

CHLORINE FIXATION ON ANTHRACITES AND CARBON BLACKS AND ITS EFFECT ON ELECTRICAL RESISTIVITY

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Abstract—A medium and a high volatile matter (VM) anthracite and a medium and low VM carbon black have been exposed to chlorine gas, at one atmosphere pressure, at temperatures between 200–1400°C. For the high VM anthracite, chlorine fixation occurred at low heat treatment temperatures (HTT) primarily by substitution of chlorine for hydrogen in aliphatic groups. At higher HTT, fixation occurred primarily by substitution of chlorine for hydrogen at the edges of aromatic platelets. For the medium VM anthracite, chlorine fixation at all HTT occurred primarily by the latter process. For the medium VM carbon black, chlorine fixation at all HTT occurred primarily by substitution of chlorine for hydrogen at the edges of aromatic platelets and by addition of chlorine on new active sites produced upon removal of the oxides of carbon from the edges of aromatic platelets. Little fixation of chlorine on the low VM carbon black occurred. Electrical resistivities of samples heated in chlorine were compared with samples heated in nitrogen. The atmosphere used influenced the change in resistivity with HTT. The effect of atmosphere on resistivity is explained on the basis of the chlorine fixation results.

1. INTRODUCTION

RECENTLY we have reported on the removal of mineral matter from anthracite, as volatile metal chlorides, upon its exposure to one atmosphere of chlorine at elevated temperatures.⁽¹⁾ It was observed qualitatively that as a result of this treatment, significant amounts of chlorine were retained by the anthracites. Workers⁽²⁻⁵⁾ have studied the interaction of activated charcoals and carbon blacks with chlorine at elevated temperatures and have found that up to 17 per cent by weight of chlorine could be retained. Generally the chlorine could not be eliminated by boiling with alkali, heating in vacuum, nor by electro dialysis, when these processes were carried out at temperatures at or below the chlorination temperature.

In this study, we have investigated the fixation of chlorine on a medium and a high volatile matter (VM) anthracite upon chlorination at temperatures between 200–1400°C. For comparison, we have also followed the chlorination of a medium and a low VM carbon black between 300–1200°C. The effects of chlorination on the electrical resistivity of the carbonaceous materials have been found to be of particular interest.

2. EXPERIMENTAL

Samples used

Two raw Pennsylvania anthracites, of particle size either 42×65 or 60×100 mesh, were used in this program. These samples were supplied by the Reading Anthracite Company. Analyses of these samples are given in Table 1. Trevorton is a high VM anthracite; St. Nicholas is a medium VM anthracite. The raw anthracites contained negligible amounts of chlorine. The Trevorton and St. Nicholas anthracites had BET surface areas, as calculated from carbon dioxide adsorption at -78°C, of 131 and 220 m²/g, respectively.⁽⁶⁾

For comparative purposes, the chlorination of a medium VM channel black, Excelsior, and a low

TABLE 1. CHEMICAL ANALYSES OF SAMPLES USED

Sample	Elemental Analysis (wt. % daf basis)			Volatile matter (%)	Ash (%)
	C	H	O		
Trevorton	92.0	3.5	2.9	8.9	10.5
St. Nicholas	94.0	2.2	1.9	4.8	6.8
Excelsior black	91.7	0.9	7.3	8.6	nil
Acetylene black	>99.5	0.1	0.2	nil	nil

VM acetylene black was also studied. Excelsior black was obtained from the Columbian Carbon Company; it had an average particle diameter of 260A and a BET surface area of 207 m²/g.⁽⁷⁾ Acetylene black was obtained from the Shawinigan Products Corporation; it had an average particle diameter of 500A and a BET surface area of 64 m²/g. Analyses of these carbons are given in Table 1.

Chlorination procedure

Chlorination was carried out in a horizontal tube furnace, with the samples held in either silica or graphite boats. In most runs, the samples were first raised to maximum temperature in an atmosphere of flowing nitrogen, at a heating rate of 5°C/min. When at maximum temperature, a gentle flow of chlorine (Matheson Company, >99.5 per cent purity) at one atmosphere pressure was started. In some runs, the furnace was first brought to maximum temperature and then the sample inserted over a period of several minutes. The flow of nitrogen was then stopped and chlorine started. The use of these different heat treatment procedures had little effect on the results. During chlorination, the sample could be periodically removed from the furnace and weighed. Generally, chlorination was discontinued when the weight increase was less than 2 per cent of sample weight per hour. Reference samples were also prepared by heating entirely in nitrogen at the same temperatures and soak times as used during chlorination.

Following chlorination, the samples were analyzed for chlorine according to the Eschka method for coals and cokes.⁽⁸⁾

Electrical resistivity measurements

Electrical resistivity measurements were made at room temperature by confining 2 g of sample between two brass-tipped steel pistons (one of which was graduated) in a glazed steatite holder, 1½ in. o.d., ½ in. i.d., and 2 in. long. The holder, constituting one arm of a Leeds and Northrup Kelvin bridge (Model 4286), was mounted in a hydraulic press. Resistance measurements were made at compacting pressures between 2,000 and 20,000 lb/in². Resistances greater than 11 ohms could not be measured on the bridge and, consequently, were determined using a vacuum tube ohmmeter. Although determinations of the highest

resistivities reported here (10⁵ ohm-cm and greater) were not precise, an indication was at least obtained of their order of magnitude and their changes following heat treatment and chlorination.

3. RESULTS

Chlorine fixation

Table 2 summarizes the results for the fixation of chlorine on the 60×100 mesh anthracites and the carbon blacks. Also included in this table are results for the loss in VM when the samples underwent identical heat treatments in nitrogen. As

TABLE 2. CHLORINE FIXATION ON ANTHRACITES AND CARBON BLACKS

HTT (°C)	Time at HTT, (hr)	VM Loss in N ₂ , (wt. %)	Chlorine Fixed, (wt. %)
Trevorton anthracite			
200	4.5	—	14.2
300	7.5	0.6	27.7
400	3.5	1.1	7.0
500	6.0	3.1	12.2
600	2.0	4.9	14.1
700	3.0	7.2	17.1
800	2.5	7.7	13.9
900	2.0	8.9	10.4
St. Nicholas anthracite			
200	2.0	—	1.1
300	2.5	—	3.2
400	2.5	—	4.2
500	2.0	—	5.9
600	4.5	1.9	13.3
700	4.5	2.4	17.5
800	2.8	3.3	14.7
900	2.0	4.4	10.7
Excelsior black			
300	2.0	—	9.5
400	2.0	0.7	11.6
500	2.0	1.2	12.4
600	1.8	2.9	12.7
700	1.0	—	10.4
900	1.0	8.5	6.0
1200	1.0	—	1.9
Acetylene black			
800	1.0	nil	1.1
1000	1.0	nil	0.9
1200	1.0	nil	0.9

expected, and as shown previously by PURI and co-workers while studying the chlorination of charcoal,⁽⁴⁾ the rate of chlorine pick-up decreased progressively with chlorination time. The chlorination time at heat treatment temperature (HTT) was either one hour or, arbitrarily, the time at which the increase in sample weight had become less than 2 per cent/hr, if this time exceeded one hour.

In agreement with PURI and co-workers for their studies on charcoal,⁽⁴⁾ the amount of chlorine taken up by St. Nicholas anthracite and Excelsior black went through one maximum with increasing HTT. By comparison, the pick-up of chlorine on Trevorton anthracite went through two maxima with increasing HTT, the maximum at *ca.* 300°C being particularly sharp. The acetylene black picked up relatively little chlorine at all HTT investigated.

As reported previously by PURI and co-workers,⁽⁴⁾ chlorination resulted in the production of significant amounts of hydrogen chloride. In this study, the amounts of hydrogen chloride produced were not measured quantitatively, but it is evident from results shown in Fig. 1 for St. Nicholas anthracite that chlorine abstracted hydrogen effectively. As HTT was increased, the effect of a chlorine atmosphere on the amount of hydrogen removed in excess of that removed thermally diminished.

In several cases, samples of chlorinated anthracite were subsequently heated in nitrogen to a temperature higher than their chlorination temperature to observe the possible removal of chlorine. For example, Trevorton anthracite chlorinated at 600°C (containing 14.1 per cent chlorine) was heated for one hour at 700°C. It underwent a weight loss of 14.6%, of which *ca.* 2 per cent was carbon monoxide and carbon dioxide. The interesting finding was that essentially all chlorine was recovered as hydrogen chloride and a negligible amount as gaseous chlorine. As the desorbed chlorine diffused from the micropore system of the anthracite, it apparently underwent sufficient collisions with the pore surface to result in its essentially complete utilization to abstract additional hydrogen.

St. Nicholas anthracite had an original sulfur content of 0.56 per cent. The majority of this sulfur was very stable thermally; in one hour at

1400°C in nitrogen it was only reduced to 0.45 per cent. The presence of a chlorine atmosphere had a negligible effect on sulfur removal.

Effect of chlorination on electrical resistivity

Table 3 summarizes the effect of heat treatment in nitrogen and chlorine at various temperatures (and times given in Table 2) on the electrical resistivity of the 60 × 100 mesh anthracites and the carbon blacks. Resistivities of the anthracites were measured at a constant sample bulk density of 1.2g/cc; those of the blacks were measured at a

TABLE 3. ELECTRICAL RESISTIVITIES OF ANTHRACITES AND CARBON BLACKS

HTT, °C	Electrical resistivity, Ω-cm	
	N ₂ atm.	Cl ₂ atm.
	Trevorton anthracite	
200	~10 ⁷	~10 ⁷
300	~10 ⁷	~10 ⁷
400	~10 ⁷	~10 ⁸
500	~10 ⁸	200
600	~10 ⁸	0.85
700	1.3	0.090
800	0.091	0.048
900	0.044	0.023
	St. Nicholas anthracite	
200	200	100
300	100	90
400	90	80
500	80	60
600	70	0.96
700	2.6	0.10
800	0.15	0.054
900	0.066	0.033
	Excelsior black	
300	0.19	0.56
400	0.17	0.39
500	0.15	0.35
600	0.14	0.26
700	0.093	0.13
800	0.059	0.076
900	0.054	0.051
1000	0.051	0.048
1200	0.044	0.043
	Acetylene black	
800	0.045	0.045
1000	0.041	0.041
1200	0.040	0.040

constant sample bulk density of 0.98g/cc. Both anthracites underwent large decreases in resistivity upon increase in HTT from 200 to 900°C. Further, samples heated in chlorine had a lower resistivity at each HTT than those heated in nitrogen. Differences in resistivity were particularly marked following heat treatment at around 600°C. Resistivities of the blacks decreased much less with increasing HTT than did the anthracites. Further, samples of Excelsior black heated in chlorine had a higher resistivity than those heated in nitrogen at HTT up to 800°C. At higher HTT there were no significant differences in resistivity. For the acetylene black, heat treatment in chlorine and nitrogen between 800–1200°C resulted in no detectable effect of atmosphere on the resistivities.

As expected, the time required for the resistivity of the samples to decrease to a limiting value at each HTT decreased with increasing temperature. Some results for the chlorination of 42×65 mesh St. Nicholas anthracite are given in Table 4. At 600°C it is seen that the resistivity was still

decreasing after a chlorination time of 6 hr. At 1400°C the limiting resistivity was reached within 15 min, small fluctuations in resistivity at longer chlorination times being within limits of experimental duplicability.

TABLE 4. CHANGES IN ELECTRICAL RESISTIVITY OF ST. NICHOLAS ANTHRACITE WITH CHLORINATION TEMPERATURE AND TIME

Chlorination time, (hr)	Resistivities (Ω -cm) following chlorination at various temperatures				
	600°C	800	1000	1200	1400
1/4	>11	0.23	0.034	0.031	0.024
1/2	>11	0.18	0.032	0.026	0.024
3/4	10.6	0.11	0.029	0.025	0.023
1	8.3	0.094	0.028	0.024	0.028
3	3.2	0.047	0.030	0.026	0.023
6	1.5	0.040	0.028	0.026	—

Figure 2 shows the resistivity of 42×65 mesh St. Nicholas anthracite as a function of one hour heat treatment at various temperatures. In the

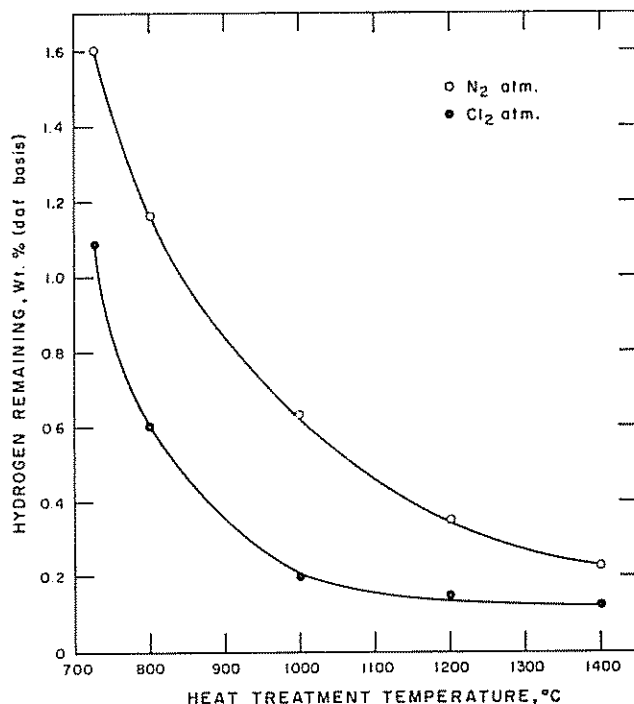


FIG. 1. Hydrogen content of 42×65 mesh St. Nicholas anthracite heated for one hour in nitrogen and chlorine at various temperatures.

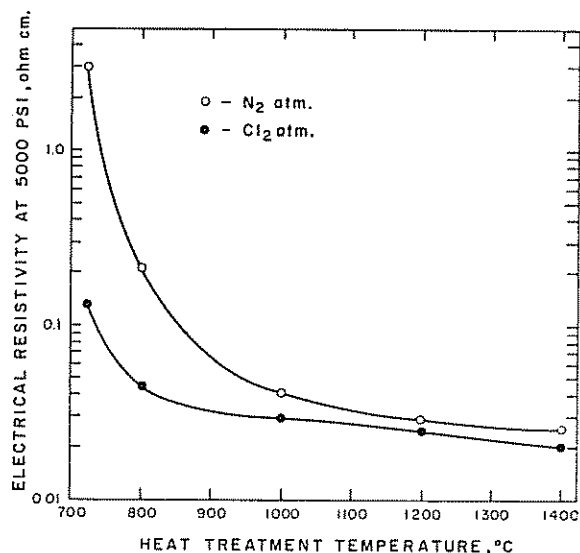


FIG. 2. Electrical resistivity of 42×65 mesh St. Nicholas anthracite heated for one hour at various temperatures in nitrogen and chlorine.

HTT range $725\text{--}1000^\circ\text{C}$, resistivities dropped sharply and the effect of a chlorine atmosphere became increasingly less marked as HTT was increased. Relatively little further decrease in resistivity occurred as HTT was increased between 1000 and 1400°C . However, for HTT up to 1400°C the St. Nicholas samples heated in chlorine continued to have significantly lower resistivities than those heated in nitrogen.

Figure 3 shows the variation of $\log(\text{resistivity})$ with $\log(\text{compacting pressure})$ for 42×65 mesh St. Nicholas anthracite heated at 800°C in both nitrogen and chlorine for one hour. Even though there was a marked difference in resistivities at each compaction pressure for samples heated in the different atmospheres, for both samples the decrease in resistivity with increasing compaction pressure was very similar. The slopes of the plots are close to -0.5 , which falls within the range of values reported by MROZOWSKI for calcined and graphitized petroleum cokes.⁽⁹⁾ A slope of *ca.* -0.5 suggests that the resistivity is decreasing with increasing compaction pressure as a result of increasing particle contact area and not as a result of increasing compression of a "surface film".

As a result of fixation of chlorine on the samples, their apparent particle densities increased; and,

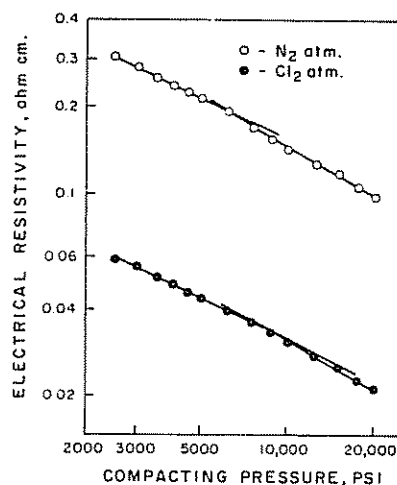


FIG. 3. Dependence of electrical resistivity on compacting pressure for 42×65 mesh St. Nicholas anthracite heated for one hour at 800°C in nitrogen and chlorine.

consequently, the bulk density of a particulate sample at a fixed compaction pressure also increased. Several results for the change in resistivity with bulk density are given in Figs. 4 and 5. For the anthracites, the compaction pressure was varied between 2000 and $15,000\text{ lb/in}^2$ to produce the increases in bulk densities observed. For

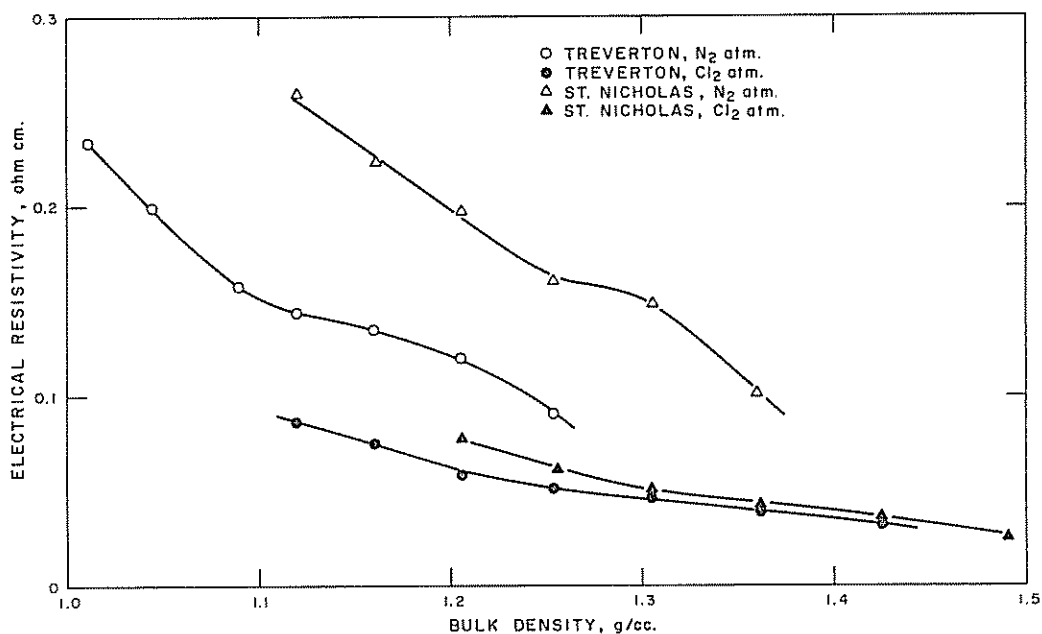


FIG. 4. Dependence of electrical resistivity on bulk density of 60x100 mesh anthracites heated at 800°C in nitrogen and chlorine.

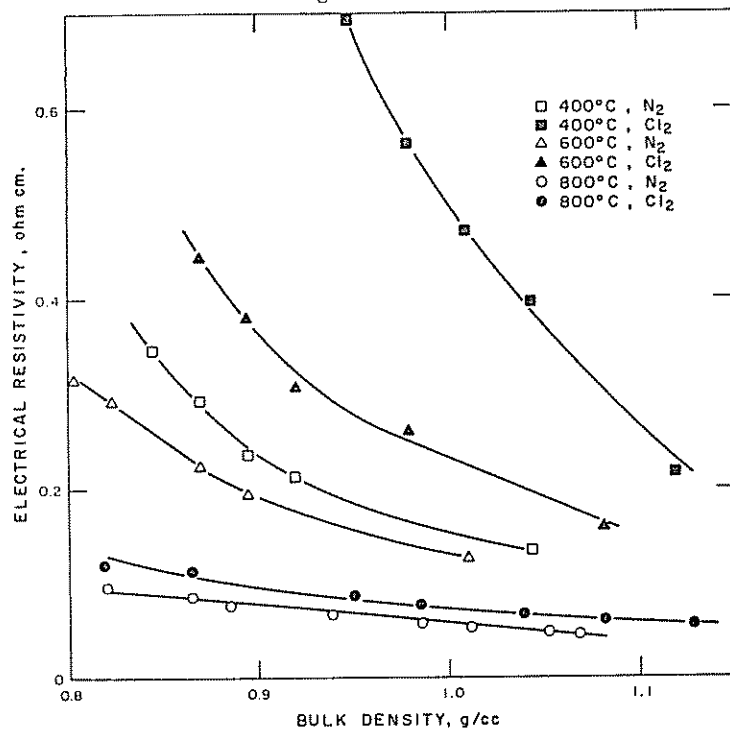


FIG. 5. Dependence of electrical resistivity on bulk density of Excelsior black heated at various temperatures in nitrogen and chlorine.

Excelsior black, the samples heated at 400 and 600°C were compressed between 2000 and 10,000 lb/in²; the samples heated at 800°C were compressed between 2000 and 15,000 lb/in².

4. DISCUSSION

Chlorination of anthracites

The results obtained in this study appear to be consistent with our present knowledge regarding the structure of anthracites and the effect of heat treatment and chlorination on carbonaceous materials containing hydrogen and oxygen. Infra-red studies have shown that coals of 90–94 per cent carbon content (that is, anthracites) contain both aromatic and aliphatic hydrogen, with the ratio CH(aromatic) to CH(aliphatic) increasing very markedly with increasing carbon content in the above range.⁽¹⁰⁾ The aliphatic hydrogen is contained both in aliphatic chains and alicyclic rings attached to the periphery of aromatic rings or platelets. The aromatic hydrogen is hydrogen essentially covalently bonded to carbon atoms at the periphery of aromatic platelets. X-ray diffraction studies have shown that the average size of the aromatic platelets in coal increases very sharply with increasing carbon content between 90–94 per cent.⁽¹¹⁾ On the basis of these previous studies on raw anthracites we conclude that: (1) Trevorton anthracite has a significant aliphatic hydrogen content and consequently a significantly lower CH(aromatic)—CH(aliphatic) ratio than does St. Nicholas anthracite and (2) the average aromatic platelet size in St. Nicholas anthracite is significantly larger than in Trevorton anthracite.

Consider now some previous results on the effect of heat treatment on coals. Infra-red studies on heat treated coals⁽¹²⁾ have shown that very little change in the spectrum occurs below 400°C, but above this temperature there is a marked decrease in the absorption due to aliphatic structures. The disappearance of aliphatic structures is considered to be caused in part by their distillation from the coal and in part by their dehydrogenation and conversion to aromatic structure. At *ca.* 600°C, the loss of aromatic hydrogen becomes substantial,⁽⁶⁾ this is accompanied by some growth in aromatic platelet size.⁽¹³⁾

Consider now the result of chlorination on the uptake of chlorine on the anthracites. As discussed by GOLDSTEIN,⁽¹⁴⁾ reaction of chlorine with

aliphatic hydrocarbons becomes significant at *ca.* 200°C, with hydrogen chloride being produced and chlorine being substituted for hydrogen in the aliphatic structure. We conclude that this accounts for the large uptake of chlorine on Trevorton anthracite at 200 and 300°C. Further supporting this conclusion, is a run where raw Trevorton anthracite was heated at 600°C in nitrogen for one hour prior to its being chlorinated at 300°C. As just discussed, much of the aliphatic structure is removed upon heating to 600°C. As expected, this resulted in a sharp decrease in subsequent chlorine uptake at 300°C. Less than 2 per cent chlorine was taken up, as compared to 27.7 per cent for the sample heated directly in chlorine at 300°C.

It is known that the introduction of halogens into aliphatic structures leads to a decrease in their thermal stability with breakdown occurring by dehydrohalogenation.⁽¹⁵⁾ Thus it appears, on the basis of the sharp decrease in chlorine uptake on Trevorton anthracite when the HTT was increased from 300 to 400°C that dehydrochlorination occurred to a substantial extent at 400°C.

The increase in chlorine uptake on Trevorton anthracite with increasing HTT from 400 to 700°C is attributed primarily to the partial substitution of chlorine for hydrogen at the edges of aromatic platelets and the addition of chlorine to a fraction of the new edge carbon atoms produced by removal of carbon monoxide and carbon dioxide. It is thought that chlorine uptake decreases with further increase in HTT above 700°C because the internal surface area of Trevorton anthracite begins to decrease rapidly above this temperature.⁽⁶⁾

For St. Nicholas anthracite, its aliphatic content was apparently too low for us to observe a maximum in chlorine uptake at *ca.* 300°C. Most of the chlorine uptake over the entire HTT range studied appears to be due to partial substitution of chlorine for aromatic hydrogen. Again the maximum in chlorine uptake at *ca.* 700°C is attributed to a decrease in internal surface area of the St. Nicholas anthracite at higher HTT.⁽⁶⁾

Our electrical resistivity results appear to be consistent with PINNICK'S studies on low temperature carbonaceous materials.⁽¹⁶⁾ From electrical resistivity and infra-red absorption studies, PINNICK showed that the energy gap between the upper valence band and conduction band for these

materials is substantial and that, consequently, their intrinsic electrical conductivity should be low. He concludes that electrical conduction in these materials can be attributed chiefly to positive charge carriers. These positive carriers are produced as a result of the removal of hydrogen, aliphatic and alicyclic hydrocarbons, and the oxides of carbon from the periphery of aromatic platelets upon heat treatment. That is, some of the σ -electrons from peripheral carbon atoms, which formed valence bonds with hydrogen, etc. are left unpaired; a π electron can now jump from the π -band into the σ -state, forming a spin pair. The effect of this is to remove an electron from the π -band and to create a hole or a positive charge carrier.

The electrical resistivity results on the anthracites heated in nitrogen are as expected. With increasing HTT, the fraction of peripheral aromatic carbon atoms covered by functional groups decreases. The decrease becomes particularly marked above *ca.* 600°C. This decreased coverage results in an increase in the number of positive charge carriers and, hence, a decrease in electrical resistivity. It is thought that differences in the fraction of peripheral aromatic carbon atoms covered by functional groups can also explain differences in electrical resistivity of the two anthracites following comparable HTT. At HTT of 600°C and below, the electrical resistivity of Trevorton anthracite is higher than St. Nicholas. This is attributed to the higher VM content of the Trevorton and, hence, a greater coverage of the peripheral aromatic carbon atoms. At HTT between 700–900°C, the electrical resistivity of Trevorton anthracite is lower than St. Nicholas. Following a HTT of 700°C, it is seen from Table 2 that the Trevorton anthracite has lost the majority of its VM and that its remaining VM content closely approximates that of the St. Nicholas anthracite. Therefore, the factor now controlling what fraction of peripheral sites is covered is the average aromatic platelet size. Since we have concluded that the platelet size is significantly smaller for the Trevorton, the peripheral area per unit weight able to accommodate functional groups is larger for Trevorton than St. Nicholas. Therefore, for small differences in VM content, the Trevorton will have a smaller fraction of peripheral aromatic carbon atoms covered than

will the St. Nicholas. This point, in so far as it affects electrical resistivity, has been discussed in some detail when considering carbons produced from carbon monoxide disproportionation.⁽¹⁷⁾

The effect of chlorination on the electrical resistivities of the anthracites also appears reasonable. At each HTT, heating the anthracites in chlorine resulted in their having a lower resistivity than when they were heated in nitrogen. As discussed by PURI,^(4,5) only a fraction of the aromatic hydrogen removed from carbon by chlorination is substituted for by chlorine. Therefore, even though some chlorine will also chemisorb on new peripheral carbon sites following removal of the oxides of carbon from anthracites, the fraction of surface covered by hydrogen plus oxygen will be greater following heat treatment in nitrogen than the fraction of surface covered by hydrogen plus oxygen plus chlorine following heat treatment in chlorine. It is noted that differences in resistivity for both anthracites were particularly marked following a HTT of 600°C. At this temperature, marked thermal removal of hydrogen from peripheral aromatic platelets just commences,⁽⁶⁾ but from results on chlorine contents of the anthracites, a significant amount of the aromatic hydrogen is removed by chlorine treatment at a HTT of 600°C.

WATERS⁽¹⁸⁾ concluded that the presence of mineral matter in coal and cokes in quantities less than 30 per cent has no significant effect on electrical resistivity measurements. Our results are in agreement with this conclusion, since we find no relationship between resistivity and ash content of the anthracites. For example, for a HTT of 600°C the ash contents of the anthracites were essentially independent of whether heat treatment was performed in nitrogen or chlorine. Yet, the resistivities were markedly dependent upon the atmosphere used during this heat treatment. On the other hand, for a HTT of 900°C both anthracites heated in chlorine had much lower ash contents than samples heated in nitrogen. At the same time their electrical resistivities were only slightly affected by the atmosphere used during heat treatment.

Chlorination of carbon blacks

Consider the results for the Excelsior black. The relatively low electrical resistivity of this black following a HTT of only 300°C in either nitrogen

or chlorine indicates that its aliphatic carbon content is very low and that the fraction of peripheral aromatic carbon atoms covered by functional groups is less than for the anthracites. The black primarily consists of aromatic structure with a fraction of the peripheral carbon atoms covered with functional groups containing hydrogen and/or oxygen.⁽¹⁹⁾

With increasing HTT from 300 to 600°C in a chlorine atmosphere, chlorine uptake increased as both increasing substitution of chlorine for hydrogen and increasing addition of chlorine to new edge carbon atoms, produced by removal of the oxides of carbon, occurred. The fact that chlorine uptake went through a maximum at a HTT of 600°C, whereas the BET surface area of Excelsior black goes through a maximum at a HTT of 1000°C,⁽⁷⁾ suggests that surface annealing of new edge carbon atoms into less active sites occurred at a significant and increasing rate as HTT was increased above 600°C. That is, annealing of these active sites apparently occurred during the heating up in nitrogen, prior to the exposure of the samples to chlorine at HTT. It would be expected that chlorine uptake would be increased if heating up to maximum temperature, as well as soaking at maximum temperature, would be performed in chlorine.

The decrease in resistivity of Excelsior black with increasing HTT in either nitrogen or chlorine is a result of increasing removal of functional groups and growth of the average aromatic platelet size. In contrast to the results for the anthracites, the electrical resistivities of the samples heated in chlorine were higher than those heated in nitrogen for HTT up to 800°C. It is felt that this is due to the ratio of hydrogen to oxygen in the raw Excelsior black being much lower than the ratio in the raw anthracites. Chlorine effectively removes hydrogen from carbon surfaces but has not been reported to remove oxygen—just to replace a fraction of it when it desorbs (as oxides of carbon). Thus, for the Excelsior black the fraction of carbon atoms at the periphery of aromatic platelets covered by hydrogen plus oxygen will be less following heat treatment in nitrogen than the fraction covered by hydrogen plus oxygen plus chlorine following heat treatment in chlorine. Because chlorine pick-up continuously decreased

with increasing HTT above 600°C, the difference between the fraction of peripheral sites covered when using different atmospheres continuously decreased. Thus, the difference in electrical resistivity also progressively decreased.

The very low uptake of chlorine on the acetylene black, particularly at 800°C, is consistent with the conclusion that chlorine chemisorbs on carbon primarily when hydrogen and/or oxygen functional groups are removed. As shown in Table I, the volatile matter content of acetylene black is negligible. As expected, heat treatment in a chlorine atmosphere rather than a nitrogen atmosphere also had a negligible effect on the electrical resistivity of acetylene black.

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