Published in Carbon 34, issue 1, 135-137, 1996
which should be used for any reference to this work

On the characterization of industrial carbon blacks by physico-chemical and by empirical parameters

H.F. Stoeckli and A. Laederach
Chemistry Department, University of Neuchâtel, Av de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

J. Affolter
* Balduin Weisser AG, Burgfelderstrasse, CH-4025 Basel, Switzerland

Key Words - Carbon black; enthalpies of immersion; DBP and AS norms

The characterization of carbon blacks [1] has made progress during the past decades and a variety of classical techniques with various degrees of sophistication are now available. For example, adsorption and immersion techniques based on the comparison with accepted standards, as described elsewhere [2,3]. On the other hand, industry also uses various empirical procedures to characterize these solids and some of the parameters are related to the performances of the black at the technical level. Two procedures, defined by internationnally acknowledged DIN or ASTM norms (German norm DIN 53199, American Society for Testing and Materials ASTM D 281-31 and Bureau of Indian Standards IS 12178-1987), are the so-called DBP (dibutylphtalate) and AS (acetone sorption) indices. The latter is related to the performance of the black when used in the paste of standard Zn/MnO_2 *Leclanché* batteries [4]. In view of the amount of information which is now available, it seems appropriate to examine critically the possible correlation between these empirical norms and basic physico-chemical characteristics of the solids and of their surface.

A number of carbon blacks have been characterized by standard adsorption and immersion techniques described earlier [2]. With the exception of XC-72 [5], the samples had little or no microporosity. The adsorption isotherms of N_2 (77K) and other vapours at 293.15K (CH_2Cl_2, C_6H_6) lead to the total surface area of the carbons. Immersion calorimetry into a variety of liquids and water at 293.15K provides further information on the solid-liquid interface through the specific enthalpy of immersion $h_i = \Delta h_i/S$. For example, in the case of water, the variation of the hydrophobic/hydrophilic character is revealed by values of $-h_i$ between 0.020 and 0.100 J/m^2, with an average around 0.040-0.060 J/m^2 for typical industrial carbon blacks. We also included immersion into DBP itself and into the standard mixture of acetone in water (1:9 in volume) used in the AS test.

In the present study, we also provide a comparison of data for the specific enthalpy of immersion of carbon blacks into 1-methylnaphtalene (1MN). This molecular probe, already used by Robert [6], is a promising candidate for the calorimetric evaluation of the surface area of carbons.

The DBP technique, as described by the DIN or the ASTM norms, is carried out as follows: Exactly 1 g (or multiple thereof) of carbon black is placed on a glass plate. DBP, contained in a 25 ml buret (accuracy 0.1 ml), is added dropwise to the carbon black and the paste is mixed and rubbed thoroughly with a large plastic spatula. The test is complete when DBP begins to wet the glass plate. The DBP number is finally obtained by calculating the volume of DBP used in the process per 100 g of carbon black.

The AS number is defined by the so-called *ball method*, as described by the Indian Standard no 12178-1987. Exactly 5 g of carbon black are introduced in a 500 ml round-bottom flask. A solution of acetone in water (1:9 in volume) is introduced in a 25 ml buret (accuracy 0.1 ml). 10 ml of the solution is added dropwise to the carbon black and the flask closed with a plastic cork. The paste is shaked one minute in a circular movement. 5 ml of the solution are added and the paste is shaked only 20 seconds in a circular movement. This adding of 5 ml is repeated until small balls of paste begin to build themselves. The solution is then added by portions of 1 ml until the number of small balls decreases to 2 or 3 greater balls. At this stage, the solution is added drop by drop and the balls are shaked and projected onto the flask wall in attempt to form one single ball. The test is complete when the ball does not break anymore. The AS number is directly obtained in ml of solution per 5 g of carbon black.

According to the experience gained by battery manufacturers, the AS number of a given carbon black is directly related to the electrochemical performances of the battery. This has also been examined recently in our laboratory [7]. High AS numbers (i.e. above 25) are therefore an important pre-requisite for the selection of the products on the battery market.

The results are shown in Tables 1 and 2. Inspection of Table 1 shows that the specific enthalpies of immersion into DBP and 1MN are quite consistent. The combination of our results with data for other

Table 1. Surface areas and specific enthalpies of immersion h_i (J/m^2).

solid	graphite	XYL-NE	N234G	Hoechst	Hum	LX-95	Ens-SS	XC-72
S_{BET} (m^2/g)	11.2	110	92	52	110	135	45	240
$-h_i(C_6H_6)$	0.114	0.112	0.111	0.109	0.113	0.114	0.114	0.123
$-h_i(H_2O)$	0.030	0.045	0.028	0.063	0.068	0.050	0.060	0.039
$-h_i$(1MN)	0.136	0.131	0.136	0.132	0.134	0.135	0.133	0.131
$-h_i$(DBP)	0.138	0.133	0.133	0.135	0.124	0.133	0.130	0.132

Table 2. AS numbers, surface areas (m^2/g) and specific enthalpies of immersion into H_2O and the standard AS solution (J/m^2).

solid	XYL-NE	N234G	Hoechst	LX-95	ENS-SS	M-100/25	DK
AS number	-	-	35	35	25	27	20
S_{BET}	110	92	52	135	45	94	95
$-h_i$(AS)	0.093	0.075	0.053	0.082	0.119	0.095	0.050
$-h_i(H_2O)$	0.030	0.045	0.028	0.063	0.060	0.059	0.022

samples, not described in this study or found in the litterature [6], leads to the following averages with their standard deviations σ,

$$-h_i\,(\text{DBP}) = 0.132 \pm 0.004\ \text{J/m}^2 \ (8\ \text{samples})$$

$$-h_i\,(\text{1MN}) = 0.135 \pm 0.006\ \text{J/m}^2 \ (10\ \text{samples, including data from [6]})$$

In the case of benzene, the combination of data from different sources leads to

$$-h_i\,(C_6H_6) = 0.113 \pm 0.010\ \text{J/m}^2 \ (15\ \text{samples})$$

It is interesting to note that the standard deviation for 1MN is smaller than for benzene, which may be due to its larger molecular surface area.

As illustrated by Fig.1, based on our data and on data supplied by carbon black manufacturers, the correlation between the DBP number and the actual surface area S_{BET} of the blacks is poor. It also appears that the scatter may be quite large, depending on the operator and the experimental conditions. A similar situation has been observed for the AS test. In view of its magnitude (typically 0.4 to 1.5 cm^3 per gram of carbon), it is likely, that the DBP number corresponds rather to the filling of larger voids between particles, than to the coating of the surface, but some proportionality between them is not excluded. However, it appears that the DBP test is not reliable for the characterization of the surface itself and its actual meaning may be questioned.

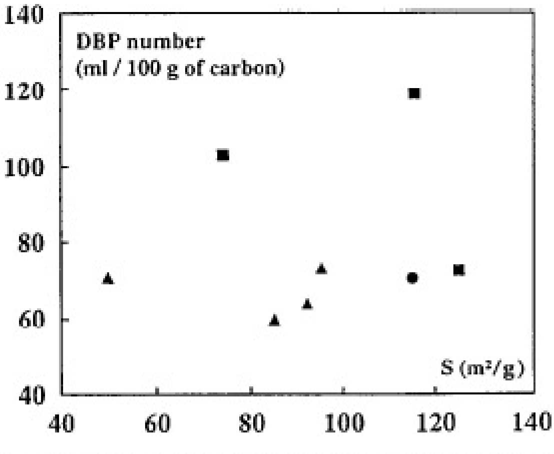

Fig.1. DBP number and BET surface areas of typical non-porous industrial carbon blacks (■ Vulcan ; ▲ Regal ; ● Mogul)

As suggested by the data of Table 2, there is no direct correlation between the AS number of typical industrial samples and the specific surface area of the solids, or the specific enthalpy of immersion into the AS mixture. With the exception of sample *Hoechst*, this enthalpy is larger than $-h_i(H_2O)$, but no systematic ratio is found. This behaviour may reflect the competition between acetone and water on the surface. On the other hand, as pointed out recently [7], the performance of *Leclanché* batteries seems to depend to some extent on $-h_i(H_2O)$, which is larger than 0.055-0.060 J/m^2 for good carbon blacks.

Like the DBP norm, the AS number itself corresponds more to a macroscopic property, than to the surface of the solid. Typical AS values represent 4-6 cm^3 of the water + acetone mixture per gram of carbon black, which suggests primarily a *volumic* effect. Since the AS number is related to the battery performance [7], the explanation probably lies in a combination of surface effects, reflected by $-h_i(H_2O)$, and the electrochemical properties of the fluid found between the carbon and MnO_2 particles. However, the standard paste used for the cells by a number of manufacturers (15 g MnO_2, 3 g carbon black, 3 g NH_4Cl, 3 g $ZnCl_2$ and 6 g of water) contains less water than found in the

AS number and no acetone at all.

To sum up, our study shows that neither the DBP nor the AS numbers can be firmly related to surface properties of the carbon blacks, but the AS number is certainly worth further investigation. On the other hand, the enthalpy of immersion into DBP provides a good assessment of the carbon blacks' specific surface area, which was unexpected but turns out to be most useful.

REFERENCES

1. J.B. Donnet, R.C. Bansal and M.J. Wang, *Carbon Black*, Marcel Dekker, New-York (1993).
2. H.F. Stoeckli, P. Rebstein and L. Ballerini, *Carbon* **28**, 907 (1990).
3. H.F. Stoeckli, D. Huguenin and A. Laederach, *Carbon* **32**, 1359 (1994).
4. D. Pletcher, *Industrial Electrochemistry*, Chapman & Hall, London (1982), pp. 239-280.
5. H.F. Stoeckli, D. Huguenin and A. Laederach, *Chimia* **47**, 211 (1993).
6. L. Robert, *Bull.Soc.Chim.Fr.* **7**, 2309 (1967).
7. H.F. Stoeckli, A. Laederach, J. Affolter and A.V. Athalye, *Progress in Batteries and Battery Materials* (in press).