BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 829—833 (1966)

The Electrical Resistivity of Carbon Black under Compression

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(Received September 21, 1965)

The electrical resistivity of carbon blacks was measured under compression (up to 9 kilobars) at room temperature using a pressure vessel of the piston-cylinder type. The slope of the log ρ vs. log P relation was about -0.5 for all the carbon black specimens except the original channel black. For the thermal blacks heat-treated above 2100°C, i. e., the graphitized thermal blacks, the linear relation between logarithms of resistivity, ρ, and of pressure, P, broke at about 2.5—4.5 kilobars. After the break the slope of the log ρ vs. log P relation for the graphitized thermal blacks had the same value as that for natural graphite. The original channel black had a value of the slope as high as -0.9, but the 1300°C-treated channel black had a value similar to that of the other samples. This was probably due to the removal of the high-resistance film on the particle surface by the heat treatment. The first stage of the decrease in electrical resistivity with an increase in the pressure seems to be due to the yielding deformation of carbon black particles caused by the increased packing of the particles, while the second stage may be due mainly to the increase in the contact of crystallites in the particles by the elastic deformation, accompanied by a change in the preferred orientation of crystallites with the pressure.

The measurement of the electrical resistivity of carbon black under compression has been carried out by a number of investigators with both technical and scientific interests. However, the measurements under pressures above 2 kilobars (kb) have been very few. According to Adelson and Austin,[1] the resistance versus pressure curves of a number of carbon blacks broke relatively sharply at approximately 30 kb; this break was assumed to be caused by the change from the elastic to the yielding deformation of carbon black particles. In their work, however, there might have been a considerable pressure gradient in the radial direction of the compressed specimen, because they used opposed anvils of a flat face as the pressure apparatus.

In the present work, the electrical resistivity of carbon black under compression was investigated under a pressure of up to 9 kb at room temperature using a pressure vessel of the piston-cylinder type. In this pressure vessel, the gradient of the pressure is negligibly small, in both the radial and the longitudinal directions of the compressed specimen, if the specimen is appropriately thin, as will be described below. Not only original carbon blacks but also heat-treated carbon blacks were used as samples.

Experimental

The materials used in the present work were two kinds of thermal black, a channel black, their heat-treated specimens and a pulverized natural graphite. The thermal blacks have no "structure"; the particle size of one of them is quite uniform, about 1000 Å on the average, while the other's is not so uniform, its average particle size being 3000 Å. The carbon blacks were heat-treated in an induction furnace at various temperatures under a reduced pressure of 10^{-2} Torr for 30 min. The natural graphite powder was also heated at 2700°C for 10 min. under 10^{-2} Torr in the same furnace. The polyhedral form of the particles of thermal blacks heat-treated above 2100°C was observed in their electron micrographs.

The density measured by the pycnometric method,[2] d_p; the density calculated from lattice constants, d_x, and the porosity, $100\,(d_x-d_p)/d_p$, of the carbon blacks are given in Table I.

The pressure vessel of the piston-cylinder type is shown schematically in Fig. 1. The piston and the cylinder were made of tool steel. The surfaces of the upper and lower pistons were plated with copper and silver in order to decrease the contact resistance between the piston and the specimen. This vessel could be used under pressures of up to 10 kb. The dimensional change of the cylinder by the elastic compression at the pressure of 10 kb was found to be negligible for the measurement of the resistivity. As an insulator between the pistons and the cylinder, a polyethylene sheet, a phenol resin pipe and a pipe made of epoxy resin reinforced with glass fibre were tested. A polyethylene sheet 0.04 mm. thick was proved to be the best among them and could be used for the measurement of the resistivity under pressures of up to 10 kb. The phenol and reinforced epoxy resin pipes, which were 2.5 mm. thick, fractured when the specimen was compressed to about 6 kb. Also, the dimensional

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[1] E. Andelson and A. E. Austin, presented at the Sixth Biennial Conference on the Carbon (1963), Pittsburgh, Pa.

[2] M. Mizutori, S. Hagiwara, K. Kawazohe and Y. Fukuda, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **66**, 1757 (1963).

TABLE I. THE DENSITIES AND POROSITY OF CARBON BLACK PARTICLES

Specimen	d_p	d_x	Porosity
Channel black			
(Spheron-9) original	1.789±0.009	—	—
1270°C HT	1.857±0.004	2.23	19.8
2020°C HT	1.933±0.002	2.24	16.1
2610°C HT	1.951±0.004	2.24	14.9
Thermal black			
(Miike ♯20) original	1.739±0.009	—	—
1340°C HT	1.860±0.002	2.24	20.2
2120°C HT	2.014±0.006	2.24	10.9
2680°C HT	2.014±0.006	2.24	9.7
Thermal black			
(Nippon Gas Chem.)			
original	1.693±0.004	—	—
2500°C HT	2.143±0.006	2.24	7.2
3000°C HT	2.167±0.006	2.24	3.2
Natural graphite	2.254±0.006	2.26	—

change in the resin pipes by compression could not be neglected in the measurement of the resistivity when the thick pipes were used. In the case of the polyethylene sheet, however, its dimensional change was negligible because it was very thin compared with the diameter of the compressed specimen. The pressure applied to a specimen was calibrated by the measurement of the volume change of NH_4F transition (3.8 kb.) The pressure loss for friction between the piston and the cylinder was found to be 5%.

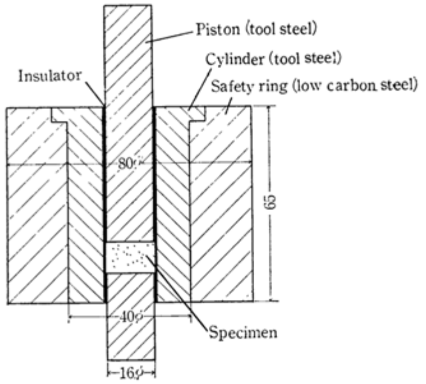

Fig. 1. The pressure vessel of piston-cylinder type.

The electrical resistance under compression was measured as a function of the thickeness of the specimen by a Kelvin bridge using the pistons as electrodes. The very good linear relation between the measured resistance and the thickness of specimen was observed, as is shown in Fig. 2. When the thickness of the specimen became too high, the measured resistance of the specimen deviated upwards from this line as a result of the non-uniformity of the pressure in the specimen. Accordingly, the thickness of the specimen was limited to about 4 mm. The electrical resistivity was determined from the inclination of this line using the least-squares calculation.

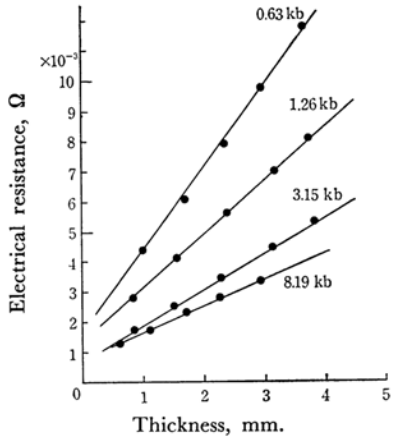

Fig. 2. Dependence of the measured electrical resistance on the thickness of the 2680°C-treated thermal black (Miike ♯20).

Results

The changes in the electrical resistivity, ρ, of the thermal blacks (Miike ♯20) and of the natural graphite with the pressure, P, are shown on logarithmic plots in Fig. 3; that of the channel black (Spheron-9), in Fig. 4 and that of the thermal black (N. G. C.), in Fig. 5.

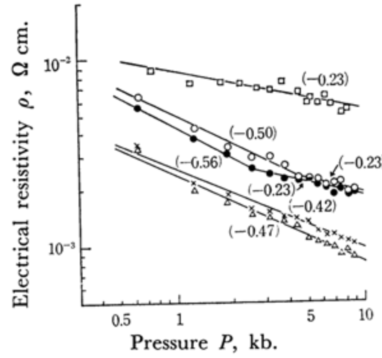

Fig. 3. Dependence of electrical resistivity ρ of carbon black on pressure P.
□: natural graphite (NG)
×: original thermal black (TBM)
△: 1340°C-treated thermal black (TBM-1300)
○: 2120°C-treated thermal black (TBM-2100)
●: 2680°C-treated thermal black (TBM-2700)
Figures in parentheses along lines are slopes of these lines.

The relation between $\log \rho$ and $\log P$ can be said to be linear. For the 2100°C-, 2700°C- and 3000°C-treated thermal blacks, the $\log \rho$ vs. $\log P$ relations break relatively sharply at the pressure of about 4.5—3.0 kb. The pressure of the break point decreases with the increase in the heat treatment temperature. However, the original and 1300°C-treated thermal blacks do not show

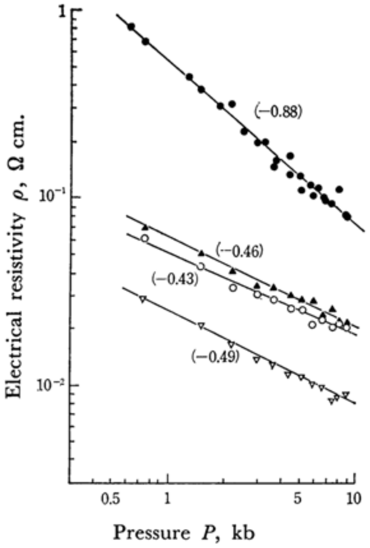

Fig. 4. Dependence of electrical resistivity ρ of carbon black on pressure P.
●: original channel black
▽: 1270°C-treated channel black (CB-1300)
○: 2020°C-treated channel black (CB-2000)
▲: 2610°C-treated channel black (CB-2600)
Figures in parentheses along lines are slopes of these lines.

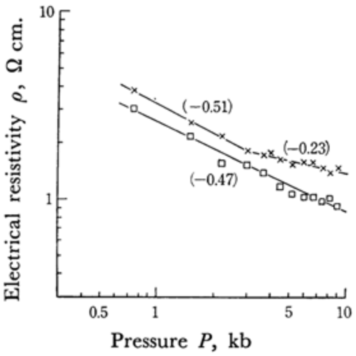

Fig 5. Dependence of electrical resistivity ρ of carbon black on pressure P.
□: original thermal black (NGC)
×: 3000°C-treated thermal black (NGC-3000)

any break within the limits of the pressure applied in the present work. In other words, the 2100°C-, 2700°C- and 3000°C-treated or graphitized thermal blacks show the change in resistivity with the pressure in two stages, while the original and 1300°C-treated thermal blacks show only the first stage of the change in resistivity. The slopes of the thermal blacks at the first stage are about -0.5, scattering somewhat from specimen to specimen. At the second stage, the relation between $\log \rho$ and $\log P$ has almost the same slope, -0.23, for all graphitized thermal blacks. This value of slope agrees with that for natural graphite.

The relation between $\log \rho$ and $\log P$ for the channel black shows no break. The original channel black has quite a high resistivity and a high slope of the $\log \rho$ vs. $\log P$ relation.

Discussion

The change in the electrical resistivity with the pressure results from the process of packing the carbon black particles. Takahashi[3] reported the dependence of the electrical resistivity of carbon black on pressures up to 200 kg./cm² to be $\rho=A/P+B$ for hard spheres and $\rho=C/P^{1/2}+D$ for deformable particles as derived from Holm's contact resistance theory. Akamatu and Inokuchi[4] observed the relation $\rho=a/P+b$ (3) for various carbon blacks in the 11—160 kg./cm² pressure range. Honda, Ouchi and Toyoda[5] reported that there was, in general, the relation $\rho=AP^{-2}+B$, where $n\approx 1$—2 for heat-treated coals, cokes and charcoals in the 400—2000kg./cm² pressure range. They also derived the relation from the relations of the void ratio to the pressure and of the void ratio to the resistivity, and deduced $n=2$ for plastically-undeformable particles. Ōtani[6] found $n=1$—0.5 for various carbons in the 500—2200 kg./cm² pressure range. According to Mrozowski,[7] the electrical resistivity of the powder

$$\rho\cong 0.34\bar{\rho}E^{1/3}/(P^{1/3}\varphi^{1.0})$$

for a purely elastic deformation (4)

and

$$\rho\cong 0.445\bar{\rho}H^{1/2}/(P^{1/2}\varphi^{3/4})$$

for a purely yielding deformation (5)

where $\bar{\rho}$ = the real resistivity; E = the elastic modulus, H = the hardness of the material of the particles, and φ = the fraction of the volume occupied by the particle. From the experimentally-established relation for the volume of a definite amount of material, $\log V=-m\log P$[7] and $\varphi\cong 1/V$,

$$\rho=k_1/(P^{(1/3+m)}) \text{ for elastic deformation} \qquad (4')$$

and

$$\rho=k_2/P^{(1/2+3m/4)} \text{ for yielding deformation} \qquad (5')$$

The pressure dependence of the resistivity caused by the change in packing is very small and leads to a small correction in the slope of the $\log \rho$ vs. $\log P$ relation. The slopes of the first stage of all the curves for $\log \rho$ vs. $\log P$ are alsmost equal to -0.5 except for the original channel black. Therefore, the first stage of the $\log \rho$ vs. $\log P$

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[3] H. Takahashi, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **71**, 361 (1950).

[4] H. Akamatu and H. Inokuchi, ibid., **70**, 185 (1949).

[5] H. Honda, K. Ouchi and S. Toyoda, ibid., **76**, 364 (1955).

[6] S. Ōtani, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **60**, 407 (1957).

[7] S. Mrozowski, Proc. Third Conf. Carbon, Pergamon (1959), p. 495.

relation may mainly correspond to the yielding deformation process of the packing of the particles, although the elastic deformation process may play some part. One can see a slight increase in the slope for the thermal black with the increase in the heat treatment temperature. As can be seen from Table I, carbon black particles are porous and are, therefore, deformable, especially when they are heat-treated at higher temperatures and become softer. The slope of the log ρ vs. log P relation for the original channel black is -0.9. This is due to the surface film on the carbon black particles.[7,8] The film on the particle surface can be removed by heat treatments at high temperatures. Therefore, the 1300°C-treated channel black has a slope similar to those of the other samples.

The pressure of the break point of the log ρ vs. log P relation for the graphitized thermal blacks conincided with the pressure at which the bulk density of the compressed mass is almost equal to the density of carbon black particles; i. e., the void ratio is almost zero (Fig. 6).

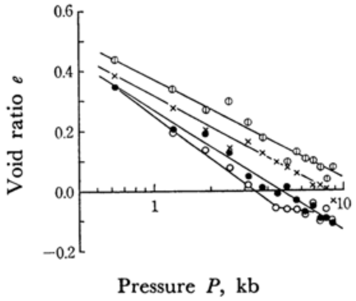

Fig. 6. Dependence of void ratio e of thermal black on pressure P.

⦶: original thermal black (TBM)
×: 1340°C-treated thermal black (TBM-1300)
●: 2120°C-treated thermal black (TBM-2100)
○: 2680°C-treated thermal black (TBM-2700)

From this point on, the particles themselves are compressed and the bulk density of particles finally reaches almost the same density as that calculated from the lattice constants, d_x. In the case of the channel black and the original and calcined (1370°C treated) thermal blacks, the bulk densities never exceeded their particle densities (Figs. 6 and 7). The plots log ρ vs. log P for these blacks had only the first stage, and not the second stage. In the second stage the dependence of the electrical resistivity on the pressure may mainly be represented by the elastic deformation mechanism, although the experimental slope, -0.23, is rather smaller than the predicted value, -0.33. There may be an increase in the preferred orientation of crystallites in the compressed mass with the increase in compression. When the distribution function of crystallite orientation is assumed to be $\sin^n \Phi$,[9] where Φ is the angle between the normal to the basal plane of crystallite and the normal to the direction of compression, the resistivity, $\overline{\rho}$, can be taken to be approximately $\rho_{\parallel c} \sin^n \Phi$, because $\rho_{\parallel c} \gg \rho_{\perp c}$, where $\rho_{\parallel c}$ and $\rho_{\perp c}$ are the resistivities of single crystals of graphite parallel to and perpendicular to the c-axis respectively. The distribution function may be related to the pressure of compression as $\sin^n \Phi = a P^b$; therefore,

$$\overline{\rho} = a \cdot \rho_{\parallel c} \cdot P^b \tag{6}$$

From Eqs. (4) or (4′) and (6)

$$\overline{\rho} \cong 0.34a \cdot \rho_{\parallel c} E^{1/3} / (P^{1/3-l} \varphi^{1.0})$$
$$\cong k_3 / (P^{1/3+m-l}) \tag{7}$$

Thus the increase in the preferred orientation decreases the slope of the log ρ vs. log P relation.

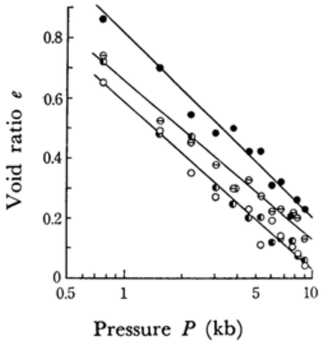

Fig. 7. Dependence of void ratio e of channel black on pressure.

●: original channel black
⊖: 1270°C-treated channel black (CB-1300)
◐: 2020°C-treated channel black (CB-2000)
○: 2610°C-treated channel black (CB-2600)

From Eq. 5 one can calculate the hardness, H, from the applied pressure, P, and the bulk density of the carbon black powder at the pressure. The resistivity at 9 kb was taken as $\overline{\rho}$, because the change in the resistivity with the increase in the pressure in the high pressure range was very small. Mrozowski[7] obtained 8×10^5 lb/in^2 = 56×10^3 kg./cm^2, which is an unreasonably high value for calcined soft carbons of coarse powder. However, he suggested the use of the calculated hardness in estimating relative values. Our results were about the same order as his value, i. e., very high. For example, the hardness was estimated to be 51×10^3 kg./cm^2 for the original thermal black, 38×10^3 kg./cm^2 for the 1340°C-treated thermal black, 28×10^3 kg./cm^2 for the 2120°C-treated thermal black, and 24×10^3 kg./cm^2 for the 3000°C-treated thermal black.

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[8] S. Mrozowski, A. Chaberski, F. E. Loebner and H. T. Pinnick, ibid., p. 211.

[9] G. E. Bacon, *J. Appl. Chem. (London)*, **6**, 477 (1956).

The original carbon blacks have about the same hardness as calcined soft carbons, and the hardness of the carbon blacks decreases to about half when they are graphitized, i. e., heat treated above 2000°C. Therefore, the graphitized carbon black particles deform easier than the original and calcined particles. In the case of the graphitized thermal black, all space in the compressed mass is filled up with material of the density of the carbon black particle at about 3—5 kb. At higher pressures the compression can be achieved only by increasing the density of the particle material, thus increasing the contact between crystallites in the particle by the elastic deformation mechanism. At the final stage of compression, the density reached 2.2 g./cm^3. This value is very near to the true density, $d_x=2.24$. The shape of the carbon black particles did not change even when the particles were compressed at pressures of 9 kb or above, where the bulk density of the carbon black was 2.2 g./cm^3 or above. The shapes of the carbon black particles before and after the compression are shown in Plate 1.

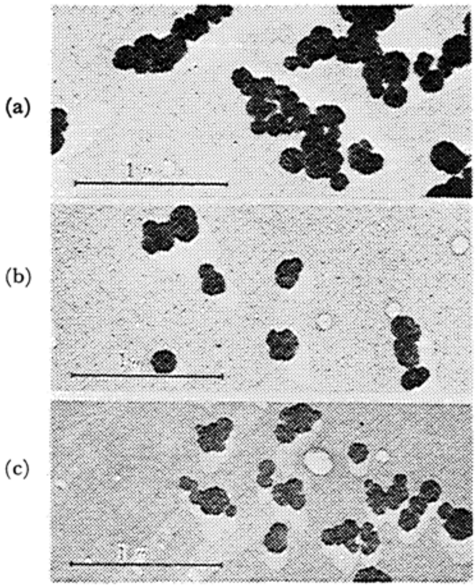

Plate 1. Electron micrographs of 2680°C-treated thermal black (Miike ♯20) Al-shadowed.
(a) before compression
(b) after compression at 8.8 kb
(c) after compression at 25 kb

In conclusion, the change in the electrical resistivity of carbon black particles with the pressure proceeds in three stages. In the lower pressure range, where the packing proceeds by filling voids by the rearrangement of carbon black particles, the resistivity changes with the number of contact points between particles. It has been reported that the resistivity changes with $1/P—1/P^{1/2}$ 3,4). However, the dependence of the resistivity of carbon black on the pressure seems to be proportional to $1/P^{1/2}$, even in a very low pressure range.10) In the medium and high pressure ranges, where the contact area increases with an increase in the deformation of the particles, the resistivity, ρ, changes with $1/P^{1/2}$. In the very high pressure range, the elastic deformation, accompanied by the change in the preferred orientation with the pressure, is the main process in determining the change in the resistivity with the pressure, $\rho \propto 1/P^{1/3-l}$. No change in the shape of carbon black particles after compression under a very high pressure could be observed.

Thanks are due to Mr. Etsuro Kato for his discussion. The authors are also indebted to the Tokai Electrode Mfg. Co. for the supply of specimens, and to the Mitsubishi Chem. Co. and the Onoda Cement Co. for taking electron micrographs.

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10) E. Kato, Private communication, to be published in *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*).