

# Development of Mesoporosity in Activated Charcoal Cloths

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## Introduction

As part of a systematic study of the production and nature of charcoal cloth, we have reported recently the influence of cations of different valency (added as their chloride salts) on the porosity generated in such materials<sup>3</sup>. Although the rates of gasification in CO<sub>2</sub> gas (expressed as burn-off) varied widely with the nature of the cation, all the activated materials produced were highly microporous with the extent of mesoporosity remaining small even at high burn-off (40-60%).

This communication describes an extension of this work to the study of anions, in particular the borate anion. Boric acid and its derivatives have been reported as acting as inhibitors in the oxidation of carbon, possibly through the development of a glassy coating on the carbon surface<sup>4</sup>. If this interpretation of their behaviour is correct, the use of such anions as impregnants could have a significant influence on the texture generated in charcoal cloths.

## Experimental

Samples of untreated Moygashel viscose rayon cloth (dimensions: 20 x 3.5 cm) were impregnated with aqueous solutions of the additives studied using the method described previously<sup>3</sup>. They were then suspended individually by means of a nichrome wire from the arm of a Cahn electrobalance mounted vertically above a tube furnace so that each sample was situated centrally within the furnace.

The samples were carbonised by heating in a stream of N<sub>2</sub> gas (flow rate, 4000 cm<sup>3</sup>min<sup>-1</sup>) up to 850°C (heating rate, 10 °C min<sup>-1</sup>), and then activated by switching the flow gas to CO<sub>2</sub> at the same flow rate. Heating was continued at 850°C for various time lengths, the weight loss of each sample being monitored continuously via a chart recorder linked to the electrobalance.

The porosity of the various activated cloth

\*A fuller account of this work will be published elsewhere<sup>1</sup>. The subject matter of this communication forms the basis of a recent patent application.<sup>2</sup>

samples was investigated by N<sub>2</sub> gas adsorption studies (at 77K) using a Carlo Erba Sorptomatic 1800 instrument.

## Results

Typical chart traces for the weight loss during activation of samples impregnated with boric acid or borax (sodium borate; Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O) are illustrated in Figure 1, where the interpolated data for the untreated cloth and for cloth impregnated with AlCl<sub>3</sub> reported previously are included for comparison<sup>3</sup>. Over the time scales employed, linear weight losses occurred in all cases but with substantial rate differences between the various samples studied.

What is interesting is that whereas boric acid inhibits the rate of activation of the untreated cloth, the addition of borax accelerates this process. Since the Na<sup>+</sup> ion is known to be extremely active promoter of carbon gasification, its presence in borax solutions may provide a simple explanation for this difference in behaviour. To test this suggestion, experiments have been conducted in which the [Na<sup>+</sup>]/[B] ratio in the impregnating solutions was varied either through the addition of borax or NaCl to an initial boric acid solution.

The results of such experiments are depicted in Figure 2. At low [Na<sup>+</sup>]/[B] ratios the rate of activation is apparently independent of the nature of the salt added to the impregnating solution, increasing in line with the Na<sup>+</sup> ion concentration in the solution. At a [Na<sup>+</sup>]/[B] ratio of ca. 4.0, however, a marked difference occurs in the behaviour of the two systems studied, which can only be attributed to the nature of the anion present. The structure of the Cl<sup>-</sup> ion is independent of pH and indeed its addition to boric acid solutions merely maintains the pH virtually constant at a value of 3.0. In contrast, increasing additions of borax progressively shift the pH of boric acid solutions to higher values; indeed, when [Na<sup>+</sup>]/[B] ≈ 4.0, the pH of the borax-containing solution was ca. 8.0. In aqueous solutions of this pH value, borate species exist as simple tetrameric ions in contrast to the caged and polynuclear structures they adopt at lower pH values. Simple borate ions probably penetrate

readily into the fibrous structure of the cloth sample during impregnation, thus achieving a more uniform distribution and facilitating ready burn-off in the presence of  $\text{Na}^+$  ions during activation.

The presence of  $\text{Na}^+$  ions and the nature of the borate species in the system also influence the porosity generated in charcoal cloths. Figure 3 illustrates the  $\text{N}_2$  adsorption isotherms obtained with activated samples initially impregnated respectively with boric acid, with boric acid plus NaCl and with borax alone. The boric acid impregnated sample exhibited a Type I isotherm with limited hysteresis typical of a microporous material (as incidentally did a sample impregnated with NaCl alone), while the other two samples exhibited Type IV isotherms with marked hysteresis loops typical of mesoporous solids. Figure 4 shows how such mesoporosity is generated as the  $[\text{Na}^+]/[\text{B}]$  ratio in the impregnating solution is increased. The influence of NaCl is now more pronounced than that of borax, certainly when  $[\text{Na}^+]/[\text{B}] \leq 0.4$ , in contrast to the corresponding influence of these salts on the rate of activation.

#### Discussion

These results indicate that the presence of  $\text{Na}^+$  ions is essential for the generation of mesoporosity in borate-containing cloths. However, the pH of the impregnating solution is also important. At low pH values, as exist in boric acid/NaCl systems, the borate species are complex and incapable of substantial penetration into the bulk of the fibre. Such species probably congregate in the readily accessible parts of the fibre, at or near to its outer surface, saturating that part of the structure. The rate of activation is thereby limited whereas rapid and uncontrolled development of mesoporosity is promoted at quite low  $[\text{Na}^+]/[\text{B}]$  ratios.

In boric acid/borax systems, however, the borate species present at  $[\text{Na}^+]/[\text{B}]$  ratios greater than 0.4 are relatively simple and readily penetrate the fibre structure. Under these circumstances not only is the rate of activation enhanced in the presence of  $\text{Na}^+$  ions, but mesoporosity develops in a more controlled manner possibly throughout the whole of the fibre cross-section.

#### Acknowledgement

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#### References

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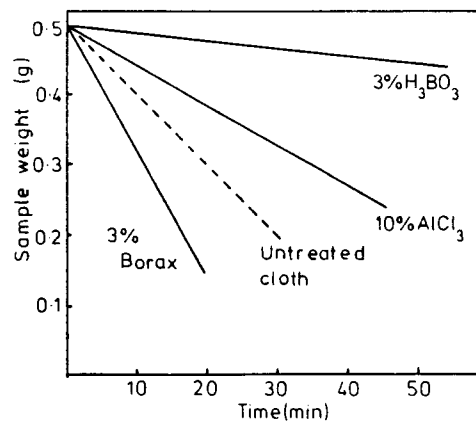


Figure 1.

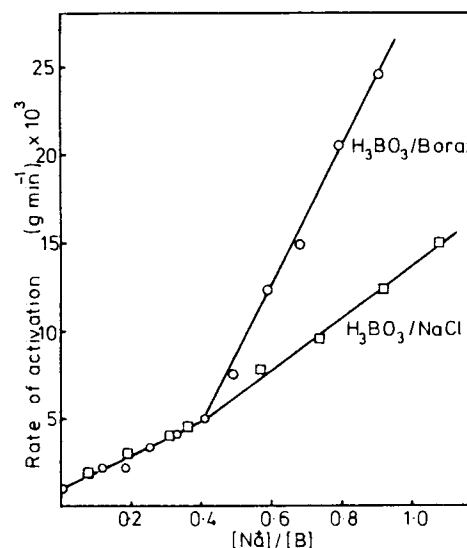


Figure 2.

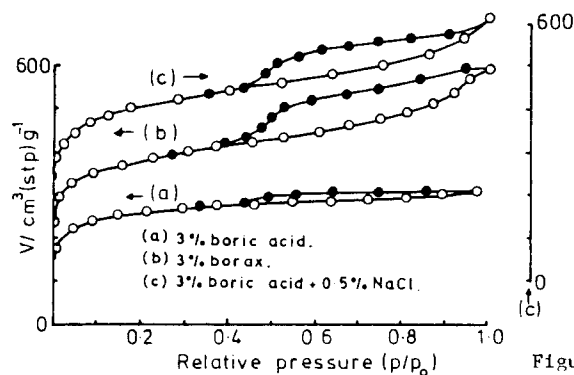


Figure 3.

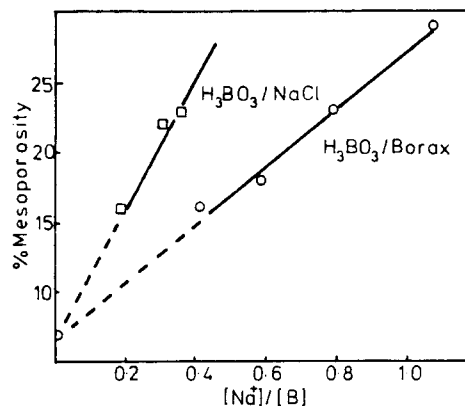


Figure 4.