

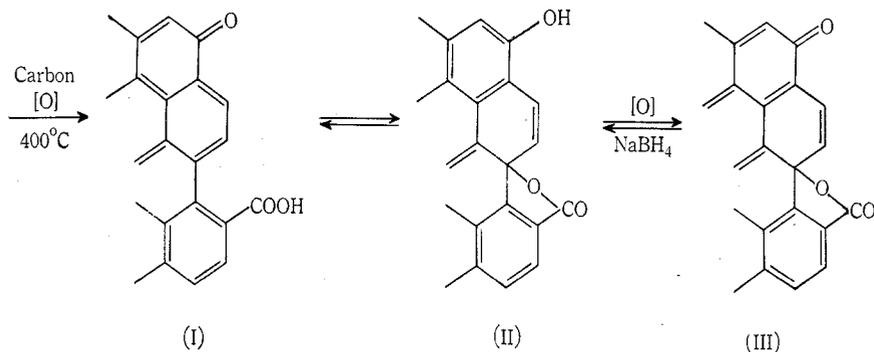
## SHORT COMMUNICATIONS

### THE REACTION OF CARBON BLACKS WITH SODIUM BOROHYDRIDE\*

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It has been shown (Garten, Weiss, and Willis 1957) that the acidity of carbon blacks is due to phenolic hydroxyls and two types of lactones. Those lactones which can be methylated by diazomethane were termed F lactones, whilst those that are not were termed N lactones.

It was also shown (Garten and Weiss 1955) that the acidity of a carbon that had been activated in air at 800 °C and cooled in nitrogen increased after reduction, and this was taken as evidence for quinones in these carbons. Studebaker *et al.* (1956) on the other hand suggested that since many carbon blacks are reduced by sodium borohydride they also contain quinones. However it was observed (Garten and Weiss 1957) that the acidity of these carbons did not change on reduction, from which it was concluded "that either quinone groups are reduced beyond the hydroquinone stage or that a group other than quinone must be responsible for the oxidation of the borohydride". It has recently been realized, however, that this conclusion is not necessarily valid and that the following mechanism for the oxidation of a carbon by air at about 400 °C would reconcile Studebaker's work with our own and also with Hallum and Drushel's (1958) polarographic evidence for quinones.



It is now postulated that the primary step in the oxidation of the carbon black during its production by the channel or roller processes is the formation of carbonyl and carboxyl groups as in (I). These groups are unstable when interconnected by conjugated double bonds and, as in the phthalein dyestuffs, revert to the more stable F lactone tautomer (II). F lactones have been shown to be

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responsible for a major portion of the acidity of ink blacks. However, the hydroxyl of an F lactone may also be conjugated with respect to that of a second F lactone elsewhere on the layer plane and should therefore behave as a hydroquinone. Hydroquinone-like properties have been reported previously for low-temperature carbons (Garten and Weiss 1955). Hence some oxidation of these to (III) is likely and this would give rise to quinones and N lactones, which are also present in carbon blacks. Thus we find that in the highly oxidized L.F.C. and L.C.C. blacks the N lactone concentration is two to three times that of the F lactones. Mild reduction, e.g. with sodium borohydride, may produce (II) but the acidity would not alter as was observed. A comparison of the N lactone concentration of some carbon blacks (Garten, Weiss, and Willis 1957) with the consumption of hydrogen after treating the same type of black, but from different batches, with sodium borohydride (Studebaker *et al.* 1956) is given below and with the exception of the H.C.C. black shows fair agreement.

Type	N Lactones (m equiv/g)	% H Consumed from NaBH <sub>4</sub> (m-equiv/g)	Type	N Lactones (m-equiv/g)	% H Consumed from NaBH <sub>4</sub> (m-equiv/g)
H.C.C. ..	0.42	1.23	H.P.C. ..	0.25	0.29
L.F.C. ..	0.64	0.70	M.P.C. ..	0.23	0.23
L.C.C. ..	0.34	0.56	E.P.C. ..	0.36	0.29

We note that the determination of N lactones is only semiquantitative and tends to give too low values as indicated by the titration curves for carbon blacks which do not show a flat plateau for high pH values. The H.C.C. black is particularly bad in this respect and this may account for the big discrepancy between the two results.

#### References

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