In further studies of the reaction between *t*-butyl perbenzoate and cyclic ethers and sulphides, we found, that if an alcohol (R—OH) is added to the substrate (tetrahydrofuran) before carrying out the reaction with *t*-butyl perbenzoate in the usual way, the alkoxy compound V is formed.

Yields cited are based on one series of experiment only and are not considered to be the maximum obtainable. A more detailed paper [8] on this subject will be published in the near future.

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Analysis of Oxide Films on Copper by Coulometric Reduction

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Several methods have been used for analysing oxide films on copper [1]. The most attractive features of the coulometric method, originally developed by Evans and Bannister [2] and by Miley [3,4], are its high sensitivity and the possibility of determining both cuprous and cupric oxide in the same run. When determining the two oxides the choice of a suitable electrolyte is important. Campbell and Thomas [5] pointed out that since copper oxide will dissolve in ammonium chloride, there is a possibility of error in earlier determinations made with NH_4Cl as electrolyte. KCl does not have this disadvantage, but it usually fails to give separation of the two oxides. Later Mills [6] suggested a phosphate buffer of pH 6.9 as a suitable electrolyte for separate determinations of the two oxides. To improve the coulometric method Lambert and Trevoy [7] recently demonstrated the importance of the complete elimination of dissolved oxygen and also of plateable cations from the electrolyte. This can be achieved by pre-electrolysis. The present paper demonstrates the possibility of using KOH (0.1 M) as electrolyte in the analysis

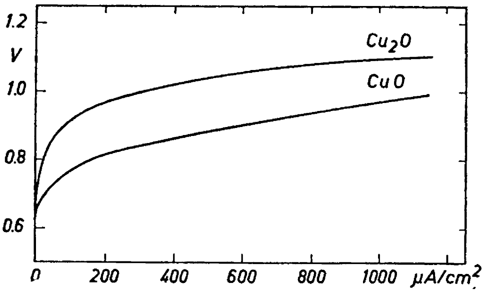

Fig. 1. Reduction potential of the two copper oxides, measured against an Ag—AgCl electrode in 0.1 M KOH, as a function of the current density.

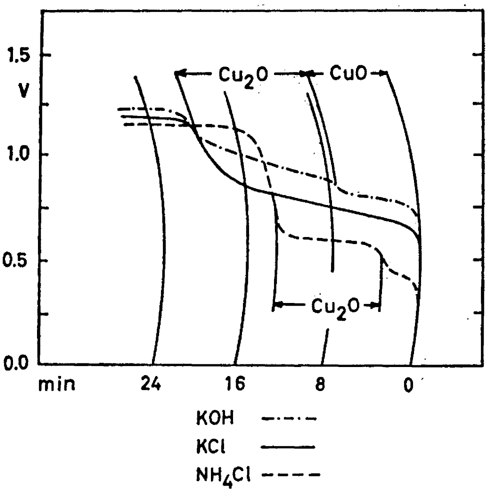

Fig. 2. Time-potential curves of coulometric runs.

Table 1.

Electrolyte	Cu_2O µg/cm^2	CuO µg/cm^2	Cu_2O+CuO µg/cm^2
KCl	—	—	51
NH_4Cl	29	10	39
KOH	37	15	52

of oxide films on copper. The use of this electrolyte has been developed during studies of morphological and kinetic phenomena in the oxidation of copper.

When KCl is used as the electrolyte, the difference between the potentials at which CuO and Cu_2O are reduced is very small and varies with the density of the reducing current. Because of this small difference potassium chloride usually fails to give separation of the two oxides. When KOH is used, the potential difference is independent of the current density and large enough to give separation in a coulometric run. Fig. 1 shows the potential at which the two oxides are reduced in KOH, measured against an Ag—AgCl electrode, as a function of the current density.

To demonstrate the possibility of using KOH as the electrolyte, the following experiment was carried out. A copper wire was mechanically polished and oxidized for one minute at 560°. The wire was then cut into three equal lengths. The amount of oxide on each part was coulometrically determined using NH_4Cl, KCl and KOH, respectively, as the electrolytes. The current density was the same in all three cases (670 µA/cm^2). The electrolytes were all cleaned by bubbling oxygen-free nitrogen through them. Oxygen was removed from the nitrogen in the usual manner with pyrogallol and a solution of chrome (II) ions. The time-potential curves for the three runs are given in Fig 2.

With KCl only one potential plateau appeared. With KOH and NH_4Cl two plateaus were obtained, indicating the presence of the two oxides. The time for complete reduction is equal in the cases of KCl and KOH, but when using NH_4Cl it becomes shorter because of dissolution of the two oxides. Table 1 gives the amount of oxide determined in the different electrolytes.

A special examination of the dissolution of the two oxides in KOH has been made. Samples of cuprous and cupric oxide powders (supplied by May and Baker Co. Ltd) were left in contact for one month with KOH of molarities 0.05, 0.1, 0.3, and 0.5. A determination of dissolved copper was then made by complexometric titration [8]. The result of the titrations showed that CuO does not dissolve. No dissolution of Cu_2O could be observed in KOH of molarities 0.05 and 0.1. In solutions of molarities 0.3 and 0.5 the amounts of dissolved cuprous oxide were determined to be less than 2.4 and 7.2 mg/100 ml, respectively. It is seen that within the normal duration of a coulometric analysis, no dissolution is to be expected.

Conclusions. The solubility of cuprous and cupric oxide in 0.1 M KOH is small enough to be neglected in this instance. The difference between the potentials at which the two oxides are reduced is nearly constant and independent of the current density. These properties make KOH (0.1 M) a possible electrolyte in the analysis of oxide films on copper.

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