APPARENT DENSITIES AND INTERNAL SURFACE AREAS OF SELECTED CARBON BLACKS

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ABSTRACT

It is shown that the open pore volume within carbon blacks can be calculated from nitrogen adsorption isotherms (77° K) on the blacks. From this volume and a helium density, the apparent density of a black can be calculated. Other properties of the blacks which then can be calculated are free surface area, internal surface area, surface roughness factor, and the average pore diameter of the internal surface. These data are presented for five selected carbon blacks.

INTRODUCTION

Carbon blacks are more or less porous depending upon the perfection of their crystallite alignment and the extent of their oxidation during preparation (1). The amount of porosity can be of importance in affecting the behavior of carbon blacks in rubber, paints, and plastics; and yet little quantitative information is available on the nature of the porosity within blacks—such information as given by apparent densities and internal surface areas.

Kotlensky and Walker (2) used a mercury porosimeter to measure the apparent densities of some carbon blacks of large particle size. The volume of mercury forced between the particles was followed by the potential drop across a platinum–iridium wire looped and held taut inside a precision bore section of a dilatometer tube. Complete filling of the void volume between particles was taken as the point where a negligible change in potential drop first occurred with increase in pressure. From a knowledge of the weights of sample and mercury and the combined volume of the sample and mercury (with mercury filling the voids between particles), a particle density could be calculated. This technique appears to be satisfactory and convenient for carbon blacks of large particle size. However, for blacks of small particle size the pressure required to completely fill the voids between particles is high. For example, for Carbolac 1, a black having an arithmetic mean diameter of 106 Å (3), a pressure in excess of 20,000 p.s.i. would be required. At such pressures, crushing and distortion of the particles are of concern (4, 5). Therefore, it is of interest to explore another approach to determine apparent densities of carbon black particles. This approach and the information which can be derived therefrom are described in this paper.

EXPERIMENTAL

The carbon blacks studied were supplied by the Cabot Corp. with some of their properties listed by them (3). Some additional properties of interest are summarized by Kotlensky and Walker (2). Carbolac 1, Carbolac 2, Monarch 71, and Mogul A are channel blacks. Vulcan 3 is an oil furnace black.

Adsorption isotherms on the blacks were measured at 77° K using a standard gas adsorption apparatus (6) with nitrogen as the adsorbate. A description of the procedure used to measure helium densities (at $30 \pm 0.1°$ C) has been given previously (2).

RESULTS AND DISCUSSION

Adsorption isotherms for the blacks studied are given in Fig. 1. Typical calculations involved in using isotherm data to calculate apparent densities and other physical properties of the blacks can be demonstrated for Carbolac 1. As suggested by Pierce (7),

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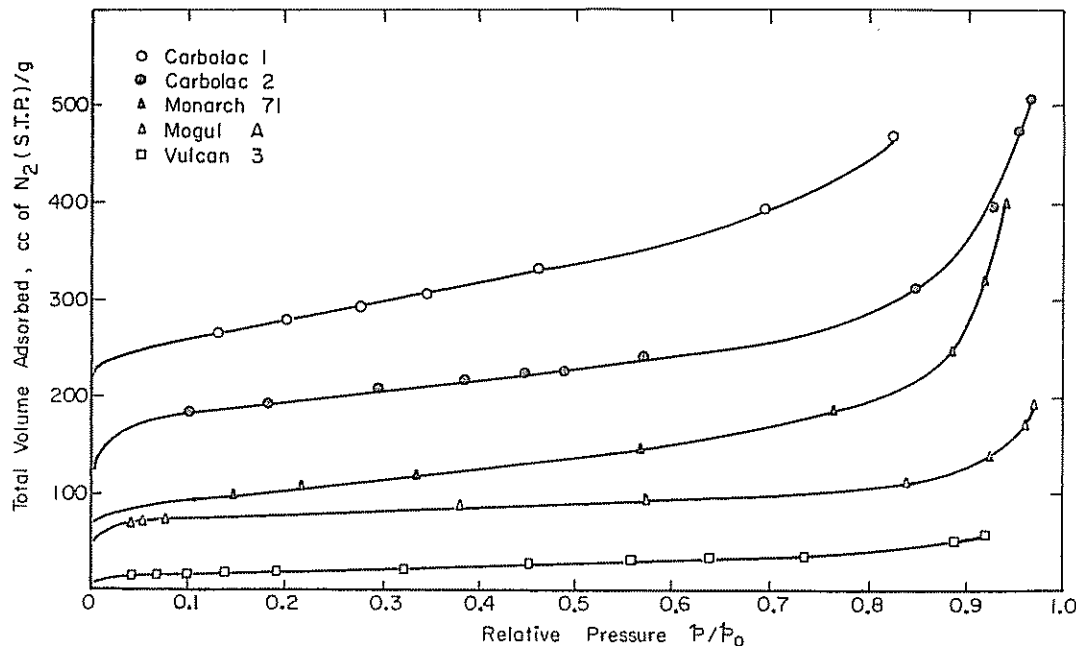
FIG. 1.   Adsorption isotherms for nitrogen at 77° K on selected carbon blacks: O Carbolac 1, ⊕ Carbolac 2, ▲ Monarch 71, △ Mogul A, □ Vulcan 3.

an isotherm for a porous solid can essentially be divided into three regions. In the middle region of the isotherm (region II), no capillary condensation occurs, but only multilayer adsorption on the free surface. In the lower region of the isotherm, monolayer and then multilayer adsorption is accompanied by the filling of the micropores within particles by capillary condensation. In the upper region of the isotherm, multilayer adsorption is accompanied by capillary condensation within the voids between particles.

In region II of the isotherm, it is possible to solve for the volume of adsorbate which completely fills the micropores (V_o) and the volume of adsorbate which covers the free surface with a monolayer (V_m'). That is, V_t, the total volume adsorbed at any relative pressure in region II, is given by

[1] $$V_t = V_o + n V_m',$$

where n is the statistical number of layers of adsorbate at a particular relative pressure.

Or since V_o is constant in region II,

[2] $$\Delta V_t = V_m' \Delta n.$$

Since n is known as a function of relative pressure for the adsorption of nitrogen on carbon at 77° K (8), ΔV_t can be plotted against Δn. From the slope of this plot, V_m' can be calculated. Figure 2 shows such a plot for Carbolac 1 over the relative pressure range 0.20 to 0.46, giving a value of V_m' of 135 cc N_2/g at S.T.P. From equation [1], then, V_o is calculated to equal 110 cc N_2/g at S.T.P.

As discussed by Pierce (8), if only multilayer adsorption is occurring, the ideal nitrogen isotherm is given by the Frenkel–Halsey–Hill equation

[3] $$(V/V_m)^b = \frac{k}{\log (p_0/p)},$$

where b equals about 2.75. Or for a porous solid, in region II, the Frenkel–Halsey–Hill isotherm can be re-expressed as
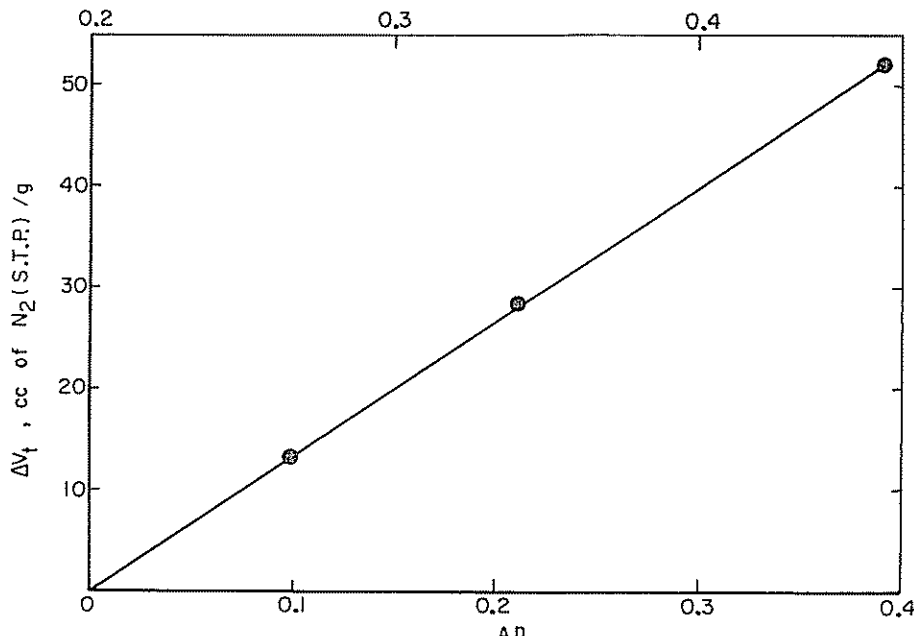
[4]
$$(V_t - V_e)^b = \frac{k'}{\log (p_0/p)}.$$

FIG. 2.   Plot of ΔV_t versus Δn for Carbolac 1 over the relative pressure range 0.20 to 0.46.

For Carbolac 1, the Frenkel–Halsey–Hill isotherm is plotted between $p/p_0 = 0.20$ and 0.46, as shown in Fig. 3. A good straight line is obtained which has a slope of 2.77.

Taking the density of liquid nitrogen at 77° K as 0.81 g/cc (6), V_e for Carbolac 1 can be re-expressed as 0.170 cc of liquid N_2/g. The total volume of a Carbolac 1 particle equals the volume of solid, plus the volume of pores closed to helium at room temperature, plus the volume of pores open to N_2 at 77° K, plus the volume between the size of pore which helium can enter at room temperature (30 minutes equilibration) and the size of pore which nitrogen can enter at 77° K (30 minutes equilibration). Assuming the latter volume to be negligible,[*] the specific volume of Carbolac 1 is given by the reciprocal of its helium density plus V_e. For Carbolac 1 the helium density is 2.02 g/cc. Therefore, the specific volume of Carbolac 1 is 0.665 cc/g, or its apparent density is 1.50 g/cc.

From the total surface area, calculated from the simplified BET equation for the isotherm data in Fig. 1, and the free surface area, calculated from V_m', the internal surface area (A) of the blacks can be calculated. Then, assuming cylindrical pores, an approximation of their average diameter can be calculated from the relationship $\bar{d} = 4V_e/A$. Further, a surface roughness factor can be calculated as the ratio of the free surface area of the blacks to the geometric surface area. The geometric surface areas are reported by Cabot (3), from electron micrograph counts.

*From studies on zeolite molecular sieves (9), it appears that this volume is in pores between ca. 2.8 and 4.2 Å in diameter. As will be seen later, the average pore size in the internal pores of the carbon blacks studied is considerably greater than 4.2 Å. Therefore, this assumption appears reasonable.
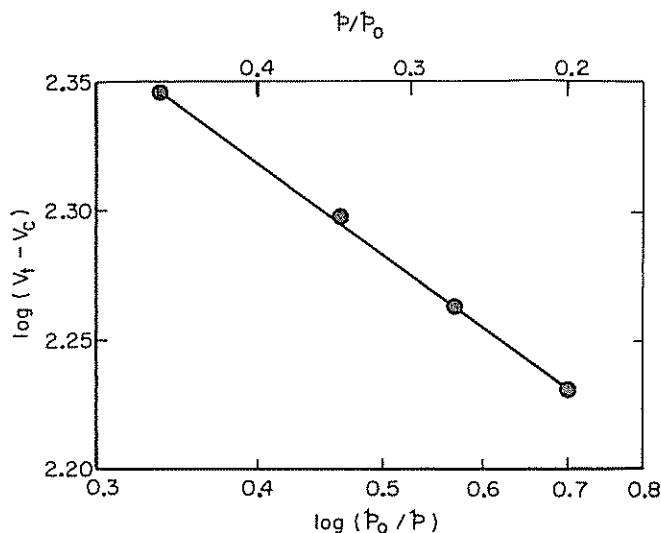
FIG. 3. Frenkel–Halsey–Hill isotherm for nitrogen on Carbolac 1 at 77° K.

Results for the five carbon blacks studied are summarized in Table I. For each black, a middle region of its isotherm was found over which the Frenkel–Halsey–Hill isotherm

TABLE I

Physical data for carbon blacks

Property	Carbolac 1	Carbolac 2	Monarch 71	Mogul A	Vulcan 3
Helium density, g/cc	2.02	2.00	2.04	2.06	2.06
Open pore volume, cc/g	0.170	0.145	0.029	0.062	0.002
Apparent density, g/cc	1.50	1.55	1.93	1.83	2.05
Total surface area, m²/g	1000	670	372	300	69
Free surface area, m²/g	587	348	304	130	65
Internal surface area, m²/g	413	322	68	170	4
Electron microscope surface area, m²/g (3)	264	178	145	82	74
Surface roughness factor	2.2	2.0	2.1	1.6	(0.9)
Average pore diameter $\bar{d}$, Å	17	18	17	14	20

for adsorption on the free surface was obeyed. The slope of the isotherms varied from 2.64 for Monarch 71 to 2.76 for Carbolac 2.

The results show that considerable variation exists in the extent of internal porosity within carbon blacks. The majority of the variation is thought to be due to differences in the extent of air after-treatment at elevated temperatures, which is a standard manufacturing step used to increase the volatile matter content of blacks (1). Carbolacs 1 and 2, with volatile matter contents of 17 and 12% respectively (3), have undergone considerable oxidation during after-treatment. Smith and Polley (10) have shown that such

oxidation can effectively open up porosity within carbon blacks. In addition, the presence of oxygen during carbon formation is known to inhibit crystallite growth and good crystallite alignment, probably because of crosslinking (11); this can result in higher porosity.

Voet (12) obtained nitrogen adsorption isotherms at 77° K on a series of carbon blacks. From these isotherms and the assumption that the amount of nitrogen filling the internal pores of the carbon blacks by capillary condensation is negligible, he calculated pore size distributions. For Carbolac 1, he reports a distribution in pore diameter between 16 and 48 Å, with the peak in the distribution occurring at ca. 20 Å. He further reports that the internal surface area of Carbolac 1 constitutes 55% of the total surface area. This can be compared with the data presented in this paper for Carbolac 1, where the average diameter of the internal pore system is 17 Å and the internal surface area constitutes 41% of the total surface area. The differences noted could possibly be due to the fact that different black samples were used in these two studies and/or to Voet's assumption of negligible capillary condensation within the internal pore system.

It is noted that the BET surface area for Vulcan 3 is less than the electron microscope surface area. This is relatively common for carbon blacks of low porosity (3, 13), and is probably due, in part, to uncertainty as to what value to use for the apparent density of the black. It does result in a surface roughness factor of less than 1 being calculated for Vulcan 3.

ACKNOWLEDGMENT

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