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Studies on Carbon Black. I. Electrometric Titration

BY D. S. VILLARS*

Introduction

Several years ago Wiegand[1] showed that the *p*H of a slurry of carbon black boiled with distilled water is a characterizing quality of the black. He found a correlation between this *p*H and the rate of cure in rubber, (accelerated) stocks with blacks of lower *p*H curing more slowly. The *p*H was also correlatable with per cent. volatile matter,[1a] decreasing as the latter increases and increasing with temperature of previous heat treatment of the black.

However, *p*H is also a function of salt content; and since the process of manufacture of some blacks deliberately introduces alkali,[2] it was felt that a more fundamental property of the black would be its complete titration curve. The present paper is intended to present results obtained some years ago of a fundamental study of this property. The first titrations of carbon black undertaken in this Laboratory were carried out for Dr. C. P. Roe by Mr. Henry Lehti. Dr. Roe concluded from their work that the "buffering capacities in alkaline titration correspond qualitatively with the oxygen content of the black."

Experimental Procedure

Exploratory work by the writer demonstrated that boiling of the black slurry was indispensable to obtaining reproducible *p*H values, that reduction of volume by boiling lowers the *p*H, that dilution raises it and that the reproducibility of the *p*H determination on boiling to constant volume is of the order of 0.1 *p*H unit.

The technique used was therefore to make a suspension of 25 g. of black by adding a slight excess over 150 ml. of distilled water and stirring. This suspension was then boiled down to a mark on a beaker, drawn to correspond to 150 ml. of water. It was then cooled and placed in a bath thermostated to 25°. *p*H measurements by glass electrode were obtained after fifteen and twenty minutes standing at 25°. If the *p*H values checked reasonably well, the beaker was removed from the bath and a measured amount of 0.5 *N* potassium hydroxide was added. The suspension was then diluted to a point about 1 cm. above the mark on the beaker and again boiled down to the mark. The beaker was cooled, set in the bath, and *p*H values measured as before. An exception had to be made for acetylene black, since its suspension with 150 ml. of water was not fluid enough to insert a glass electrode without danger of breaking it. Twenty-five grams of this black was accordingly suspended in 500 ml. of water. This volume was corrected for in comparing results with other blacks.

Results

Except for those marked "Experimental" the carbon blacks investigated were regular commercial samples of acetylene black, easy processing channel (EPC), medium processing channel (MPC), and ink black. These classifications have become standard terminology[3] in the industry and refer to ease of handling in the factory. They are related to particle size of the blacks. The numbers following the abbreviations designating type refer to manufacturer and lot. Blacks of the same general type are not believed to differ greatly among suppliers. Of the "experimental" blacks, no. 1 is a low oxygen black prepared by heating a standard EPC to a temperature above 1000° in an inert atmosphere, no. 2 and 3 are believed to be special lots of hard processing channel (HPC) treated to give high initial *p*H without appreciable removal of oxygen. Further details of preparation are not available from the supplier.

For detailed results, see Table I. A typical titration curve plotted in the usual way, *p*H *vs.* ml. of alkali, is given in Fig. 1. In this figure the circles give the results of the titration of one sample of experimental black 1, the crosses the results on a duplicate sample. The agreement between the points indicates the reproducibility of the measurements. It may be immediately seen that there is no inflection point, *p*H values rising steadily to an asymptotic value corresponding to the *p*H of the potassium hydroxide used in the titration. There is thus no stoichiometric titer for the carbon black.

On the other hand, it was discovered that plotting *p*H *versus* logarithm of ml. of alkali, *x*, does give a straight line (see Fig. 2). Table I summarizes the slopes, *b′*, and intercepts, *a′*, of the straight lines representing the data. Below

$$pH = a' + b' \log x \qquad (1)$$

these values are given the standard deviations of the points from their least squares lines. The fact that the average of these standard deviations (0.15 *p*H) is of the same order as that of the reproducibility of the determination ($\sim$0.10 *p*H) means that this straight line relationship is entirely adequate to represent the data.

The slopes of the individual lines were compared with each other by means of Fisher's statistical procedure of Variance Analysis.[4] The results obtained were that the external consistency is good enough to show that the probability is less than one in one thousand that these estimated

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* Present address: Jersey City Junior College.

[1] W. B. Wiegand, *Ind. Eng. Chem.*, **29**, 953 (1937).

[1a] For a discussion on the nature of this volatile matter see reference (1). A further discussion will be presented in the second paper of this series.

[2] W. B. Wiegand, U. S. Patent 2,178,382; 2,178,383, October 31, 1939.

[3] L. H. Cohan, *Chem. Eng. News*, **23**, 2078–2085 (1945).

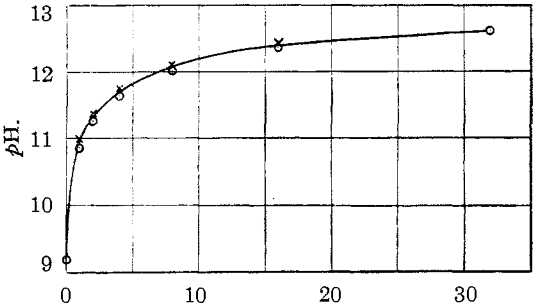
[4] R. A. Fisher, "Statistical Methods for Research Workers," Oliver and Boyd, London, 9th ed., 1944, Chap. VIII; L. H. C. Tippett, "Methods of Statistics," 2nd ed., William and Norgate, Ltd., London, 1937; G. W. Snedecor, "Statistical Methods," 4th ed., Collegiate Press, Inc., Ames, Iowa, 1946.

TABLE I

DETAILED TITRATIONS, *p*H's

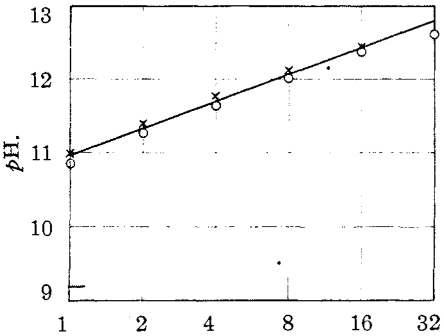
Ml. 0.5 *N* KOH	Exptl.-1		Acetylene		MPC-1		MPC-2	Exptl.-2		EPC-1	
0		9.19	7.33	6.99	4.11	4.05	4.05	8.11	7.77	4.58	4.47
1	10.98	10.85	9.53	9.08		6.01		8.84	8.57		6.50
2	11.37	11.26	10.03	9.73	7.40	7.31	8.09	9.27	9.01	7.65	7.77
4	11.75	11.64	10.33	10.33	8.82	8.72	9.30	10.01	9.94	9.30	9.01
8	12.11	12.01	10.59	10.57	9.97^{6a}	10.79	9.93^{6}	11.05	10.91	10.15^{6}	10.63
16	12.43	12.37	11.29	11.20	10.54^{8}	12.10	10.67^{8}	12.04	11.96	10.71^{8}	12.09
32		12.61	11.40	11.88	11.05^{10}		11.05^{10}	12.53	12.43	10.59^{10}	
					11.09^{12}					11.05^{12}	
a'	11.00	10.90	10.24^{b}	10.06^{b}	5.77	5.86	6.77	8.64	8.39	6.15	6.39
b'	1.209	1.187	1.271	1.770	5.293	5.202	4.241	2.638	2.764	5.106	4.664
Standard dev. (from regression)	0.025	0.055	0.129	0.124	0.094	0.234	0.098	0.207	0.214	0.073	0.136

[a] Exponents give total ml. of 0.5 *N* potassium hydroxide added in case amount disagrees with that indicated in first column. [b] Corrected from 500 to 150 ml. by adding log 500/150 to log ml. 0.5 *N* potassium hydroxide.



Ml. 0.5 *N* KOH.

Fig. 1.



Log ml. 0.5 *N* KOH.

Fig. 2.

constants for the different blacks would differ among themselves as much as they did, by chance alone. We therefore conclude that the intercepts and slopes for the different blacks are indeed different. The slopes and intercepts are compared with other properties of the blacks in Table II. Figure 3 shows that the intercepts increase in the same order as slopes decrease.

TABLE II

TITRATION RESULTS

Carbon black[a]	Sp. S. m²/g.[b]	Total Ox.[c] %	Initial *p*H	Intercept *a'*	Slope[d] *b'*
	Data of Villars				
Exptl. black-1	110	0.08	9.19	10.95	1.20
Acetylene	75.4	.27	7.16	10.15	1.52
MPC-1	134 (N)	2.12	4.08	5.81	5.25
MPC-2	126	2.76	4.05	6.77	4.24
Exptl. black-2	147	3.37	8.94	8.52	2.70
EPC-1	99.8 (N)	3.93	4.53	6.27	4.89
	Data of Roe and Lehti				
MPC-3			4.58	5.39	4.39
Exptl. black-3			8.13	8.08	2.20
EPC-2	106.5	3.30	4.55	4.87	5.09
Ink black-1	422	4.38	4.63	4.28	4.34
Ink black-2	694	6.30	3.26	1.92	4.72

[a] Following standard terminology[3] MPC 1, 2, 3 are medium processing channel blacks differing in manufacturer and lot; EPC are easy processing channel blacks. [b] Determined by Emmett[5] method. We are indebted to Professor P. H. Emmett for determining for us the values marked by N. He used nitrogen. The remaining values were determined in this Laboratory by means of butane. They have been corrected to nitrogen by multiplying by 1.5, an average empirical correction factor obtained by comparison of the nitrogen values with butane values. The necessity of this correction probably arises from an arbitrary choice of the area occupied per butane molecule and from differences between butane and nitrogen as to penetration of cracks in the surface. [c] Determined by analysis of oxygen volatilized at 1000°. [d] Slope units *p*H (log ml. 0.5 *N* KOH)$^{-1}$.

To summarize, we find that, (1) the titration curve for each black is adequately representable by the linear logarithmic relationship, equation 1, and (2) the slopes of the curves characterizing the different blacks are linearly correlated with their intercepts. In the next section a hypothesis is proposed to account for these facts.

Theoretical

If it were assumed that carbon black had no effect on the *p*H in a titration, one would expect a linear logarithmic relationship as observed above. However, the slope of such a line should be unity for all blacks. No room would be allowed on this explanation for slopes (statistically) significantly differing among themselves. Similarly, any explanation invoking differences in effective volume

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(5) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309–319 (1938).

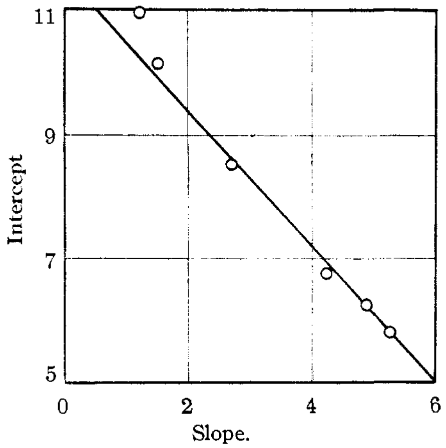

Fig. 3.

of the water in the carbon black suspension could also account for straight lines but they would likewise have to have unit slope.

A hypothesis has been set up in terms of Langmuir's "checkerboard" adsorption mechanism[6] to account for slopes differing from unity. Suppose that the carbon black surface adsorbs water and that the latter dissociates electrolytically in a manner depending on the amount of oxygen chemisorbed on the carbon surface. To account for the observations, this dependence will have to be in a direction such that if no oxygen is present, hydroxyl ion tends to come off; if a large amount of oxygen is present on the surface, hydrogen ions tend to come off. Consider the latter case, as it corresponds to the usual commercial type of carbon black. The other case is amenable to the same equations as a consequence of the reciprocal relationship between H^+ and OH^- ions.

Let

V = volume of aqueous phase
s = total surface of carbon black
h_0 = number of equivalents H^+ ion per unit area which could dissociate off into solution
sh_0/V = a = "concentration" of total acidic material
α = degree of dissociation of H^+ ion equivalents on black

Then the concentration, A, of "weak acid ion" in the solution will be

$$A = \frac{sh_0}{V}\alpha \qquad (2)$$

and the "concentration" of "undissociated weak acid," HA, will be

$$\mathrm{HA} = \frac{sh_0}{V}(1 - \alpha) \qquad (3)$$

In order to account for varying slopes in equation (1) we postulate that H^+ ions may adhere only when m adjoining spaces on the "checkerboard" surfaces are empty (of H^+) and can escape into the liquid only when n H^+ ions touch each other.[6a] Equilibrium will obtain then when the rate of dissociation equals the rate of adsorption.

$$\text{Rate of adsorption} = k_1 H\alpha^m$$
$$\text{Rate of escape} = k_2(1 - \alpha)^n$$

or

$$k_2/k_1 = K = H\alpha^m/(1 - \alpha)^n \qquad (4)$$

In the above, H designates the H^+ ion concentration.

Putting equation 2 in 4 and substituting a for sh_0/V, one gets

$$H = K(a - A)^n a^{m-n} A^{-m} \qquad (5)$$

or

$$-\log H \equiv p\mathrm{H} = m \log A - n \log (a - A) + (n - m) \log a - \log K \qquad (6)$$

For electrical neutrality

$$B + H = A + \mathrm{OH} = A + K_w/H \qquad (7)$$

where B is concentration of strong base ion added and OH is hydroxyl ion concentration. In the pH range 4 to 11, $K_w/H - H$ is negligible compared with B, neglecting initial pH when B is zero. In the region where a is much larger than A, equation (6) becomes approximately

$$\begin{aligned} p\mathrm{H} &= m \log B - m \log a - \log K \\ &= m \log B + m \log V/sh_0 - \log K \end{aligned} \qquad (8)$$

Such a contingency simply implies that water on the black surface is very little dissociated.

Discussion

Equation 8 portrays the behavior observed experimentally. With values of a less than unity, intercepts of the pH *versus* $\log B$ lines tend to occur in inverse order to that of slopes. Increase in volume V should increase pH. The intercept of equation 8

$$\text{Intercept} = a' = -\log K + m \log V/sh_0 \qquad (9)$$

when plotted *versus* slope, m, should give a straight line as long as K, V and s remain constant. Rough evaluation of the constants of the line from Fig. 3 gives

$$\log K = -11.57$$
$$a = sh_0/V = 0.0413$$

Also, according to equation 8, a black of high specific surface (large s) should give lower intercepts. This is confirmed by the data obtained by Roe.

The slope m has been pictured as representing the number of free spaces on the carbon black surface before a colliding H^+ ion can stick to the surface. Note that the parameter n, the number of H^+ on the surface which have to touch before one can escape, has cancelled itself from consideration. Why the system behaves as if extra free spaces are required may be pictured by considering the energetics of the process. A hydrogen ion arriving at the surface has to dispose of most

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(6) I. Langmuir, THIS JOURNAL, **38**, 2221–2295, esp. 2268, 2288 (1916); *ibid.*, **40**, 1361–1403, esp. 1369–1375 (1918).

(6a) This type of attack originated with Langmuir.[6] It may be considered to represent a specific application of the more general case where the probabilities of adsorption and of escape are not independent events.

of its excess heat of adsorption energy within one vibration period; otherwise it will retain so much that it will immediately evaporate back into the solution. A certain fraction of these ions fails to dissipate the necessary amount of energy. This fraction corresponds to a reflection coefficient and constitutes part of the kinetic adsorption constant, k_1. Now, the presence of other hydrogen ions in the neighborhood of a free space to which the adsorbing ion is heading will raise the potential energy *versus* distance curve. This gives it a shallower and narrower minimum. The ion has a shorter distance to travel and consequently a shorter time is available to it for dissipating its kinetic energy. Therefore, a smaller fraction of attaching collisions will occur.

The effect of neighboring ions is dependent upon the type of surface bonds or the distribution of types in a material like carbon black where several types are possible. Thus, in high oxygen black, where the carbon valences are mostly occupied by a layer of oxygen atoms upon the surface, little attraction is left over to adsorb hydrogen ion. What hydrogen ions are present are left free to interfere, by their force fields, with oncoming prospective adsorbing ions. On the other hand, the purified blacks, having a minimum oxygen content may exert all their attractive forces to hold hydrogen ion. The force fields of the hydrogen ions already present are thus partially occupied and have less opportunity to interfere with oncoming ions. This would account for a lower slope constant, m.

It may be noted that experimental black no. 2 is out of line in that it does not show the high slope which we have been led to expect in view of its high oxygen content. This may be more apparent than real. It is presumed that this black was manufactured according to the process described in reference 2. If an amount of base, c, has already been added in the manufacture of the black, it is obviously incorrect to consider the argument of the logarithm in equation (1) to be only base, B, added in the titration. It should be $B + c$. The slope m' of the curve pH *versus* log B is related to the true slope, m, by the equation

$$m' = m(B + c)/B \qquad (10)$$

The true slope is therefore greater than the apparent one, m', and this tends to remove the discrepancy in the correlation curve of slope *versus* oxygen content for this black.

In closing it may be well to point out that there are of course alternative points of view which could be used for developing a theory to account for the experimental data. For example, one could consider the carbon black surface as a multibasic acid with a distribution of basicity over the surface. The actual distribution would naturally be a function of the oxygen content and the number of negative ions in the immediate neighborhood. Titration of such a multi-basic acid would not be expected to give an inflection point when the data are plotted in the conventional fashion. The constant $K = 10^{-11.57}$ might represent the value of the mean ionization constant over the region titrated. Furthermore, a relationship is to be expected between the degree of dissociation on the carbon black surface and the zeta potential it develops. Abramson[7] has shown that the titration curve of a protein is closely correlated with the curve relating electrophoretic mobility with pH.

Acknowledgment.—Thanks are expressed to Dr. C. P. Roe for the use of those of his results included in this report and to Dr. H. M. Smallwood for helpful advice while the work of the writer was being carried out.

Summary

Commercial carbon blacks have been titrated electrometrically with alkali using a glass electrode. As the curves of pH *versus* ml. of base show no inflection point, it is concluded that carbon black has no stoichiometric titer in the ordinary sense. However, a linear relation is found between pH and log ml. of base. The slopes of these curves are negatively correlated with their intercepts, and, particle size remaining constant, are positively correlated with oxygen content of the black. A theory is described which accounts for the observations by postulating that a number of neighboring empty spaces greater than unity is required before H^+ ion can adhere to the carbon black surface. This number is greater, the greater the oxygen content of the black. The system behaves as if presence of oxygen combined on the surface increases the free space required by hydrogen ions before they can successfully adhere to the surface.

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[7] Abramson, Moyer and Gorin, "Electrophoresis of Proteins," Reinhold Publishing Corp., New York, N. Y., 1942, p. 146.