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APPLICATION OF THERMAL ANALYSIS TO CARBON BLACK–ELASTOMER SYSTEMS

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In this study a relationship between the surface and textural properties of carbon blacks and the gasification process induced thermally in air is noted. A temperature jump method was used to follow the gasification in air and to establish the relevant Arrhenius parameters. This can be associated with the activity of 'basal' plane carbon atoms as well as 'edge' carbon atoms at the surface. This is based on a model of carbon black structure consisting of the irregular packing of small graphite carbon structures. The carbon black surface was measured using a single measurement of adsorption based essentially on the BET volumetric method. The carbon black surface had a rate of oxidation per unit area which clearly indicated that the lower area carbon blacks had a predominately active area of 'edge' atoms at the surface while the surface of the higher area carbon blacks had a predominate amount of 'basal' plane graphite carbon atoms.

Keywords: carbon black–elastomer system, oxidation kinetics

Introduction

This study details surface area characteristics and oxidation rates for various carbon blacks used in elastomer formulations. The oxidation kinetics have been determined by thermogravimetric runs with the carbons in an atmosphere of air. The Arrhenius parameters are calculated from this data. The determination of the surface area was by nitrogen adsorption using a specifically designed unit. The activity of the carbons was judged by expressing the specific reaction rate per unit area instead of per gram.

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Carbon blacks are formed by the degradation of organic compounds from the vapor phase. They are used as reinforcing fillers in rubber and coloring agents in plastics and inks [1]. A carbon black usually contains 90–99% elemental carbon. Oxygen and hydrogen make up the remaining major elements present [2]. Carbon blacks differ from other carbons (e.g., graphite, charcoals, and coke) because they are composed of spherical particles and are quasi-graphitic in structure [3]. The primary particle size is found to be small (diameters with high largely external surface areas as determined from the BET adsorption techniques employing nitrogen (up to 150 m^2g^{-1} [4]. These differences have a profound effect upon the incorporation of carbon blacks into the rubber tire formulation which is the subject of the following publications. Carbon black is characterized with regard to the particle size, the extent of the particle fusion into aggregates, and specific surface area. Particle fusion is referred to as the structure of carbon black and samples are characterized as being of high structure or low structure carbon. Particle size is measured by electron microscopy. In the ASTM nomenclature for carbon black, the first digit is based on the mean particle diameter determined by electron microscopy. The most commonly used tests in the industry for surface area evaluation are iodine number and nitrogen adsorption. The structure is measured by how much dibutyl phthalate (DBP) is adsorbed by the carbon black [5]. The method of determining surface area of carbon black used in this study is based on the adsorption onto the carbon of nitrogen at the temperature of boiling liquid nitrogen [6]. The ASTM classification system for carbon blacks is given in report D1765 [7]. A typical ASTM designation is N110. The first letter denotes the effects the black has on the cure rate. N is for the normal cure and S is for slow-curing blacks. The first digit following the letter indicates the particle size as indicated in Table 1.

Table 1 Particle size as determined by ASTM

Group	Particle diameter in nanometers
0	1–10
1	11–19
2	20–25
3	26–30
4	31–39
5	40–48
6	49–60
7	61–100
8	101–200
9	201–500

The iodine number is described in ASTM report D1510 [8]. The third and fourth digits used in the ASTM system are arbitrarily assigned by the ASTM Committee but do indicate specific properties. The carbon blacks studied here were made from the oil furnace process. Thermogravimetry (TG) is used extensively in the study of elastomer systems including the carbon black components. There has been renewed interest in this technique because of its ability to record simultaneously the first derivative of mass loss (DTG). An example involving carbon black may be used as an illustration. In elastomer mixes a typical TG run provides data which can be utilized for compositional analysis. This is a typical TG run initially in nitrogen when the percentages of oil and polymer can be calculated from the TG curve. The percentages of carbon black and ash it is claimed can be calculated from the TG graph by changing the atmo-sphere to air [9]. Ash is a collective term which encompasses the inert inorganic fillers such as clays, carbonates, and zinc oxide. A temperature jump method of following carbon *oxidation* was used in this study. This is a method that combines two techniques, namely the rising temperature and isothermal techniques. It is an important feature of the present study. A sample is placed into the TG balance and it is heated to the starting temperature. The temperature is held there for a given amount of time, then the temperature is increased in small increments and held constant for the same time interval as before. The temperature is then increased again and held isothermally for that given amount of time. This process is repeated until the sample is burned off or six good plots of mass against time at noted temperatures have been completed. In the case of carbon black the carbon is burned off ideally in the following reaction:

$$C(s) + O_2(g) \longrightarrow CO_2(g).$$

However, the carbon rarely gives 100% CO_2 as product gas and the evolved gas stream will contain both CO and CO_2. The TG follows this as a mass loss. Each carbon black with known surface area was subjected to this process. The kinetic rates were then determined for each temperature, when

$$\frac{d\alpha}{dt} = k\,(T)$$

and

$$\alpha = k\,(T)\,t$$

where α is the fraction decomposed, t is the time, $d\alpha/dt$ is the observed rate and $k(T)$ is the specific reaction rate at temperature T, where T is the temperature imposed on the system (in Kelvin) for that particular region. In the present study the carbon black as applied were subjected to this TG technique.

Experimental

Carbon blacks

The carbon blacks used in the formulations tests here are from various suppliers and are listed in Table 2. This table indicates the nitrogen surface area, the iodine number, and the suppliers.

Table 2 Characteristics of carbon blacks used in this study

Sample	Grade	Iodine number	Nitrogen adsorption surface area /$m^2 \cdot g^{-1}$	Supplier
1	N774	24	29	Cabot
2	N774	24	29	Witco
3	N660	36	30–40	Cabot
4	N683	34	37	Ashland
5	N683	37	37	Witco
6	N650	36	38	Cabot
7	N650	36	38	Witco
8	N650H	36	38	Columbian
9	N650	39	38	Columbian
10	N550	44	42	Witco
11	N550	44	42	Cabot
12	N330	82	83	Cabot (bead)
13	N330	82	83	Cabot (powder)
14	N330	82	83	Witco
15	N330	82	83	Columbian
16	N326	81	84	Columbian
17	N339	90	96	Witco
18	N234	120	126	Witco
19	N234	120	126	Cabot
20	N234	120	126	Ashland
21	N110	146	143	Ashland

Equipment

A Stanton Redcroft TG unit model TGA 100 was used with an Omnitherm computer. All samples were tested with a temperature range up to 600°C. The nitrogen surface area unit was an empirical single point unit described by Dollimore *et al.* [10]. Being modified from previous equipment described by Haynes [11] and Klyackko–Gurvich [12]. The experimental procedure used on the temperature jump method was as follows:

1. A sample of carbon black was placed into the sample pan of the TG balance and was weighed.
2. The furnace was then placed around the sample and heated to 450°C, and held constant for twenty minutes.
3. The temperature was then raised 10°C and held constant for twenty minutes. This pattern was continued until most of the carbon black was burned off.
4. A graph of weight loss *vs.* temperature can also be plotted. The time of twenty minutes was arbitrary and can be altered in other systems so as to give optimum results. The procedure used for N_2 adsorption has previously been outlined [10–12]. The sample of carbon blacks were dried for one hour at 100°C.

Table 3 Results of nitrogen adsorption

Carbon black	Supplier	ASTM surface area / $m^2 \cdot g^{-1}$	Nitrogen adsorption surface area $m^2 \cdot g^{-1}$
N774	Cabot	29	30
N774	Witco	29	30
N660	Cabot	30–40	35
N683	Ashland	37	39
N683	Witco	37	36
N650	Cabot	38	42
N650	Witco	38	41
N650H	Columbian	38	37
N650	Columbian	38	37
N550	Cabot	42	42
N550	Witco	42	48
N330	Columbian	83	83
N330	Witco	83	83
N330	Cabot (bead)	83	83
N330	Cabot (ground)	83	83
N326	Columbian	84	84
N339	Witco	96	127
N234	Ashland	126	127
N234	Cabot	126	126
N234	Witco	126	126
N110	Ashland	143	141

Note: Witco N330 was used as the standard to calibrate the surface area apparatus. At least three trials were averaged to calculate surface area on each sample.

Results and discussion

The results of the nitrogen adsorption are seen in Table 3. The temperature jump method applied to the oxidation of carbon black in air has been outlined earlier in this study. A typical graph of mass loss time is shown in Fig. 1. It appears at first glance that the line has taken the shape of a curve. Upon closer investigation the curve is seen to be made up of a series of straight lines. The rates can be considered to be zero order, the rate of the reaction can be calculated from the percent weight loss over a given time. To make this calculation easier, graphs of mass loss *vs.* temperature were constructed. A typical graph of this kind is shown in Fig. 2.

From the above data for each carbon black, a table was constructed which consisted of the sample number and weight loss percent, time in minutes, time in seconds, temperature in degrees °C and degree K, and calculated values of ln*K* and 1/*T*. A typical set of values can be seen in Table 4. All the data for each carbon gave good Arrhenius plots (Fig. 3). A summary of these results giving values of the Activation Energy (*E*) and the Pre-Exponential term (*A*) is provided in Table 5. The data obtained in this table shows a good compensation plot with the

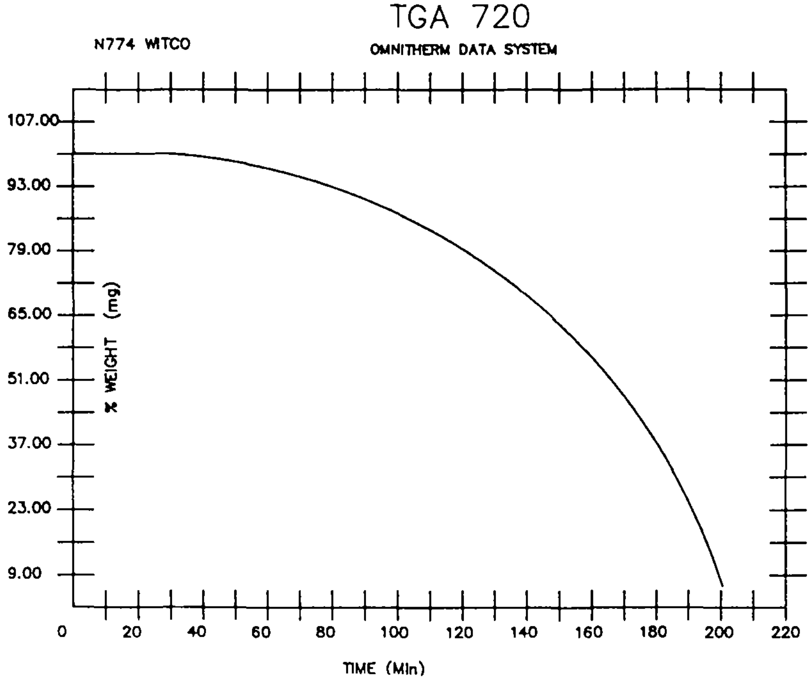

Fig. 1 Temperature jump plot for carbon black Witco N774 oxidized in air using 20-minute periods at each temperature

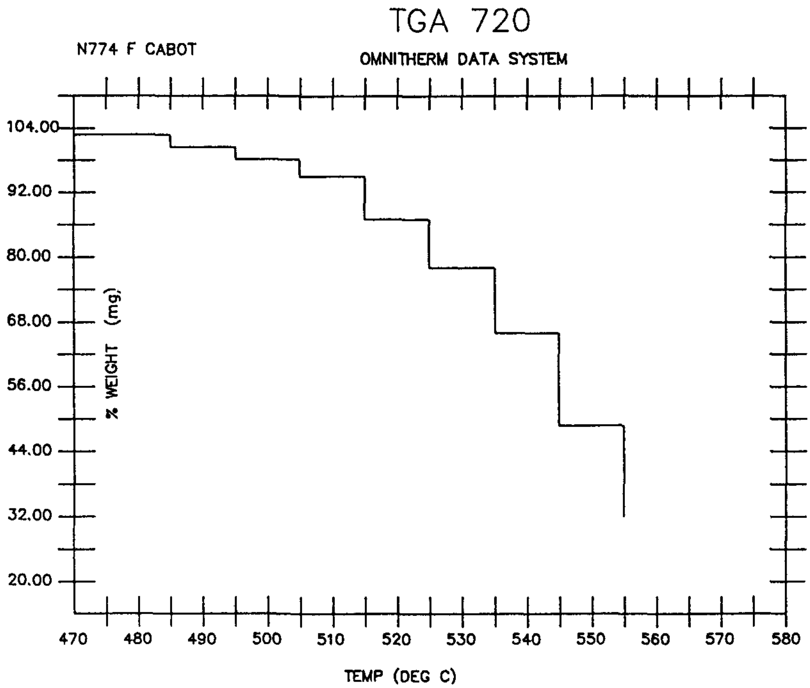

Fig. 2 A typical plot of mass loss *vs.* temperature for carbon black Cabot N774 oxidized in air using the temperature jump method using 20-minute periods at each temperature

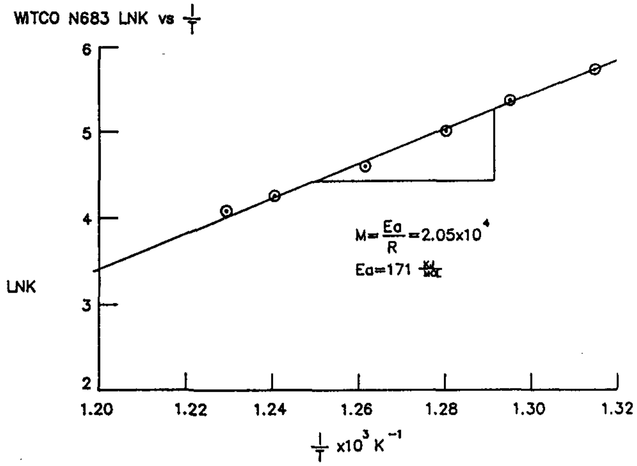

Fig. 3 Arrhenius plot for oxidation of carbon black Witco N683

value of E ranging from 125 kJ·mol^{-1} to 195 kJ·mol^{-1} (Fig. 4). These values agree with earlier work done on α and β resins extract from coal [13]. These authors conclude that the reaction of carbon with oxygen produces surface oxygen complexes which decompose to form gaseous products. It appears that there are at least two components to the carbon surface. One of these components is called the active surface, associated with the oxidation and gasification process while the other components are relatively inactive.

Table 4 A typical result of the oxidation jump method applied to carbon black Witco N683

Mass loss / %	Time / s	Temp. / K	k / s^{-1}	–ln K	$1/T \times 10^3$ / K^{-1}
4.13	1200	763.15	3.44×10^{-3}	5.67	1.310
5.74	1200	773.15	4.78×10^{-3}	5.34	1.293
8.4	1200	783.15	7.00×10^{-3}	4.98	1.277
11.62	1200	793.15	9.68×10^{-3}	4.64	1.261
15.61	1200	803.15	0.0130	4.34	1.245
20.02	1200	813.15	0.0167	4.09	1.230

Slope = 2.05×10^4 E_a = 171 kJ·mol^{-1} A = 1.57×10^9 s^{-1}

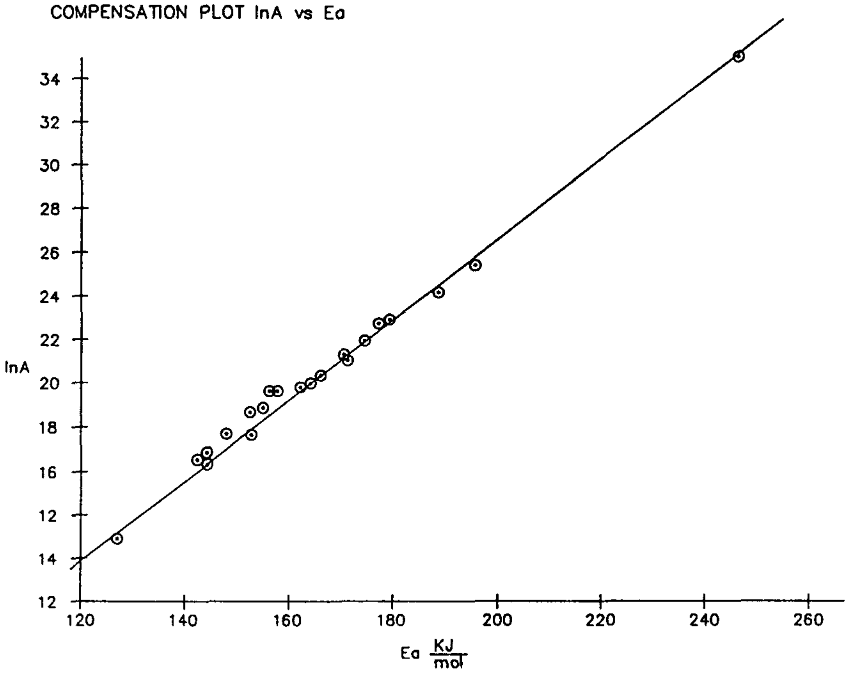

Fig. 4 Compensation plot for oxidation of carbon blacks in air

Table 5 Calculated values for the Arrhenius parameters for the oxidation for carbon blacks

Sample	Manufacturer	A / s^{-1}	E / kJ·mol^{-1}
N774	Cabot	2.3×10^{10}	189
N774	Witco	1.38×10^{14}	247
N683	Ashland	6.34×10^{9}	178
N683	Witco	1.57×10^{4}	171
N660	Cabot	6.48×10^{8}	166
N650	Witco	5.02×10^{8}	163
N650	Cabot	7.28×10^{9}	180
N650H	Columbian	3.24×10^{9}	176
N650	Columbian	1.76×10^{9}	170
N550	Cabot	4.20×10^{8}	162
N550	Witco	5.28×10^{10}	196
N330	Columbian	2.71×10^{7}	143
N330	Witco	2.09×10^{6}	127
N330 (bead)	Cabot	1.25×10^{8}	152
N330 (ground)	Cabot	1.96×10^{7}	142
N339	Witco	1.64×10^{8}	155
N326	Columbian	2.03×10^{7}	143
N234	Ashland	3.42×10^{4}	158
N234	Cabot	3.57×10^{8}	157
N234	Witco	5.16×10^{7}	147
N110	Ashland	6.57×10^{7}	152

A comparison of the oxidation rates of carbon blacks was done at three different temperatures and this information is given in Tables 6, 7 and 8. It was found to be more informative to transform the specific reaction rate to specific reaction rate per unit area for the purposes of comparison to refer this rate per unit area to the oxidation rate of N774. (This carbon black was chosen as a point of reference due to its low surface area.) Figures 5, 6 and 7 show plots of specific reaction rate per unit area against the total surface area for the oxidation of carbon blacks at 773, 793 and 813 K. The choice between active sites (for the gasification by oxygen) and the inactive sites would be a choice 'edge' carbon atoms at the surface and the 'basal' plane atoms. According to Grisdale [14] and Smith and Polley [15]. The rate of oxidation of carbon crystallites is about 17 times faster in the direction parallel to the basal planes (along their edge atoms – described here as 'edge atoms') than perpendicular to them. From Tables 5, 6 and 7 it can be seen that the low surface area carbon blacks tended to have faster rates per unit area of surface than the height surface area carbons (Figs 5–7). The

Table 6 Comparison of rates of oxidations of carbon blacks at 773K

Grade	Manufacturer	Surface area $m^2 \cdot g^{-1}$	The specific reaction rate, k / s^{-1}	$k \times 10^5$ Surface area = k_s *	k_s (Carbon) ** k_s (carbon N774)
N774	Cabot	30	0.0036	12.00	1.00
N774	Witco	30	0.0029	9.54	0.795
N660	Cabot	35	3.7810^{-3}	10.79	0.899
N683	Ashland	39	6×10^{-3}	15.5	1.29
N683	Witco	36	4.79×10^{-3}	13.3	1.11
N650	Cabot	42	4.71×10^{-3}	11.2	0.933
N650	Witco	41	4.91×10^{-3}	12.0	1.00
N650H	Columbian	37	4.00×10^{-3}	10.81	0.90
N650	Columbian	37	6.11×10^{-3}	16.52	1.37
N550	Cabot	42	5.32×10^{-3}	12.67	1.06
N550	Witco	48	3.33×10^{-3}	6.9	0.58
N330	Columbian	83	5.9×10^{-3}	7.12	0.59
N330	Witco	83	5.32×10^{-3}	6.41	0.53
N330 (bead)	Cabot	83	6.66×10^{-3}	7.91	0.66
N330 (ground)	Cabot	83	4.86×10^{-3}	5.86	0.49
N336	Columbian	84	5.03×10^{-3}	6.00	0.50
N339	Witco	92	5.85×10^{-3}	6.35	0.53
N234	Ashland	127	7.27×10^{-3}	5.72	0.48
N234	Cabot	126	8.63×10^{-3}	6.85	0.57
N234	Witco	126	5.89×10^{-3}	4.68	0.39
N110	Ashland	141	3.45×10^{-3}	2.44	0.20

* This column gives the specific reaction rate per unit area

** This column gives the relative reaction rate per unit area normalized by putting N774 Cabot as unity

Table 7 Comparison of rates of oxidation of carbon blacks at 793.15 K

Grade	Manufacturer	Surface area / $m^2 \cdot g^{-1}$	The specific reaction rate k / s^{-1}	$k\times10^5$ / surface area = k_s*	k_s (Carbon)** / k_s (carbon N774)
N774	Cabot	30	7.55×10^{-3}	25.2	1.000
N774	Witco	30	7.54×10^{-3}	25.1	0.996
N683	Ashland	39	0.012	31.1	1.234
N683	Witco	36	9.35×10^{-3}	26.0	1.03
N660	Cabot	35	7.25×10^{-3}	20.72	0.82
N650	Witco	41	9.30×10^{-3}	22.7	0.90
N650	Cabot	42	9.55×10^{-3}	22.7	0.90
N650H	Columbian	37	7.99×10^{-3}	21.6	0.86
N650	Columbian	37	0.0119	32.1	1.27
N550	Cabot	42	0.0110	23.8	0.94
N550	Witco	48	7.16×10^{-3}	14.91	0.59
N330	Columbian	83	0.0104	12.5	0.50
N330	Witco	83	8.76×10^{-3}	10.6	0.42
N330 (bead)	Cabot	83	0.0119	14.3	0.57
N330 (ground)	Cabot	83	8.49×10^{-3}	10.2	0.40
N339	Witco	92	0.0107	11.6	0.46
N326	Columbian	84	8.8×10^{-3}	10.5	0.42
N234	Ashland	127	0.0134	10.6	0.42
N234	Cabot	126	0.0156	12.7	0.50
N234	Witco	126	0.0105	8.33	0.33
N110	Ashland	141	6.27×10^{-3}	4.45	0.18

* This column gives the specific reaction per unit area

** This column gives the relative specific reaction rate per unit area by putting N774 Cabot as unity

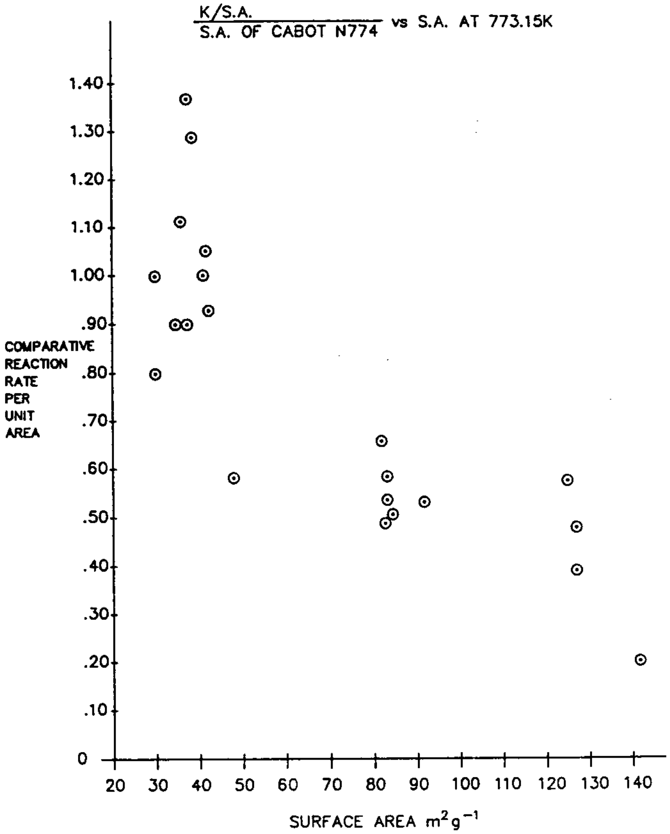

Fig. 5 Plot of specific reaction rate per unit area against the total surface area for the oxidation of carbon blacks at 773K

order of reactivity is shown in Table 9. The results show that the lower surface area carbon blacks are more reactive towards oxygen than the higher nitrogen surface area carbons. The conclusion from these results must be that the lower surface area carbon blacks have a greater proportion of their surface consisting of 'edge' carbon atoms whilst the higher area carbon blacks expose a larger proportion of the relatively inactive basal plane carbon atoms. A similar conclusion has been drawn by us on a much more limited study with only eight carbon blacks [16]. Armington found a similar relationship between specific reactivity and surface area of carbon blacks [17]. Their findings help in indicating the reinforcing action noted when carbon blacks are incorporated in elastomer systems. Lower surface area carbon blacks act mainly as fillers in carbon black–elastomer systems while reinforcement is clearly seen in carbon black–elastomer systems with

Table 8 Comparison of rates of oxidation of carbon blacks at 813.15 K

Grade	Manufacturer	Surface area / $m^2 \cdot g^{-1}$	The specific reaction rate k / s^{-1}	$k \times 10^5$ surface area = k_s*	k_s (Carbon)** k_s (carbon N774)
N774	Cabot	30	0.0153	5.09	1.00
N774	Witco	30	0.0189	6.31	1.24
B683	Ashland	39	0.0236	6.05	1.19
N683	Witco	36	0.0177	4.91	0.96
N660	Cabot	35	0.0135	3.85	0.76
N650	Witco	41	0.0171	4.17	0.82
N650	Cabot	42	0.0187	4.46	0.88
N650H	Columbian	37	0.0154	4.17	0.82
N650	Columbian	37	0.0224	6.05	1.19
N560	Cabot	42	0.0183	4.35	0.85
N550	Witco	48	0.0148	3.08	0.61
N330	Columbian	83	0.0176	2.13	0.42
N330	Witco	83	0.0141	1.70	0.33
N330 (bead)	Cabot	83	0.0210	2.5	0.49
N330 (ground)	Cabot	83	0.0144	1.74	0.34
N339	Witco	92	0.0191	2.08	0.41
N326	Columbian	84	0.0149	1.77	0.35
N234	Ashland	127	0.0231	1.82	0.36
N234	Cabot	126	0.0287	2.28	0.45
N234	Witco	126	0.0182	1.44	0.28
N110	Ashland	141	0.0111	0.784	0.15

* This column gives the specific reaction rate per unit area

** This column gives the relative reaction rate per unit area normalized by putting N774 Cabot as unity carbon black, of high external surface area. This would suggest that the interactions between the elastomer and the basal carbon atoms is the feature which imparts reinforcing action in the carbon–elastomer composite. It is therefore suggested that this kind of oxidation study might be a useful criteria in selecting suitable carbon fillers which would have a reinforcing action in carbon–elastomer composites. In future publications this rheology between the local plane carbon atoms and elastomer systems will set out in more detail.

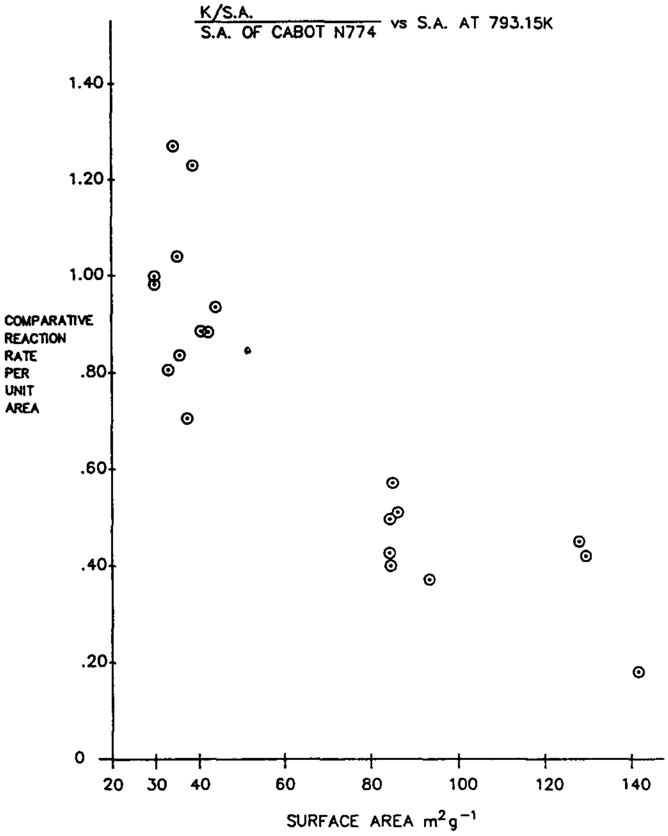

Fig. 6 Plot of specific reaction rate for unit area against the total surface area for the oxidation of carbon black at 793 K

Table 9 Carbon blacks listed in order of decreasing reaction rates / S.A. at 773 K, 793 K and 813 K

	At 773 K	At 793 K	At 813 K
1	Columbian N650	Columbian N650	Witco N774
2	Ashland N683	Ashland N683	Ashland N683
3	Witco N683	Witco N683	Columbian N650
4	Cabot N550	Cabot N774	Cabot N774
5	Witco N650	Witco N774	Witco N683
6	Cabot N774	Cabot N550	Cabot N650
7	Cabot N650	Cabot N650	Cabot N550
8	Columbian N650H	Witco N650	Witco N650
9	Cabot N660	Columbian N650H	Columbian N650H
10	Witco N774	Cabot N660	Witco N550
11	Cabot N330 (bead)	Witco N550	Cabot N660
12	Columbian N330	Cabot N330 (bead)	Cabot N330 (bead)
13	Witco N550	Cabot N234	Cabot N234
14	Cabot N234	Columbian N330	Columbian N330
15	Witco N330	Witco N339	Witco N339
16	Witco N339	Ashland N234	Ashland N234
17	Columbian N326	Witco N330	Columbian N326
18	Cabot N330 (ground)	Columbian N326	Cabot N330 (ground)
19	Ashland N234	Cabot N330 (ground)	Witco N330
20	Witco N234	Witco N234	Witco N234
21	Ashland N110	Ashland N110	Ashland N110

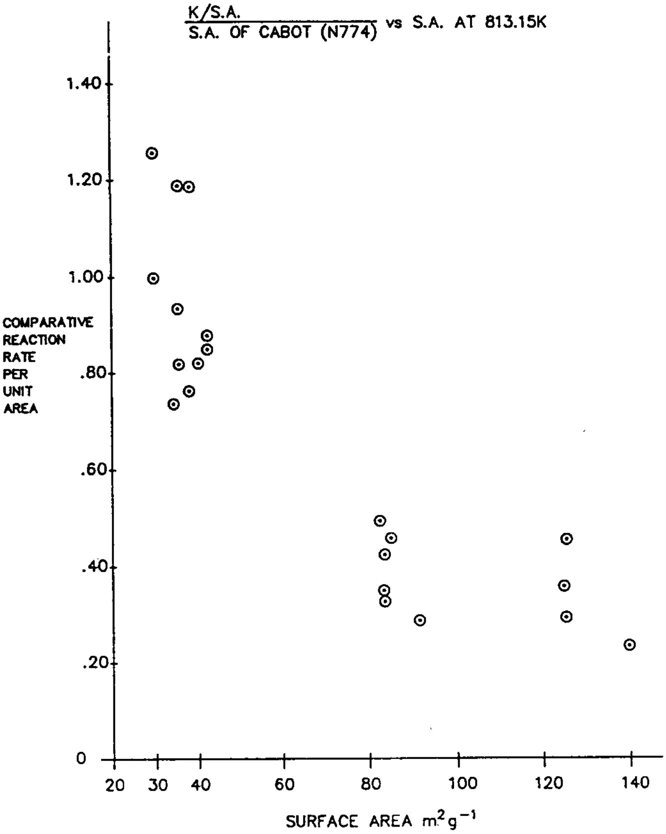

Fig 7 Plot of specific reaction rate per unit area against the total surface area for the oxidation of carbon blacks at 813K

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Zusammenfassung — Es wird eine Beziehung zwischen den Oberflächen- und Texturmerkmalen von Ruß und den in Luft thermisch induzierten Vergasungsvorgängen hergestellt. Unter Anwendung der Temperatursprung-Methode wurde die Vergasung in Luft verfolgt, um die relevanten Arrhenius'schen Parameter zu ermitteln. Dies kann mit der Aktivität der "basalen" Ebenenatome sowie der "Kanten"atome in Verbindung gebracht werden. Dies basiert auf einem Modell der Rußstruktur, bestehend aus einer unregelmäßigen Packung von kleinen Graphit- Strukturen.Die Rußoberfläche wurde mit einer Adsorptions-Einzelmessung vermessen, die im wesentlichen auf der volummetrischen BET Methode basiert. Die Rußoberfläche besaß eine Oxidationsgeschwindigkeit pro Flächeneinheit, die eindeutig zeigt, daß Ruß mit geringerer Fläche an der Oberfläche ein vorwiegend aktives Gebiet von "Kanten"atomen besitzt, während die Oberfläche von Ruß mit größerer Fläche eine vorwiegende Menge von "basalen" Graphitebenen-Atome besitzt.