Size and Structure of Commercial and Graphitized Carbon Blacks by Low-angle X-Ray Scattering and Colloid-chemical Methods

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Introduction

The measurement of size of colloidal perticles has been one of the most extensively investigated subjects in colloid science. Among various procedures for measuring the particle size, some methods have been adopted for routine industrial assessment of the colloidal products. However, little has been known on the mutual relationships between the values obtained by different methods, and the lack of knowledge in the correlation has lead to the equivocal elucidation of properties.

It seems very desirable, therefore, that some experiments to compare results from different methods for the same sample should be carried out.

Carbon black is an industrially available colloid, the properties of which have been investigated by means of various methods including electron-microscope[1)], X-ray scattering[2–5)], adsorption[1,6–16)], or heat of wetting[10)] methods, and distinguished, in most cases, in the spherical particle shape and absence of internal surface, in other words, an example of colloid of simple structure. The general properties and industrial applications of carbon blacks are to be referred to ref. (17).

In the present work, the average particle size values obtained from low-angle X-ray scattering, electron-microscope, molecular adsorption and heat of wetting with methanol for various carbon black samples have been compared and discussed. It appears that there is no need to assert the importance of the study of this kind to the industrial uses of the samples for rubber reinforcing filter, printing ink, coloring pigment and other miscellaneous purposes.

Description of Samples

Carbon Blacks.—The data characterizing fourteen carbon black samples investigated in the present work are summarized in Table I. These samples (five Japanese and nine American) appear to be representative of modern commercial carbon blacks with various general properties and uses. The designating symbols in the type of the samples are those widely adopted in the rubber industry and denote the process in manufacturing and uses: LCC, low color channel; FT, fine thermal; SRF, semi-reinforcing furnace; HAF, high abrasion furnace; HPC, hard processing channel; LFI, long flow impingement; MT, medium thermal; MAF, medium abrasion furnace; ISAF, impingement super abrasion furnace, SAF, super abrasion furnace. No pretreatment of extracting tarry matters attached to the carbon surfaces has been applied in this work.

Graphitized Carbon Black.—A gas thermal black, No. 1 in Table I, Tokyo Gas 300 (LCC), was subjected to heating and graphitization up to various temperatures.

To prepare the samples heated up to temperatures below 1000°C, a muffle furnace was employed. The carbon black was filled, in order to avoid oxidation by air, in a silica tube, which was thickly covered by asbestos to control the rate of heating, the temperature being measured by a thermo-couple inserted into the center of the

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9) M. L. Corrin, ibid., **73**, 4061 (1951).

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14) F. K. Shoenfeld, ibid., **27**, 571 (1935).

15) W. R. Smith, F. S. Thornkill and R. I. Bray, ibid., **33**, 1303 (1941).

16) J. Sameshima, H. Akamatu, K. Inouye, S. Kawamura, R. Matsuura and K. Tamaru, *Reviews of Modern Colloid Science*, **1**, 250 (1948).

17) W. R. Smith, "Encyclopedia of Chemical Technology," Vol. 3, The Interscience Encyclopedia, Inc., New York (1949).

TABLE I

DESCRIPTION OF CARBON BLACKS

No.	Carbon black	Type	Process	Manufacturer
1	Tokyo Gas 300	LCC	Gas thermal	Tokyo Gas Co.
2	Miike 20	FT	Gas thermal	Miike-gosei Co.
3	Asahi Carbon 40	SRF	Oil furnace	Asahi Carbon Co.
4	Seast 285	HAF	Oil furnace	Tokai Electrode Co.
5	Shoden Acetylene black	Acetylen black	Thermal	Showa-denko Co.
6	Micronex 2	HPC	Channel	Columbia Carbon Co.
7	Kosmos 15A	LFI	Channel	United Carbon Co.
8	Peerlees IIA	LFI	Channel	Peerless Carbon Black Co.
9	Thermax	MT	Gas thermal	Thermatomic Carbon Co.
10	Sterling S	SRF	Oil furnace	Cabot Inc.
11	Philblack A	MAF	Oil furnace	Phillips Petroleum Co.
12	Philblack O	HAF	Oil furnace	Phillips Petroleum Co.
13	Philblack I	ISAF	Oil furnace	Phillips Petroleum Co.
14	Philblack E	SAF	Oil furnace	Phillips Petroleum Co.

tube. The samples heated up to 420, 620 and 990°C were obtained at an average heating rate of 50 ± 10°C/min. The graphitized carbon black samples heated at temperatures above 1000°C were prepared by means of a Tammann furnace at the Omachi Factory of Showa Denko Co. Ltd. by the average rate of temperature rise of 50 ± 10°C/min. up to 1300, 1700, 2100, 2420, 2630 and 3170°C, maintaining at the final temeratures for further 25 minutes.

Experimental Procedures

Low-angle X-ray Scattering.—Several workers[2-5] have applied the low-angle X-ray scattering method to derive the particle size of carbon blacks as a modern tool of particle size determination. Biscoe and Warren[2] employed a camera of 47.6 cm. specimen-to-film distance to record the scattering and calculated the particle size of three samples based on the Guinier's scattering intensity formula[18]. These authors showed the size in fair agreement with that obtained by the electron-microscopic method. Jellinek, Solomon and Fankuchen[3] have proposed a graphical method to obtain the particle size distribution from a single scattering recorded film and demonstrated it for a carbon black by means of a camera of specimen-to-film distance of 23.5 cm. This procedure was also applied to another sample by Turkevich and Hubbell[5] who used a camera of 70 cm. specimen-to-film distance with the Geiger counter to record the scattered X-rays. Brusset[4] also reported the size of five samples.

The calculation of particle size has been carried out by the theoretical functions relating the intensity of scattered X-ray to the scattering angles. Various functions have been proposed which differ in the treatments of the characteristics of the sample material, particle shape, particle distribution, etc. and the readers are raferred to excellent reviews by Yudowitch[19].

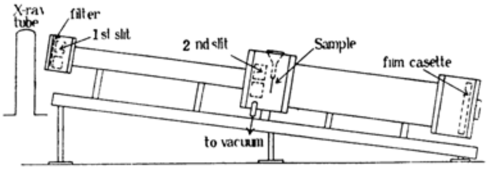

Fig. 1. A sketch of low-angle X-ray scattering camera.

The apparatus used in this work is a type of two-aperture collimating system camera. A sketch of the apparatus is drawn in Fig. 1. A first aperture of width a_1 and length b_1 is placed in metal block A. At a distence l from the first aperture is the second aperture in block B with width a_2 and length b_2. The scattering specimen is placed close to the second aperture. At a distance L from this specimen aperture is placed a cassette, in which the recording film is set, in the block C. The blocks A, B and C are tightly connected by means of rubber packings with two metal tubes to enable the inside of the apparatus to be evacuated. After Yudowitch[19], the intensity of the scattered rays, I, is considered to be

$$I \propto a_1 b_1 a_2 b_2 R^5 \rho^2 / l^2 L^2 \lambda^2 u^2, \tag{1}$$

where, R is the particle radius, ρ the electron density, λ the X-ray wave length and

$$u = 2\pi \varepsilon R/\lambda, \tag{2}$$

where, ε is the scattering angle. From Eqs. (1) and (2), it is noted that to give a strong intensity short length of l and L and a wide aperture as possible are recommended. On the other hand, Yudowitch[19] has given also the following conditions of camera geometry for the most intense usable data in the case of the slope analysis using the Guinier's equation:

$$l = L, \tag{3}$$

$$a_1 = 2\ a_2 = \lambda L \delta u / 4\pi R \tag{4}$$

$$b_1 = b_2, \tag{5}$$

and at a tolerable error,

$$a_1 < \lambda l / 3R, \tag{6}$$

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[18] A. Guinier, *Ann. Phys.* **12**, 161 (1939).

[19] K. L. Yudowitch, *Rev. Sci. Instr.*, **23**, 83 (1952); *Anal. Chem.*, **25**, 721 (1953).

where, δu denotes the collimation error. These relations imply that a long camera is useful to have the scattering pattern in a limited error and at the same time to employ wider apertures which are apparently easy to be made and operated. A sufficiently long specimen-to-film distance (L) is also necessary to assure a reasonable pattern. However, it is also clear that the long camera necessitates longer exposure time to obtain a scattering pattern on the film suitable to calculate the particle size. Fortunately, we have known that the average diameter of carbon blacks lies usually in the range of some hundreds angstrom, except very few thermal blacks with diameters of some thousands angstrom. The author has used the values of l and L of approximately 100 cm. (exactly, l is 1013 mm. and L is 993 mm.). From Eqs. (4), (5) and (6), the maximum value of a_1 may be calculated as shown in Table II in the case of the camera dimension described above and copper $K\alpha$ or chrome $K\alpha$ radiations. These values suggest that the exposure time may be shortened by employing a wider aperture system. In the present experiment, the dimentions of first and second appertures were taken as follows: (1) a_1 1.00 mm. and a_2 0.50 mm. for Cu $K\alpha$ radiation and (2) a_1 1.00 mm. or 0.50 mm. and a_2 0.50 mm. or 0.25 mm. for Cr $K\alpha$ radiation. In each condition, the relation (4) is applied. The height of apertures ($b_1=b_2$) is 3.00 mm. In the case of (1), the samples with the average diameter less than 1000 Å. are expected to be analyzed, while in (2) the maximum diameter to be covered would be up to nearly 4000 Å. It is thus expected that almost all carbon black samples are tested by this camera in a reasonable accuracy. Other cautions to shorten the exposure have been taken in minimizing the absorption of X-rays by air in this very long (2 m.) camera by evacuating the whole path continuously during the exposure up to 10^{-2} mmHg and also the absorption by foil windows and filter. As is obvious in Fig. 1, the only source of absorption by camera window is the filter (Ni for Cu ray and V_2O_5 on Al foil for Cr ray) which is cemented with the first aperture and at the same time constitutes the window to keet the vacuum.

TABLE II

THE MAXIMUM WIDTH OF THE FIRST APEATURE IN A FUNCTION OF PARTICLE DIAMETER

Diameter, Å	a_1 maximum, mm.	
	Cu $K\alpha$ (1.54Å)	Cr $K\alpha$ (2.29Å)
100	10.4	15.5
500	2.08	3.10
1000	1.04	1.55
2000	0.52	0.78
5000	0.21	0.31

To reduce spurious radiations scattered from the apertures, the apertures have been designed to have a depth of 10 mm., so that a very clear-cut slit image is obtained in blank tests. A beam-stopper was used with the width of 2.5 mm. in the case of a_1 width 1.00 mm. or 1.4 mm. for a_1 0.50 mm.

The sample powder is extruded from a capillary in a small bar of 1 mm. diameter and set on a mount which is inserted inversely from the top of block B close to the second apperture and the sample mount is screwed in tightly to keep the vacuum.

By employing Cu radiation generated at 35 kV. and 20 mA. or Cr radiation at 35 kV. and 15 mA. Eastman-Kodak "No-screen" X-ray film, the exposure of 30 to 60 minutes was sufficient to give the suitable scattering patterns. A necessary by-earth voltage was applied to the filament of X-ray tube to reduce the focal spot width up to the same width of the first slit a_1; this procedure has resulted in strengthening the X-rays efficiently to pass through the camera. An example of the scattering patterns is shown in Fig. 2.

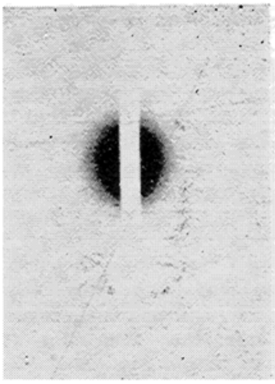

Fig. 2. An example of scattering pattern (×I). Sample: Philblack E.

The film obtained was micro-photometered by a reading photometer for each 0.25 mm. of film at a constant photometer condition. The calibration of the photographic density has been carried out by the graded-indensity scale method. The curves of the logarithm of measured (calibrated) intensity versus square of scattering angle (or of distance on film) showed a general shape as exemplified in Fig. 3. The average particle size was calculated from the straight part of the curve for each sample by use of the equation proposed by Guinier[18].

$$I=CWR^3e^{-0.221k^2R^2}, \tag{2}$$

where, I is the intensity, C a constant particular to the sample, W the mass of scattering elements, R the particle radius and k is $4\pi\sin(\varepsilon/2)/\lambda$. The Eq. (7) is changed to the following form:

$$\log I=A-BR^2f^2, \tag{8}$$

where, A and B are constants and f is the distance on film of a scattering with intensity I.

It has been found the reproducibility of the experiment by these procedures is approximately 10% or, in most cases, with higher accuracy for the carbon blacks of less than 1000 Å. diameter.

X-Ray Powder Method.—The commonly used powder method was employed, using filtered

TABLE

No.	Carbon Black	Dia. from low-angle scattering, Å	Modal dia. by electron-microscope, Å	Iodine adsorption	
				Surface area, m²/g.	Dia., Å
1	Tokyo Gas 300	732	500	37.8	848
2	Miike 20	1140	1120	8.77	3650
3	Asahi Carbon 40	1390	1020	7.75	4580
4	Seast 285	572	640	48.8	661
5	Shoden Acetylene black	1420	1250	22.3	1450
6	Micronex 2	576	250	47.3	713
7	Kosmos 15A	686	460	83.7	387
8	Peerless IIA	608	370	76.1	459
9	Thermax	1940 (Cu) 4890 (Cr)	3300	—	—
10	Sterling S	636	620	11.5	2730
11	Philblack A	620	450	17.4	1930
12	Philblack O	454	380	35.3	994
13	Philblack I	445	280	45.9	746
14	Philblack E	396	220	57.9	615

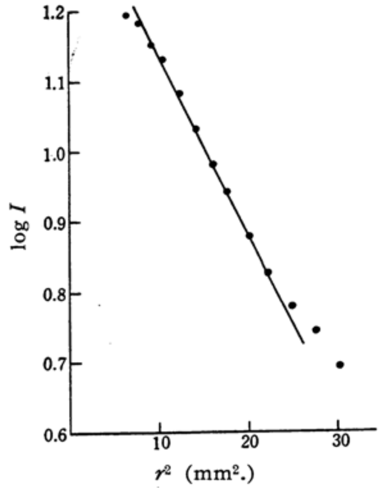

Fig. 3. An example of the relation between log I and r^2. Sample: Philblack E, I: absolute intensity, r: distance on film

copper $K\alpha$ radiation at 30 kV. and 20 mA. A calibrated camera (radius 45 mm.), powder specimen of 0.5 mm. diameter and Kodak "No-screen" films were used. The patterns of (002) and (100) indices were microphotometered for each 0.5 mm. of film and the crystallite dimensions were calculated for both patterns, Lc and La respectively, by the Laue-Brill procedure[20]. The crystallite dimension observed in carbon blacks implies the size of fundamental structural units of which the carbon black particle (a cluster of units) is constructed.

Electron-microscopic Method.—The enlarged electron-micrographs obtained for the samples have varying magnifying ratios between 14000 and 79000 according to the range of particle dimension. The sizes of numerous particles on the photographs were measured with the help of a magnifying glass and transparent scale, and the diameter of the most frequent counting (called the modal diameter) was determined.

Adsorption Measurements.—The most accurate method to evaluate the surface area will be the low-temperature adsorption method of nitrogen at liquid-air temperature[1,6-10] but a more feasible and rapid method of determining the specific surface area by adsorption of molecules from solutions has been applied to carbon blacks is frequently adopted. The compounds used for adsorbent are organic acids[11,12], iodine[13-16], diphenylguanidine[13], methylene blue[16], etc. In this work, the iodine and the methylene blue adsorption measurements were made which had been previously applied by the author to carbon black[16], coal[21] and coke[22].

The dried sample (0.5 g.) was added to 25 cc. of 0.1 N iodine solution at 25.0°C and the mixture stirred from time to time. The change in iodine concentration was determined after 1 hour. The specific surface area value could be derived from the adsorption per unit weight of sample, it being assumed that the adsorption is monomolecular and that the cross sectional area of adsorbed iodine molecule is $16.1\ \text{Å}^2$[23,24].

A 25 cc. portion of 0.4% methylene blue solution was added to 0.5 g. dried sample and stirred occasionally. The change in concentration after 24 hours at 25.0°C was determined with a photoelectric colorimeter. The specific surface area was again given from the adsorption data, the molecular area on solid surfaces being taken as $1.0 \times 10^3 \text{m}^2/\text{g}$[25]. The surface area value was then calculated in diameter by use of real density for each sample. The density was obtained picnometrically at 25.0°C with methanol after replacing

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[20] K. Inouye, H. Tani and M. Abiko, *J. Fuel Soc. Japan*, **32**, 292, 386 (1953).

[21] K. Inouye, ibid., **29**, 112 (1950).

[22] K. Inouye and H. Tani, *Fuel* (London), **34**, 356 (1955).

[23] E. J. Mack, *J. Am. Chem. Soc.*, **47**, 2468 (1925).

[24] L. H. Reyerson and A. W. Wishart, *J. Phys. Chem.*, **42**, 683 (1938).

[25] F. Paneth and W. Thimann, *Ber.*, **57**, 1215 (1924).

III

Dye adsorption		Heat of Wetting			Crystallite dimensions	
Surface area, m^2/g.	Dia., Å.	Heat, cal./g.	Surface area, m^2/g.	Dia., Å	La, Å	Lc, Å
35.4	906	4.25	42.5	755	16.5	10.9
—	—	3.00	30.0	1070	15.4	12.0
—	—	—	—	—	17.5	11.4
53.3	606	2.83	28.3	1100	18.2	13.8
—	—	2.82	28.2	1150	43.1	24.8
61.0	553	—	—	—	16.5	14.3
189.	172	12.6	126.	257	19.5	10.1
120.	291	11.3	113.	309	20.9	12.4
—	—	—	—	—	21.5	11.9
17.8	1800	0.60	6.0	5350	17.3	14.2
27.1	1240	0.72	7.2	4680	20.7	13.6
50.3	689	1.95	19.5	1810	15.5	11.8
64.6	444	2.12	21.2	1660	18.2	11.1
81.7	365	3.47	34.7	1030	16.4	12.5

the occluded air by evacuating below 1 mmHg for several hours.

Heat of Wetting Method.—Kraus[10] has reported recently the heat of immersion of nine carbon black samples in water, methanol and *n*-hexane. The results was discussed in comparison with the specific surface area obtained by the nitrogen adsorption method at very low temperature and it was shown that the value of heat evolved by wetting the unit area varies with the nature of the sample, particularly the content of oxygenic radicals in carbon blacks.

In the present work, the heat-of-wetting measurements were made in order to derive the specific area on an assumption that the area per unit heat evolved is identical. The aparatus is a calorimeter comprising a Dewar flask with bakelite lid which is fixed to the flask by screws and supports all the working parts of the calorimeter: a stirrer which serves at the same time as a support of sample bulb, electrical heater and a Beckmann's thermometer to which a bulb-breaking device is attached. The Dewar vessel is immersed in a thermostat regulated at 25.0°C, which is situated in an air-bath controled at approximately 25°C. The construction and procedure are not very different from those proposed by earlier workers, in particular, by Griffith and Hirst[26]. Approximately 0.3–2.5 g. sample dried at 100–110°C for 1.5 hour and weighed in a thin-walled glass bulb, was evacuated at 10^{-4} mmHg for 5–6 hours at room temperature. After an equilibrium of temperature in Dewar vessel was attained, the bulb was broken in methanol (120 cc.) by a breaking device attached to the thermometer and the elevation of temperature was recorded at each 0.5 or 1 minute until when an equilibrium was again attained. The heat capacity was measured for each run by heating with known electrical energy supplied from a battery.

To derive the surface area from the heat-of-wetting, a value of area per unit heat of 10.0 m^2/cal. obtained by Bangham[27] and Maggs[28] for several carbonaceous substances was used.

The diameter was obtained from a specific surface area similarly as the absorption method by use of real density.

Electrical Resistivity Measurement.—The sample was dried at 110°C for 1 hour and the electrical conductivity of the compressed sample was then measured at various successive pressures with an apparatus constructed by Honda et at.[29]. The powder was placed in a steel tube and the pressure up to 3000 kg./cm^2 was exerted on it by a hydraulic system. The specific resistivity was plotted against $1/P$, $1/P^2$ or $1/\sqrt{P}$; where P denotes the pressure applied. The best linearlity has been found at the relations between the specific resistance and $1/\sqrt{P}$; the value of resistivity when P reaches infinity was taken as the characteristic value for each sample.

Results and Discussions

Carbon Blacks.—Table III summarizes the values of particle diameter obtained from the methods explained in the preceding section. The surface area and heat of immersion as well as crystallite dimension by powder method are also tabulated for reference.

The diameters obtained by low-angle scattering method and by electron-microscope are in fairly good agreement. However, it seems important to note that the value from low-angle scattering is, in most

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[26] M. Griffith and W. Hirst, "Proc. of Conf. on the Ultra-fine Structure of Coals and Cokes," British Coal Utilization Research Association, London (1944), p. 80.

[27] D. H. Bangham and R. I. Razouk, *Proc. Roy. Soc* (London), **A166**, 572 (1938).

[28] F. A. P. Maggs, "Proc. of Conf. on the Ultra-fine Structure of Coals and Cokes," British Coal Utilization Research Association, London (1944), p. 95.

[29] H. Honda, K. Ouchi and T. Toyoda, *J. Chem. Soc. Japan* (Pure Chem. Sect.), **76**, 364 (1955).

cases, larger than the value from the latter; the cause of this discrepancy may be due to some experimental errors, but it is also probable that the particles of carbon black have some connection with each other by means of bridges made of carboneceous substance with not a very different nature from the particles themselves, and the scattering dimension by X-ray is apparently larger than that expected by electron-micrographs in which all particles, even though they connect and form a skeleton or guitarshaped agglomerate, are recognized as separate particles piled up one above another. (See Fig. 4). Watson[30] has suggested that in the electron-micrographs of shadowed carbon black particles some kinds of "essential" bridge forming between neighboring particles are observed. The possibility of the occurrence of the jointing particles as shown in Fig. 4 is also supported by the correlation between particles size and electrical resistance described in the next section. It is assumed from the results in Table III that the joining of this kind may be more noticeable in the samples with finer particle size, which showed larger discrepancy.

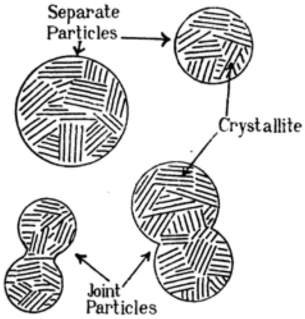

Fig. 4. Models of carbon black particles.

The particle diameter values obtained from adsoption methods and the heat-of-wetting measurement are somewhat parallel to those by X-ray and electron-microscopic method, but an exact comparison indicates that these colloid-chemical procedure, which are often employed in carbon black assessment, are by no means recognized as giving absolutely accurate results, and should be used only for a conventional qualitative comparison. As pointed out by Kraus[10], the adsorption or heat of immersion is largely affected by the chemical composition of reagents used as well as of carbon black itself, especially by the nature of surface of particles.

The crystallite size derived from line broadening of powder diffraction method gave almost similar dimensions of La (size in a-axis of hexagonal lamellae) and Lc (size in c-axis) ranging from approximately 10 to 20 Å, excluding only acetylene black which has more developed ultimate units. The concept of carbon black structure that the crystallites are piled in a very packed state so as to embrance no internal surface has been widely accepted (cf. Fig. 4). This is supported by the results of the present work (Table III) which show particle sizes from adsorption or heat of wetting methods, which will be able to measure the internal surface, are of approximately similar order as those from purely physical methods.

Graphitized Carbon Blacks.—The diameter revealed by low-angle method and the specific resistance method are tabulated in Table IV. The preparation of samples and measuring procedures are to be referred to the earlier descriptions.

As widely accepted, the crystallite dimensions increase with the elevation of graphitization temperature. Meanwhile, the size of particles, which are clusters of the ultimate unit crystallites, shows a very interesting change during the course of graphitization. On the other hand, the change in specific resistance is also particular. The relations between these three factors are illustrated in Fig. 5.

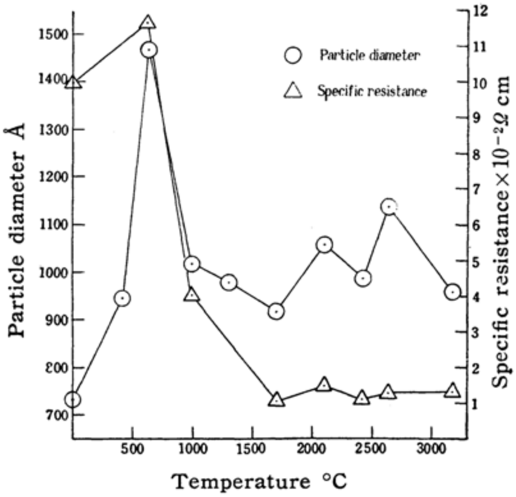

Fig. 5. Variations of particle size and specific resistance with treating temperature.

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30) J. H. L. Watson, *J. Appl. Phys.*, **20**, 747 (1949).

Schaeffer et al.[31] have reported the electrical resistance variations with graphitization of some kinds of carbon black; they observed a sharp minimum of resistivity at approximately 1200°, followed by increase up to approximately 2500°C, and the second decrease at higher temperatures. An interpretation of these results was tried as the evolution of combined gaseous materials from the samples and the growth of the crystallite.

TABLE IV

PROPERTIES OF GRAPHITIZED BLACKS

Temp., °C	Diameter, Å	Dimension Å Lc	Crystallite La	Specific resistance, Ω cm.
Untreated	732	16.5	10.9	0.100
420	950	—	—	—
620	1470	21.1	14.1	0.117
990	1020	23.9	13.6	0.0410
1300	982	—	—	—
1700	920	50.8	36.9	0.0110
2100	1060	75.7	38.1	0.0158
2420	990	99.1	41.1	0.0119
2630	1140	47.8	50.0	0.0129
3170	960	61.9	40.8	0.0134

However, the present correlation between electrical resistance and particle diameter in Fig. 5 would suggest that the variation in resistivity is caused by a change in the state of agglomeration of the particles. As discussed in the earlier section, it has been indicated that the carbon black particles tend more or less to combine with each other to form conjoint particles that act as the scattering sources by X-rays and give large apparent diameter values. It is apparent that the conjoint particles shown in Fig. 4 can form only a loosely packed state and that such loose packing results in a difficulty of electrical conduction. The maxima in both electrical resistance and particle size at 620°C are most noticeable and it is expected that the carbonization of tarry substances on the surface of particles will play a part in forming a scaffolding particle system. The electron-micrographs also show somewhat agglomerated particle images for the samples treated at such temperature range. The linearity between particle size and resistance is also observed at higher temperature range in Fig. 5, but it seems that the formation of conjoint particles at higher temperature range than 1000°C is improbable. Another reason is therefore to be considered that the increase in particle size is also derived from extinction of smaller particles by heat treatment and vice versa. Based on the similar concept as suggested above, the increase in average particle size will cause a loosely packed state and have a high electrical resistance.

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