the present invention to add both a rubber-like material and polymethyl methacrylate to the polypropylene. Examples of the rubber-like material are acrylonitrile-butadiene rubber (NBR), butyl rubber (IIR), styrene-butadiene rubber (SBR), etc. It is to be understood that the rubber-like materials contribute to a further improvement in internal loss.

In general, the modulus of elasticity of a resin gradually decreases as the surrounding temperature is raised. The temperature at which modulus of elasticity decreases to one-half of the original value at room temperature is referred to as half-modulus temperature in this specification. When the half-modulus temperatures of resins of interest are compared, the half-modulus temperature of polypropylene is higher by about 25 degrees Centigrade than that of normal PVC, and PMMA is higher by 10 degrees Centigrade than the latter. Accordingly, molding materials comprising flaky graphite powder, polypropylene and optionally, PMMA have a higher half-modulus temperature and hence, improved temperature resistance as compared with the previous PVC-based molding materials.

The flaky graphite powder contributes to an improvement in modulus of elasticity, which cannot be expected in the case of resin components per se. The modulus of elasticity is substantially increased when graphite flakes are oriented in one direction, preferably parallel to the surface of a molded product. Graphite flakes have a thin disc- or platelet-form and preferably have an average particle size of about 0.1 to about 20 microns, particularly about 0.1 to about 5 microns. An improvement in modulus of elasticity attributable to graphite flakes and satisfactory moldability can be expected and such moldings are free of embrittlement when about 10 to 90 parts by weight of graphite powder is combined with 90 to 10 parts by weight of the resin component. An outstanding improvement is achieved when about 50 to 75 parts by weight of graphite powder is combined with about 50 to 25 parts by weight of the resin component.

PMMA is widely used with polypropylene as its processing aid and the amount of PMMA to be added may be varied in the range of 1-30%, preferably 10-25% by weight of the polypropylene, depending on the shape and properties of the intended product. The rubber-like materials may be added in an amount of about 2 to 50 parts per 100 parts by weight of the resin component. The addition of about 10 pph of the rubber-like material will result in a 20% reduction of modulus of elasticity while internal loss is increased about 1.5 to 2.0 times.

The present invention will be more fully understood by referring to the preferred embodiments in conjunction with the drawing.

Tone-arm elements may be fabricated by first mixing flaky graphite powder with a resin component which may be polypropylene alone or its admixture with polymethyl methacrylate and an optical rubber-like material. Also, a plasticizer and/or stabilizer may optionally be added. The thus obtained mixture is fully kneaded by means of a conventional kneader or roll mill while heating to a temperature of 190°-210° C. at which the resins will soften or melt. The kneaded mass is designated at 3 in FIG. 1 as containing graphite flakes 2 in a resin matrix 1. As seen from FIG. 1, graphite flakes 2 are randomly distributed throughout the resin matrix 1.

The kneaded mixture 3 is ready for use in molding. Tone-arm elements such as head shells, arm bases and cartridge bodies may be directly molded from the kneaded material 3 by any suitable molding methods including compression molding, injection molding and press molding. A process of compression molding, for example, is illustrated in FIG. 2. Upper and lower mold halves 4 and 5 define a cavity having a configuration corresponding to the shape of a desired tone-arm element, when mated together. A portion of the kneaded material 3 is placed on the cavity-defining surface of the lower mold half 4 to compress the material while heating, allowing the material to flow throughout the cavity. Thereafter, the mold halves 4 and 5 are cooled and then separated. The molded element 6 is then removed.

The molded element 6 may take the form of a head shell 7, a cartridge body 8, and an arm base 9 shown in FIGS. 3a, 3b, and 3c, respectively.

The kneaded material 3 containing randomly distributed graphite flakes or the element 6 molded therefrom has a modulus of elasticity which is about $\frac{1}{2}$ or $\frac{1}{3}$ of that of a material of the same composition, but having the graphite flakes oriented. However, their internal losses are equal independent of graphite orientation. Elements

molded from a kneaded material containing randomly distributed graphite flakes are suitable as elements constituting a tone-arm system which need not vibrate at a high reproduction frequency range, but must have sufficient damping characteristics to externally induced low-frequency range vibrations and vibration due to a warped record.

In another embodiment requiring an increased modulus of elasticity, the kneaded material 3 is repeatedly rolled by means of a roll mill into a sheet 10 as shown in FIG. 4. The rolling of the kneaded material causes the graphite flakes 2 to be oriented parallel to the surface of the sheet 10. As a result of graphite orientation, the modulus of elasticity of the rolled sheet is increased two to three times over kneaded materials containing randomly distributed graphite flakes. The sheet 10 or a laminate of two or more sheets 10 if desired may be fabricated into a tone-arm element of a desired shape by any suitable method including vacuum forming, air-pressure forming or press molding while heating.

In fabricating a head shell as shown in FIG. 3a, a plurality of sheets 10 are laminated to a desired thickness and the laminate is press molded between upper and lower mold halves. The resulting head shell 7 exhibits a high stiffness and a high modulus of elasticity as graphite flakes 2 are oriented parallel to the surface of the shell as shown in FIGS. 5a and 5b.

In general, an arm pipe should bear a relatively large load or should have a high stiffness and modulus of elasticity as it is equipped with a balance weight and a head shell and is to be manually manipulated by the operator. Therefore, the arm pipe is preferably fabricated from the sheet 10 having graphite flakes oriented. The arm pipe may be fabricated by spirally winding a strip cut from the sheet 10 around a core 11. The tightly wound strip is heated to cause heat bonding of adjoining edges. Alternatively, a sandwich assembly of a core 12 between two sheets 10 is subjected to pressure forming at elevated temperatures in a press mold 13 as shown in FIGS. 7 and 8. The thus fabricated tone-arm pipe is designated at 14 in FIG. 9. In this arm pipe 14, graphite flakes 2 are oriented parallel to the surface of the pipe or both in the axial and the circumferential directions as shown in FIGS. 10a and 10b.

Examples of the present invention are described below.

EXAMPLE 1	Parts by weight
Polypropylene	100
Flaky graphite powder	200

EXAMPLE 2	Parts by weight
Polypropylene	100
Flaky graphite powder	300

EXAMPLE 3	Parts by weight
Polypropylene	80
Polymethyl methacrylate	20
Flaky graphite powder	250

EXAMPLE 4	Parts by weight
Polypropylene	100
IIR	10
Flaky graphite powder	200

EXAMPLE 5

	Parts by weight
Polypropylene	80
Polymethyl methacrylate	20
IIR	10
Flaky graphite powder	250

CONTROL

Polyvinyl chloride	100
Flaky graphite powder	200
Lead stearate (stabilizer)	5
Dioctyl phthalate (plasticizer)	10

In each Example, power ingredients were fully kneaded in a kneader at a temperature of 190°–210° C. using the above-mentioned formulation. A portion of the thus kneaded material was rolled several times by means of a twin-roll mill, obtaining a sheet in which graphite flakes were oriented parallel to the surface. Samples of the kneaded materials and rolled sheets were determined for their physical properties. The results are shown in the following Table.

Various tone-arm elements were fabricated from the kneaded mixture and the rolled sheet of each Example. Particularly, head shells, cartridge bodies and arm bases were compression molded from the kneaded mixture having randomly distributed graphite flakes. Head shells, arm pipes and arm bases were vacuum formed from the rolled sheet having graphite flakes oriented.

The thus obtained tone-arm elements are light weight or have a low density as the molding material is based on the synthetic resin and graphite. They show sufficient internal loss due to the crystalline structure of graphite and the softness of the rubber-like material when used. Further, those tone-arm elements in which the graphite flakes are oriented exhibit a significantly increased stiffness and modulus of elasticity. That is, tone-arm elements having sufficient internal loss can be fabricated without losing physical strength. In addition, the tone-arm elements of the present invention are satis-

factorily heat resistant as proved by a heat distortion temperature of above 120° C.

What we claim:

1. A tone-arm element fabricated from a kneaded mixture comprising polypropylene, polymethyl methacrylate and flaky graphite powder.
2. The tone-arm element according to claim 1 wherein the kneaded mixture further contains a rubber-like material.
3. The tone-arm element according to claim 2 wherein said rubber-like material is selected from the group consisting of acrylonitrile-butadiene rubber, butyl rubber and styrene-butadiene rubber.
4. The tone-arm element according to any one of claims 1, 2 or 3 wherein the graphite flakes of said powder are oriented substantially parallel to the surface of the element.
5. A tone-arm element according to claim 1 wherein said kneaded mixture contains 90 to 10% by weight of polypropylene and 10 to 90% by weight of flaky graphite powder and based on the weight of the polypropylene 1–30% by weight of polymethyl methacrylate and 2–50% by weight of a rubber-like material.
6. The tone-arm element according to claim 5 wherein said kneaded mixture contains 50 to 25% by weight of polypropylene and 50 to 75% by weight of flaky graphite powder.
7. The tone-arm element according to claim 5 wherein the graphite flakes have a particle size of 0.1 to about 20 microns.
8. The tone-arm element according to claim 7 wherein the graphite flakes have a particle size of 0.1 to about 5 microns.
9. The tone-arm element according to claim 1 wherein the element is fabricated directly from the kneaded mixture by compression molding, injection molding or press molding.
10. The tone-arm element according to claim 1 wherein the element is fabricated by rolling the kneaded mixture into a sheet and then forming the sheet into a desired shape by way of vacuum forming, air-pressure forming or press molding.

Example	Graphite distribution	Modulus of elasticity E (x 10 ¹⁰ N/m ²)	Density ρ (x 10 ³ kg/m ³)	Internal loss tan δ	Half-modulus temperature* (°C.)
1	random	1.6	1.47	0.05	80
1	oriented	3.2	1.47	0.05	80
2	random	2.5	1.60	0.04	80
2	oriented	4.3	1.60	0.04	80
3	random	2.0	1.55	0.04	80
3	oriented	3.8	1.55	0.04	80
4	random	1.25	1.45	0.07	80
4	oriented	2.50	1.45	0.07	80
5	random	1.5	1.52	0.06	80
5	oriented	3.0	1.52	0.06	80
Control	random	2.2	1.8	0.03	55
Control	oriented	6.0	1.8	0.03	55
Aluminum		7.1	2.7	0.003	—
Kraft paper		0.2	0.6	0.05	—

* Temperature at which the modulus of elasticity is reduced to one-half its room temperature value.

FIG. 1

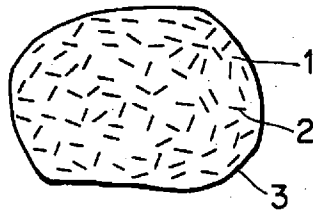


FIG. 3a

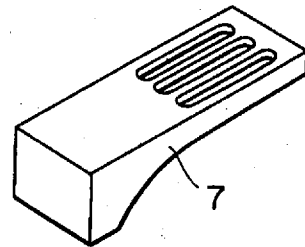


FIG. 2a

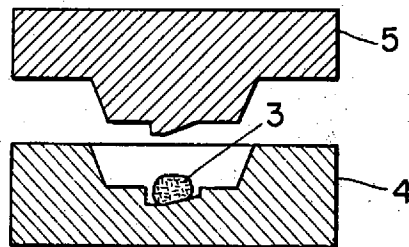


FIG. 3b

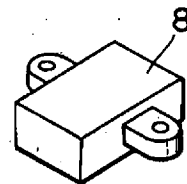


FIG. 2b

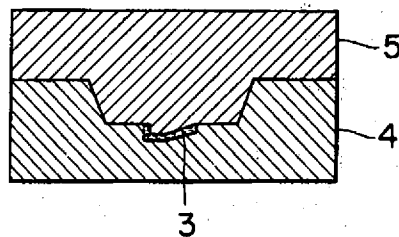


FIG. 3c

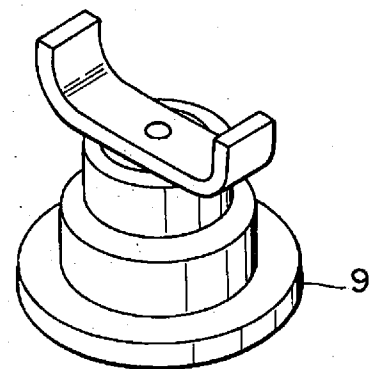


FIG. 2c

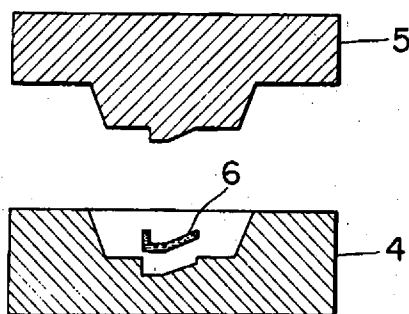


FIG. 4

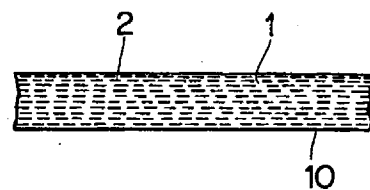


FIG. 5a

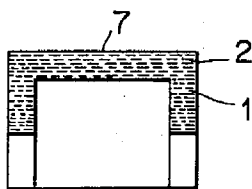


FIG. 5b

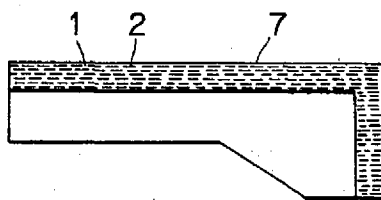


FIG. 8

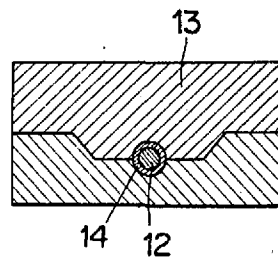


FIG. 6

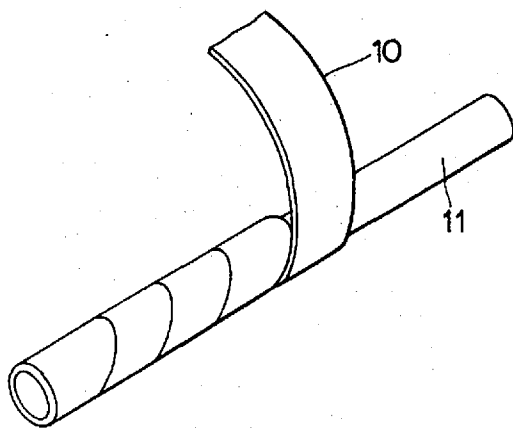


FIG. 7

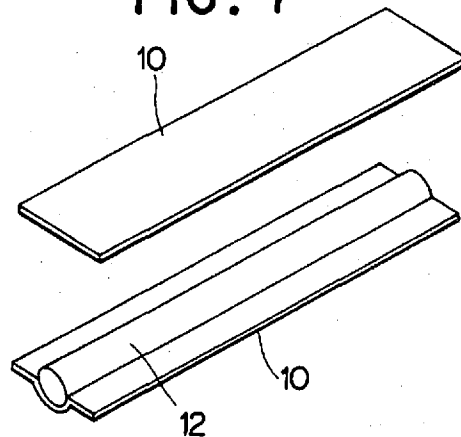


FIG. 9

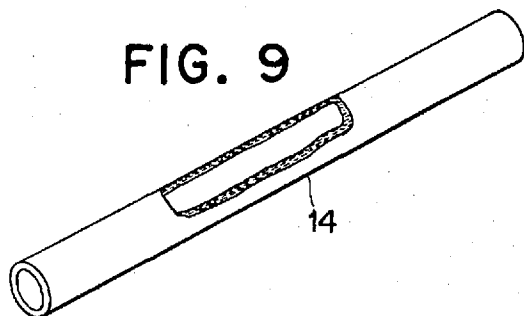


FIG. 10a

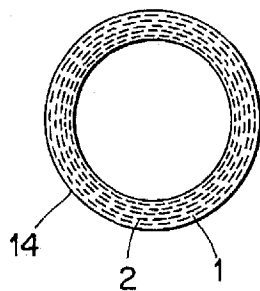
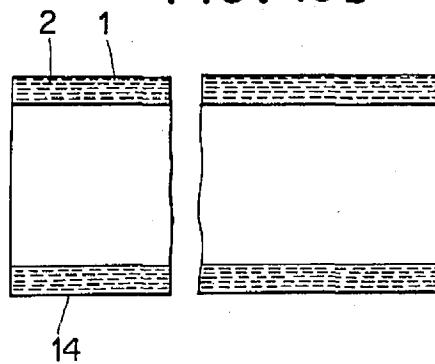


FIG. 10b



[54] ACOUSTIC VIBRATING ELEMENT OF GRAPHITE AND METHOD OF MANUFACTURING SAME

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[73] Assignee: Pioneer Electronic Corporation, Tokyo, Japan

[21] Appl. No.: 315,564

[22] Filed: Oct. 27, 1981

Related U.S. Application Data

[63] Continuation of Ser. No. 880,747, Feb. 24, 1978, abandoned.

[30] Foreign Application Priority Data

Feb. 28, 1977 [JP] Japan 52/20192

[51] Int. Cl.³ H04R 31/00

[52] U.S. Cl. 29/594; 181/167; 423/445; 423/448; 423/458

[58] Field of Search 423/448, 445, 458; 181/157, 166, 296; 264/29.1; 427/249; 29/594

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Primary Examiner—Edward J. Meros

Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak and Seas

[57] ABSTRACT

An acoustic vibrating element, such a domed speaker diaphragm A or a phonographic pickup cantilever B, is formed by vapor deposition on an easily separable mold member 5 of tantalum or tantalum alloy when a mixture of a hydrocarbon gas and an inert gas is passed through a furnace heated to a temperature of 1150° C.–1250° C. at a flow rate in excess of 200 cm/min. The c-axis crystalline orientation of the resulting graphite element is substantially perpendicular to its surface, which provides a Young's modulus above 16,000 Kg/cm².

5 Claims, 2 Drawing Figures

ACOUSTIC VIBRATING ELEMENT OF GRAPHITE AND METHOD OF MANUFACTURING SAME

This is a continuation of application Ser. No. 880,747, filed Feb. 24, 1978, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to acoustic vibrating elements such as the diaphragms in loudspeakers or microphones and the cantilevers in phonographic pick-up cartridges, and to a method of manufacturing such elements from carbon.

Heretofore, aluminum and titanium have been commonly employed as materials for manufacturing electro-acoustic transducers of this type. Although these materials have a high workability factor and low densities ρ , 2.69 and 4.54 for aluminum and titanium, respectively, since they do not have a very high Young's modulus E it is difficult to manufacture high performance diaphragms from them.

On the other hand, beryllium and boron have a high Young's modulus E and low densities ρ , and thus have a high relative modulus of elasticity E/ρ . These materials have thus been commonly employed to produce high performance diaphragms. As beryllium is poisonous, however, there are considerable environmental risks during manufacture, and the necessary equipment and safeguards for preventing such risks are quite expensive. Beryllium also has poor workability, whereby vibrating elements made thereof are very costly. Boron, on the other hand, is relatively brittle and thus low in mechanical strength, and has a low workability factor. Furthermore, it is difficult to obtain high purity boron. Accordingly, as in the case of beryllium, the cost of manufacturing boron vibrating elements is relatively high.

SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to eliminate the above-described drawbacks by providing an acoustic vibrating element of crystalline oriented carbon which has an excellent high frequency response characteristic due to a high relative modulus of elasticity, a good transient characteristic, and a flat frequency response owing to a high internal loss characteristic. The cost of such vibrating elements is relatively low because the material thereof is carbon, which is inexpensive, and the cost of the manufacturing equipment required is also quite low.

BRIEF DESCRIPTION OF THE DRAWING

In the drawing:

FIG. 1 shows a vertical sectional view of an apparatus for manufacturing a dome-shaped acoustic diaphragm in accordance with the present invention, and FIG. 2 shows a vertical sectional view of an apparatus for manufacturing a cylindrical cantilever.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIGS. 1 and 2 illustrate apparatuses for manufacturing a dome-shaped speaker diaphragm A and a cylindrical phonographic pickup arm cantilever B, respectively. Reference numeral 1 designates a high temperature furnace made of a material such as alumina having a high coefficient of heat conductivity. An electrical

heater coil 2 is wound around the furnace 1, and reference numerals 3 and 4 respectively designate a gas inlet and outlet provided in the walls of the furnace. A mold box or former 5 made of heat-resisting material such as graphite or tantalum is in the form of a hemisphere in FIG. 1 to manufacture a dome-shaped speaker diaphragm A, and in the form of a tapered cylinder in FIG. 2 to manufacture a cylindrical cantilever B. The configurations of the mold formers 5 thus correspond to those of the vibrating elements A and B to be manufactured. Reference numeral 6 designates a stand for supporting the mold former 5.

The method of manufacturing the vibrating elements will now be described. First, in order to remove oxygen and water which hinder or retard the deposition of carbon, the furnace 1 is evacuated whereafter an inert gas such as argon is introduced through the gas inlet 3. After the pressure in the furnace becomes higher than atmospheric pressure the gas outlet 4 is opened, and the furnace is then heated by energizing the heater coil 2. When the temperature in the furnace reaches 1150°–1250° C. a gaseous phase carbon compound is mixed with the inert gas and the flow rate of the gas mixture through the furnace is adjusted to exceed 200 cm/min. The gaseous phase carbon compound is preferably a gaseous phase hydrocarbon, such as methane, ethane, propan or acetylene. When an unsaturated gaseous phase hydrocarbon is employed, it is preferable to introduce hydrogen gas together with the gaseous phase hydrocarbon or the gas mixture so that the unsaturated gaseous phase hydrocarbon may be converted into a saturated hydrocarbon by adding hydrogen atoms.

As a result the hydrocarbon in the gas mixture is thermally decomposed, and a layer of carbon is gradually and uniformly deposited on the surface of the mold former 5. When the thickness of this carbon layer reaches a desired predetermined value the introduction of the hydrocarbon gas mixture is suspended. After the furnace has cooled down the thus formed carbon element or layer deposited on the surface of the mold former, that is, the diaphragm A or cantilever B, is separated or removed from the mold former. If the mold former is made of tantalum or a tantalum alloy the carbon element can be readily removed because the coefficient of thermal expansion of the mold former differs greatly from that of the carbon element deposited thereon, and because the bonding strength between the carbon element and the tantalum or tantalum alloy is very weak. If the mold former is made of graphite or a mixture having graphite as its major component, the carbon element can also be readily removed due to the difference between the respective coefficients of thermal expansion, i.e. $3.7\text{--}4.4 \times 10^{-6} \text{ } ^\circ\text{C.}^{-1}$ for graphite and $1.7 \times 10^{-6} \text{ } ^\circ\text{C.}^{-1}$ for the carbon layer.

The c-axis of the resulting graphite crystal diaphragm A or cantilever B is oriented substantially perpendicular to the surface of the element owing to the high flow rate of the gas mixture, its density ρ is accordingly higher than approximately 2.0 to 2.1 g/cm³, and its Young's modulus exceeds 16,000 Kg/mm².

If the diaphragm A or cantilever B is further subjected to heat treatment in an inert gas atmosphere at a temperature higher than 2000° C. but lower than the melting temperature of graphite, for example in a range of from 2400° C. to 2700° C. for 3 to 60 minutes, the c-axis of the graphite crystal becomes even more perpendicularly oriented to the surface of the element, and

hence the Young's modulus increases to above 20,000 Kg/mm².

As is apparent from the above description, a mixture of a hydrocarbon gas and an inert gas or hydrogen is introduced into a heated furnace at a flow rate higher than 200 cm/min, as a result of which the c-axis of the resulting graphite crystal vibrating element is oriented perpendicular to the surface thereof, and its Young's modulus exceeds 16,000 Kg/cm². Therefore, if the configuration of a vibrating element according to the invention is made identical with that of a conventional one and the other elements such as a magnetic circuit therefor remain the same, the vibrating element according to the invention has a higher maximum resonance frequency and internal loss characteristic, and a correspondingly flat frequency response curve.

What is claimed is:

1. In a method for producing an electro-acoustic transducer comprising a vibrating member and means for vibrating the vibrating member, the improvement comprising the step of: introducing a mixture of a gaseous carbon compound and an inert gas and/or hydrogen into a furnace; subjecting said mixture to thermal decomposition to thereby deposit a layer of carbon on a surface of a mold former having a desired configura-

tion, wherein the flow rate of said gaseous carbon compound is sufficiently high that the crystallographic c-axis of said layer of carbon is substantially perpendicular to the surface of said layer of carbon; separating said layer of carbon from said mold former to thus obtain said vibrating member; and mounting said vibrating member in a position to be vibrated by said vibrating means.

2. The method of claim 1 wherein said carbon layer has a Young's Modulus above 16,000 kg/cm².

3. The method of claim 1 wherein, in said step of subjecting said mixture to thermal decomposition, a temperature in a range of 1,150° C. to 1,250° C. is utilized.

4. The method of claim 3 wherein, in said step of introducing said mixture into said furnace, said mixture has a continuous flow rate above 200 cc/min.

5. The method of claim 1 further comprising the step of, following said step of subjecting said mixture to thermal decomposition, subjecting said layer to a heat treatment in an inert gas atmosphere at a temperature in a range of 2400° C. to 2700° C. for a time in a range of 3 to 60 minutes.

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FIG. 1

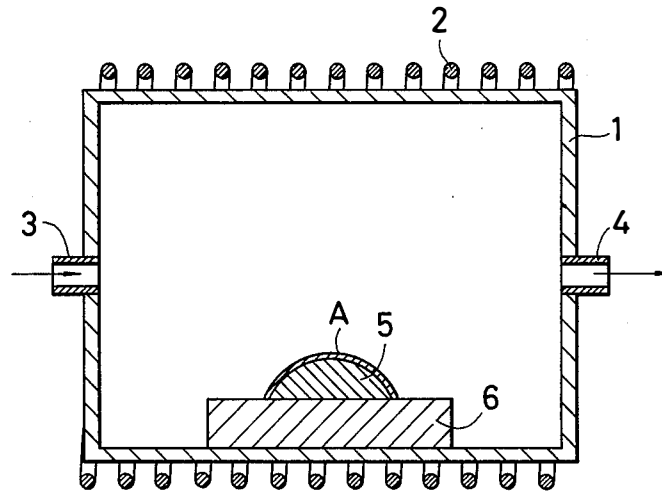
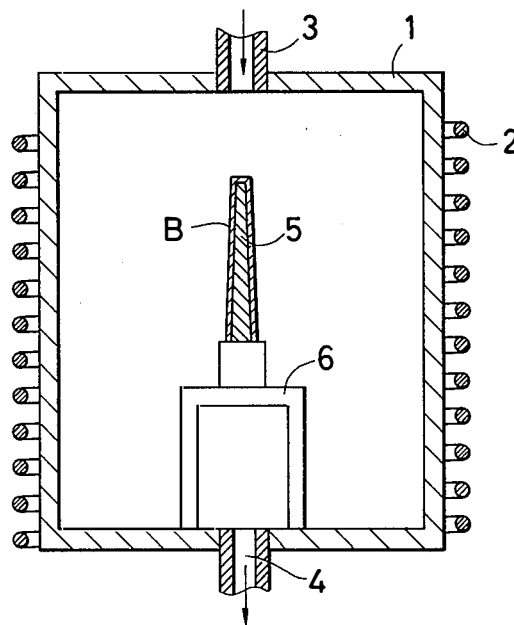


FIG. 2



United States Patent [19]

Murakami et al.

[11] Patent Number: 5,064,019

[45] Date of Patent: Nov. 12, 1991

[54] ELECTROACOUSTIC DIAPHRAGM AND METHOD FOR MAKING SAME

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[73] Assignees: Matsushita Electric Industrial Co., Ltd.; Research Development Corporation of Japan, both of Japan

[21] Appl. No.: 334,519

[22] Filed: Apr. 7, 1989

[30] Foreign Application Priority Data

Apr. 8, 1988 [JP] Japan 63-87517

[51] Int. Cl.⁵ G10K 13/00; H04R 7/00

[52] U.S. Cl. 181/170

[58] Field of Search 181/167, 170

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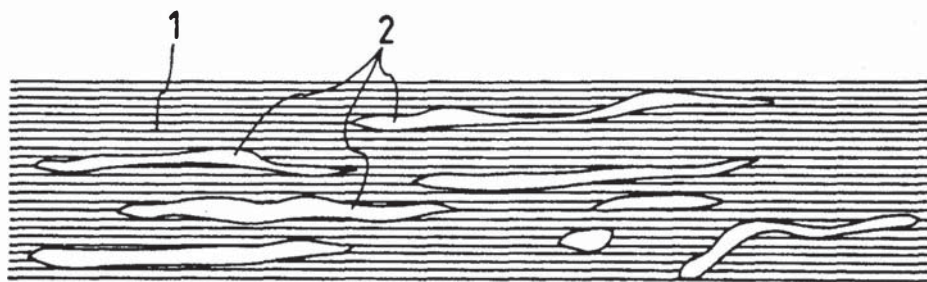
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Primary Examiner—Brian W. Brown
Attorney, Agent, or Firm—Lowe, Price, LeBlanc,
Becker & Shur

[57] ABSTRACT

An electroacoustic diaphragm is provided, which diaphragm comprising a pyrolytic graphite film obtained from a polymer selected from polyoxadiazole, an aromatic polyimide obtained by polycondensation or pyromellitic acid and an aromatic diamine, polybenzothiazole, polybenzobisthiazole, polybenzoxazole, polybenzobisoxazole, poly(pyromellitimide), poly(m-phenyleneisophthalamide), poly(m-phenylenebenzimidazole), poly(m-phenylenebenzobisimidazole), polythiazole and poly-p-phenylenevinylene. The graphite film has a discontinuous layer of a polymeric material formed on and in the film whereby not only good electroacoustic characteristics, but also good mechanical strength and good adhesion of an adhesive applied thereof are obtained. A method for fabricating such diaphragm is also described.

5 Claims, 1 Drawing Sheet



ELECTROACOUSTIC DIAPHRAGM AND METHOD FOR MAKING SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to carbonaceous diaphragms which exhibit electroacoustic characteristics suitable for use in speakers, microphones and the like and a method for making such diaphragms.

2. Description of the Prior Art

A recent growing tendency toward digitalization of acoustic apparatus requires very high performance of diaphragms for use in speakers or the like. The diaphragm adapted for this purpose should have a small degree of deformation when applied with an external force with a small degree of sound distortion and is able to reproduce a clear sound whose range is wide. To this end, it is necessary that the diaphragm be light in weight and have a good modulus of elasticity and good rigidity. More particularly, the diaphragm should have (1) a large Young's modulus (E), (2) a small density (ρ), (3) a large sound velocity (transmission velocity V of sound wave), (4) an appropriate value of internal loss ($\tan \delta$). It will be noted that the values of V , E and ρ have the relationship that $V = \sqrt{E/\rho}$.

Aside from the above physical properties, it is important that the fabrication be easy and that the diaphragm be stable against heat and humidity.

The currently employed materials for the diaphragm are, for example, paper, plastic resins, aluminium, titanium, magnesium, beryllium, boron, silica and the like. These materials or metals have been employed singly or in combination with glass fibers, carbon fibers and the like. Alternatively, some of them have been used in the form of metal alloys. However, paper or plastic resins are not satisfactory for use as a diaphragm with respect to the physical and acoustic characteristics such as the Young's modulus, density and sound velocity. In particular, the frequency characteristic in a high frequency range is very poor, which makes it difficult to obtain a clear sound when these materials are applied as a diaphragm of a tweeter. On the other hand, aluminium, magnesium and titanium are excellent in sound velocity but has so small an internal loss of the vibrations that a high-frequency resonance phenomenon undesirably appears. Thus, these metals are not satisfactory for use as a diaphragm for high-frequency service. Moreover, boron and beryllium exhibit better physical properties than those of the above-mentioned materials or metals and can reproduce a sound of good quality when applied as a diaphragm. However, boron or beryllium is very expensive and has very poor workability.

On the other hand, diaphragms made of carbon or carbonaceous materials have been recently developed in order to overcome the drawbacks involved in the above-described materials. As is known in the art, graphite has a number of good physical properties which are favorable when graphite is applied as a diaphragm. Several techniques of making diaphragms from graphite or other carbonaceous materials have been proposed including (1) a technique wherein graphite powder is dispersed in a polymer resin or resins, (2) a technique using a polymer sheet which has been carbonized and graphitized, and (3) a technique which makes use of a graphite/carbon combination which is

obtained by firing a sheet of graphite powder and a polymer resin or resins.

A typical example of the diaphragm obtained by (1) is one which is made of a dispersion of graphite powder in polyvinyl chloride resin matrix. This diaphragm is readily influenced by humidity and temperature and its vibration characteristic considerably deteriorates at temperatures over 30° C.

With the technique (2), several types of polymer films have been investigated but initially expected characteristics could not be obtained because plastic films used are hard to graphitize. For example, the resins including epoxy resins, phenolic resins, furfuryl alcohol resins have been used for this purpose. These plastic resins exhibit a low rate of graphitization and are shrunk to an appreciable extent when thermally treated, so that defects such as deformation, crackings and the like are often produced. This technique does not ensure fabrication of a diaphragm of graphite or a carbonaceous material having good characteristics under well-controlled quality control.

The technique (3) includes a method wherein a liquid component of a pitch obtained by cracking of crude oil is mixed with graphite powder and the mixture is thermally treated for carbonization, and a method wherein a monomer or oligomer capable of yielding a thermosetting resin is used as a binder for graphite powder and a thermoplastic resin having functional groups capable of thermal decomposition and crosslinkage under heating conditions are mixed with graphite powder as a binder, followed by thermal carbonization. These methods have been developed in order to increase a yield of graphite or carbon and to prevent shrinkage or deformation when thermally treated. A diaphragm obtained from the resultant graphite exhibits good electroacoustic characteristics.

However, the methods of the technique (3) require complicated fabrication procedures which are inconvenient for industrial mass production. In order to industrially obtain the pitch and liquid component by cracking of crude oil in the former method, a very complicated procedure of thermal treatment at high temperatures and fractional solvent extraction is necessary. The latter method requires a high technic wherein graphite powder and a binder are sufficiently kneaded by the use of a kneader operating under high shear force conditions. Subsequently, cleft graphite crystals and the binder resin are strongly dispersed to impart affinity for each other by mechanochemical reaction thereby causing the crystal planes of the graphite to be oriented along the direction of the sheet plane. Although the diaphragm obtained using the resultant combination has very excellent characteristics, those characteristics are slightly inferior to those of a beryllium diaphragm which is believed to have the highest characteristics attained among existing diaphragms. In addition, the modulus of elasticity of the combination is significantly poorer than the theoretical value of 1020 GPa. of a graphite single crystal.

SUMMARY OF THE INVENTION

An object of the invention is to provide a carbonaceous or graphite diaphragm which has good mechanical strength and good electroacoustic characteristics as will not be expected by prior art diaphragms.

Another object of the invention is to provide a carbonaceous or graphite diaphragm which ensures good

adhesion of adhesives and can be manipulated as desired.

A further object of the invention is to provide a method for fabricating a graphite diaphragm which is very simple in procedure thereby producing the diaphragm having excellent mechanical and electroacoustic properties.

A still further object of the invention is to provide a method for fabricating a graphite diaphragm by a simple and industrially advantageous manner.

The diaphragm according to the invention comprises a pyrolytic graphite film obtained from a polymer selected from polyoxadiazole, an aromatic polyimide obtained by polycondensation of pyromellitic acid and an aromatic diamine, polybenzthiazole, polybenzobisthiazole, polybenzoxazole, polybenzobisoxazole, poly(pyromellitimide), poly(m-phenyleneisophthalamide), poly(m-phenylenebenzimidazole), poly(m-phenylenebenzobisimidazole), polythiazole and poly-p-phenylenevinylene and a discontinuous layer of a polymeric material formed on and in the graphite film. The polymeric material is formed by impregnation in the graphite film after dissolution in a suitable solvent.

The diaphragm is fabricated by a method which comprises providing a film of a polymer defined above, subjecting the film to pyrolysis or thermal treatment at a temperature of not lower than 2000° C. in vacuum or in an inert gas for a time sufficient for the pyrolysis to obtain a graphite film, impregnating a polymeric material in the graphite film to form a discontinuous layer of the polymeric material on or in the graphite film, and drying the thus impregnated film.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic sectional view of part of a diaphragm fabricated according to the invention; and

FIG. 2 is a schematic sectional view of part of a known diaphragm using a dispersion of graphite powder in a plastic resin.

DETAILED DESCRIPTION AND EMBODIMENTS OF THE INVENTION

Reference is now made to the accompanying drawings. In FIG. 1, there is generally shown part of a diaphragm D which includes a graphite film 1 and a polymer resin 2 formed on and in the graphite film 1 in the form of, for example, islands.

The graphite film 1 used in the practice of the invention is obtained from a film of a polymer which is selected from polyoxadiazole, an aromatic polyimide obtained by polycondensation of pyromellitic acid and an aromatic diamine, polybenzthiazole, polybenzobisthiazole, polybenzoxazole, polybenzobisoxazole, poly(pyromellitimide), poly(m-phenyleneisophthalamide), poly(m-phenylenebenzimidazole), poly(m-phenylenebenzobisimidazole), polythiazole and poly-p-phenylenevinylene. These polymers are known in the art. In particular, the aromatic polyimide useful in the present invention is described, for example, in Japanese Laid-open Patent Application No. 60-181129, which is incorporated herein by reference. In the practice of the invention, a preferred aromatic polyimide is a poly-N,N'-(P,P'-oxydiphenylene)pyromellitimide.

For the formation of the graphite film, the polymer film is pyrolyzed or thermally treated at a temperature of not lower than 2000° C. in vacuum or in an inert gas such as nitrogen, argon or the like for a time sufficient for the pyrolysis. The time is generally in the range of

from 10 minutes to 10 hours. By the pyrolysis, the polymer film is carbonized to give a graphite film which is slightly reduced in size. When the graphite film obtained is used as a diaphragm, the graphite film should preferably have a thickness of from 5 to 50 micrometers in view of the mechanical and electroacoustic characteristics.

Of the graphite films, those films obtained from polyoxadiazole, polybenzimidazole and the aromatic polyimide are preferred because of their high sound velocities.

The diaphragm of the invention should further comprise a polymeric material applied to the graphite film. The polymeric material is formed in or on the graphite film by which the mechanical strength, electroacoustic characteristics and the adhesion of an adhesive to the graphite film can be significantly improved. The polymeric material is formed, for example, as islands which mean discontinuous layers. For this purpose, carbonaceous substances such as pitches, organic polymers and the like may be used provided that they have high affinity for the graphite film sufficient to cause the impregnation. If the affinity is low, the polymeric materials tend to come off from the graphite film after application and are not impregnated. Preferably, epoxy resins, polyorganosiloxane resins, cyanoacrylate resins, and furan resins are used. Useful epoxy resins include, for example, Sumiepoxy ELM 120 available from Sumitomo Chem. Co., Ltd. The polyorganosiloxane is, for example, Silaplane available from Chisso Corporation.

The cyanoacrylate resin is, for example, one which is available under the name of Aron α from Toa Synthetic Chem. Co., Ltd. of Japan. The furan resin is a product of a furfuryl alcohol oligomer which has been thermally polymerized after application. The amount of the polymer resin to be applied to the graphite film may vary depending upon the type of resin and should be sufficient to improve physical properties including adhesiveness. The amount is generally in the range of from 0.2 to 25 wt %. When the preferred resins are used, the amount is in the range of from 0.5 to 15 wt % of the graphite film for the epoxy resin, from 0.5 to 25 wt % for the organosiloxane resin, from 0.2 to 15 wt % for the cyanoacrylate resin, and from 1.0 to 20 wt % for the furan resin. Less amounts for the respective resins are unfavorable because physical strength is not improved significantly. On the other hand, when larger amounts are used, there is the tendency that the electroacoustic characteristics including the sound velocity, Young's modulus and the like lower.

The diaphragm of the invention may be considered to have a structure similar to known diaphragms obtained from graphite powder and a polymer resin. However, the diaphragm of the invention is completely different from the known diaphragms. Part of a typical known diaphragm is shown in FIG. 2, in which a diaphragm D includes islands of a graphite powder 3 dispersed in a polymer resin matrix 4. This is completely different from the diaphragm of the invention shown in FIG. 1, in which graphite is a matrix in which a polymeric material is contained. With the diaphragm of the invention, the characteristics of the diaphragm depend greatly on the graphite. This is why the diaphragm of the invention is better than the known diaphragm.

In the above embodiment, the graphite film is applied or impregnated with a polymeric material. The graphite film obtained from the aromatic polyimide or polyoxadiazole shows better mechanical and electroacoustic

characteristics without application of any polymeric material than the graphite films obtained from the other polymers. The diaphragm using this graphite film without application of any polymeric materials is also within the scope of the invention.

Fabrication of the diaphragm according to the invention is described.

In the method of the invention, a film of the polymer defined before is first provided. This film is subjected to pyrolysis at temperatures not lower than 2000° C. in vacuum or in an inert gas for a time set forth before. As stated in examples, the polymer film may be first thermally pretreated at temperatures not higher than 1000° C. in an inert gas. The resultant film is relatively fragile and may be reduced in size. Subsequently, the pretreated film is pyrolyzed at temperatures of not lower than 2000° C., e.g. at 3000° C. For the pyrolysis, the polymer film or pre-treated film is usually sandwiched between graphite plates so as to prevent breakage during the pyrolysis. The pyrolyzing conditions may be varied during the course of the pyrolysis. Preferably, the film is thermally treated in vacuum up to a temperature not higher than 2000° C., followed by further treatment in an inert gas, such as argon, at a temperature higher than 2000° C. The heating rate is not critical but is preferably in the range of from 1° C./minute to 50° C./minute. The polymer or pretreated film is substantially graphitized for a time of from 10 minutes to 10 hours. The resultant film is relatively flexible in nature.

This graphite film has good electroacoustic characteristics but has relatively poor mechanical strength and adhesion of an adhesive.

In the practice of the invention, the problem is solved by applying the graphite film with a solution of a polymeric material to cause the polymer to be formed as islands in and/or on the graphite film.

A solution of a polymer, which is preferably an epoxy resin, an organosiloxane resin, a furan resin or a cyanoacrylate resin as stated before, is prepared. The solvents used to prepare the solution may be any ones which are able to dissolve an intended polymer. Examples of such solvents include ketones such as acetone, ethers such as ethylene glycol monoalkyl ethers, hydrocarbons such as toluene, 1,4-dichlorobenzene and the like, alcohols such as isopropyl alcohol and NMP, and the like. When the polymer is a liquid having a low viscosity, it may be used without dilution with any solvent. For instance, an oligomer of a furfuryl alcohol may be applied as it is, after which it is polymerized by application of heat. However, it is usual to dissolve the polymer in a solvent. This is advantageous in that the amount of the polymer being applied or impregnated can be relatively precisely controlled by controlling the concentration in the solution. For facilitating the impregnation, the applied graphite film may be placed under reduced pressure conditions, under which the applied polymer may be conveniently included in the graphite film as shown in FIG. 1.

The applied film is dried or thermally treated at temperatures which may depend upon the type of applied polymer resin. In general, the temperatures are appropriately in the range of not higher than 1000° C., preferably from 200° to 800° C. Thus, a graphite film applied or impregnated with a polymer resin can be obtained. This film has good electroacoustic characteristics and good mechanical strength. In addition, the film has good adhesion of an adhesive, which is particularly

effective for application in speaker or microphone systems.

The applied graphite film may be fabricated in any size and can be applied as a diaphragm for acoustic devices without difficulties.

The present invention is more particularly described by way of examples.

EXAMPLE 1

A 50 μ m thick polyimide film (Kapton H film, available from Du Pont De Nemours & Co.) was cut into a piece having a size of 80 mm Φ . This piece was placed between quartz plates and thermally treated in an electric furnace at a temperature of 1000° C. in an atmosphere of nitrogen at a heating rate of 20° C./minute. After the treatment at 1000° C. for 10 minutes, the film was cooled down to room temperature and removed from the furnace. The resultant film was shrunk to an extent of 60 mm Φ and was relatively hard and brittle.

This sample was placed between graphite plates and subjected to pyrolysis in a carbon heater furnace, Model 46-5, available from Shinsei Electric Furnace Co., Ltd. of Japan while heating up to 3000° C. In this pyrolysis, the film was first heated up to 2000° C. in vacuum at a heating rate of 40° C./minute and then in an atmosphere of argon at a heating rate of 40° C./minute up to 3000° C. The film was kept at the maximum temperature for 1 hour, after which it was cooled down to room temperature. The resultant graphite film was relatively flexible and soft. This film was subjected to measurement of physical properties by the use of the Dynamic Modulus Tester of Toyo Seiki K. K. of Japan.

The above procedure was repeated at different pyrolysis temperatures.

The results of the measurement of the graphite films are shown in Table 1. Moreover, the characteristics of known materials used as a diaphragm were also subjected to measurement of the characteristics. These results are shown in Table 2.

TABLE 1

Thermal Treatment Temp. (°C.)	Sound Velocity (Km/sec.)	Young's Modulus (GPa)	Density (g/cm ³)	Internal Loss tan δ
1400	4.6	31	1.5	2.0×10^{-2}
1600	3.7	21	1.5	3.0×10^{-2}
1800	4.4	30	1.6	2.2×10^{-2}
2000	7.4	76	1.4	2.0×10^{-2}
2200	7.9	100	1.6	4.2×10^{-2}
2400	9.4	158	1.8	3.6×10^{-2}
2600	12.3	364	2.4	3.3×10^{-2}
2800	18.1	692	2.1	2.3×10^{-2}
3000	18.9	750	2.1	2.2×10^{-2}

TABLE 2

Material	Sound Velocity (Km/sec.)	Young's Modulus (GPa)	Density (g/cm ³)	Internal Loss tan δ
Paper (pulp)	1.0-2.0	0.2-4.0	0.2-0.6	$2-6 \times 10^{-2}$
Polypropylene	1.3	1.5	0.9	6.0×10^{-2}
Aluminium	5.1	70	2.7	$2-3 \times 10^{-3}$
Titanium	4.9	110	4.5	"
Magnesium	5.1	44	1.7	"
Beryllium	12.2	270	1.8	"
Graphite/carbon	11.0	175	1.45	9×10^{-3}

The sound velocity and Young's modulus of the graphite films obtained from the polyimide film sharply increase at thermal treatment temperatures near 2000°

C. When pyrolyzed at 2600° C., the sound velocity is 12.3 Km/second and the Young's modulus is 364 GPa. These values are higher than those of beryllium, as particularly shown in Table 2, which has been accepted as having the most excellent characteristics for diaphragm among existing diaphragm materials. Thus, it will be seen that the pyrolysed polyimide film has good characteristics as a diaphragm. The characteristics of the pyrolysed film are more improved at higher temperatures, e.g. the Young's modulus reaches 750 GPa when the temperature is 3000° C. This value is as high as 74% of the theoretical value of single crystal graphite which is 1020 GPa.

As will be appreciated from the above, when the polyimide film is thermally treated at temperatures of not lower than 2000° C., a graphite film having good characteristics can be obtained by a very simple procedure as compared with complicated fabrication procedures of known techniques as stated before.

The graphite films obtained above are relatively low in mechanical strength and adhesion of an adhesive. This is solved by application or impregnation of an organic polymer. This is described below.

The graphite film obtained by the thermal treatment of the polyimide film at 2800° C. was immersed in each of solutions of an epoxy resin (Sumiepoxy ELM 120, available from Sumitomo Chem. Co., Ltd.) dissolved in a mixed solvent of ethylene glycol monomethyl ether (methyl cellosolve) and acetone in different concentrations, thereby changing an amount of the epoxy resin impregnated in the graphite film. After the impregnation, each film was dried at 100° C. for 1 hour and thermally treated at 150° C. for further 1 hour. After the drying treatment, the film was weighed to determine an amount of the impregnated resin. In this manner, the graphite films impregnated from 0 to 100 wt % based on the film were made. These films were subjected to measurement of the sound velocity, Young's modulus, internal loss and tensile strength. The results are shown in Table 3 below.

TABLE 3

Amount of Impregnated resin (wt %)	Sound velocity (Km/sec.)	Young's Modulus (GPa)	Internal Loss tan δ	Tensile Strength (MPa)
0	18.1	692	2.3×10^{-2}	85
0.2	18.1	690	2.3×10^{-2}	85
0.5	17.9	680	2.8×10^{-2}	180
5	16.8	590	3.1×10^{-2}	300
15	12.2	380	2.3×10^{-2}	500
25	7.5	72	2.0×10^{-2}	600
100	3.5	25	1.8×10^{-2}	600

As will be apparent from the above results, when the amount of the epoxy resin exceeds 15 wt % based on the film, the characteristics including the Young's modulus abruptly decrease. On the other hand, when the amount is less than 0.5 wt %, little improvement of the tensile strength is expected. From this, the amount of the epoxy resin is conveniently in the range of from 0.5 to 15 wt %.

When the impregnated diaphragm is applied as a diaphragm, the adhesion of various types of adhesives and particularly an epoxy resin adhesive is improved remarkably. This makes it very easy to assemble electroacoustic devices such as speakers, microphones and the like.

EXAMPLE 2

A 50 micrometer thick polyoxadiazole film (available from Furukawa Electric Ind. Co., Ltd.) was cut into pieces having a size of 60 mm Φ . This piece was placed between quartz plates and thermally treated in an electric furnace (Model LTF-8, available from Sankyo Electric Furnace Co., Ltd. of Japan). The thermal treatment was effected at 1000° C. while heating at a rate of 20° C. in an atmosphere of nitrogen and the sample was kept at 1000° C. for 10 minutes, after which it was cooled down to room temperature and removed from the furnace. The resultant sample was reduced in size to an extent of 48 mm Φ and was relatively hard and brittle.

This sample was placed between graphite plates and subjected to pyrolysis in a carbon heater furnace, Model 46-5, available from Shinsei Electric Furnace Co., Ltd. of Japan while heating up to 2800° C. In this pyrolysis, the film was first heated up to 2000° C. in vacuum at a heating rate of 40° C./minute and then in an atmosphere of argon at a heating rate of 40° C./minute up to 3000° C. The film was kept at the maximum temperature for 1 hour, after which it was cooled down to room temperature. The resultant graphite film was relatively flexible and soft. This film was subjected to measurement of physical properties by the use of the Dynamic Modulus Tester of Toyo Seiki K. K. of Japan.

The above procedure was repeated at different thermal treatment temperatures.

From the above test, it was found that the graphite films thermally treated over 2000° C., inclusive, had large sound velocity and Young's modulus with a small density, so that they were suitable as a diaphragm. For instance, the graphite film obtained at a thermal treatment temperature of 2800° C. had a sound velocity of 8.0 Km/second, a Young's modulus of 140 GPa, a density of 2.2 g/cm³ and an internal loss of 7.7×10^{-2} .

Subsequently, the graphite films were each immersed in an oligomer of furfuryl alcohol (Hitafuran 302, available from Hitachi Chem. Ind. Co., Ltd.), followed by polymerization by application of heat. The film was thermally treated at 800° C. for 40 minutes in an electric furnace (Model UTF-8, available from Sankyo Electric Furnace Co., Ltd.) After the thermal treatment, the respective films were weighed to determine an amount of the impregnated resin. These films were subjected to measurement of the sound velocity, Young's modulus, internal loss and tensile strength. The results are shown in Table 4 below.

TABLE 4

Amount of Impregnated resin (wt %)	Sound velocity (Km/sec.)	Young's Modulus (GPa)	Internal Loss tan δ	Tensile Strength (MPa)
0	8.0	140	7.7×10^{-2}	80
0.2	9.5	175	4.0×10^{-2}	85
0.5	11.0	260	3.1×10^{-2}	280
5	16.0	400	2.8×10^{-2}	400
20	12.0	310	2.8×10^{-2}	460
30	7.0	70	2.3×10^{-2}	520
50	5.2	50	2.0×10^{-2}	600
100	3.1	25	1.8×10^{-2}	600

As will be apparent from the above result, the amount of the furfuryl alcohol polymer is suitably in the range of from 0.5 to 20 wt % based on the film.

EXAMPLE 3

Graphite films were obtained by treating polyoxadiazole films at a temperature of 2800° C. in a manner similar to Example 2 and then impregnated with an organosiloxane polymer in different amounts.

After completion of the impregnation, the films were each dried at 100° C. for 1 hour and thermally treated at 200° C. for 2 hours. The resultant films were subjected to measurement of characteristic properties as in the foregoing examples. As a result, it was found that when the amount of the polymer was in the range of from 0.5 to 25 wt % based on the film, the sound velocity was not lower than 10 Km/second and the Young's modulus was not less than 200 GPa. The tensile strength was not less than 180 MPa when the amount of the impregnated resin was not less than 0.5 wt %. The thus treated films had all good adhesion of adhesives thereto.

EXAMPLE 4

Graphite films were obtained by treating polyoxadiazole films at a temperature of 2800° C. in a manner similar to Example 2 and then immersed in solutions of a cyanoacrylate resin (Aron α) in an acetone solvent with different concentrations. After removal of the films from the respective solutions, the films were dried at 80° C. for 1 hour. The resultant films were subjected to measurement of characteristic properties as in the foregoing examples. As a result, it was found that when the amount of the resin was in the range of from 0.2 to 20 wt %, the sound velocity was not lower than 10 Km/second and the Young's modulus was not lower than 200 GPa. The tensile strength was 180 MPa or over when the amount was not less than 0.2 wt %. The adhesion of adhesives to the impregnated films was good.

EXAMPLE 5

The general procedure of Example 1 was repeated except that a polybenzimidazole film was used and thermally treated at a final temperature of 2800° C. The resultant film has a sound velocity of 5.0 Km/second, a Young's modulus of 120 GPa, an internal loss of 2.6×10^{-2} and a tensile strength of 350 MPa.

The film was impregnated with an epoxy resin in the same manner as in Example 1 in different amounts.

When the amount of the impregnated resin was in the range of from 0.5 to 15 wt %, the sound velocity was not lower than 10 Km/second, the Young's modulus was not lower than 200 GPa and the tensile strength was not less than 400 MPa.

It was confirmed that when the polybenzimidazole was thermally treated at not lower than 2000° C., similar results were obtained.

The general procedure of the foregoing examples was repeated using 50 micrometer thick films of polybenzobisthiazole, polybenzoxazole, polybenzobisoxazole, poly(pyromellitimide), poly(m-phenyleneisophthalamide), poly(m-phenylenebenzimidazole), poly(m-phenylenebenzobisimidazole) and polythiazole. Similar results were obtained when these films were thermally treated at temperatures not lower than 2000° C.

What is claimed is:

1. An electroacoustic diaphragm which comprises a pyrolytic graphite film having a modulus of elasticity and rigidity suitable to exhibit electroacoustic characteristics obtained from a polymer selected from the group consisting of polyoxadiazole, an aromatic poly-

imide obtained by polycondensation of pyromellitic acid and an aromatic diamine, polybenzthiazole, and an aromatic diamine, polybenzthiazole, polybenzobisthiazole, polybenzoxazole, polybenzobisoxazole, poly(pyromellitimide), poly(m-phenyleneisophthalamide), poly(m-phenylenebenzimidazole), poly(m-phenylenebenzobisimidazole), polythiazole and poly-p-phenylenevinylene, and a discontinuous layer of a polymer resin formed on and in the graphite film, wherein said discontinuous layer is in the form of islands formed on and in the graphite film, wherein said discontinuous layer is made of a polymer selected from an epoxy resin, an organosiloxane resin, a cyanoacrylate resin and a furan resin, wherein said polymer is an epoxy resin and is used in an amount of from 0.5 to 15 wt % of the graphite film, and said electroacoustic diaphragm has a tensile strength of from 180 to 500 Mpa, a Young's modulus of from 380 to 680 GPa., and said electroacoustic diaphragm has a measured sound velocity from 12.2 to 17.9 Km/sec.

2. An electroacoustic diaphragm which comprises a pyrolytic graphite film having a modulus of elasticity and rigidity suitable to exhibit electroacoustic characteristics obtained from a polymer selected from the group consisting of polyoxadiazole, an aromatic polyimide obtained by polycondensation of pyromellitic acid and an aromatic diamine, polybenzthiazole, and an aromatic diamine, polybenzthiazole, polybenzobisthiazole, polybenzoxazole, polybenzobisoxazole, poly(pyromellitimide), poly(m-phenyleneisophthalamide), poly(m-phenylenebenzimidazole), poly(m-phenylenebenzobisimidazole), polythiazole and poly-p-phenylenevinylene, and a discontinuous layer of a polymer resin formed on and in the graphite film, wherein said discontinuous layer is in the form of islands formed on and in the graphite film, wherein said discontinuous layer is made of a polymer selected from an epoxy resin, an organosiloxane resin, a cyanoacrylate resin and a furan resin, wherein said polymer is an epoxy resin and is used in an amount of from 0.5 to 15 wt % of the graphite film, and said electroacoustic diaphragm has a tensile strength not less than 400 MPa, a Young's modulus of not less than 200 GPa, and said electroacoustic diaphragm has a measured sound velocity not less than 10 Km/sec.

3. An electroacoustic diaphragm which comprises a pyrolytic graphite film having a modulus of elasticity and rigidity suitable to exhibit electroacoustic characteristics obtained from a polymer selected from the group consisting of polyoxadiazole, an aromatic polyimide obtained by polycondensation of pyromellitic acid and an aromatic diamine, polybenzthiazole, and an aromatic diamine, polybenzthiazole, polybenzobisthiazole, polybenzoxazole, polybenzobisoxazole, poly(pyromellitimide), poly(m-phenyleneisophthalamide), poly(m-phenylenebenzimidazole), poly(m-phenylenebenzobisimidazole), polythiazole and poly-p-phenylenevinylene, and a discontinuous layer of a polymer resin formed on and in the graphite film, wherein said discontinuous layer is in the form of islands formed on and in the graphite film, wherein said discontinuous layer is made of a polymer selected from an epoxy resin, an organosiloxane resin, a cyanoacrylate resin and a furan resin, wherein said polymer is an organosiloxane resin and is used in an amount from 0.5 to 25 wt % of the graphite film, and said electroacoustic diaphragm has a measured sound velocity of not less than 10 Km/sec., a Young's modulus of not less than 200 GPa,

and the tensile strength of said electroacoustic diaphragm is not less than 180 MPa.

4. An electroacoustic diaphragm which comprises a pyrolytic graphite film having a modulus of elasticity and rigidity suitable to exhibit electroacoustic characteristics obtained from a polymer selected from the group consisting of polyoxadiazole, an aromatic polyimide obtained by polycondensation of pyromellitic acid and an aromatic diamine, polybenzthiazole, and an aromatic diamine, polybenzthiazole, polybenzbis-thiazole, polybenzoxazole, polybenzbisoxazole, poly-(pyromellitimide), poly(m-phenyleneisophthalamide), poly(m-phenylenebenzoimidazole), poly(m-phenylenebenzobisimidazole), polythiazole and poly-p-phenylenevinylene, and a discontinuous layer of a polymer resin formed on and in the graphite film, wherein said discontinuous layer is in the form of islands formed on and in the graphite film, wherein said discontinuous layer is made of a polymer selected from an epoxy resin, an organosiloxane resin, a cyanoacrylate resin and a furan resin, where said polymer is a cyanoacrylate resin and is used in a amount of from 0.2 to 20 wt % of the graphite film, and said electroacoustic diaphragm has a measured sound velocity of not less than 10 Km/sec., a Young's modulus of not less than 200 GPa, and the

tensile strength of said electroacoustic diaphragm is 180 MPa or greater.

5. An electroacoustic diaphragm which comprises a pyrolytic graphite film having a modulus of elasticity and rigidity suitable to exhibit electroacoustic characteristics obtained from a polymer selected from the group consisting of polyoxadiazole, an aromatic polyimide obtained by polycondensation of pyromellitic acid and an aromatic diamine, polybenzthiazole, and an aromatic diamine, polybenzthiazole, polybenzbis-thiazole, polybenzoxazole, polybenzbisoxazole, poly-(pyromellitimide), poly(m-phenyleneisophthalamide), poly(m-phenylenebenzoimidazole), poly(m-phenylenebenzobisimidazole), polythiazole and poly-p-phenylenevinylene, and a discontinuous layer of a polymer resin formed on and in the graphite film, wherein said discontinuous layer is in the form of islands formed on and in the graphite film, wherein said discontinuous layer is made of a polymer selected from an epoxy resin, an organosiloxane resin, a cyanoacrylate resin and a furan resin, polymer is a furan resin and is used in an amount from 0.5 to 20 wt % of the graphite film, and said electroacoustic diaphragm has a tensile strength from 280 to 460 MPa, Young's modulus of from 260 to 400 GPa., and said electroacoustic diaphragm has a measured sound velocity from 11.0 to 16.0 Km/sec.

* * * * *

30

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60

65

FIG. 1

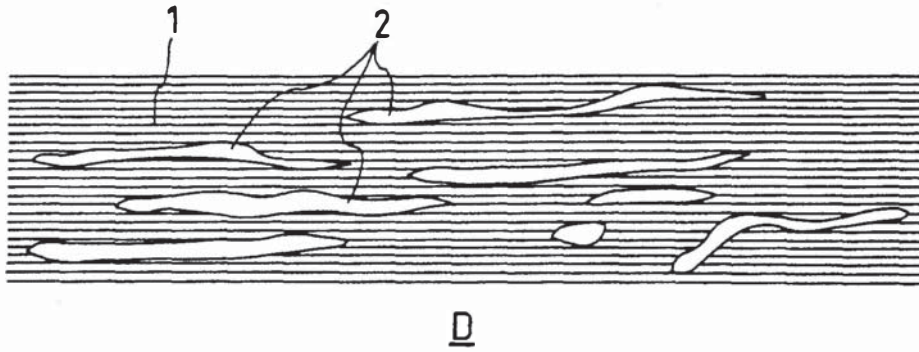
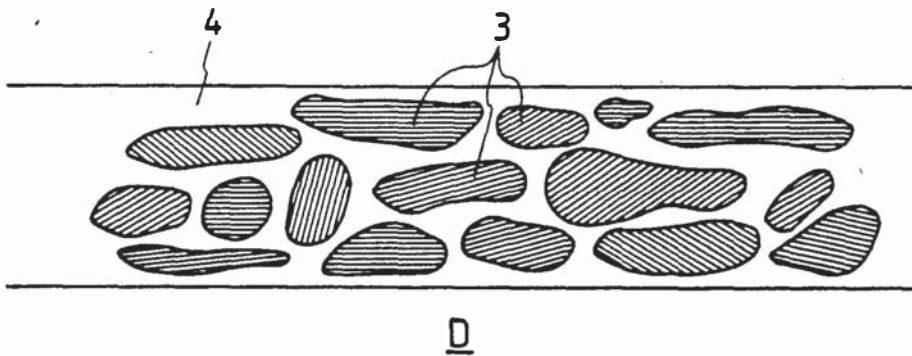


FIG. 2
PRIOR ART



KNG™-150 Graphene Nanoplatelets

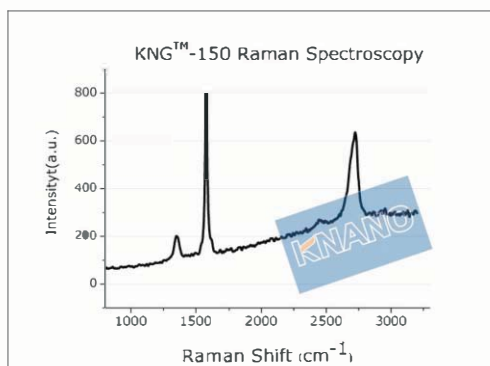
KNG™-150 graphene nanoplatelets are stacks of multi-layered graphene sheets having a platelet morphology. The KNG™-150 graphene nanoplatelets have a high aspect ratio (width to thickness)

Bulk Powder Characteristics

Appearance	Bulk density	Powder conductivity	Specific surface area
A black and grey powder	~0.3g/cm ³	~12000S/m	40-60m ² /g

Graphene Nanoplatelets Properties

Diameter	Thickness	Carbon content	Pure density	Thermal conductivity	Tensile Modulus	Young's Modulus
1-20um	5-15nm	>99.5wt%	~2.25g/cm ³	~3000W/m K	~1000Gpa	~1060Gpa



Applications

- The high performance composite nano-additives.
- To improve composites thermal conductivity and diffusion, anti-static electricity properties, tensile strength, stiffness, corrosion resistance and lubricant properties.

Use methods

- KNG™-150 is suggested to mix with the target polymer via the general plastics machines. Please discuss with us for the related issues of best dispersion.
- Some kinds of performance graphene nanoplatelets master batches are available.
- amounts for modifications depend on actual uses.

Attentions

- The effectiveness of modification may depend very much on the type and the amount of surface modifiers used. It would be our great pleasure to have discussions with you for the related issues and for the best dispersion.

Package

- KNG™-150 package: 10kg or tailor-made for your specific need.