The Electrosynthesis of Organic Compounds

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The development of electrochemical routes in the industrial production of organic compounds is beginning to attract considerable interest. Already two large-scale processes are in operation, one producing adiponitrile from acrylonitrile, an intermediate step in the manufacture of Nylon 66, and the other producing lead tetra-ethyl anti-knock compounds. This article reviews the basic electrochemistry involved in this type of synthesis and outlines the great possibilities being opened up by advances in technique, in reactor design and in the development of new types of electrode structures in which platinum and its associated metals will play an important part.

In recent years research in the field of organic electrosynthesis has received considerable stimulation from the forecast that, with the advent of nuclear power, electricity will become cheaper compared to chemical oxidants and reductants. Furthermore, the reasons for the failure of earlier workers to achieve selective reactions have become apparent and by controlling the electrode potential, the solution conditions (solvent, pH, concentration of species, etc.) and by choice of suitable electrode materials, some measure of selectivity is now possible. It therefore seems likely that electrochemical techniques will have an increasing role in preparative organic chemistry, both in industry and in the laboratory as a standard method for oxidations and reductions as well as other reactions such as substitutions and cyclisations.

In order to explain the interest in electrochemistry it is convenient to contrast electrochemical reactions with homogeneous or heterogeneous reductions and oxidations using hydrogen and air or oxygen. The free energy change, $\Delta G°$, of these processes is equivalent to a cell potential, $E°$, given by

$$\Delta G = -nFE°$$

By referring to a scale of free energies or electrode potentials, Figure 1, it is evident that such spontaneous reactions are only possible within the potential range limited by the reduction of oxygen or the oxidation of hydrogen. This driving force only amounts to approximately 0.5 eV or 10 kcals/mole. By contrast, it is possible to carry out electrochemical reactions at potentials between +3.5 V and −2.5 V even in aqueous solution, if suitable electrolytes and electrodes are chosen. Thus, the driving force for an electrode process is of the order of 3eV or 60 kcals/mole. Electrochemical reactions therefore enable one to introduce considerable energy into molecules at low temperature and the order of magnitude of this energy is, in fact, that required to break chemical bonds. Figure 2 compares the energy ranges in which different methods of activating molecules will be effective.

Clearly, in view of the energy which may be introduced, it is not surprising that many "high energy" chemicals that are used as oxidants and reductants in synthesis are prepared electrochemically (e.g. sodium, manganese dioxide, chlorine) and there are obvious advantages in avoiding such intermediates.
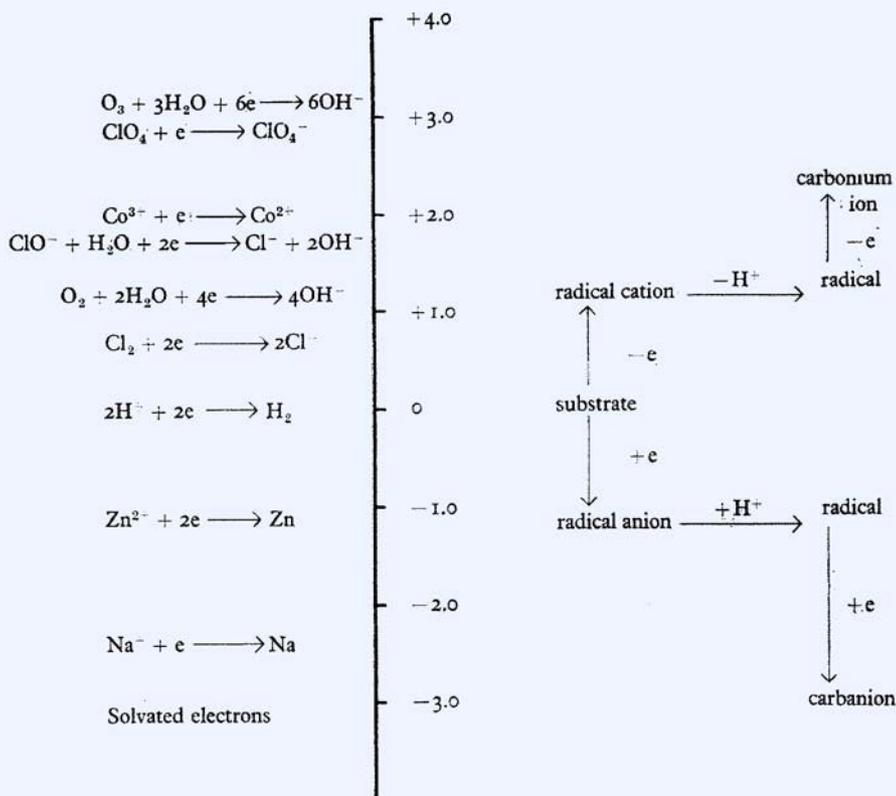
$$O_3 + 3H_2O + 6e \longrightarrow 6OH^-$$
$$ClO_4 + e \longrightarrow ClO_4^-$$

$$Co^{3+} + e \longrightarrow Co^{2+}$$
$$ClO^- + H_2O + 2e \longrightarrow Cl^- + 2OH^-$$

$$O_2 + 2H_2O + 4e \longrightarrow 4OH^-$$

$$Cl_2 + 2e \longrightarrow 2Cl^-$$

$$2H^+ + 2e \longrightarrow H_2$$

$$Zn^{2+} + 2e \longrightarrow Zn$$

$$Na^+ + e \longrightarrow Na$$

Solvated electrons

+4.0
+3.0
+2.0
+1.0
0
−1.0
−2.0
−3.0

carbonium
↑ · ion
| −e
radical cation ——−H⁺——→ radical
↑
| −e
substrate
| +e
↓
radical anion ——+H⁺——→ radical
| +e
↓
carbanion

Fig. 1 *The scale of free energies or electrode potentials. This shows the approximate potentials (in volts) at which various electron transfer reactions take place and indicates the intermediates that may be formed in electrode processes*

The intermediates formed in electrode processes are indicated in Figure 1 and are entirely consistent with the large driving force of such reactions. While the figure is not drawn to scale, it nevertheless shows the approximate points at which radical ions, radicals, carbanions and carbonium ions would be expected to form. Thus it can be seen that by controlling the electrode potential a measure of selectivity may be achieved. The classical example of this idea is the reduction of nitrobenzene where phenylhydroxylamine may be produced at low negative potentials and aniline at more negative potentials (1).
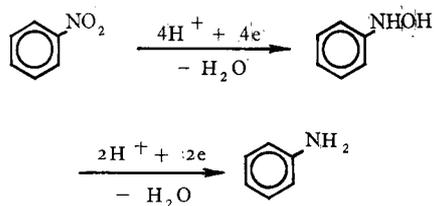
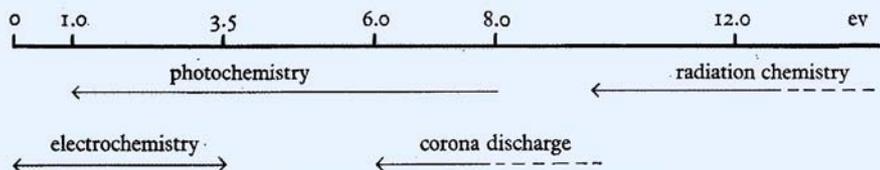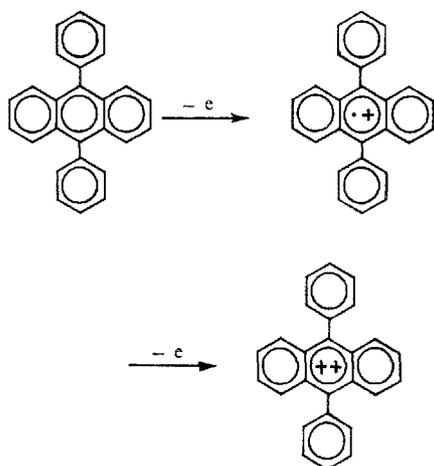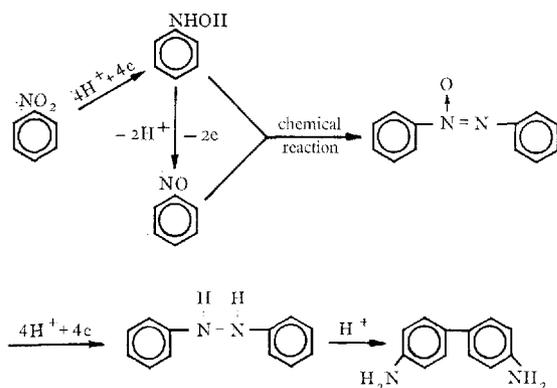

A further example is the oxidation of 9, 10-

Fig. 2 *The diagram illustrates the range in energy (1 electron volt = 23 k.cal mole⁻¹) which may be introduced into molecules by various 'high energy' techniques*

diphenylanthracene at platinum electrodes in aprotic solvents. At low potentials this leads to the radical cation and at high potentials to the dication (2).


It is also possible to exert a measure of control over electrode reactions by maintaining the electrode at a series of potentials for controlled durations. In this way it is possible, for example, to switch successively from oxidation to reduction and thus to change the products of the reaction (3).
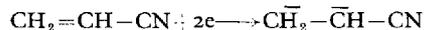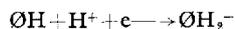

A further important application of pulse electrolysis is likely to be the control of electrode activity by control of the electrode history. For example, in the use of platinum metal electrodes for the oxidation of hydrocarbons in non-aqueous solutions the elec-

trode activity rapidly falls with time. In view of the wide range in potential over which the inert metals may be used the polarisation can be reversed for short controlled periods of time and the electrode reactivated cathodically. In this way controlled successful oxidation of hydrocarbons may be achieved.
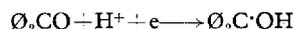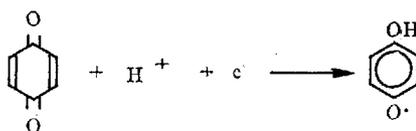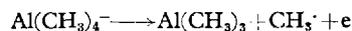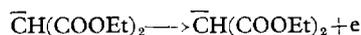
Intermediates of the kind shown in Figure 1 will be formed in many electrode reactions. For example, carbonium ions will be generated at platinum electrodes during the oxidations of alkyl halides (4), carboxylic acids (5), hydrocarbons (6), and amines (7).

$$RI \longrightarrow R^+ + \tfrac{1}{2}I_2 + e$$

$$RCOO^- \longrightarrow R^+ + CO_2 + 2e$$

$$RH \longrightarrow R^+ + H^+ + 2e$$
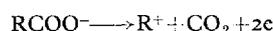
Carbanions and dianions are generated in the reduction of alkyl halides, aromatic hydrocarbons (9), quinones (10), nitrocompounds (11), and activated olefins (12), e.g.

$$RI + 2e \longrightarrow R^- + I^-$$

$$\emptyset H + H^+ + e \longrightarrow \emptyset H_2^-$$

$$CH_2 = CH - CN + 2e \longrightarrow C\overline{H}_2 - \overline{C}H - CN$$

Radicals are also frequently produced as in the oxidation of carboxylic acids (13) and of carbanions (14, 15), and the reduction of some alkyl halides (8), ketones (13), quinones (17) and tetra-alkylammonium salts (18), e.g.

$$RCOO \cdot \longrightarrow R \cdot + CO_2 + e$$

$$\overline{C}H(COOEt)_2 \longrightarrow \dot{C}H(COOEt)_2 + e$$

$$Al(CH_3)_4^- \longrightarrow Al(CH_3)_3 + CH_3 \cdot + e$$

$$\emptyset_2CO + H^+ + e \longrightarrow \emptyset_2C \cdot OH$$

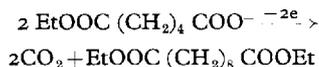$$RI + e \longrightarrow R \cdot + I^-$$

In order to study these highly reactive intermediates, it is clearly necessary to use unreactive solvents and electrode materials. Indeed, it is the advent of aprotic polar solvents in which the intermediates have an appreciable half life that has allowed the characterisation of many intermediates by electrochemical and spectroscopic methods (in particular ESR). In many other cases the nature of the intermediates has been inferred from the products of the reaction and by analogy to known reaction mechanisms.
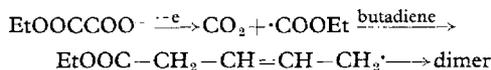
Reactions at Platinum Electrodes

The generation of the reactive species naturally also demands inert electrode substrates and platinum metals have been widely used in aprotic solvents over the range $+3.0$ to -3.0V. On the other hand, in water or other protic solvents the use of platinum metals has been confined to anodic reactions because the decomposition of solvent to form hydrogen is strongly favoured. However, at the present time a considerable research effort is being devoted to investigations of the oxidation and substitution of organic compounds and for these processes the use of inert platinum electrodes is of key importance. Indeed, most of the oxidative reactions listed in this article have been carried out on platinum metal electrodes.

The formation of the intermediates has been written as if the electrode surface is not directly involved in the reaction step. In many cases, however, the reactive species will be adsorbed on the surface and the catalytic role of the electrode will be of key importance. For example, the reductive hydrogenation of olefines is dependent on the use of platinum blacks (19) as is the dissociative adsorption of saturated hydrocarbons or methanol as an essential step in the overall reactions on fuel cell electrodes (20). Again the coupling of radicals produced from carboxylic acids in the Kolbe or Brown-Walker reaction is dependent on the electrode surface, being favoured by platinum in aqueous solutions (13).

The intermediates which are formed react in similar ways to those observed when they are generated in homogeneous processes, although their reactions will often be modified by the adsorption on the electrode. In typical reactions, radicals will dimerise (21),

$$2 \text{ EtOOC (CH}_2)_4 \text{ COO}^- \xrightarrow{-2e}$$
$$2CO_2 + \text{EtOOC (CH}_2)_8 \text{ COOEt}$$

attack double bonds (22),

$$\text{EtOOCCOO}^- \xrightarrow{-e} CO_2 + \cdot \text{COOEt} \xrightarrow{\text{butadiene}}$$
$$\text{EtOOC}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2\cdot \longrightarrow \text{dimer}$$

or react with certain electrode metals (23),

$$\text{R Mg I} \xrightarrow{-e} \text{MgI}^+ + \text{R} \cdot \xrightarrow{\text{Pb}} \text{PbR}_4$$

Carbanions or dianions formed from aromatic hydrocarbons will protonate to form dihydroaromatic compounds (9) or undergo other typical coupling reactions such as that with carbon dioxide (17).
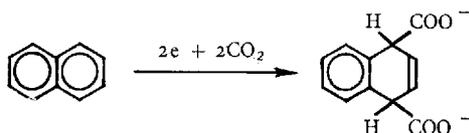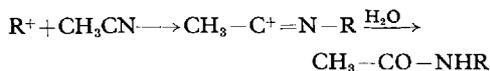

Similarly, the dianions formed from activated olefines will react with unsaturated compounds as in

$$\overline{\text{CH}}_2-\overline{\text{CH}}-\text{CN}+\text{CH}_2=\text{CHCN}+2\text{H}^+ \longrightarrow$$
$$\text{NC}-(\text{CH}_2)_4-\text{CN}$$
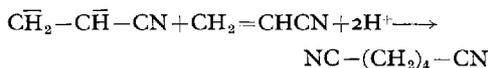
and intramolecular reactions leading to cyclisation are also possible (24),
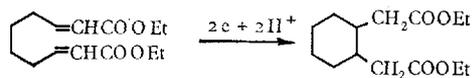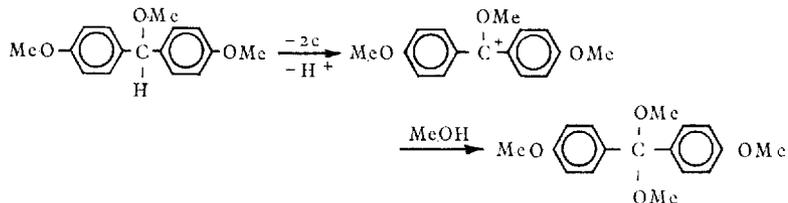

Carbonium ions are naturally highly reactive and usually attack the solvent or deprotonate to form olefines. For example, in acetonitrile amides are formed (4)
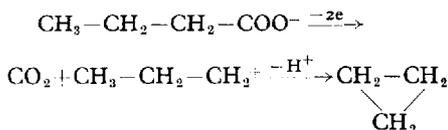
$$\text{R}^+ + \text{CH}_3\text{CN} \longrightarrow \text{CH}_3-\text{C}^+=\text{N}-\text{R} \xrightarrow{\text{H}_2\text{O}}$$
$$\text{CH}_3-\text{CO}-\text{NHR}$$

and in methanol ethers are the products (25)

as shown by the reaction

$$\text{MeO}–\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{OMe}}{|}}{\text{C}}}–\text{OMe} \xrightarrow[-\text{H}^+]{-2e} \text{MeO}–\underset{}{\overset{\overset{\text{OMe}}{|}}{\overset{+}{\text{C}}}}–\text{OMe}$$

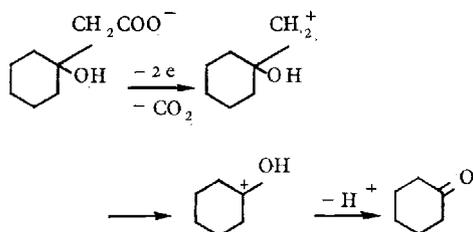$$\xrightarrow{\text{MeOH}} \text{MeO}–\underset{\underset{\text{OMe}}{|}}{\overset{\overset{\text{OMe}}{|}}{\text{C}}}–\text{OMe}$$

In other cases carbonium ions show their typical rearrangements as in the oxidation of neopentyl iodide (4), ring formation (26), e.g.

$$\text{CH}_3–\text{CH}_2–\text{CH}_2–\text{COO}^- \xrightarrow{-2e}$$

$$\text{CO}_2 + \text{CH}_3–\text{CH}_2–\text{CH}_2^+ \xrightarrow{-\text{H}^+} \underset{\diagdown\text{CH}_2\diagup}{\text{CH}_2–\text{CH}_2}$$

ring expansion (27), or ring contraction (28), e.g.

The substitution, for example cyanation or acetoxylation, of aromatic compounds also takes place via cationic intermediates since the reaction will only take place at potentials at which the hydrocarbons are oxidised even if the substituting anion is oxidised at lower potentials (29).

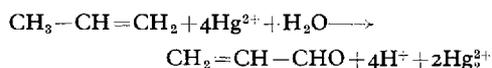## Industrial Processes in Operation

It will be seen that many of these reactions lead to industrially useful products, for example, diterminal substituted compounds. Indeed, the formation of lead tetra-alkyl and of adiponitrile have been made the basis of new commercial synthetic processes by Nalco and Monsanto respectively.

Figure 1 also indicates the potential regions in which a number of inorganic intermediates are generated. For example, Co^{III} may be generated in situ at an electrode and allowed to react with an organic substrate with re-

generation of Co^{II}. In this way reaction occurs within a zone adjacent to the electrode and the actual electrode process

$$\text{Co}^{II} \longrightarrow \text{Co}^{III} + e$$
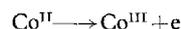
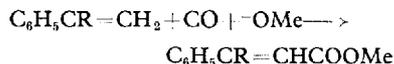serves to "drive" the homogeneous catalytic reaction (30). Other examples of such reactions are the oxidation of propylene by Hg^{II}

$$\text{CH}_3–\text{CH}=\text{CH}_2 + 4\text{Hg}^{2+} + \text{H}_2\text{O} \longrightarrow$$
$$\text{CH}_2=\text{CH}–\text{CHO} + 4\text{H}^+ + 2\text{Hg}_2^{2+}$$

where the mercuric ion is regenerated electrochemically (31). These indirect reactions which involve highly oxidising conditions can again only be achieved by the use of inert platinum metal electrodes. The oxidation of propylene to propylene oxide

$$\text{CH}_3–\text{CH}=\text{CH}_2 + \text{ClO}^- \longrightarrow$$
$$\underset{\diagdown\text{O}\diagup}{\text{CH}_2–\text{CH}}–\text{CH}_3 + \text{Cl}^-$$
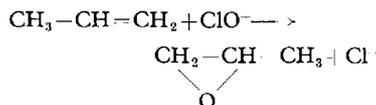
by electrochemically generated hypochlorite (32) and the reaction of olefines with carbon monoxide and methanol in the presence of platinum carbonyls to give methyl esters of $\alpha – \beta$ unsaturated acids (33)

$$\text{C}_6\text{H}_5\text{CR}=\text{CH}_2 + \text{CO} + {}^-\text{OMe} \longrightarrow$$
$$\text{C}_6\text{H}_5\text{CR}=\text{CHCOOMe}$$

are further interesting examples of indirect processes.

Some of the most extreme oxidations carried out at present are the perfluorinations of aliphatic hydrocarbons in anhydrous hydrogen fluoride. It is not clear, however, whether these proceed via the generation of oxidised aliphatic species or of fluorine (34, 35).

Figure 1 also shows that highly reducing species may be generated and the ultimate

limit is, in fact, the formation of solvated electrons in suitable solvents such as ammonia, amines, or hexamethyl phosphoramide (36, 37). The electrons will react with aromatic hydrocarbons and give di- or tetrahydro derivatives.
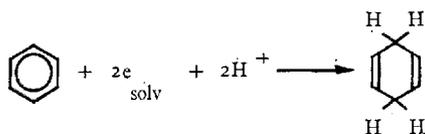
It may be noted that benzene cannot be directly reduced at electrodes.

Importance for Large-scale Synthesis

It will be apparent that many of the intermediates which have been described are of considerable importance for large-scale synthesis. A major aim of these synthetic procedures in the coming years will undoubtedly be the build-up of complex molecules from relatively simple starting materials as might be achieved by the reaction of radicals with olefines.

Linked to this aim will be the activation of unreactive substrates such as carbon dioxide and saturated hydrocarbons by utilising the high driving force of electrochemical processes. Of equal importance to the development of new synthetic routes will be the use of electrochemical procedures to increase the selectivity of existing reactions and to reduce the number of steps in a synthesis as well as simplifying the work-up by avoiding the introduction of reagents which must subsequently be removed.

Development of Reactors and Electrodes

A further major development is likely to be the construction of new electrochemical reactors which will permit an easier scale-up. In recent years the bulk of the effort has been devoted to the development of highly active catalytic electrodes for fuel cells, the aim being the complete oxidation of hydrocarbons to carbon dioxide. It is likely that further research will lead to structures capable of giving, for example, controlled partial oxidations but utilising many of the advantages inherent in the design of the porous fuel cell electrodes.

The development of these and other new types of electrode structures such as fluidised beds and packed beds and the development of membranes suitable for separating electrode compartments will undoubtedly lead to the construction of low cost reactors having a high throughput. The operation of many of these electrodes will be dependent on the use of finely divided platinum metals imbedded in the structure to give a high surface area for the surface reactions at low cost. There is every prospect, therefore, that the chemical engineering technology to make use of the chemical advantages of electrosynthetic procedures on the industrial scale will be available.

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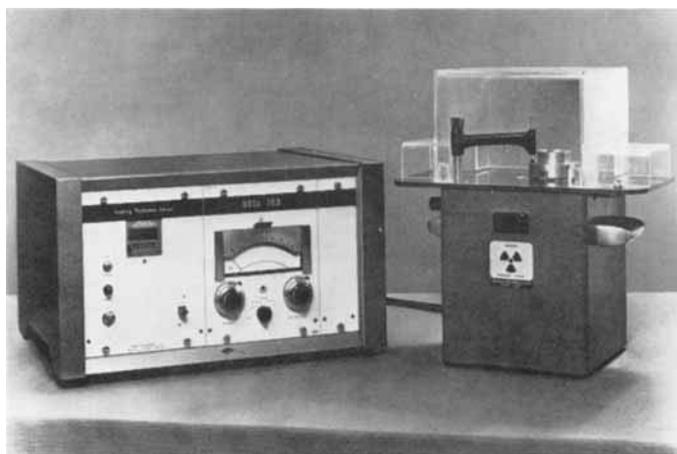
Measurement of Electrodeposit Thickness

The use of the beta back-scatter technique for the non-destructive measurement of the thickness of electrodeposited coatings – and the basic design of a commercial instrument, the Beta 750 – were described some two years ago (*Platinum Metals Rev.*, 1967, **11**, 13). The success of this equipment has now led to the introduction of an extended range of instruments to meet specialised needs and to satisfy the increasingly stringent demands for consistency and accuracy, particularly where electrodeposits such as rhodium, palladium and gold are involved.

The Beta 751 provides a four-figure digital read out of the beta count over a pre-selected time, this figure being related to deposit thickness by reference to a calibration graph. Variations of this equipment provide the facility to pre-set a minimum thickness or a range of thicknesses, pass or fail lights being activated by the count figure obtained.

A direct reading instrument, the Beta 752, incorporates a meter reading of deposit thickness in micro-inches, based upon calibrated scales for specific combinations of deposit and basis metal. This instrument is particularly suitable where large numbers of tests must be carried out and maximum accuracy is not a vital consideration.

The units are produced by Panax Equipment Limited and marketed by Johnson Matthey.

The Beta 752 unit is fitted with a calibrated scale for the direct reading of electro-deposit thickness. Zero and full-scale deflection points are set by adjusting the two potentiometers