

DENSITY-RESISTIVITY RELATIONSHIPS FOR BAKED CARBONS*

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Carbon samples were prepared by molding mixtures of petroleum coke particles and coal tar pitch and baking them to 1000°C. The coke particle size, the binder content and the molding pressure were varied so as to give samples with a wide variation in apparent density d , filler density d_0 and resistivity ρ . The apparent densities of samples were increased by impregnation with pitch and rebaking. The relationships between apparent density, filler density and electrical resistivity were investigated and the range of applicability of Mrozowski's formula was experimentally tested. The results yield information concerning an undetermined parameter in the theory.

The relationships between the densities and electrical resistivities of baked carbons, as presented in the preceding paper by Mrozowski¹, have been subjected to an experimental study. The carbons which were studied were prepared in the laboratory by molding mixtures of coke particles and binder. The coke used was Texas-Lockport petroleum coke, which had an ash content of about 0.5% and was calcined to approximately 1200°C. Coal tar pitch, medium grade, was used as binder.

The coke was crushed, ground in a roll mill and sorted according to particle size by standard Tyler sieves. The sizes of the sieves are given in Table I. All samples were made of coke particles whose sizes were determined by two neighboring sieves in the Tyler sieve series. The "particle size" is defined by the two limiting sieves. Thus, for example, particle size 48/65 refers to particles that passed through the No. 48 sieve and were caught on the No. 65 sieve. A sufficient amount of coke for the samples in this study as well as for future needs was crushed and sorted by sieving at the early stages of the work, and each group of coke

particles of a given size was thoroughly mixed after all sieving was done in order to assure reproducibility of results.

The samples were prepared in the following manner. A "green mix" was prepared by mixing coke particles and coal tar pitch binder in the desired proportions in a paddle type mixer for about 15 minutes at a temperature of 150°C. In this type of mixer the particles were coated with binder without being crushed. The green mix was prepared in batches of about 300 grams. Small amounts of the mix were molded in a cylindrical mold on a Carver Laboratory hydraulic press while the mold was maintained at a temperature of 100°C. The molded green carbon samples usually weighed between 5 and 7 grams and were $\frac{3}{4}$ inch in diameter and were approximately $\frac{3}{4}$ inch in height, the height varying slightly from sample to sample.

The green carbon samples were baked in a silicon carbide crucible 30 inches in height and 17 inches inside diameter which was placed inside the baking oven. The samples were imbedded within the crucible in a packing which consisted of an equal mixture by weight of 50 mesh white sand and coke particles of 35 mesh size or smaller, and the top of the crucible was covered with a layer

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¹ S. Mrozowski, This volume, page 195.

TABLE I
Tyler Sieve Sizes

Mesher to the Inch	Opening (mm)
48	.295
65	.208
100	.147
150	.104
200	.074
270	.053

of asbestos to prevent entry of oxygen into the crucible during baking. The temperature of the oven was measured by a thermocouple in contact with one of the inner walls of the oven, the temperature being controlled by means of a Wheelco instrument. A three-day baking cycle was used during which the temperature was gradually increased at the rate of 11 degrees per hour from room temperature up to 700°C and then at the rate of 15 degrees per hour from 700°C to 1000°C.

The apparent density d of each baked carbon sample was determined from the weight of the sample and from measurements of its length and diameter as obtained with a micrometer. The filler density d_0 was obtained by dividing the weight of the coke particles in the sample by the total volume of the baked carbon sample. The weight of the coke particles was easily determined from the weight of the sample before baking (green sample) and the known binder content of the mix. The coke particles did not lose any weight in baking because the coke was previously heat treated to a higher temperature during calcination.

The electrical resistivity was determined by a potentiometric method. The sample was placed between the flat ends of two large brass cylinders through which the current was supplied. Natural graphite powder was compressed between the ends of the sample and the brass so as to insure uniform contact along the end faces of the sample. A pair of knife-edges of fixed

separation was placed in contact with the sample, and the difference of potential between the knife-edges was measured. Since the carbon samples have an inhomogeneous particle-binder structure, there are statistical fluctuations in the density and also fluctuations in the resistivity within the samples. The knife-edges were therefore rotated in steps about the circumference of each sample, and an average of the potential differences measured was used to calculate the resistivity of the sample. The current through the sample was determined from the voltage drop across a standard 0.1 ohm resistance in series with the sample.

The factors varied in the preparation of samples were the molding pressure, the binder content and the particle size. The molding pressure was varied from 1000 to 15,000 psi; the binder content of the green mix was varied from 10 to 50 parts binder to 100 parts coke particles by weight; and five different coke particle sizes were used, the sizes ranging from 48/65 to 200/270. A total of about 700 samples has been thus far prepared in this study.

Both the apparent and the filler densities of the green samples vary with molding pressure and binder content. An increase in molding pressure leads to an increase in these densities, but there is an upper limit to the densities that can be obtained from a given green mix by just increasing the molding pressure. When the coke particles which are all in direct contact with neighbors are compressed to the extent that the binder which originally coats the particles fills all the interstices between particles, no further increase in pressure can cause the filler density to increase. From there on the extra pressure causes a reversible elastic compression of the mix, the pressure being transmitted mainly by the fluid binder. An increase in binder content in this case causes a decrease in the maximum obtainable filler density and consequently also in the

maximum apparent green density, since relatively more space is filled by the lower density binder.

All samples showed shrinkage after baking so that the filler densities increased, but the apparent densities of most samples decreased because the binder gave off volatile material and lost weight during baking. However, in a few samples, namely those made of coke with small 200/270 size coke particles and 30 and 40 parts binder, the shrinkage more than compensated for the loss of weight of the binder so that the densities of those samples actually increased slightly in going from the green to the baked state. For samples made of a given particle size and at a given pressure, there appeared to be an optimum binder content which would yield the highest apparent density in the baked state. The best carbons, as judged mainly by appearance, were those made of mixes with 20 to 40 parts binder. Samples with low binder contents were mechanically weak and crumbled at the touch, and they had low apparent densities and high resistivities. On the other hand, when green carbons with a very high binder content were baked, part of the binder was pushed out of the sample into the packing material during the early stages of the baking process and solidified around the sample in the form of a crust which could be removed by scraping.

In order to determine the type of relationship that may exist between the electrical resistivity and the apparent density, a plot was made as is shown in Fig. 1. Here the resistivities of baked carbons made of size 100/150 coke particles are plotted against their apparent densities. The molding pressures and binder contents of the samples were varied, and all the samples were baked to 1000°C. The points on a given curve correspond to samples molded under the same pressure. The shape of the curves appears to be typical for all particle sizes; similar families of curves were obtained for

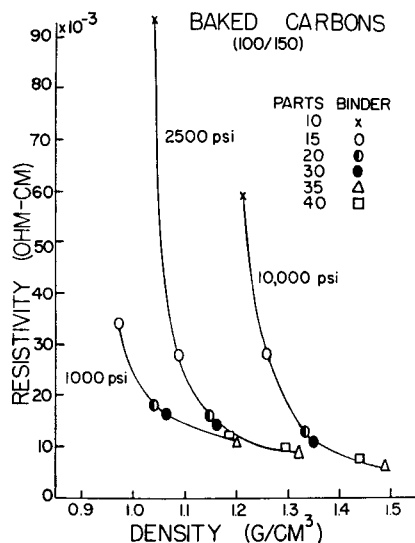


FIG. 1. Electrical resistivity vs. apparent density for carbon samples of different binder contents baked to 1000°C. The curves connect points corresponding to samples molded at the same pressure.

samples made of 48/65 and 200/270 particles. As was to be expected, the results show that there is no relation between the apparent density and the electrical resistivity of a baked carbon involving only those two quantities. It can easily be seen from the figure that baked carbons can be prepared with a large variation in apparent density and resistivity just by varying the molding pressure and the binder content. It is also found, but not seen directly from Fig. 1, that the filler density d_0 varies as well as the apparent density when the binder content and molding pressure are varied.

It is possible to draw a curve on Fig. 1 which will form an envelope for the curves drawn. Such an envelope will represent a lower limit for the resistivity which can be obtained for a carbon with a given apparent density when both binder content and molding pressure are varied. A curve of the resistivity proportional to d^{-3} fits quite well as an approximate envelope in Fig. 1, and the same curve with the same constant of

proportionality was found to be a good limiting curve for the similar data for the 48/65 and 200/270 particle size samples. Such a d^{-3} relation was actually found by manufacturers to be roughly applicable in many instances¹. A system of curves like those of Fig. 1 and the expression for the envelope might be of interest to a manufacturer of carbons as a very rough guide in the production of carbons with specific properties. However, they are not convenient for theoretical interpretation because both densities d and d_0 are simultaneously varying.

In the preceding article, Mrozowski has derived a formula relating the resistivity and apparent density of a baked carbon, introducing the filler density d_0 as a variable. The resistivity ρ and apparent density d were shown to be related by the equation

$$\rho = B/d_0^x(d - d_0)^{\frac{1}{3}} \quad (1)$$

where B is a constant that is dependent in the first approximation on the true resistivity and real density of the coke particles and x is an undetermined exponent. For the purpose of convenience, equation (1) can be re-written in the form of two relations:

$$\rho = A/(d - d_0)^{\frac{1}{3}} \quad (2)$$

and

$$A = B/d_0^x \quad (3)$$

Relation (2) is amenable to an experimental check because it is possible to increase the apparent density d while the filler density d_0 remains almost constant. The apparent densities of baked carbons can be increased by impregnation with pitch and rebaking, and this was done for several groups of samples. In the process of impregnation, liquid pitch was forced into the pores of the baked carbon samples. This was done by placing the samples in a glass tube containing some solid Resin C pitch, evacuating the tube and heating it while

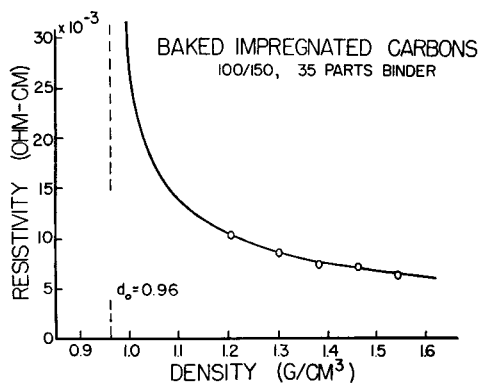


FIG. 2. Electrical resistivity vs. apparent density for a group of baked carbon samples before and after each of the four successive impregnations and bakings to 1000°C. The curve corresponds to relation (2) of the text and the points are averages of experimentally obtained values.

under vacuum. When the samples became completely submerged in the liquid pitch, air was allowed into the tube. The liquid pitch was thereby forced into the pores of the baked carbons by atmospheric pressure. After being removed from the liquid pitch, the impregnated samples were baked as before to a temperature of 1000°C. It was found that each sample that was impregnated shrank slightly after rebaking so that not only the apparent density increased, but the filler density d_0 also increased slightly. However, the relative increase of the filler density was less than 1%, which was very small compared to the increase of the apparent density of the sample.

Fig. 2 shows a plot of resistivity vs. apparent density for a group of samples with $d_0 = 0.96$ that were successively impregnated and rebaked four times. The curve is that obtained from relation (2), where a value of A was chosen which would best fit the data. The value of A was determined from a best fit with all the points rather than by determining it from the experimental values of d , d_0 and ρ for the unimpregnated samples because of the slight changes in d_0 after impregnation. Each circle on the curve represents an average

for ten samples, and the circle showing the lowest density is an average for the baked samples before impregnation. The points for the individual samples show a small scatter of about 1% in both d and d_0 about their average values, but it was found that points from individual samples fell consistently either on or slightly above or slightly below the drawn curve, which is what is to be expected for carbons of only slightly different d_0 's. The agreement of experiment with theory for this group of samples can therefore be considered to be very good. The densities and d_0 in Fig. 2 are fairly low because these samples were molded at the relatively low pressure of 1000 psi, but the samples were very useful experimentally as they showed large increases in apparent density with impregnation. Several other similar curves for impregnated samples made with the same size coke particles and the same binder content, but having different d_0 's were also obtained and agreed very well with relation (2).

To determine the value of the exponent x in relation (3), the factor A was plotted against d_0 as obtained for several groups of nonimpregnated baked carbons and the plot is shown in Fig. 3. The values of A were determined from relation (2) using the experimentally determined values of d , d_0 and ρ . The points in the graph correspond to samples made of coke particles of five different sizes, but with the same binder content of 35 parts binder to 100 parts coke particles by weight. The three different points for samples made with coke of a given particle size correspond to three different molding pressures of 1000, 2500 and 10,000 psi, and each point represents an average for ten samples. The 100/150 samples for which the results are plotted in Fig. 1 and Fig. 2 are not the same as those samples used for the results in Fig. 3 which were made at a later time. The estimated probable error in the value of A is about

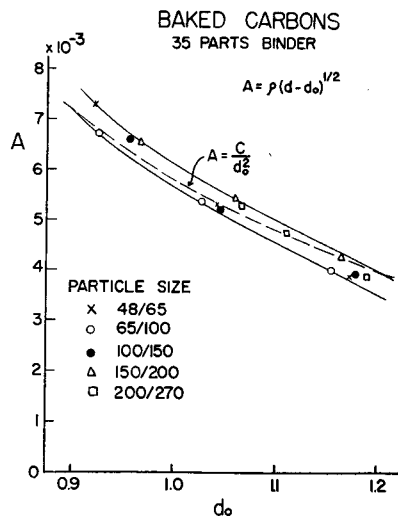


FIG. 3. Dependence of the coefficient A on the filler density d_0 for carbon samples made of mixtures of different single size coke particles and the same binder content, molded at three different pressures and baked to 1000°C.

5%. The points in Fig. 3 do not fall on a single curve, but the different groups of samples were baked in different runs and the scatter of the values obtained may be due to this fact. The broken curve in Fig. 3 was drawn for $x = 2$, and one can see from the location of the points that x is definitely greater than 2. The exponent corresponding to the two solid curves which bound the region containing the points is about 2.4. However, on the basis of presently available data, it is difficult to assign precise values to x and to B .

From Fig. 3 there appears to be, in the first approximation, no dependence of the values of A and B on the coke particle size. This result was to be expected from general reasons given in the preceding paper by Mrozowski¹. Curves of A vs d_0 have also been obtained for several groups of samples with particle sizes 48/65, 100/150 and 200/270 and with different binder contents, but the results are at present incomplete. The shape of the A vs. d_0 curve for each group of samples made of coke particles in a

given size range and of a given binder content was found to satisfy, relation (3) fairly well with a value of x in the neighborhood of 2.

The value of the factor B was found to be the same, within the limit of experimental error, for samples with binder contents of 30 and 40 parts binder and in-between. However, as the binder content was lowered, the value of B was found to increase. This variation of B at low binder contents can be understood, though, from the process of manufacture and the particle-binder nature of the baked carbons. The samples are formed by molding a green mix, consisting of coke particles coated with layers of binder, the thickness of the layers being proportional, for a given coke particle size, to the binder content. The particles come into direct contact when under pressure within the mold, but the sample expands slightly on leaving the mold and many of the direct contacts between the particles are opened. If the binder content is low, the binder bridges at this kind of contact will break, though some of these contacts may be re-established in the baking due to shrinkage. For a given (not too high) molding pressure, the filler density varies little with the binder content in the low binder range. The very low binder content samples do not pack well and have slightly lower densities, however, because in molding the particles do not slip as well past each other as they do when they are surrounded by thicker binder layers. While the apparent and filler densities of these very low binder

content samples differ only slightly from those samples with higher binder contents, the number of effective interparticle bridges in these low binder content samples is so much lower due to the effect of severance of some of the bridges that very much higher resistivities are obtained, and this in turn leads to higher values of B . As found by experiments, the small gaps between particles may be filled by impregnation and the bridges restored. This leads to a decrease in the resistivity greater than expected by formula (1) and results in the lowering of the value of B .

At the present time, a more thorough investigation of the variation of A with d_0 is being carried out in an effort to determine more precisely the value of the exponent x and its possible dependence on the packing of the particles. The effects of impregnation of baked carbons with low binder contents are also being studied in order to clarify the nature of the deviations from the theoretical relations. Furthermore, samples with different proportions of mixed particle sizes are being prepared. It is also felt that a study of the flow or diffusion of liquids and gases through these porous baked carbons will give complementary information concerning the nature of the interconnected system of pores within the samples.

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