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BRONZE PLATING IN CUTLERY MANUFACTURE.

by

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The results obtained during the course of this work are to the best of my knowledge original, except where reference is made to other work.

This thesis or any part, has not been submitted for a degree at any other university or polytechnic.

A Medlock
November 1993.

Preface and Objectives

The objectives of the work carried out in this thesis was to assess the appeal and relative properties of bronze plated cutlery. This was with particular respect to imported bronze cutlery and traditional silver plated cutlery.

Although bronze plating has been carried out for many years, its main use has been in industrial and mining applications. However due to an increasing awareness of nickel sensitivity by skin contact with nickel plated articles, and impending legislation, a resurgence in bronze plating as an alternative to nickel is expected.

Silver plated cutlery is well established and has a significant share of the market. It was therefore considered that the quality of silver plated cutlery and imported cast bronze cutlery could be taken as benchmark in relationship to the "fit for purpose" requirement of the Sale of Goods Act.

As a final coating for cutlery, the bronze deposit would need to possess satisfactory tarnish resistance, wear resistance and be sufficiently ductile to withstand some deformation. In addition under normal commercial plating conditions the alloy composition and hence colour and other properties would need to be predictable and consistent.

Abstract

The quality and aesthetic appeal of imported cast bronze cutlery has been assessed and found to be inferior to cutlery of U.K. origin produced from traditional materials. Gold coloured finishes on traditional cutlery were popular indicating that bronze plated cutlery should be marketable.

Samples which were bronze plated using commercial processes were found to be as good or superior to the cast bronze product with respect to tarnish resistance. The wear properties of bronze coatings as a whole were superior to those of electrodeposited silver which is used extensively in cutlery production.

A new commercial bronze plating bath was assessed for the production of cutlery. The effect of electrolyte pH and current density on deposit composition and distribution were investigated.

In production it would be necessary to tightly control the tin content of the bronze deposit at about twenty percent to achieve a satisfactory colour, tarnish resistance and ductility. This would necessitate changes to the electrolyte to maintain chemical stability. A modified electrolyte composition has been proposed.

Contents

Page

Page

3.0 **Results** 41

1.0 Introduction to Cutlery

1.1 Origins of The Project

This project arose out of CATRA'S ongoing interest in the development of new materials and finishes for cutlery. Interest had been shown by some member companies in alternative finishes to the traditional silver and gold coatings, especially for use with contemporary designs. In particular, gold coloured finishes which could be produced substantially cheaper than gold or gold alloys were generally considered to be the most desirable.

A brief outline of the development of the cutlery industry together with descriptions of the relevant trade and technical associations follow. These are included to provide an understanding of the cutlery industry in Sheffield as it currently stands.

1.2 The Development of Sheffield as a Centre for Cutlery Manufacture

Cutlery is known to have been produced in the Sheffield region since the fourteenth century, although at this time London was the major cutlery centre.

London was displaced by Sheffield as the centre for the cutlery trade during the sixteenth and seventeenth centuries. This occurred due to a plentiful supply of indigenous sandstone used to produce high quality grinding stones and, more importantly, the availability of water power (1, 2).

In 1624 the Cutlers Act was passed by Parliament leading to the formation of a controlling body, The Company of Cutlers in Hallamshire. The company still exists today although not as a controlling body. However, the company still endows the title of Master Cutler to a member, who must also be a director of an edge tool company, at the annual Cutlers Feast. An account of the companies origin through to the mid-twentieth century is given by L.du.Garde Peach (3)

1.3 Trade and Research Organisations in the Cutlery Industry

1.3.1 Research and Development

The Cutlery Research Council was formed in January 1952 following the recommendations of the Cutlery Working Party of 1947. The council was funded by a grant from the Department of Scientific and Industrial Research and by a compulsory annual levy on cutlery companies based on turnover of stainless steel cutlery (4). The objectives of the council were to improve quality and reduce manufacturing costs in cutlery production. In November 1962 at the request of the Board of Trade, the council became a limited company with limited liability named The Cutlery and Allied Trades Research Association (CATRA). The compulsory research levy was discontinued in 1987 and replaced by a voluntary membership subscription.

1.3.2 Trade Associations

Commercial interests of the cutlery and silverware industries are represented by The British Cutlery and Silverware Association (BCSA). Membership of the association is open to individuals or companies manufacturing in the U.K. cutlery, holloware and silver or silver plated goods.

The association which was formed in 1985 is controlled by a Management Committee formed from elected representatives of member companies.

The association offers a number of services including negotiations with trade unions on wages and working conditions, seminars, business trend reports, trade statistics, trade fairs and legal advice. (5)

1.4 Cutlery Production

1.4.1 Materials used in Early U.K. Cutlery Production

Before the late eighteenth century knife blades were produced from shear or double shear steel which were in turn produced from blister steel. This was later replace by crucible steel, which was of much higher quality, developed by Benjamin Huntsman whilst working in Sheffield. In 1913 stainless steel was produced by the Sheffield metallurgist Harry Brearley and this eventually gained acceptance in the 1920's after initial resistance by the cutlers. (2)

Handles were produced in a wide variety of designs, colours and textures. A large range of natural materials were used including rosewood, beech, ebony, agate, jet and amber. Animal products commonly used were stag, bone, horn, ivory and mother of pearl. Metal usage in the manufacture of handles was mainly confined to brass, nickel-silver, silver and gold (2, 6).

Synthetic materials such as cellulose nitrate, know as Xylonite or celluloid, became available in the latter half of the nineteenth century. Between the 1920's and 1950's most table knives produced had celluloid handles and an estimate of 1947 was that 24,000 of these handles were needed annually for Sheffield Table Knife Cutlers (7).

1.4.2 Materials Used in Current U.K. Cutlery Production

The range of materials used in table cutlery manufacture is much smaller than that used in the past. This is due in part to environmental considerations and the need for modern materials to fulfil strict hygiene requirements and withstand dishwasher use.

Material and performance requirements of cutlery are specified in BS5577 (8). This standard specifies the requirements for stainless steel, silver plated nickel-silver (EPNS) and silver plated stainless steel cutlery. Non metals such as ceramics, woods and plastic, are included provided that they fulfil the requirements of various performance tests.

As a consequence of modern requirements, the majority of table cutlery produced in the U.K. is either in stainless steel or EPNS. Some gold plated cutlery is produced, either as a complete finish or partially to highlight silver, although these ranges tend to be produced to special order.

1.5 Electroplating Processes in Cutlery Production

1.5.1 Silver Plating

Silver was one of the first metals to be commercially deposited and in 1840 the electrodeposition of silver from cyanide baths was patented by the Elkington Brothers (9). Silver is still commercially deposited from cyanide baths despite research into non-cyanide electrolytes including those based on thiosulphate, pyrophosphate and ferrocyanides (10).

Today brightening additives are added to the electrolyte to obviate or reduce the amount of final polishing of the silver deposit. These additives can be broadly split into the following three groups; sulphur compounds, selenium or tellurium salts and antimony salts (10, 11).

The latter two classes of addition agents are known to have a profound effect on the hardness of a silver deposit. Claims are often made that silver deposits with a high hardness will possess superior abrasion resistance despite the work of Weiner (12). This work demonstrated that there was little correlation between hardness, abrasion resistance and scratch resistance on spoons silver plated from a number of commercial electrolytes.

Silver tarnishes readily when exposed to sulphur containing environments. Although the tarnish film can be easily removed using any one of many proprietary products the possibility exists that the deposits intrinsic tarnish resistance might be improved by the co-deposition of a suitable alloying addition. However, a literature survey carried out in 1976 (13) on the tarnishing of silver observed that there had been no successful development in tarnish resistant alloys. In 1984 Farr concluded following 5 years of research that the development of a tarnish resistant silver alloy by either conventional metallurgy or by electrodeposition was unlikely (14). A literature search carried out as part of the present work confirmed that there has been no further changes in this respect.

1.5.2 Gold Plating

The development of gold plating has been similar to that of silver using cyanide solutions. Acid type baths have been developed which have improved both stability and deposit characteristics. Electrolytes are available which co-deposit small proportions of alloying additions. In commercial gold baths currently used for cutlery either cobalt or nickel brightening additions are used. These additions are reported to improve the hardness, brightness and wear resistance of the deposit (15).

1.6 Imported Bronze Cutlery

The bulk of U.K. cutlery production is in a "silver" colour since gold plated cutlery is prohibitively expensive and impractical for the majority of consumers.

It is against this background that cast tin-bronze cutlery imported from Thailand has found a niche in the market place. Although of poor quality it has continued to sell, principally through mail order outlets and a limited number of department stores. Import figures for cast bronze cutlery alone are not available. However, some indication may be obtained from U.K. import statistics under the category of flatware other than precious metals and stainless steel. It can be assumed that the bulk of this figure is attributable to bronze cutlery. With this assumption, the value of imports from Thailand of bronze cutlery has been typically £200,000 per annum over the last 5 years (16).

It is likely that a superior quality British product could be produced using traditional materials with bronze plated coatings. It is anticipated that such cutlery offered in appropriate designs and suitably marketed would achieve a significant turnover.

1.7 Bronze Plating

The first thorough and systematic investigation of bronze plating solutions based on cyanide and stannate was carried out in 1936 by Baier and MacNaughton(17). Little commercial interest was shown until the 1950's when a nickel shortage in the West lead to research into possible replacement coatings particularly as an undercoat for chromium. Bronze was found to perform as well as nickel in this respect, the protective properties of bronze-chromium were considered equivalent to nickel-chromium and superior to copper-chromium coatings (18).

The use of tin-copper alloy coatings with an optimum composition of 45% Sn, 55% Cu called speculum, became established for decorative applications and for tableware. The deposit was hard, white resembling silver in colour and had a high tarnish resistance (19,20).

Despite this interest in bronze coatings during the 1950's, their use did not really become established. The main use of bronze coatings today is as a "stop-off" for components to be nitrided and for corrosion protection of mining equipment. Electrodeposited bronze has been found to offer good corrosion and wear resistance in mining environments (21).

However interest in bronze plating as an alternative to nickel has been revived largely due to the concern about nickel sensitivity. This condition is mainly confined to women and future legislation within the European Economic Community is likely to ban the use of nickel plate on jewellery and other items which come into contact with the skin (22).

Work is currently being carried out by the major suppliers to produce both yellow and white bright bronze deposits to act as direct replacements for nickel plate. Results from this work confirm that copper-tin and copper-tin-zinc coatings do not cause any allergic reactions(23).

1.7.1 Control of Bronze Deposit Composition

Commercially available bronze plating solutions are of the cyanide-stannate type. Early electrolytes were sodium salts but potassium salts are now used exclusively due mainly to their increased plating speed (21).

The basic reactions can be summarised by the following equations:

$$K_2CuCN)_3 = 2K^+ + CuCN)_3^{--} \quad \text{(i)}$$

$$Cu(CN)_3^{--} = Cu^+ + 3CN^- \quad \text{(ii)}$$

$$K_2SnO_3 = 2K^+ + SnO_3^{--} \quad \text{(iii)}$$

$$SnO_3^{--} + 3H_2O = Sn^{4+} + 6OH^- \quad \text{(iv)}$$

It can be seen that the amount of copper or tin deposited can be varied by changes in the cyanide and hydroxyl ion concentrations in the bath. By maintaining the cyanide and metal contents at a constant concentration the tin content of the deposit may be controlled by carefully monitoring the amount of hydroxide. Increasing the hydroxyl ion concentration, i.e. by making potassium hydroxide additions, depresses the dissociation of stannate resulting in less tin being deposited.

Inert anodes are usually used and these may consist of graphite, platinised titanium or austenitic stainless steel although oxygen free high purity copper is sometimes used (24). Replenishment of the metal content of the bath is carried out by carefully controlled chemical additions. In addition to the concentration of the bath constituents other important parameters which affect the deposit composition are bath temperature and plating current density. The effects of varying these parameters have been investigated by a number of workers (25, 26,27).

Increasing the temperature of the plating bath has been found to increase both the tin content of the deposit obtained and the cathode current efficiency. However a practical temperature limit of 60 to 70°C must be set to avoid relatively rapid cyanide decomposition.

Decreasing the cathode current density used was found to result in higher cathode current efficiencies by most workers but in contrast Sing and Siddhanta observed the reverse of this situation.

1.8 Technical Requirements of Cutlery

At this stage it is necessary to review cutlery materials against which the properties of cast and plated bronze products can be assessed. For convenience the properties of bronze plate will be discussed in this section.

1.8.1 Current Materials

The material and constructional requirements for table cutlery are specified in BS5577:1984 (1989) which is technically equivalent to ISO 8442. This applies to stainless steel and EPNS cutlery only.

The performance requirements for metals relate mainly to stainless steel and include corrosion, bend and hardness tests. These tests are specified to ensure that the knife blades, which are produced from martensitic stainless steel, have been suitably heat treated in order to optimise corrosion resistance, cutting edge retention and ductility.

Flatware of any alloy is required to withstand a strength test which attempts to simulate the bending stresses which may be applied in use. The test requires the item under test to withstand a specified load, dependent on size, of the item being tested, without plastically deforming it by more than 1 mm.

Two grades of EPNS cutlery are specified in BS5577 relating to a standard and special thickness. The average coating thicknesses for these grades are specified as 20 and 33 microns respectively. In addition a minimum local thickness of 60% for significant surfaces is specified. Significant surfaces are those points of the cutlery in contact with a surface when at rest. Consequently significant surfaces are the points at which wear becomes apparent.

Silver is a relatively soft metal and in its electrodeposited form has a Brinell hardness of 60 to 180 kg mm^{-2} depending on bath additions (II). In practice silver plated cutlery scratches easily and wear at the contact points may be a problem depending on how frequent it is used. Forks may exhibit wear on the backs of prongs due to the abrasive action of knife blades cutting. Spoons may exhibit regions of wear around the outer edges of the bowl due to abrasion during contact with ceramic tableware.

1.8.2 Bronze Plate

Copper-tin bronzes can be deposited in a wide variety of colours ranging from copper to white with approximate tin contents of five to twenty five per cent respectively. Gold coloured bronze deposits are attained with a tin content of about fifteen per cent (21,28).

Copper-tin-zinc bronze plating baths are commercially available from a number of suppliers. Bronzes deposited from these ternary systems have a wider range of colours than those obtained from binary systems. A composition of 75-85% copper, 13-23% tin and 2-3% zinc is reported to be a deep yellow colour (23). A bright alloy for decorative applications was developed by Westinghouse which had a composition of 55% copper, 30% tin and 15% zinc (29).

White bronzes containing approximately 45% (speculum) have been widely reported as possessing superior tarnish resistance to silver and therefore suitable for indoor decorative applications, particularly tableware (28,19,30,31,32 33). However investigations on the tarnish resistance of yellow bronzes has been relatively limited. A proprietary bronze with a composition of 75-85% copper 13-23% tin and 2-3% zinc is recommended by the supplier for food applications and others requiring tarnish and corrosion resistance (23).

The hardness of bronze deposits is largely a function of deposit composition. Lee (26) reported that deposits of about five per cent tin and a hardness of 199 VHN rising to 314 VHN at sixteen per cent tin. These results were largely in agreement with those obtained by Ramanathan (34) who recorded a maximum hardness of 520 VHN at forty two per cent tin. Menzies and Ng (25) investigated the hardness of bronze deposits with tin contents of less than twelve per cent obtained under a variety of deposition conditions. They found that hardness was not solely a function of tin content but that increasing bath temperatures at a given current density resulted in an increase in hardness.

Bronze plate with a tin content between sixteen and twenty percent would be expected to possess a hardness in excess of 300 VHN and therefore a superior wear resistance.

1.9 Objectives

The overall objective of the present work was to assess the appeal and properties of bronze plated cutlery relative to those of imported cast bronze cutlery and silver plated cutlery. It was considered that as these already have a significant share of the cutlery market then their quality could be taken as a benchmark in relationship to 'the fit for purpose' requirement of the Sales of Goods Act. In addition, it was necessary to ascertain whether or not cutlery could be bronze plated with a sufficiently consistent alloy composition thickness and colour, commensurate with the normal commercial practice.

2.0 Experimental Design

2.1 Market Survey

A survey was conducted to assess the relative appeal of various coatings and selective gold plating on table cutlery to consumers.

Two examples of imported cast bronze cutlery were included in the survey. This cutlery has found a niche in the market, providing an opportunity for consumers wishing to convey a sense of individuality.

This survey was not intended to provide a detailed analysis of consumer preferences but rather to identify those finishes suitable for further evaluation. Further details regarding the methodology involved in the survey are given below.

2.1.1 Cutlery Samples

Only table knives were used in the survey. These were preferred to flatware samples, since they enabled the visual contrast of the stainless steel blades and bronze finish to be featured. Two and three piece settings, although initially considered, were discounted on the grounds that the survey would have become static rather than mobile.

The samples used are shown in Figures 1a to c and comprised the following:

Harley pattern Hollow handle knives,

1. Gold plate
2. Bronze plate
3. Silver plate
4. Silver plate with selective gold plate
5. Red, Albrafin lacquer
6. Green, Albrafin lacquer
7. Blue, Albrafin lacquer

Monobloc Knives

8. Forged stainless steel, Overture patterned
9. Forged stainless steel, with selective gold plate,
10. Imported cast bronze, Heritage pattern
11. Imported cast bronze, Rosewood pattern

2.1.2 Survey Procedure

Visitors to CATRA's laboratories were asked to complete a questionnaire (Figure 2). Questionnaires completed by senior personnel within the cutlery industry were not included in the analysis. Interviews were also carried out at local factories and at local educational establishments. Only staff were interviewed at the latter.

2.2 Assessment of Imported Cast Bronze Cutlery

Four patterns of bronze cutlery imported from Thailand were assessed with respect to BS5577: Table Cutlery, where applicable. This cutlery has proved to be marketable and is offered for sale by various High Street retail outlets.

All four patterns were of cast bronze construction, with one pattern incorporating rosewood scales. The patterns used are shown in Figure 3.

2.2.1 Visual Assessment

Each item of cutlery was visually assessed with particular emphasis on finish, symmetry and freedom from rough unfinished edges.

2.2.2 Strength Tests

Spoons and forks were subjected to the strength test specified in BS5577 using a calibrated and NAMAS accredited test rig. During the test a force of 100 N is applied to the handle neck with the item at rest on a plane surface. The criteria for passing this test is that any permanent deformation, measured by a dial gauge, must not exceed 1mm.

The strength test specified in BS5577 for knives is intended for hardened and tempered martensitic stainless steel and was considered inappropriate for the bronze knives under consideration.

2.2.3 Dishwasher Trials

A bronze knife, fork and spoon were subjected to dishwasher trials. Although these products were not claimed to be dishwasher safe the trials were carried out to provide a comparison of the performance with those of stainless steel and EPNS cutlery. The trials were carried out using a Hoover Dishwasher model 4804 and using 2 sets of control samples as listed below.

a) Three piece stainless steel set: 17% chromium ferritic stainless steel spoon and fork. 13% chromium martensitic stainless steel forged monobloc knife.

b) Three piece EPNS set, nominal silver thickness 30 microns: EPNS spoon and fork. EPNS Hollow handle knife with 13% Chromium martensitic stainless steel blade.

Detergent powder and rinse agent were prepared, for use in the trial, as specified in BS3999: Part II. These had the following compositions and were prepared from laboratory grade reagents.

Standard Detergent

Ingredient	Formula	%Wt
Pentasodium triphosphate	$Na_5P_3O_{10}$	20
Sodium hexametaphosphate	$(NaPO_3)_6$	40
Sodium metasilicate (anhydrous)	Na_2SiO_3	30
Sodium sulphate (anhydrous)	Na_2SO_4	6
Sodium dichloroisocyanurate	$Cl_2Na(NCO)_3.2H_2O$	2
Low foaming non-ionic wetting agent		2

Rinse Agent

Ingredient	%Vol
Low foaming non-ionic wetting agent	60
Propan -2-ol	20
Water	20

The trial was conducted for 20 cycles using the intermediate wash setting. Fifteen grams of detergent powder was placed in the dispenser before each cycle. The rinse agent was added via the automatic dispenser set on the soft water setting which is the condition of the normal Sheffield domestic water supply.

Each item of cutlery was placed in the plastic cutlery basket in the dishwasher and secured using nylon cable ties. Care was taken to ensure that there was no metallic contact between individual items of cutlery which might have given rise to galvanic corrosion.

The waste water was monitored during the 10th cycle for any change in pH, which was measured using an electronic pH meter.

On completion of each wash cycle, the cutlery was removed, examined and its appearance noted.

2.2.4 Microstructural Examination

Optical microscopy was carried out using a Vickers M17 metallurgical microscope with a 35 mm camera attached. Microsections were prepared by mounting samples in thermosetting plastic resin. Grinding was carried out using 120, 240, 400 and 600 grit silicon-carbide papers. Polishing was done in three stages. The first two on rotary pads impregnated with 6 micron and 3 micron diamond compounds respectively. A napped cloth impregnated with alumina and distilled water as a lubricant was used for the final polish.

Following a number of trials to determine the best etching reagent, electrolytic etching using chromic acid solution was found to produce the best results.

2.2.5 Mechanical Properties

A 4 mm diameter tensile specimen was machined from a dessert spoon handle which appeared free from porosity. A tensile test was carried out in accordance with BS18 Category 2 procedure. Hardness tests were carried out with a NAMAS accredited Vickers Hardness machine using a 10 kg load. The reported hardnesses are the average of three measurements.

2.2.6 Chemical Composition

The chemical compositions of a bronze knife and fork were determined using Inductively Coupled Plasma Emission Spectroscopy.

2.3 Adhesion Tests

Adhesion tests were carried out on a commercially available bronze coating, Ronalloy 2N plated on both 3% nickel-silver and 17% chromium ferritic stainless steel substrate.

2.3.1 Sample Preparation

Polished coffee spoon blanks were supplied to LeaRonal Ltd and were plated to the following specifications in their laboratory:

a) Stainless steel, Woods nickel strike, 6 micron bright nickel and 15 micron bronze.

b) Stainless steel, Woods nickel strike, 3 micron bright nickel and 15 micron bronze.

c) Stainless steel, Woods nickel strike and 15 micron bronze.

d) Stainless steel, Woods nickel strike, acid activate, 15 micron bronze

e) Nickel-silver, 6 micron nickel and 10 micron bronze.

Three samples were plated to each of the above specifications. Appropriate pre-treatment and plating details are given in tables 1 and 2.

2.3.2 Test Method

A number of simple qualitative tests for adhesion exist which are used on a routine basis with production samples. The ball burnishing test is one which is applicable to a wide range of coatings and is also specified as an adhesion test for silver plate on cutlery (8).

Alternative tests involving heating and quenching the samples can lead to erroneous results because of the diffusion of elements between the substrate and coating or by the formation of intermetallic compounds. Tests based on deformation of the sample can be subjective in their interpretation.

On this basis, the ball burnish test was used as a test for adhesion. The test also has the advantage that all the test specimens are tested simultaneously under identical conditions.

The bronze plated samples were burnished in a rubber lined, rotating drum containing hardened steel balls and soap solution along with EPNS control samples. After a period of 40 minutes the samples were removed, rinsed and dried prior to examination at a magnification of 50X for blistering and or peeling plate.

2.4 Bronze Coating Composition and Coating Thickness Measurements using XRF

A significant proportion of the experimental work involved measurements using X-Ray fluorescence and its validity is first be considered.

This work was carried out using a Fischerscope XRF 1200 which is of the energy dispersive type fitted with a dedicated micro computer.

2.4.1 Operating Principles

Radiation from an X-Ray tube is collimated to achieve a high intensity beam which is directed onto a small area of the test specimen measuring 0.3 mm x 0.5 mm. Impingement of this high intensity beam onto the specimen results in the production of secondary radiation which is measured using a proportional counter. The mass per unit area of the coating and the intensity of the secondary radiation are related. This relationship is established by calibration using standards having known mass per unit area.

It is also possible for the instrument to simultaneously measure both the coating thickness and composition of simple alloys such as bronze under certain conditions.

2.4.2 Calibration for Coating Thickness Measurements on Nickel-Silver Test Specimens

Separate calibrations were carried out for each of the following bronze coatings:

Degussa Miralloy 845

Schloetter RP 13-50

LeaRonal Ronalloy 2N

Calibration for each coating was achieved over the thickness range 10 to 50 microns using plated test specimens whose coating thickness had been determined by microscopic examination of a metallographically prepared cross section. Measurement was made using a NAMAS certified eye piece graticule. As copper was present as the major element in both the coating and the substrate, calibration using the conventional copper tin procedure was not possible. Instead calibrations were carried out using the tin window only i.e., by establishing the relationship between coating thickness and secondary radiation intensity attributable to tin only. The calibration standards used for each coating were nickel silver sheet test samples plated by the respective companies to the following nominal thicknesses.

Coating	Nominal Thickness (Microns)
Degussa Miralloy 845	10, 15, 20 and 50
Schloetter RP 13-50	10, 20, 50
LeaRonal Ronalloy 2N	10, 20, 25, 30 and 50

After calibration, the thickness of each calibration standard was re-measured using the instrument to determine the accuracy. Five measurements were made on each standard and the mean value of these taken as the coating thickness.

2.4.3 Calibration for Simultaneous Thickness and Composition Measurements on Ferritic Stainless Steel

Calibration of the instrument for simultaneous thickness and composition measurements on ferrous substrates of binary copper-tin - bronze coatings is a standard procedure. However, the coating under investigation, Schloetter RP13-50, was a ternary bronze containing copper, tin and up to six percent zinc.

It was considered by Fischer Co., that accurate measurements would still be possible because the instrument would interpret the zinc signal as that of copper. This being attributable to the fact that zinc and copper "channels" are adjacent and thus allowing tin measurements to be made.

Calibration of the instrument was carried out using commercial certified and traceable thickness standards for tin on iron, copper on iron and composition standards for tin-copper. The instrument parameters were set in accordance with data supplied by Fischer as given in Table 3.

After calibration, the compositions of the bronze composition standards were remeasured by XRF. The tin contents of the 5 standards were 3.2, 5.4, 12.4, 14.8 and 25.2% respectively. Each standard was remeasured ten times and the mean of these measurements recorded. This enabled the accuracy of the instrument to be determined over the anticipated compositional range at 'saturation' thickness.

Simultaneous coating thickness and composition measurements were made on each of 5 tin-bronze plated steel reference standards. The standards had nominal tin contents of 14%. The thickness of these standards were reported as 17.6, 24.3, 29.7, 36.5 and 40.6 microns. Each standard was remeasured 10 times and the mean of these measurements recorded. This enabled the accuracy of the instrument to be determined over the anticipated thickness range for a given tin content.

Additional reference standards were produced by plating ferritic stainless steel teaspoons using the Schloetter Company Ltd bronze bath. This was carried out to determine whether or not the presence of zinc in the deposit or the stainless steel substrate had any detrimental effect on the accuracy of the thickness and composition measurements obtained. The teaspoons were plated in the pH range 12.3 to 12.8 (measured at 35°C) to obtain a series of deposits having different compositions. Twenty thickness measurements were made on the corresponding area of each sample and their mean thickness recorded. The thickness of the coatings were then measured by microscopic examination of their cross sections.

2.4.6 Comparison of Average Coating Thickness Determination by the Strip and Weigh Technique and by XRF

CATRA have established that average silver thickness determinations on spoons using XRF give comparable results to those obtained by the strip and weigh method specified in BS5577. Determinations using XRF involves thickness measurements at 4 positions on the spoon; upper and lower surfaces of the handle and the centres of the bowl. The mean of these 4 measurements are reported as the average silver thickness for that piece.

In general, the average silver thickness determined by XRF is I to 3 microns below the result obtained by stripping and weighing. This is attributable to the deposit being thicker along the edges due to current density effects at these areas.

The surface areas of spoons were determined by the Schleigal Technique as specified in BS5577. In this test spoons are coated with adhesive and weighed to an accuracy of ± 0.001 g. The spoon is then immersed in a heated fluidised bed of graded glass beads having a diameter of between 200 and 250 microns. After drying, the spoon, its surface now covered with a monolayer of glass beads is reweighed. A reference standard of known surface area is tested in parallel with the spoon. This test procedure is then repeated. The area of the spoon (A cm^{-2}) is calculated using the formula:

$$A = \frac{M}{F}$$

Where M = mean mass of beads adhering to the spoon (g)

F = mean mass of beads adhering to the reference standard (g cm^{-2}).

Three ferritic stainless steel spoons were plated using the Schloetter RP 13-50 bronze bath. Plating was carried out using the manufacturers recommended parameters to produce deposits with a coating thickness of approximately 15-20 microns.

After plating the average coating thickness was determined by the XRF method as previously described for silver. The spoon was weighed to an accuracy of 0.001 g and the coating stripped in warm nitric acid. The spoon was then reweighed and the average coating thickness (t) calculated using the expression:

$$t = \frac{M \times 10000}{A \times D}$$

Where M = loss in mass (g)

A = surface area of bronze coating (cm^2)

D = density of bronze coating

2.5 Evaluation of the Wear Resistance of Bronze Coatings

The wear resistance of bronze coatings were evaluated in relation to the wear of gold and silver coatings. Two tests were employed. One involved exposure of plated specimens to a tarnish promoting atmosphere followed by hand polishing. The second test utilised a purpose built test rig.

2.5.1 Preparation and Testing of Samples

The base material used for the wear and micro hardness tests was 3% nickel-silver with a hardness of 90HV10. The dimensions of the test specimens were 25 mm x 50 mm x 3 mm for the hardness tests and Wear Test 1 and 75 mm x 10 mm x 3 mm for Wear Test 2.

The bronze plated test specimens were plated to a nominal thickness of 10 microns and the coatings evaluated were:

Degussa Miralloy 845

Schloetter RP 13-50

LeaRonal Ronalloy 2N

Hard Gold and silver plating was done by jobbing platers to the cutlery industry using commercial plating baths. Silver was plated to a nominal thickness of 20 microns and the hard gold was plated to a nominal thickness of 5 microns on a 20 micron thick underplate of silver.

2.5.1.1 Bronze Coating Composition

Scrapings were carefully taken from each of the bronze coatings. Each sample of scrapings was weighed, dissolved in acid, diluted to a known volume and analysed using Inductively Coupled Plasma Atomic Emission Spectrometry.

2.5.1.2 Microhardness Tests

Microhardness values were obtained for the bronze and silver deposit by measurements normal to the coating surface using a Vickers indentor. The relevant test specification (35) states that "the applied force shall be such that the depth of indentation is less than one-tenth of the thickness of the coating". For bronze coatings it has been shown that hardness values are not significantly affected if the depth of indentation is less than one-eigth of the coating thickness. Loads were selected for micro-hardness testing which satisfied this latter criteria.

2.5.2 Combined Wear Test and Tarnish Test

2.5.2.1 Wear Test 1

The bronze, silver and gold plated test specimens were exposed to an atmosphere containing volatile sulphides at a constant relative humidity of 75% for 6 hours. The tests were carried out at an ambient temperature of 20°C ± 3°C. The test specimens were suspended by nylon thread, enclosed in a perspex chamber over a plate on to which thioacetamide had been sprinkled. A saturated solution of sodium acetate within the base ensured the constant humidity. The apparatus was constructed to comply with 1S04538-1978(e) (36).

Prior to testing the coating thickness of each specimen was determined by XRF at 5 positions on each side along its length and the mean coating thickness recorded. The test specimens were then placed in the chamber for a period of 6 hours. On completion of the test, the specimens were removed and vigorously hand polished for a period of one minute each. Polishing was carried out using Goddards Silver Plate Powder, an inert, abrasive polishing compound, applied with a damp Selvyt cloth.

The specimens were subjected to a total of 12 tarnishing and cleaning cycles. The coating thicknesses were remeasured after 3,6,9 and 12 cycles.

2.5.2.2 Tarnish Test

Tarnish tests were carried out in parallel with the wear tests. The degree of tarnish was visually assessed after each 6 hour period of exposure to the atmosphere containing volatile sulphides. For the tarnish assessment only, an additional specimen of solid bronze prepared from a cast bronze knife blade was included.

On completion of each 6 hour exposure period the test specimens were removed from the chamber and the degree of tarnishings was visually assessed according to the following scale and the corresponding value recorded.

1. Unaffected
2. Very slight tarnish
3. Slight tarnish
4. Moderate tarnish
5. Severe tarnish
6. Very severe tarnish

The specimens were then cleaned and the coating thickness measured as described in 2.5.2.1. The degree of tarnishing on each sample was assessed after each of the 12 cycles. The mean value was calculated from the 12 sets of values assigned to each sample to enable a comparison of the tarnish susceptibility of the coatings and solid bronze to be made.

2.5.3 Wear Test 2

The procedure used for the wear test described above, although reproducing actual conditions of use may be expected to produce varying results depending upon the person carrying out the test.

A wear test rig was designed and built to eliminate operator bias and to investigate the wear resistance of bronze coatings using a popular household cleaner JIF.

A diagram of the test rig is shown in Figure 4. The plated test specimen was clamped to a frictionless slide which was driven by a pneumatic cylinder. The test sample was reciprocated back and forwards whilst a static slide was adjustable using limit switches. Hydraulic flow regulation using Hydrocheck, a proprietary device, enabled the speed to be regulated. The adjustable wear probe was produced from hardened steel and was 12 mm in diameter. The contact surface of the probe was flat and covered in napped cloth, glued in place. Loads were applied using weights fitted to the cantilever arm. A standard load of 20 N was adopted for the tests.

The coating thickness of the test specimens was determined at the mid-length position of the wear path prior to testing the probe and test specimen immersed in JIF cleaner. The test specimen was then subjected to 1000 cycles; a cycle consisting of one forward and one reversed stroke. After 1000 cycles the test specimen was removed, cleaned and the coating thickness remeasured using XRF at the same position as before. This procedure was repeated a number of times, dependent upon the coating thickness under test, which enabled wear curves to be plotted.

2.6 Assessment of a Commercial Bronze Plating Bath

On the basis of the encouraging results of the market survey and wear tests it was decide to commission a commercial alkaline cyanide bronze plating bath with a view to producing bronze plated prototype cutlery. The bath was installed at Lathco Ltd a subcontract silver plating company.

2.6.1 Equipment and Operating Details

Six hundred litres of RP13-50 plating solution, supplied by Schloetter Company was made up from 2X liquid concentrate, diluted with de-ionised water. The solution was contained in an insulated polypropylene tank which was maintained at a rate of 2 to 3 bath volumes per hour. The filter particle retention size was 10 microns. Platinised titanium or Type 317 austenitic stainless steel anodes were specified for use with the bath. However, due to financial constraints and the unavailability of Type 317 stainless steel in the UK, Type 316 stainless steel was used as anode material.

The power supply used was a single phase rectifier with a smooth output. Current consumption was monitored using an ampere minute meter. Solution maintenance is by a 2 part replenisher system and the following maintenance rates were used, as specified by Schloetter Company, for every 5000 A min:

122 g replenisher 1
160 ml replenisher 2

Operating data specified by Schloetter Company is given in Table 4.

2.6.2 The Effect of pH on Deposit Composition

Seventeen percent chromium ferritic stainless steel teaspoons were used for these trials since their use enabled the local tin content of the deposit to be determined by XRF, thereby allowing any variation across one item to be detected.

Preliminary trials were carried out using Lathco's existing pretreatment line used to plate stainless steel. The pretreatment sequence employs a high chloride, nickel strike. Satisfactory adhesion (determined by the ball burnish test) was obtained in contrast to previous laboratory trials where it has been found necessary to use a nickel underplate.

Batches, each of 6 teaspoons, were plated using current densities in the range 2 to 2 A dm^{-2} at pH values in the range 12.2 to 12.8. The solution as initially made up had a pH of 12.8 (measured at 35°C) and this was allowed to fall as a result of plating dummy batches during which no additions of potassium hydroxide were made.

The tin content of each spoon was determined at four positions by XRF on the upper and lower surfaces of both the bowl and handle. The mean tin content of each batch was therefore calculated from 24 measurements.

As previously discussed the zinc content of the deposits could not be determined using XRF due to the proximity of the zinc and copper "channels". Therefore, the zinc content was determined by atomic absorption spectroscopy (AAS) after the stripping of the coating in warm dilute nitric acid. The zinc content was determined for one spoon taken from each batch and taken from the same plating jig position to give an indication of the zinc content for that batch.

Potassium hydroxide was added at the end of the first trial to raise the pH to its original value and the trial was repeated. Replenishers were added to the bath as required and the solution was analysed during the trials to ensure that the solution was within the specified operating parameters.

2.6.3 Effect of Current Density on Composition and Thickness Distribution at pH 12.4

The trials reported above established that the bath became relatively unstable at a pH of about 12.3. Therefore it was decided to investigate the effect of current density on the deposit composition and thickness of a bath having a pH of 12.4. it was anticipated that at this pH, samples could be plated with deposits containing the maximum tin content possible in a consistent and repeatable manner.

Four batches of 36 stainless steel teaspoons were bronze plated at current densities of 0.5, 1.0, 1.5 and 2.0 A dm^{-2} respectively. Each batch of spoons was wired and each spoon individually identified as shown in Figure 5. Each batch was plated using a nominal quantity of electricity of 1440 ampere minutes and the bath pH was maintained at a value of 12.4 by potassium hydroxide additions.

The mean bronze plate coating thickness and tin content of each spoon were determined from 4 results obtained from XRF measurements (on the upper and lower surfaces of the bowls and handles).

The mean zinc content of the deposit based on 2 spoons taken from each batch was determined by stripping of the coating using warm dilute nitric acid followed by analysis of the resulting solution by AAS. Samples for zinc determination were selected from jig positions 1 and 15 (see figure 5) from each batch. These positions were expected to be representative of high and low current density areas respectively.

A control batch of teaspoons was silver plated under normal conditions for comparison with the bronze plated batches.

2.6.4 Effect of Current Density on Cathode Current Efficiency at pH 12.4

The cathode current efficiency of the bronze bath was determined at current densities of 0.6, 1.0, 1.5 and 2.0 A dm^{-2}. Seventeen percent chromium ferritic stainless steel test specimens measuring 15 cm x 7.5 cm were used in these runs to facilitate strip and weigh tests, and XRF measurements made following the plating. Each test specimen was plated using a nominal quantity of electricity corresponding to 200 A min., measured using an ampere hour meter. The electrolyte was maintained at a pH of 12.4 (measured at 35°C) during plating.

Electrolyses were carried out using current densities of 0.6, 2.0, 1.0 and 1.5 A dm^{-2} in that order. The current densities were not used in sequentially ascending or descending order to avoid misinterpretation of results which might have been the case had a second variable depending upon bath usage been operating.

The tin content and deposit thickness of deposits were determined simultaneously using XRF. The values quoted were the mean of 20 individual measurements per test specimen. Zinc was determined by AAS after stripping of the bronze deposit in dilute nitric acid.

The test specimens were weighed before and after plating to an accuracy of ± 0.001 g using an electronic balance.

In order to ensure satisfactory adhesion of the deposit a nickel strike was used prior to bronze plating. The weight gain attributable to the nickel strike was not considered significant having been established prior to these experiments as 5 milligrams.

The cathode current efficiency was calculated by applying the formula:

$$\% \text{ Cathode Efficiency (for metal deposition)} = \frac{\text{I (theory) to deposit xg}}{\text{I (practical) to deposit xg}} \times 100$$

The method of calculating I(Theory) is shown in Appendix 1.

2.7 The Effect of Tin Content on Deposit Ductility

It is well known that the presence of intermetallic compounds can lead to brittleness of the deposits produced. As cutlery is often subject to some deformation during use it is a requirement of any coating that it be relatively ductile.

2.7.1 Test Specimens and Plating Procedure

Copper strips measuring 10 mm x 0.8 mm were cut from commercially annealed copper sheet. These strips were plated using various current densities and electrolyte pH values in order to obtain bronze deposits of 20 microns nominal thickness with tin contents ranging from 12 to 39%. The copper strips were simultaneously plated along with similar sized stainless steel strips which were used to determine the actual tin content of the deposit. It was assumed that the substrate material did not effect the tin composition of the deposits obtained using identical plating conditions.

2.7.2 Test Method

The bronze plated strips were bent by hand around a spiral bend test former which is shown pictorially in Figure 6. This technique was first described by Edwards (37) as a method for measuring the ductility of electrodeposited coatings.

The spiral of the former is described by the formula

$$r = 0.4473\, e^{0.5\theta}$$

The radius at which cracks formed during bending was noted.

Those strips on which cracking was not observed were bent around successively smaller cylindrical mandrels and the smallest diameter at which cracking did not occur was noted.

The test was carried out on three test specimens for each tin content and the mean calculated.

The percentage elongation was calculated using the equation

$$e = \frac{t \times 100}{d + t}$$

where e = percentage elongation,

t = total thickness of plated strip,

and d = diameter of smallest mandrel at which cracking does not occur.

3.0 Results

3.1 Results of the Market Survey

The results of questionnaires completed by 120 people are given in Figure 7. The main age groups interviewed were in the 18 to 25 and 26 to 35 age groups. It is envisaged that these groups are those most likely to purchase cutlery when setting up home. In addition, these age groups are likely to account for a large proportion of wedding gifts. The age distribution of respondents is shown in Figure 8.

The income groups of those interviewed are shown in Figure 9. The largest group was that of professional / managerial personnel. This group may be assumed to possess the greatest disposable income and therefore, the most likely to purchase cutlery.

The main results of the survey are shown in Figures 10 to 13 and a breakdown of overall preferences for each age group is shown in Figure 14. Silver plated cutlery was found to be the most preferred finish in each group of samples by each age group. The second most popular finish was silver with selective gold plating. The bronze plated hollow handled knife was preferred to gold, the opinions of many people being that the bronze colour was more subtle. By combining the results of the gold and bronze plate it can be seen that a considerable proportion of the sample population had a preference for a "gold" colour. The imported solid bronze knife with rosewood handle was unusual in that it attracted similar response to the most disliked and most preferred options. However, there is a clear correlation between age and preference for this design, which was preferred by the younger age groups. The coloured handles, in particular red, were generally disliked.

3.2 Assessment of Imported Bronze Cutlery

3.2.1 Visual Assessment

The cast bronze cutlery examined was free from rough unfinished edges and the overall finish was of an acceptable standard. However, the symmetry of the cutlery was generally poor and inconsistent.

All spoon bowls were asymmetric, this was more pronounced on the larger spoons.

The alignment of the knife blades with respect to their handles was poor on each of the four knives examined. These knives failed to meet the construction requirements of BS5577.

In addition, remnant machining marks were visible on each knife blade, particularly near the bolster.

3.2.2 Strength Tests

Each spoon and fork tested met the requirements of the strength tests.

3.2.3 Dishwasher Trials

The pH of the waste water from the dishwasher was found to vary during the wash cycle as follows:

Intermediate Wash Cycle (60 minutes)

Cold pre-wash	pH 7.3
50°C wash	pH 9.7
Cold rinse	pH 8.3
Cold rinse	pH 7.8
60°C final rinse	pH 7.4
Dry (30 minutes)	

The EPNS and stainless steel cutlery were completely unaffected at the end of the trial.

The bronze knife developed two small oval blemishes on the handle during the third cycle. These marks corresponded with the position where the handle had rested against the plastic cutlery basket. In addition, dark areas began to develop from the eleventh cycle on each item of bronze cutlery. At low magnification the dendritic structure of the bronze was visible within the darkened areas and the blemishes as shown in Figure 15.

The bronze cutlery was easily restored to its former polished appearance using proprietary abrasive metal cleaners.

3.2.4 Microstructural Examination

Fine interdendritic porosity was observed in some samples. Typical Microstructures taken from such samples and consisting of heavily cored solid solution and phase are shown in Figures 16a and b.

No evidence of cold working was observed in the cutlery examined. This suggests that the spoon bowls and knife blades had not been formed by stamping or rolling.

3.2.5 Mechanical Properties

The results of tensile tests are given in Table 5 together with typical properties of traditional cutlery materials. The results show that although the tensile strength of the cast bronze is comparable with nickel-silver and stainless steel, it is a much more brittle material. Hardness test results are given in Tables 6 and 7.

3.2.6 Chemical Composition

Bronze was identified as a simple binary tin-bronze with a nominal tin content of 20%. The full compositions are given in Table 8.

3.3 Bronze Plate Adhesion

The results of bronze plate adhesion tests are given in Table 9. The bronze plated nickel-silver samples were satisfactory and passed the test.

However, only bronze plated stainless steel samples with nickel underplates passed the adhesion test. The use of a Woods nickel strike resulted in the poorest adhesion, and Figure 17 shows the high degree of blistering typically found on these samples after testing.

3.4 Bronze Coating Measurements using XRF

3.4.1 Thickness Measurements on Nickel-Silver Substrates

The mean thickness measured for each coating obtained by the XRF method is given in Table 10 together with the measurements obtained by microscopical examination.

3.4.2 Simultaneous Thickness and Composition Measurements on Ferritic Stainless Steel Substrates

The results of tin measurements using XRF of the bronze composition standards are given in Table 11. The results of simultaneous coating thickness and composition measurements using XRF of the bronze plated steel reference standards are given in Table 12.

The results of thickness and composition measurements using XRF on plated stainless steel spoons are given in Table 13 together with thickness measurements obtained by the microscopic examination of metallographically prepared cross sections.

All measurements made using XRF were comparable with the quoted compositions and thicknesses and those thicknesses measured optically using a microscope.

3.4.3 Comparison of Average Coating Thickness Determination using the Strip and Weigh Technique and XRF

The results of average coating thickness determinations obtained using the strip and weigh technique and XRF on bronze plated stainless steel teaspoons are given in Table 14.

The average thickness determined by both techniques were in close agreement. The value obtained by XRF was 1.6 to 3.8 microns less than that given by stripping and weighing. This was consistent with previous comparisons carried out on silver plate at CATRA. This difference is attributable to the build up of deposit at high current density areas which is not detected by the 4 point XRF method.

3.5 Wear Resistance of Bronze Coatings

3.5.1 Bronze Coating Composition

The compositions of the coatings are given in Table 15. The Ronalloy coating was a binary bronze of similar composition to the cast bronze cutlery. The Miralloy 845 and RP13-50 coatings were ternary bronzes containing zinc. Lead was detected in Miralloy 845 and this was thought to have been introduced via the brightener system. The other bronzes had been plated from baths without brightener additions. Nickel detected in each deposit was thought to have been introduced using a bath operated with stainless steel anodes.

3.5.2 Microhardness Measurements

The microhardness of the bronze coatings are given in Table 16 together with those of silver plated from a commercial bath. Gold deposits are generally too thin for accurate hardness measurements to be made and the manufacturers claimed hardness of 150HV is used for comparison purposes in this work.

The bronzes as a group possessed the greatest hardness ranging from 292 to 324 HV 0.025 compared with 91 HV 0.015 for silver.

3.5.3 Combined Wear Test and Tarnish Test

3.5.3.1 Wear Test 1

The results are shown in Figure 18 which shows that silver possessed the poorest wear resistance and hard gold the greatest. The bronze deposits had an intermediate wear resistance and the results show a high degree of scatter.

3.5.3.2 Tarnish Test

The results of tarnish tests are shown in Figure 19. Gold was found to be completely tarnish free throughout the tests and silver was only very slightly tarnished. The bronze coatings as a group were found to be significantly more susceptible to tarnishing than the silver. However, the bronze coatings were marginally less susceptible to tarnishing than was the cast bronze.

3.5.4 Wear Test 2

The results of wear tests are shown in Figure 20 and 21. Silver was again found to possess the poorest wear resistance and hard gold the greatest. The results of this wear test for the bronze coatings showed much less scatter than those obtained by hard polishing (see Section 2.5.3).

3.6 Evaluation of a Commercial Bronze Plating Bath

3.6.1 Effect of pH on Deposit Compositions

The effect of pH on deposit composition is shown in Figures 22 to 25 and can be summarised as follows:

i) For a given pH the use of the lower current density of 1 A dm^{-2} results in higher levels of zinc and tin in deposits than at 2 A dm^{-2}.

ii) The zinc content of the deposit is reduced by plating at lower pH values for both current densities although the slope of the graph at 1 A dm^{-2} is much less than at 2 A dm^{-2}.

iii) The tin content of the deposit is increased by plating at lower pH values for both the current densities investigated.

iv) There is a linear relationship between both the tin and zinc contents with pH.

The results of plating solution analyses are given in Table 17 in the chronological order in which they were determined.

The pH values measured by Schloetter Co. differ from those determined during the trial. Measurements during the trial were made at operating temperature of 35°C whilst those measured by Schloetter Co. were at 20°C. A conversion chart was plotted from both sets of data and is given in Figure 26.

The colour of the as-deposited bronze with 7.4% tin was copper coloured and became paler with increasing tin content until at 21.7% tin the deposit appeared white. However, after buffing the white deposit took on a pale straw colour and in general the apparent colour difference across the composition range was reduced.

3.6.2 Effect of Current Density on Composition and Thickness Distribution at pH 12.4

The effect of current density on the average thickness of a batch of 36 spoons is shown in Figure 27. The effect of current density on zinc content of the deposit measured at two jig positions is shown in Fig.28. A decrease in current density was found to result in a corresponding increase in zinc content of the deposit. The zinc content of deposits from jig position 15 (i.e., low current density area) was found to be marginally greater than those from jig position 1 (i.e., high current density area) at each current density.

The effect of current density on the average tin content of a batch of spoons is shown in Figure 29. A reduction in current density was found to result in an increase in tin deposited.

Thickness measurement results for the silver plated batch of spoons were as follows:

Average thickness 14.9 microns

Min average thickness 13.1 microns

Max average thickness 17.3 microns

3.6.3 Effect of Current Density on Cathode Current Efficiency at pH 12.4

The cathode current efficiency average thickness and composition at each current density are given in Table 18. The effect of current density on efficiency is shown in Figure 30.

The cathode current efficiency was found to be at its optimum value of 54% at a current density of 1 A dm^{-2}. The average thickness measurements, as would be expected, gave a good indication of relative cathode current efficiency for each current density.

3.7 Effect of Tin Content on Deposit Ductility

The results of ductility tests are shown in Figure 31 which shows the relationship between tin content and deposit ductility. Ductility was found to be a sensitive function of tin content. Deposits with tin contents of 25% and 39% were found to be unacceptably brittle.

4.0 Discussion of Results

4.1 Market Survey

The market survey revealed that silver plated cutlery (EPNS) was the most preferred finish in each group of cutlery samples and by each age group of respondents. However, it can be seen from Figure 10 that by combining the results of gold and bronze plate a considerable proportion of the population, thirty percent, had a preference for the "gold" colour.

In addition, the bronze plated cutlery was considered aesthetically superior to gold plated cutlery due to the more subtle colour of the bronze. However, the appearance of both finishes could in practice be varied by adjusting the plating parameters.

The imported bronze cutlery was generally well received by the younger age groups reflecting the sales potential for similar bronze plated cutlery to newly married couples and young people setting up home.

4.2 Assessment of Imported Bronze Cutlery

4.2.1 Visual Assessment

The overall standard of the cast bronze cutlery was of an acceptable standard and of suitable quality. However, in comparison to traditional British cutlery the finish and general quality was poor.

4.2.2 Strength Tests

The spoons and forks tested were found to meet the requirements of the strength tests specified in BS5577. The knives were not tested to this standard as the relative strength test was devised for specific grades of martensitic stainless steel heat treated to give a minimum hardness of 560Hv 30.

4.2.3 Dishwasher Trials

The cutlery performed better than might have been expected in the dishwasher trials. The contact corrosion which occurred on the bronze cutlery during the dishwasher trials appears to have been caused by the retention of water between the cutlery and plastic basket. This resulted in interdendritic corrosion of the bronze by differential aeration.

It appears from the trial results that corrosion of bronze cutlery would be inevitable in the long term when subjected to cleaning using a dishwasher. However, if bronze cutlery was market suitably it well might find a section of buyers who are prepared to hand clean it as is the case with silver and gold plated cutlery.

4.2.4 Microstructural Examination

Areas of corrosion observed in the dishwasher trials had a dendritic structure which was subsequently confirmed by metallographic examination of the bronze cutlery.

Examination of the copper-tin equilibrium diagram (Figure 32) shows that bronzes containing more than about 1% tin at room temperature should consist of two phases α and ε. However, the eutectoid reaction $\delta \rightarrow \alpha + \varepsilon$ is only achieved by prolonged heat treatment within the temperature range 200-350°C. As a result of the sluggishness of this reaction it is possible to consider δ phase as existing at room temperature under most conditions (38, 39, 40).

The heavy coring arises as a consequence of the wide freezing range of the alloy and at 798°C the remaining interdendritic liquid peritectically reacts with α:

$$\alpha + \text{liquid} \rightarrow \beta$$

On cooling some β decomposes to α until at 568°C the remaining β decomposes:

$$\beta \rightarrow \alpha + \delta$$

Further cooling through 520°C results in the reaction:

$$\alpha \rightarrow \alpha + \delta$$

The δ phase, a brittle intermetallic, is retained under normal conditions as previously described down to room temperature.

An homogenisation treatment within the temperature range 593-787°C for several hours is required to remove or minimise the dendritic segregation in bronze castings (41). However, this is only applicable to bronzes with tin contents of 15% or less.

4.2.5 Mechanical Properties

Although the tensile strength of the cast bronze was found to be comparable to those of nickel silver and stainless steel the measured elongation of 12.5% was relatively low. The brittle nature of the bronze together with the likelihood of casting defects occurring raises the possibility of the cutlery fracturing during use, especially where the cross-sectional area is small.

4.3 Bronze Plate Adhesion

Adhesion tests on stainless steel plated in the laboratory with Ronalloy 2N revealed the necessity for a nickel underplate otherwise severe blistering occurred. However, in subsequent trials in a commercial plating shop, satisfactory adhesion of RP13-50 on stainless steel was achieved by the use of a high chloride nickel strike.

The conflicting results may be attributable to the different bronze bath formulations. However, it is more likely that satisfactory adhesion was achieved as a direct result of a more efficient, large scale pretreatment cycle in contrast to a small laboratory line.

4.4 Bronze Coating Measurements using XRF

4.4.1 Thickness Measurements on Nickel-Silver Substrates

Thickness measurements using XRF and by microscopic examination were found to be comparable for each of the bronze coatings within their respective calibration ranges. Each calibration was intended for, and only suitable for, these very specific conditions and erroneous results might be expected under different applications such as variations in the substrate or underplates used.

4.4.2 Simultaneous Thickness and Composition Measurement on Ferritic Stainless Steel.

Simultaneous thickness and composition measurements of the bronze coatings on a ferrous substrate were found to be accurate. Routine measurements of this type on binary Cu-Sn bronze coatings are a standard feature of the particular XRF instrument used in this work. The UK agents for the instruments believes that the presence of zinc up to about 8% would not have any adverse effect on the ability of the instrument to simultaneously measure the percentage tin and coating thickness.

4.4.3 Comparison of Average Coating Thickness Determination using the Strip and Weigh Technique and XRF

Four point thickness measurements on the teaspoons were found to give a rapid and reasonably accurate indication of the average thickness of bronze plate.

The absolute densities of the bronze were unknown and for comparison purposes in the strip and weigh tests average thicknesses were calculated assuming densities of 8.5 gm cm^{-3} and 8.7 gm cm^{-3}. Average thicknesses determined by the strip and weigh technique were approximately 2 to 3 microns greater than those determined using XRF. This was expected and consistent with results obtained over a number of years with silver coatings at CATRA. The apparently greater thickness being attributable to the increased coating thickness along the edges due to the increased current density at these areas. This increase in thickness is not detected using XRF as the thickness is measured only at four points on the relatively flat surfaces.

4.5 Wear Resistance of Bronze Coatings

4.5.1 Coating Compositions

The three proprietary bronze coatings tested were found to differ markedly in composition but still possessed similar "bronze" colours.

Lead was present in Miralloy 845 deposit and was thought to have been introduced via the brightener system during plating. The remaining bronzes had been plated without brightener additions because of the manufacturers fears regarding co-deposition of lead. Obviously lead is an undesirable element for articles intended for use in contact with food.

4.5.2 Microhardness Measurements

Each of the bronze coatings was found to be significantly harder than the cast bronze. Although hardness values are affected by the load used during such measurements, microhardnesses could not be carried out on the cast bronzes for direct comparisons due to heavy segregation. Miralloy 845 was found to have the greatest hardness at 324 HV .025 and this is thought to be due to this bronze being a bright deposit.

Safranek, Hespeneide and Faust (42) reported bronze deposits with tin contents of 7-15% and 17-20% Sn having Knoop hardnesses of 260-280 and 300-320 respectively. Ramanathan (34) reported DPH numbers of 300 and 350 kg mm^{-2} for bronze coatings containing 12.5% and 21% Sn respectively.

Although hardness measurements are dependent on the load and the indentor used, hardness has also been shown to be a function of deposition conditions (25, 43).

4.5.3 Combined Wear Test and Tarnish Test

The high degree of scatter in the wear measurements observed for each coating is thought to be attributable to the inconsistency of hand polishing. Despite the scatter, gold was clearly the most wear resistant coating. The particular gold tested, was a hard gold plate intended for applications where wear can be anticipated. Such gold coatings are plated from acid gold baths containing transition metal brighteners. These additions result in a finer grain size which causes the gold to appear brighter while increasing the deposits hardness and wear resistance (15).

In addition to the gold plate being by design a wear resistant coating it is also inert to the test environment and therefore unaffected by the tarnishing component of the test.

The bronzes performed similarly in the wear test and although possessing inferior wear resistance to gold were clearly superior to that of silver.

The bronze coatings were, however, visibly inferior to silver with regards to tarnishing. Of the bronze coatings Miralloy 845 was the least susceptible to tarnishing. This may be attributable to the relatively high zinc content of the deposit. This is claimed to be added specifically to enhance corrosion resistance by the manufacturer.

Significantly of the various materials tested cast bronze was found to be the most susceptible to tarnishing.

<u>4.5.4 Wear Test</u>

The benefit of using a test rig with standard conditions of stroke and load are obvious. The results obtained were much more reproducible than those obtained by hand polishing tests. As in previous wear tests, gold was again found to posses the greatest wear resistance. However, the bronzes were only marginally superior in terms of wear resistance to silver as measured by this test.

From the results of both wear tests it is reasonable to assume that bronze deposits would perform satisfactorily as a coating where applied to cutlery. The expected life of a bronze coating given the same thickness is likely to be greater than a silver coating.

4.6 Effect of Tin Content on Deposit Ductility

Increasing tin content of the bronze deposit was found to have a profound effect on the ductility, the coating becoming unacceptably brittle at twenty five percent tin. According to Raub and Sautter (44) the alpha phase in electrodeposited bronzes extends to about fifteen percent tin compared to one or two percent tin for the thermally prepared equilibrium alloy. Bronzes containing less than fifteen percent tin can therefore be expected to be ductile. However delta phase, a metastable intermetallic compound was reported in deposits with tin contents ranging from about fifteen to fifty eight percent. The brittleness of the bronze deposits containing twenty five percent tin appears to be attributable to the presence of this phase.

4.7 Optimum Plating Bath Conditions

It is necessary to operate the plating bath under optimum conditions to ensure an even as possible deposit thickness and composition across a batch. In particular, a consistent composition is desirable to avoid colour charges across a batch or even across an item of complex shape.

4.7.1 Electrolyte pH

It has been established using this bath that to obtain deposits with tin contents greater than 15% it is necessary to maintain a pH of less than 12.4 (measured at 35°C) when using a current density of 1 A dm^{-2}. However, the bath has been found to behave in an erratic manner at these low pH values. It would be necessary to develop the electrolyte formulation further before plating under normal routine production conditions could begin.

4.7.2 Current Density at pH 12.4

The effect of current density at a pH of 12.4 on thickness and composition was investigated over the range of 0.5 to 2.0 A dm^{-2}. The smallest variation in thickness measured on a batch of 36 spoons was observed on samples plated at 2.0 A dm^{-2}. This variation became progressively greater with the use of decreasing current density over the range investigated.

The tin content of the deposit was found to increase in a linear manner with decreasing current density over the range from 0.5 to 2.0 A dm^{-2}. However, in contrast to the thickness distribution, the variation in content across a batch of spoons was of a similar range at each current density.

The zinc content of the deposit was found to vary from 0.8 to 2.3% over the current density range investigated. The minimum content was observed at a current density of 1.5 A dm^{-2}. These results were significantly below that of 4 to 6% claimed by the manufacturer.

The cathode current efficiency was found to be at its optimum level of 54% at a cathode current density of 1 A dm^{-2}. An increase or decrease in current density from this value was found to markedly reduce the efficiency.

It can therefore be seen that a current density of 1 A dm^{-2} would provide the most efficient plating rate whilst maintaining a reasonable thickness and composition range.

4.8 Potential Use of Bronze Plate in Cutlery Manufacture

Desirable material properties for cutlery are strength, non-toxicity, tarnish resistance, wear and aesthetic appeal. Traditionally these have been mainly satisfied by stainless steel and electroplated nickel-silver. Coatings currently used in cutlery production are almost exclusively electroplated silver and hard gold alloys.

Solid bronze with a nominal tin content of 25% is a brittle material and this combined with the likely occurrence of casting defects may lead to an unacceptably high failure rate during service. However, the present work suggests that bronze plating of traditional materials could add to the range of cutlery available. This would possibly extend the market, and in particular, to second time buyers.

It has been demonstrated that the mechanical properties of bronze plate are comparable in terms of wear with those of silver and gold which as previously discussed are well established. The ductility whilst perhaps not so good is sufficient provided the tin content is maintained at a suitable level. In practice this is easily attained as ductility is only poor when the tin content is such that white deposits are obtained.

Although bronze is not tarnish free, the present work suggests that the tarnish resistance is sufficiently high when considered in relation to high quality cutlery. Silver plated cutlery for example is subject to tarnishing and requires frequent hand cleaning but because it is perceived as a luxury item consumers will accept the need to hand clean it from time to time. As such items tend to be used on special occasions then the disadvantage associated with hand washing and cleaning are not so great as for items used on an everyday basis.

Bronze is one of the few coloured finishes available for cutlery and it therefore adds scope for design in an industry which at present is particularly stagnant. Gold which fulfills the same objective is too expensive to allow this design feature to be exploited so well in the production of cutlery aimed at such a large sector of the public.

This work has shown that satisfactory deposits can be achieved using the RP13-50 bath on a small scale. However, before large scale production of bronze plated cutlery could begin it would be necessary to alter the formulation of the bath to maintain stability and hence colour consistency, ductility and optimum tarnish resistance.

5.0 Conclusions:

1. A significant demand for gold coloured cutlery has been identified by the market survey especially amongst younger age groups.

2. The overall standard of imported cast bronze cutlery is inferior to British cutlery produced from stainless steel and nickel silver. Bronze plating of these materials would produce stronger and more aesthetically pleasing products.

3. The wear resistance of bronze coatings plated from proprietary baths have been found to be superior to silver coatings. Therefore it is expected that for a given coating thickness the life of a bronze coating would be at least equal to that of silver.

4. The tarnish resistance of bronze is inferior to that of gold and silver. However it is anticipated that by suitable marketing techniques this would still be acceptable for luxury goods which require special care.

5. White bronze coatings with tin contents greater than twenty five percent were extremely brittle. The ductility of yellow bronze coatings containing less than twenty percent tine were judged to be ductile.

6. To achieve satisfactory deposits with tin contents between fifteen to twenty percent it is necessary to maintain an electrolyte pH of 12.4 or less. However

for the plating bath investigated this was the lowest pH at which the electrolyte remained stable.

7. The optimum cathode current density for the electrolyte at pH 12.4 was found to be 1 A dm^{-2}. Compositional and thickness variations on batches of bronze plated spoons were found to increase with decreasing current density.

8. To achieve a bronze deposit of constant composition and hence colour it would be necessary to closely control the electrolyte pH and temperature. Metal content, hydroxide and cyanide concentrations would need to be monitored, otherwise differences in colour and thickness would result between batches of work. To avoid variations across a bath it would be necessary to maintain a sufficiently high cathode current density.

6.0 Further Work

The present work has shown that to obtain bronze deposits with the required tin contents the electrolyte has to be maintained at a relatively low pH at which it becomes chemically unstable. It is anticipated that an electrolyte of the following composition would be stable and produce bronze coatings of the desired composition.

Tin	10 g/1
Copper	10 to 15 g/1
Zinc	3 g/1
Potassium Cyanide	50 g/1

The concentration of potassium hydroxide required would need to be established on site.

Although bronze coatings could be applied to traditional "Parish" patterns of cutlery the greatest potential may be on contemporary designs given the preference of younger age groups. Detailed market surveys incorporating bronze plated contemporary and traditional designs would identify any trends.

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Table 1

Manufacturers process sequences for Ronalloy 2N on stainless steel

	PROCESS SEQUENCE	TEMPERATURE	TIME	CURRENT DENSITY
1	Alkali soak clean - Ronaclean GP300	60°C	2 mins.	
2	Alkali anodic clean - Ronaclean GP300	60°C	1 min.	2 Adm^{-2}
3	Rinse			
4	Acid activate - Activator No 2	Ambient	2 mins.	
5	Rinse			
6	Nickel strike - Woods nickel strike	Ambient	3 mins.	2 Adm^{-2}
7	Rinse			
8	Acid activate - Activator No 2	Ambient	2 mins.	
9	Rinse			
10	Bright nickel plate - Spectronal	60°C	(a) 6 mins. - 3 um. (b) 12 mins. - 6 um.	3 Adm^{-2}
11	Rinse			
12	Bronze plate - Ronalloy 2N (no brightener)	50°C	60 mins. - 15 um.	1 Adm^{-2}
13	Rinse			
14	Dry			

NOTE

Samples (a) plated with stages 1-7 and 10B-14
Samples (b) plated with stages 1-7 and 10A-14

Samples (c) plated with stages 1-7 and 12-14
Samples (d) plated with stages 1-9 and 12-14

Table 2

Manufacturers process sequence for Ronalloy 2N on nickel-silver

PROCESS SEQUENCE	TEMPERATURE	TIME	CURRENT DENSITY
1 Alkali soak clean - Ronalloy GP300	60°C	1 min.	
2 Cathodic alkali clean - Ronalloy GP300	60°C	2 mins.	3 Adm^{-2}
3 Rinse			
4 Activate - Activator No 2	Ambient	1 min.	
5 Rinse			
6 Nickel plate - Spectronal	60°C	9 mins. - 6 um	3 Adm^{-2}
7 Rinse			
8 Bronze plate - Ronalloy 2N (no brightener)	55°C	20 mins. - 10 um	2 Adm^{-2}
9 Rinse and dry			

Table 3

Fischerscope XRF instrument parameters for simultaneous bronze composition and thickness measurements

Element	Density ($g\ cm^{-3}$)	Region of Interest*		Normalisation Time (s)	Measurement Time (s)
		Lower Limit	Upper Limit		
Tin Copper	7.30 8.93	155 55	233 79	120	20

*NOTE

The region of interest is the energy range used for counting purposes.

Table 4

Operating parameters of RP 13-50 solution as specified by the supplier

	Operating Parameters	
	Optimum	Range
Tin (g/1)	9	(7 - 11)
Copper (g/1)	18	(15 - 21)
Zinc (g/1)	3	(2 - 4)
Potassium Cyanide (g/1)	40	(35 - 45)
Potassium Hydroxide (g/1)	10	(8 - 15)
pH (at 20°)	-	(12.5 - 13.0)
Temperature (°C)	35	(33 - 37)
Cathode C.D. (A/dm^2)	2	(1.5 - 2.5)

Table 5

The mechanical test results of cast bronze and typical properties of traditional cutlery materials

Sample/Material	0.1% Proof N mm^{-2}	0.2% Proof N mm^{-2}	0.5% Proof N mm^{-2}	Max. Stress N mm^{-2}	Elongation %	Reduction of Area %	Vickers Diamond Hardness kg mm^{-2}
Bronze Handle	296	328	374	682	12.5 (On 20 mm)	20.6	215
10% Nickel-silver Sheet Typical annealed Typical hard work	 100 600	 - -	 - -	 350 690	 65 5	 - -	 70 210
Type 304 Stainless Sheet Typical annealed	-	265	-	600	55	-	155

Table 6

The hardness of bronze forks and spoons

Item		Vickers Diamond Hardness kg mm^{-2}	
		Handle	Bowl/Bosom
"Heritage"	Dessert Fork	195	206
	Dessert Spoon	230	215
"Hexagonal"	Dessert Fork	182	195
	Dessert Spoon	209	209
"Bamboo"	Dessert Fork	209	222
	Dessert Spoon	215	188
"Rosewood"	Dessert Fork	206	192
	Dessert Spoon	228	240

Table 7

The hardness of bronze knives

Item	Vickers Diamond Hardness kg mm^{-2}	
	Handle	Blade
"Heritage" Knife	288	232
"Hexagonal" Knife	230	209
"Bamboo" Knife	215	204
"Rosewood" Knife	215	215

Table 8

The chemical composition of bronze cutlery

Item	Composition %										
	Cu	Sn	Zn	Pb	Ni	Fe	Sb	As	Bi	P	Cd
Bamboo Knife	78.2	20.6	0.14	0.04	<0.05	0.06	0.01	0.02	<0.01	<0.01	0.002
Hexagonal Fork	80.1	19.2	0.02	0.04	<0.05	0.07	0.02	<0.01	<0.01	<0.01	<0.002

Table 9

The results of adhesion test on bronze plated samples

SAMPLE	AS PLATED APPEARANCE	APPEARANCE AFTER BALL BURNISHING
Ronalloy 2N/Stainless Steel (a)	Satisfactory	Satisfactory
Ronalloy 2N/Stainless Steel (b)	Satisfactory	Satisfactory
Ronalloy 2N/Stainless Steel (c)	Slight random blistering	Badly blistered along edges and about handle neck
Ronalloy 2N/Stainless Steel (d)	Slight random blistering better than (c)	Additonal random blistering but less than (c)
Ronalloy 2N/Nickel-Silver (e)	Satisfactory	Satisfactory

Table 10

Comparison of local bronze thickness measurements on nickel-silver substrates using XRF and by microscopical measurement of microsections.

Sample	Nominal Thickness (microns)	Local Coating Thickness (microns)	
		Microsection	XRF
Miralloy 845	10	10.0	10.5
	15	14.8	14.2
	20	19.5	18.4
	50	43.8	46.3
RP 13-50	10	8.7	8.3
	20	17.0	16.2
	50	38.9	38.1
Ronalloy 2N	10	10.5	10.4
	20	23.3	22.7
	25	26.6	25.7
	30	31.7	30.7
	50	51.5	48.4

Table 11

Tin measurements on solid bronze reference standards using XRF

Tin Content of bronze std. (%)	Tin content using XRF (10 measurements) %	
	Mean	Std Deviation
3.2	3.0	0.2
5.4	5.1	0.3
12.4	11.2	0.4
14.8	14.7	0.4
25.2	24.8	0.4

Table 12

Coatings thickness and composition measurements made simultaneously by XRF on bronze plated steel reference standards

Bronze plated steel reference standards	Measurements using XRF Mean of 10 measurements	
Thickness (microns)	Thickness (microns)	Tin (%)
17.6	17.9	13.7
24.3	23.2	15.4
29.7	30.8	13.7
36.5	33.9	13.8
40.6	39.2	13.4

Table 13

Coating thickness and composition measurements made simultaneously using XRF on ferritic stainless steel

Measurements using XRF 20 measurements				Measurements by microscopical examination of cross section
Thickness (microns)		Tin (%)		Thickness (microns)
Mean	Std Deviation	Mean	Std Deviation	
18.7	0.3	8.8	0.2	18.2
12.7	0.2	10.8	0.2	13.0
22.8	0.5	15.0	0.1	21.8
18.9	0.3	22.6	0.3	18.5
13.9	0.9	39.2	0.4	13.0

Table 14

Comparison of average coating thickness determination of bronze plated spoons by the stripping and weigh and XRF methods

Average Thickness of Bronze Deposit on Teaspoon (microns)			% Sn
Strip and Weigh		XRF 4 Point Measurement	
Density 8.7 g cm^{-3}	Density 8.5 g cm^{-3}		
23.8	24.4	20.6	10.8
15.8	16.2	14.7	10.0
21.0	21.5	19.9	13.7

Table 15

The compositions of bronze coatings

Coating	Composition %			
	Cu	Sn	Zn	Others
Degussa Miralloy 845	73.5	13.0	12.5	0.3 Pb 0.7 Ni
Schloetter RP13-50	91.0	7.0	2.0	0.6 Ni
Lea Ronal Ronalloy 2N	79.7	20.3		0.9 Ni

Table 16

The microhardness of silver, gold and various bronze coatings

Coating	Mean Microhardness
Degussa Miralloy 845	324 HV 0.025
Schloetter RP13-50	306 HV 0.025
Lea Ronal Ronalloy 2N	292 HV 0.025
Silver	91 HV 0.015
Hard Gold (0.15% Ni)	150 HV (Manufacturers claimed hardness)

Table 17

The results of solution analyses made on samples taken from the bronze plating bath

	Operating Parameters	Analysis Results (in order of sampling)			
Tin	9 g/1 (7 - 11)	7.8	8.3	8.8	9.4
Copper	18 g/1 (15 - 21)	17.2	16.6	16.3	19.1
Zinc	3 g/1 (2 - 4)	3.4	3.3	3.3	3.3
Potassium Cyanide	40 g/1 (35 - 45)	40.4	41.6	41.9	37.7
Potassium Hydroxide	10 g/1 (8 - 15)	0.4	0.3	0.00	0.6
Potassium Carbonate		8.3	6.9	6.9	18.0
pH (at 20°C)	12.5 - 13.0	13.1	12.9	12.6	13.2
pH (at 35°C)		12.6	12.4	12.2	12.7
A mins.		73060	105957	138172	194879

Table 18

The cathode current efficiency, average thickness and composition of bronze deposits at different current densities.

Current Density (A dm^{-2})	Cathode Current Efficiency (%)	Average Thickness (microns)	Deposit Composition (Wt %)		
			Zn	Sn	Cu (balance)
0.6	49	14.2	1.44	15.90	82.66
1.0	54	15.6	0.91	15.11	83.98
1.5	49	13.1	0.86	13.46	85.68
2.0	29	8.7	0.98	11.40	87.62

Figure 1a — Electroplated hollow handle knives.

Top to bottom: Gold, gold on silver, bronze, silver
(Original in colour)

Figure 1b — Hollow handle knives finished in Albrafin lacquer.

Figures 1a and 1b — Hollow handled knives used in the market survey.
(Original in colour)

Figure 1c Monobloc knives used in the market survey.

Top to bottom: Imported bronze, imported bronze with rosewood handle, stainless steel, gold on stainless steel
(Original in colour)

Select a knife from each group which you would most like to own on the basis of colour finish only.

Hollow handle knives

1. Gold ☐ Bronze ☐

2. Silver ☐ Silver/Gold ☐ Gold ☐ Bronze ☐

3. Silver ☐ Silver/Gold ☐ Gold ☐ Bronze ☐ Red ☐ Green ☐ Blue ☐

Monoblock handle knives

4. Stainless steel ☐ Stainless steel/Gold ☐

5. Stainless steel ☐ Stainless steel Gold ☐ Imported Bronze ☐

6. Imported Bronze ☐ Rosewood ☐

7. Of all the knives which did you prefer the most ?

8. Of all the knives which did you dislike the most ?

9. Are you 18-25 ☐ 26-35 ☐ 36-45 ☐ 46-55 ☐ 56-65 ☐ Over 65 ☐

10. Do you own a dishwasher ?

Yes ☐ No ☐

11. Are you employed within the cutlery industry or have any connection with the cutlery industry ?

Yes ☐ No ☐

12. Is the majority of your household income earned from:

Manual employment ☐ Trade ☐ Professional/ Managerial work ☐ Are you retired ☐

Figure 2

Format of the questionnaire used in the market survey.

Figure 3

The patterns of imported cast bronze cutlery which were assessed.

Top to bottom: Contemporary, hexagonal, rosewood, bamboo
(Original in colour)

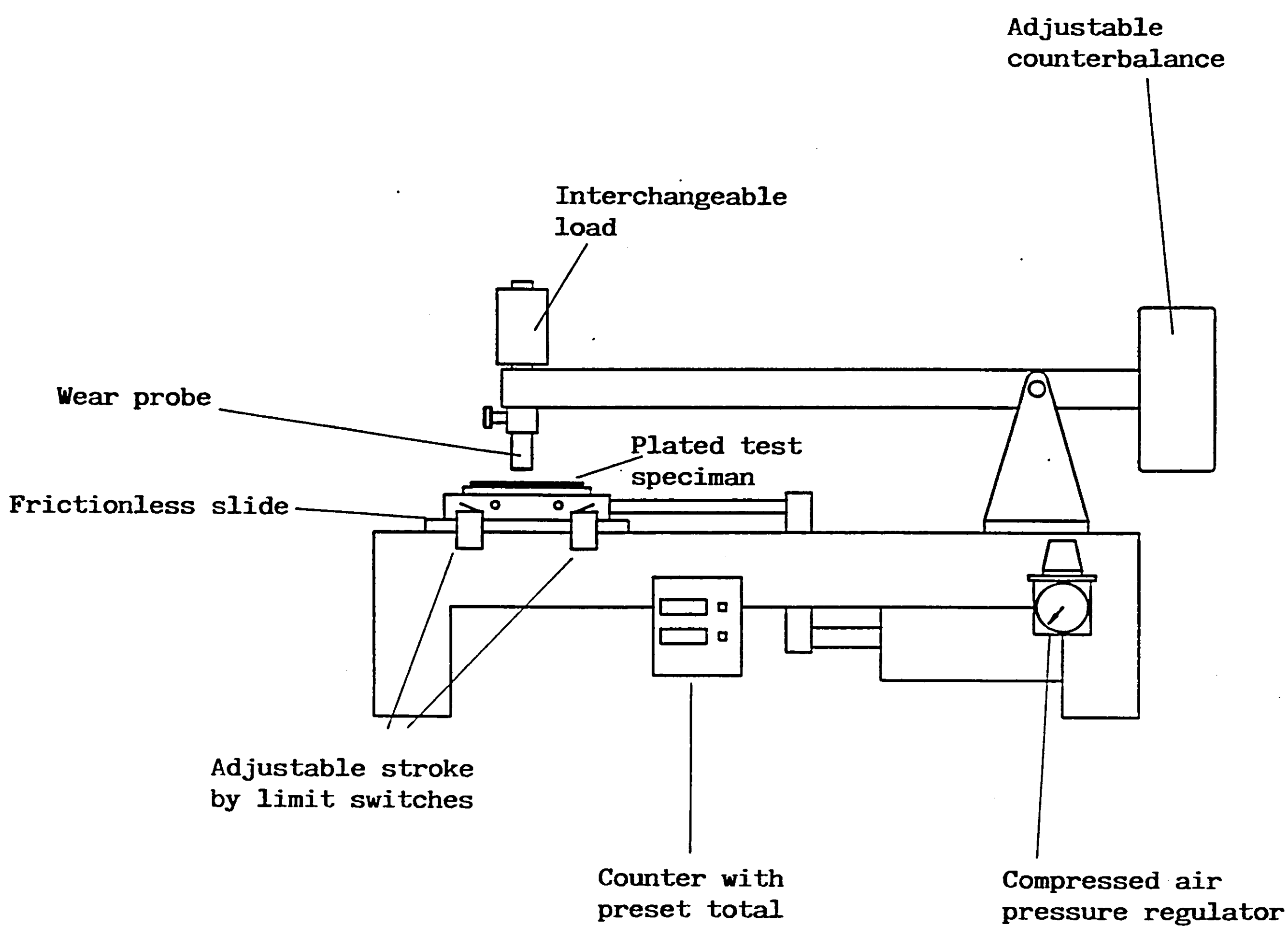

Figure 4

Diagram of wear test apparatus.
(Conditions used were, 20 N load and 25 mm sec^{-1} stroke speed)

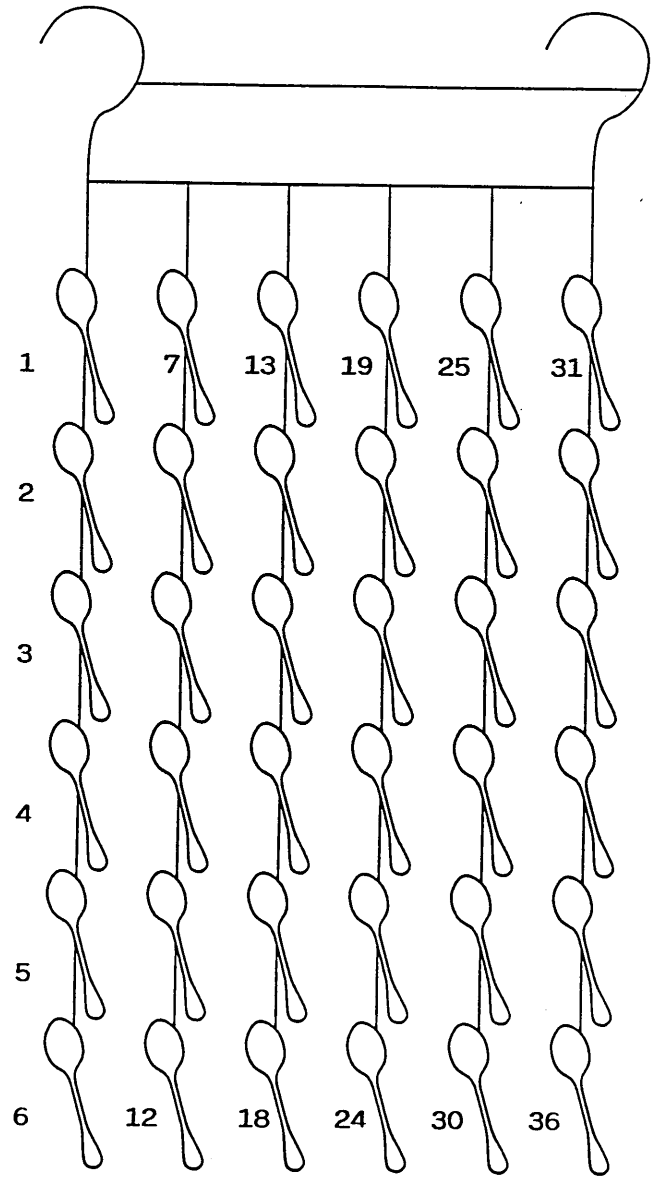

Figure 5

Wiring configuration of each batch of teaspoons adopted during plating.

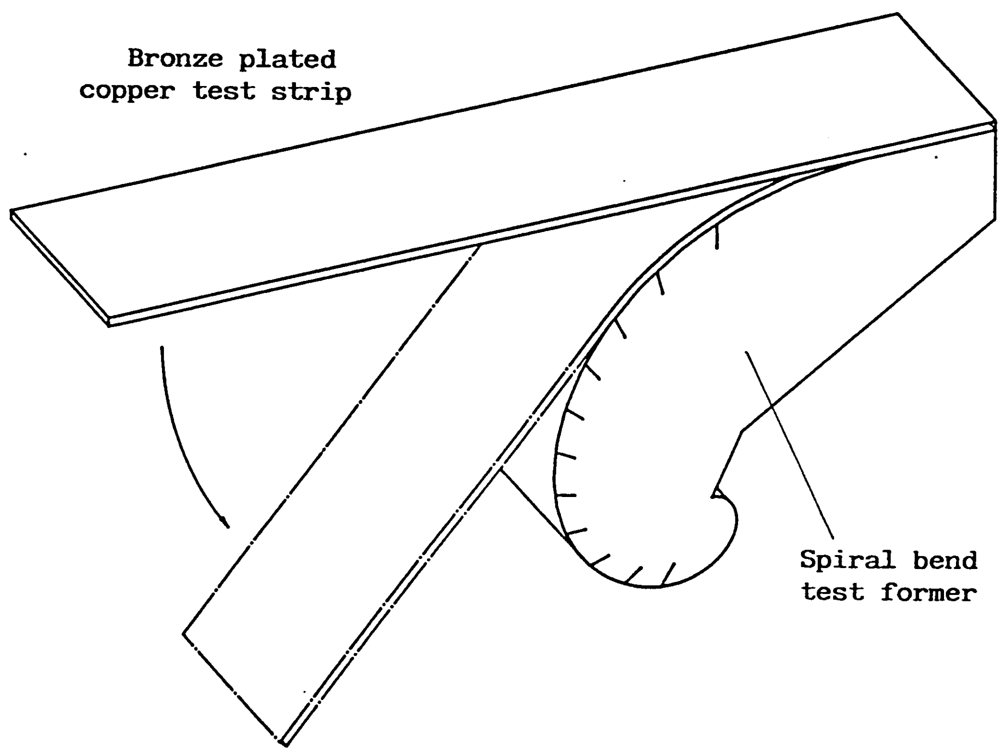

Figure 6

Diagram showing spiral bend test former used to measure the ductility of bronze coatings with different tin contents.

Select a knife from each group which you would most like to own on the basis of colour finish only.

Hollow handle knives

1. Gold 35 Bronze 65

2. Silver 47.5 Silver/Gold 22.5 Gold 10 Bronze 20

3. Silver 43 Silver/Gold 17 Gold 9 Bronze 17 Red 1 Green 4 Blue 9

Monoblock handle knives

4. Stainless steel 68 Stainless steel/Gold 32

5. Stainless steel 53 Stainless steel Gold 18 Imported Bronze 29

6. Imported Bronze 44 Rosewood 56

7. Of all the knives which did you prefer the most ?

8. Of all the knives which did you dislike the most ?

9. Are you

18-25	26-35	36-45	46-55	56-65	Over 65
27	27	14	17	10	5

10. Do you own a dishwasher ?

Yes 12 No 88

11. Are you employed within the cutlery industry or have any connection with the cutlery industry ?

Yes 34 No 66

12. Is the majority of your household income earned from:

Manual employment 28 Trade 6 Professional/ Managerial work 63 Are you retired 3

Figure 7

Questionnaire showing overall response to survey (%)

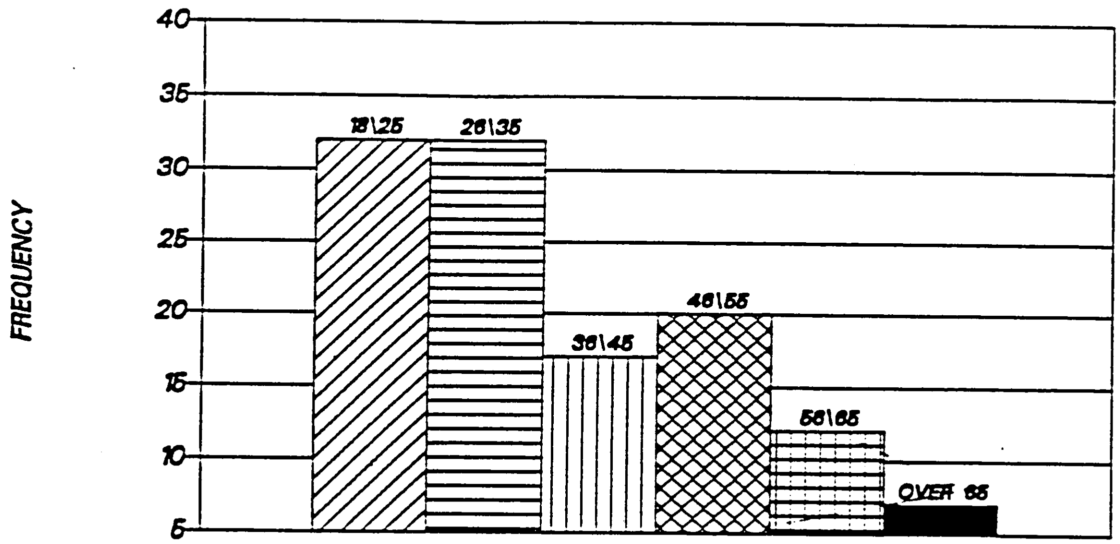

Figure 8

The age distribution of respondents to the market survey questionnaire.

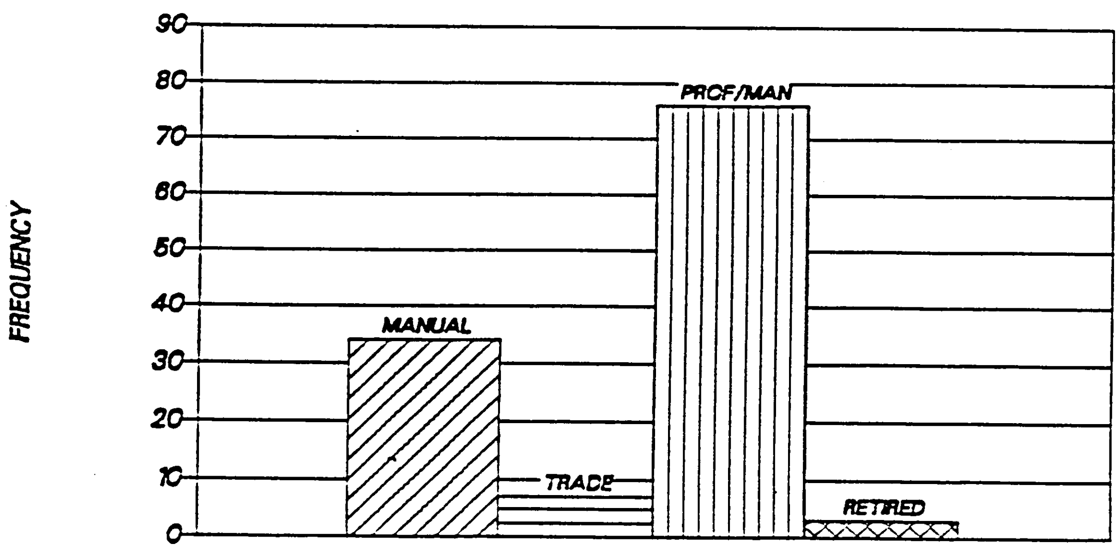

Figure 9

The classification of respondents to the market survey questionnaire by type of occupation and income.

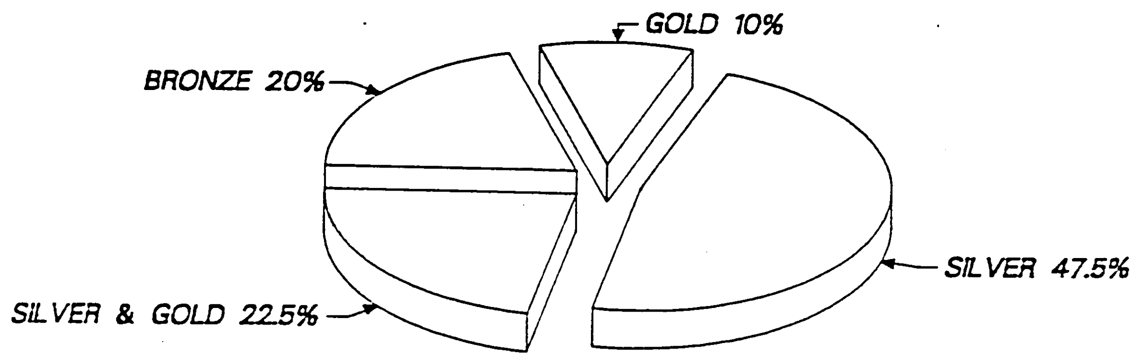

Figure 10

Pie chart showing percentage breakdown of response to question number 2 of the market survey questionnaire. The preferences of the sample population between electroplated hollow handles.

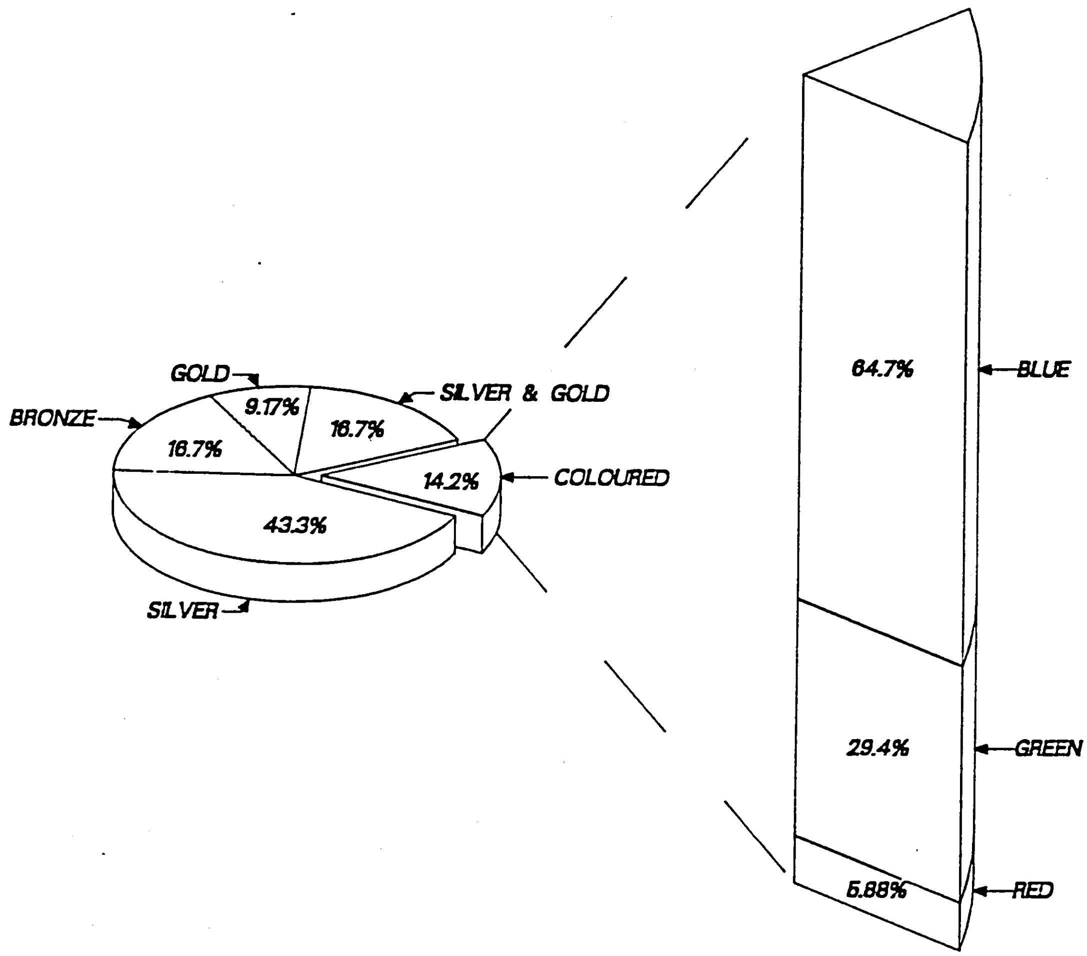

Figure 11

Pie - bar chart showing percentage breakdown of response to question number 3 of the market survey questionnaire. The preferences of the sample population between electroplated and coloured hollow handle knives.

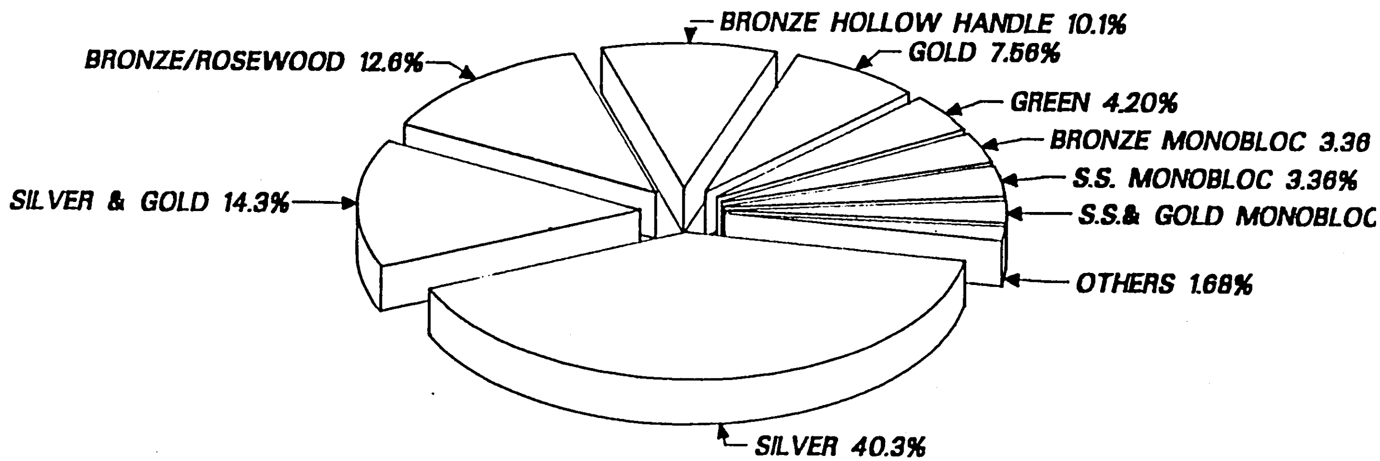

Figure 12

Pie chart showing percentage breakdown of response to question number 7 of the market survey questionnaire. The preferred finish of all sample knives used in the survey.

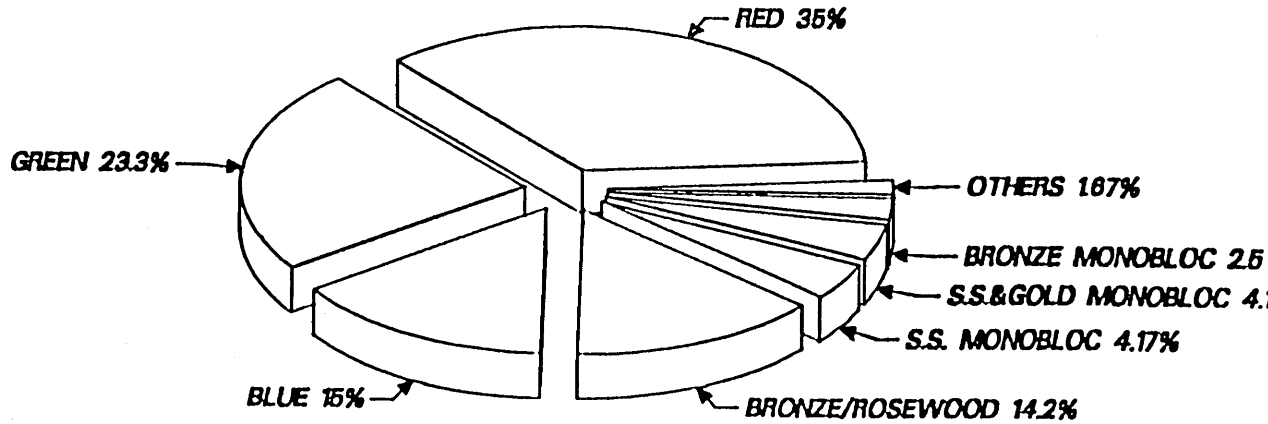

Figure 13

Pie chart showing percentage breakdown of response to question number 8 of the market survey questionnaire. The most disliked finish of all sample knives used in the survey.

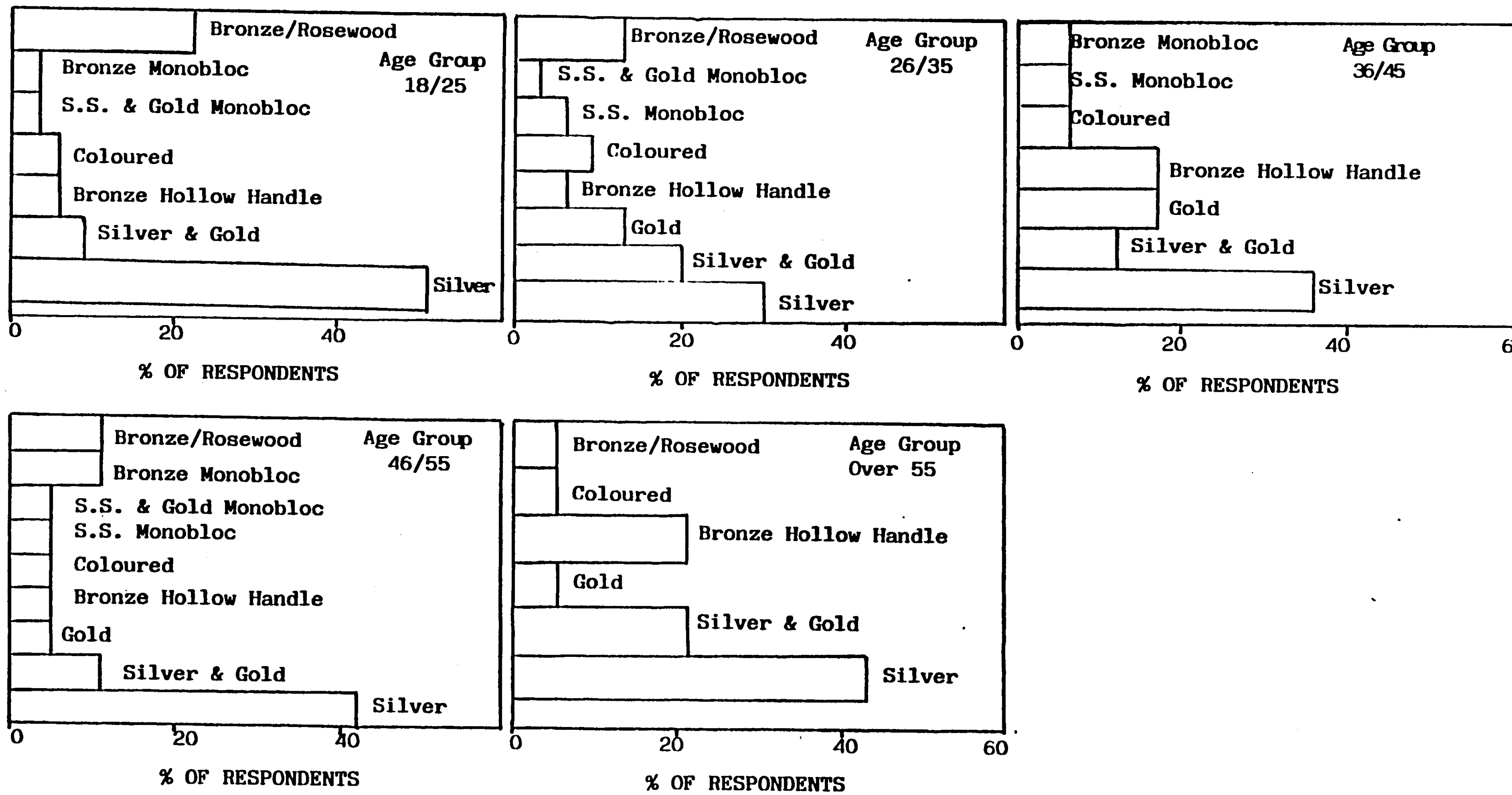

Figure 14

Bar charts showing percentage breakdown of response to question 7 of the marketsurvey questionnaire by various age groups. The preferred finish of all sample knives used in the survey.

Figure 15

Surface appearance of cast bronze knife handle after the dishwasher trial. Magnification X25.

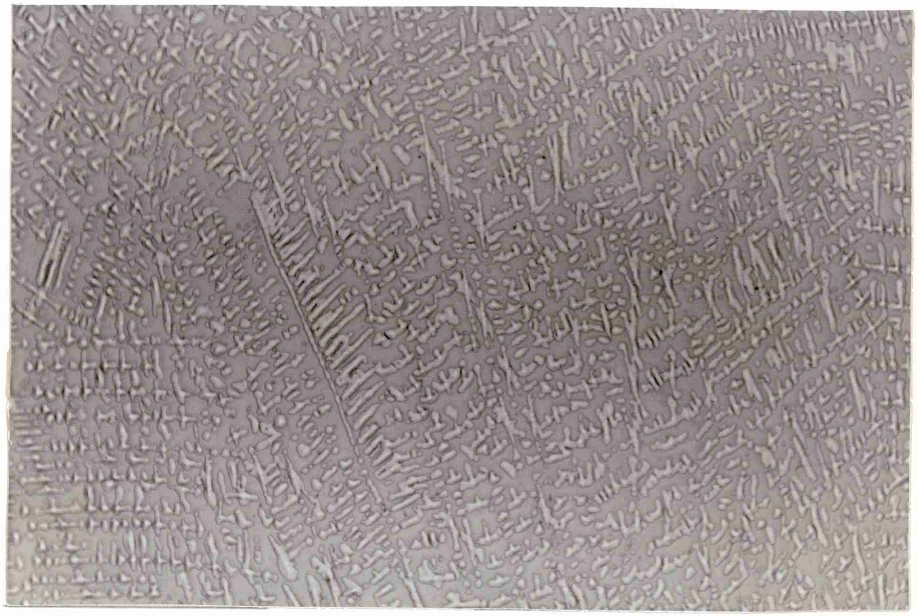

Figure 16a Transverse microsection prepared from cast bronze handle. Magnification X45.

Figure 16b Longitudinal microsection prepared from cast bronze handle. Magnification X45.

Figures 16a and 16b Microstructures of cast bronze. Electrolytic etch in chromic acid solution.

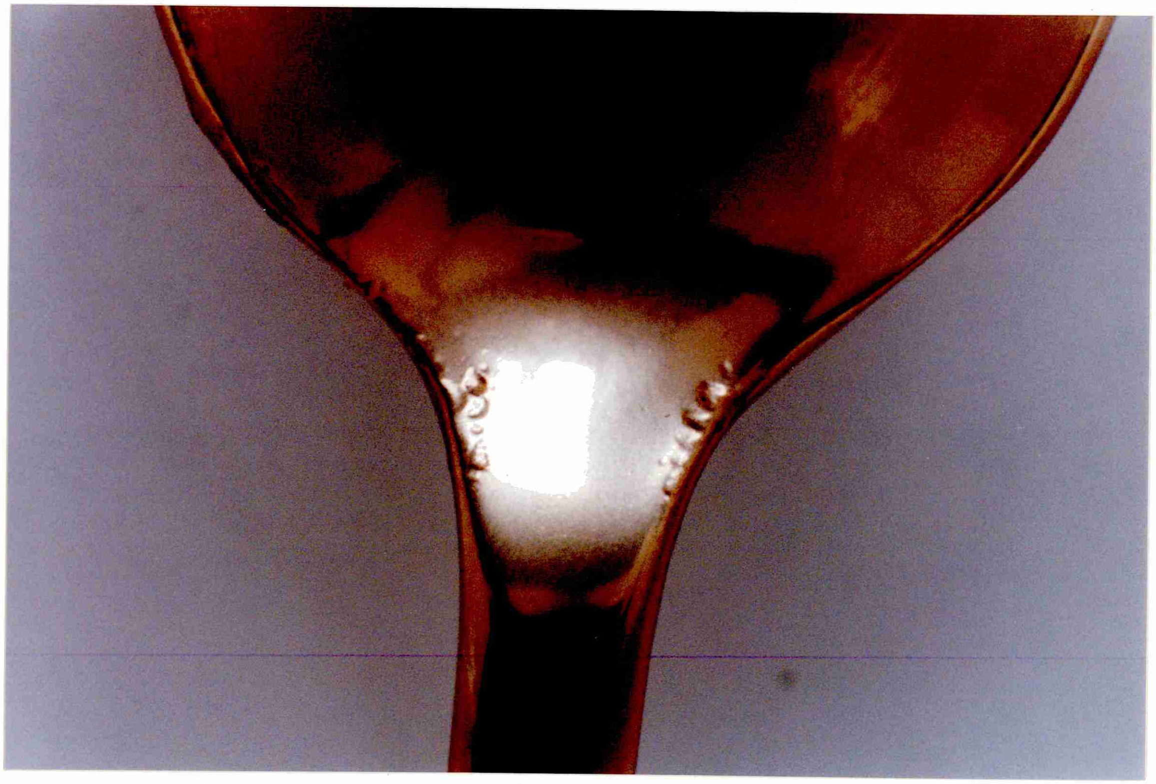

Figure 17

Blistered areas of bronze plate after the adhesion test.
(Original in colour)

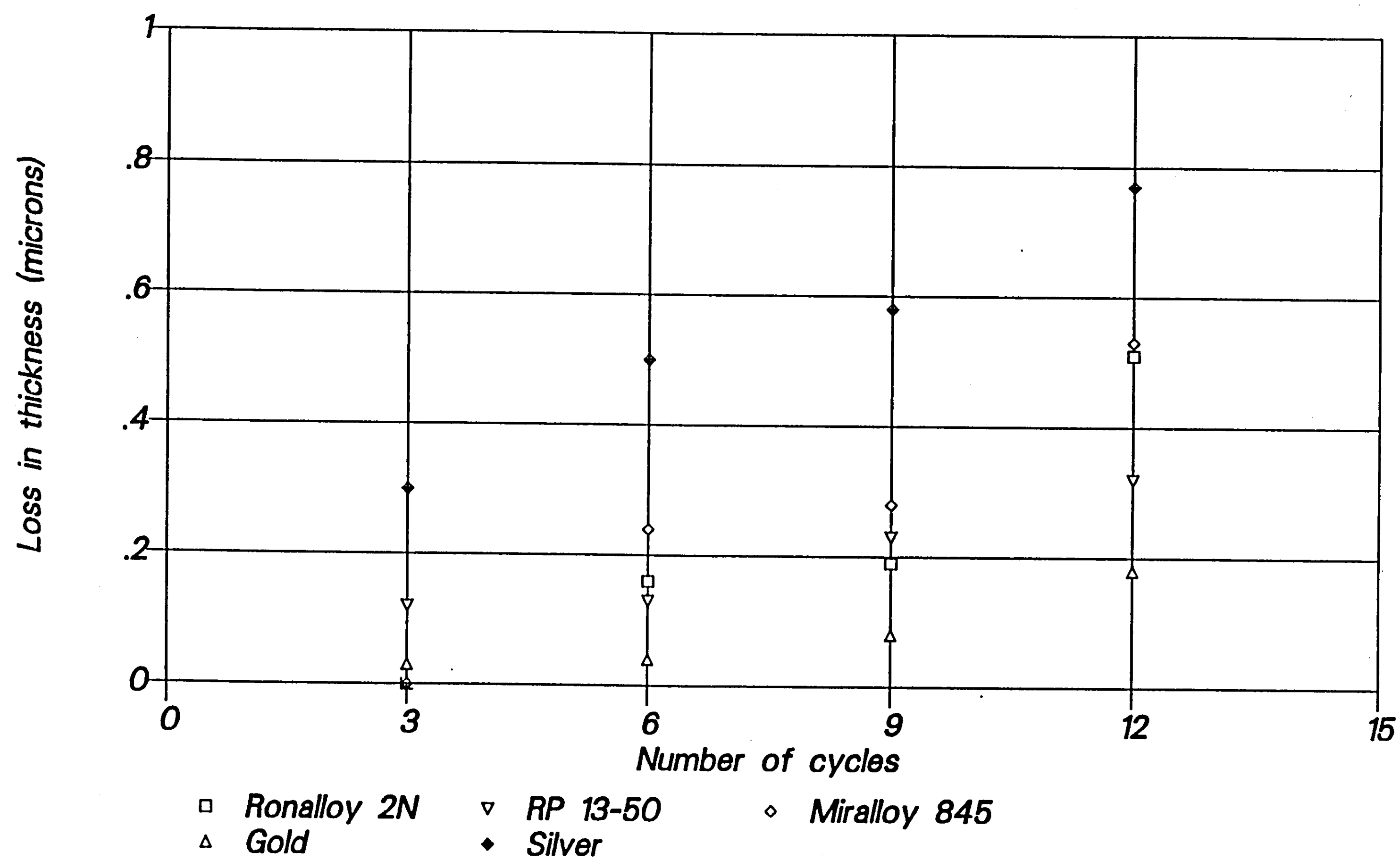

Figure 18

Comparison of wear rates for gold, silver and bronze coatings by hand polishing. One cycle consisted of hand polishing after a 6 hour test duration in the thioacetamide chamber.

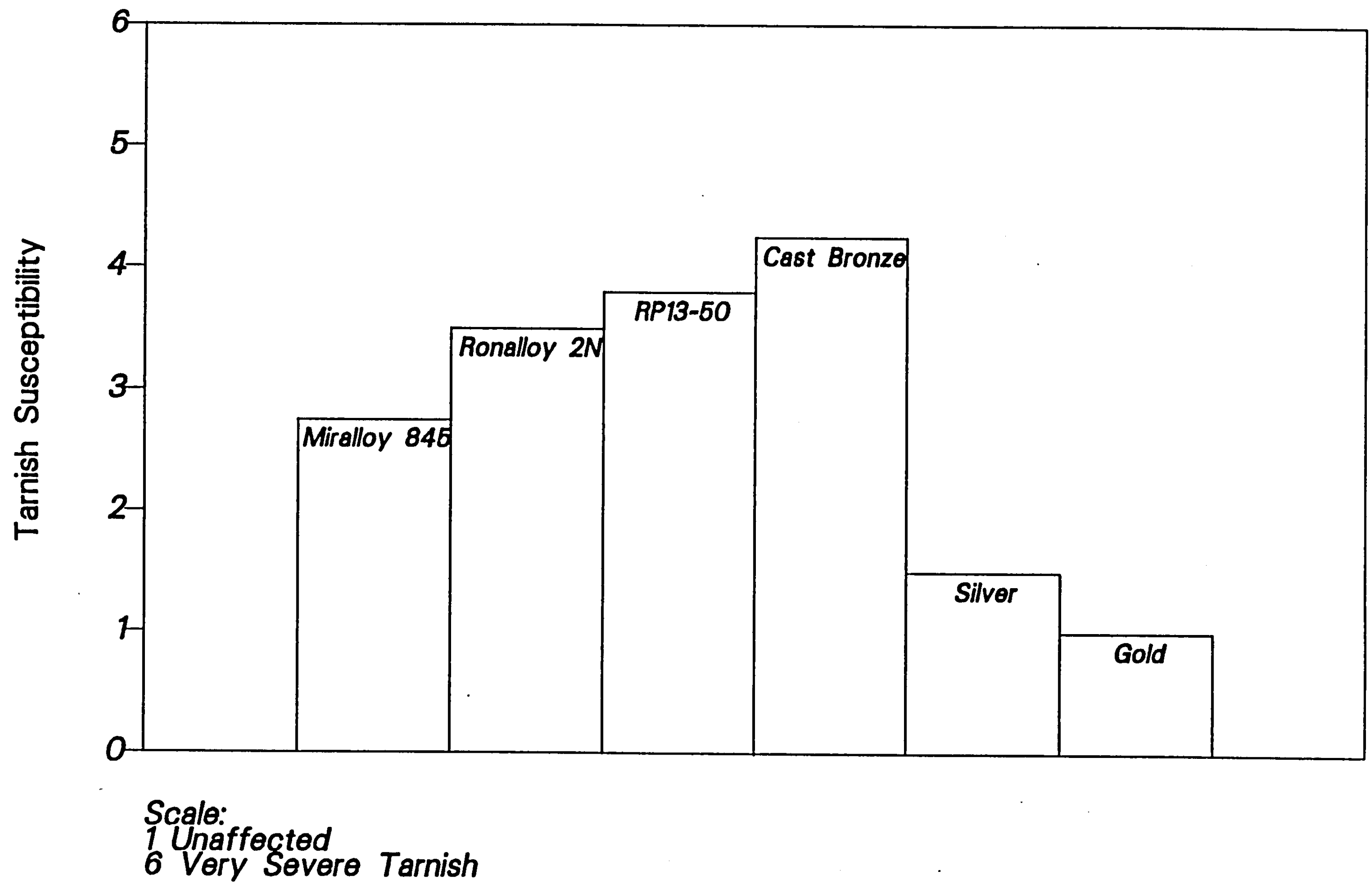

Figure 19

The results of tarnish tests carried out in the thioacetamide chamber. (The tarnish susceptibility rating is the mean of 12, 6 hour, cycles).

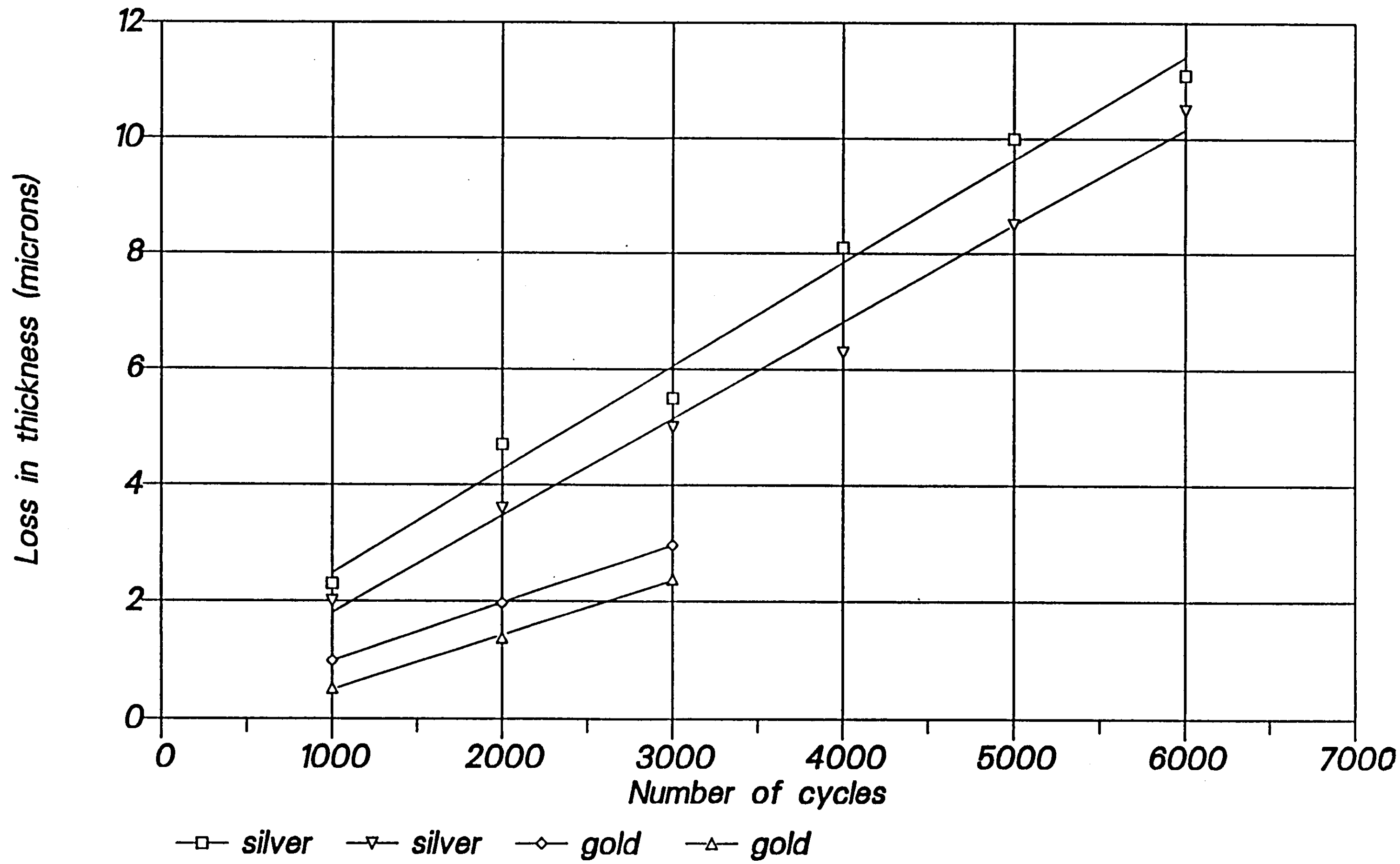

Figure 20

Comparison of wear rates for gold and silver, plated from commercial baths, using the wear test rig.

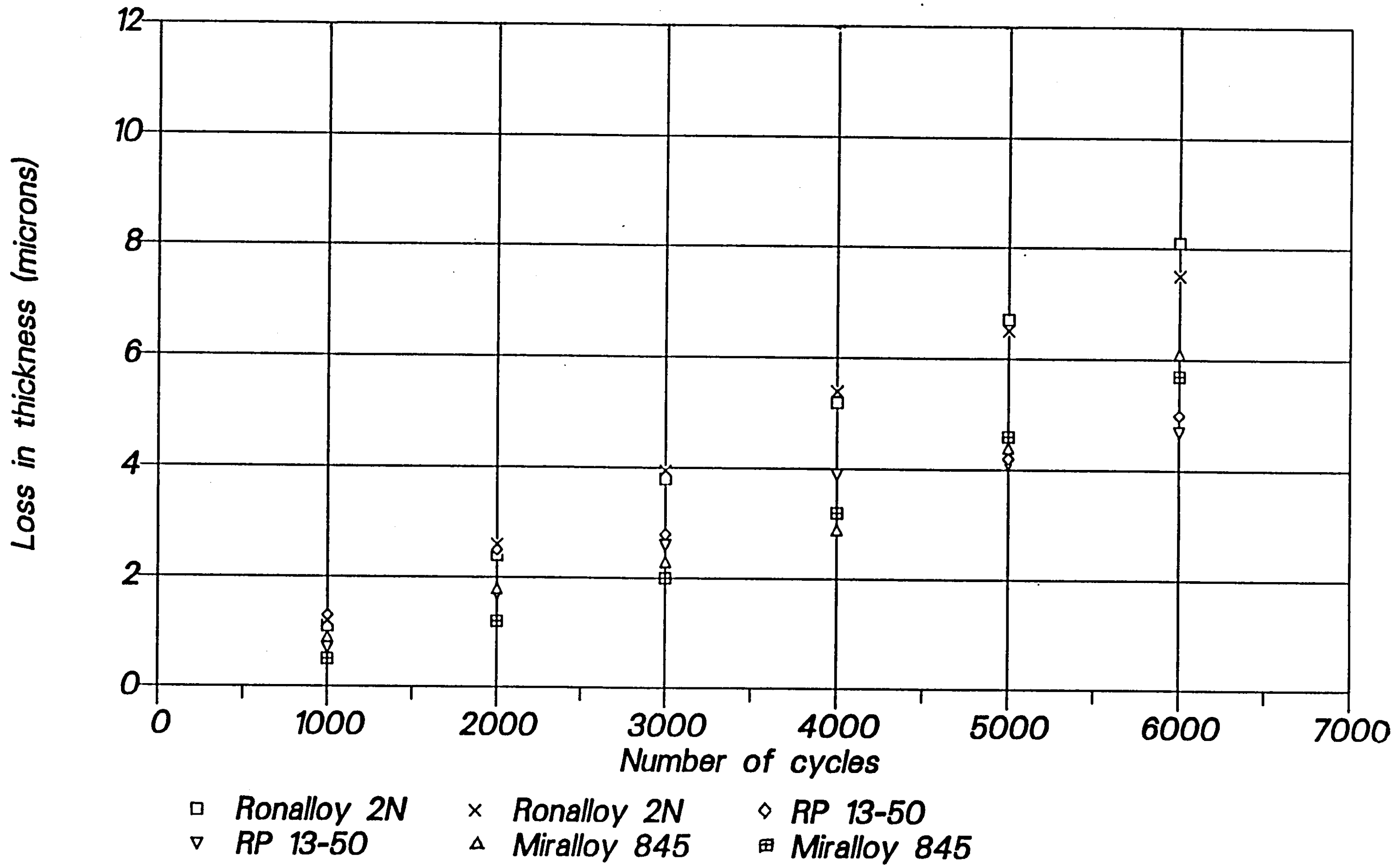

Figure 21

Comparison of wear rates for bronze coatings, plated from commercial baths, using the wear test rig.

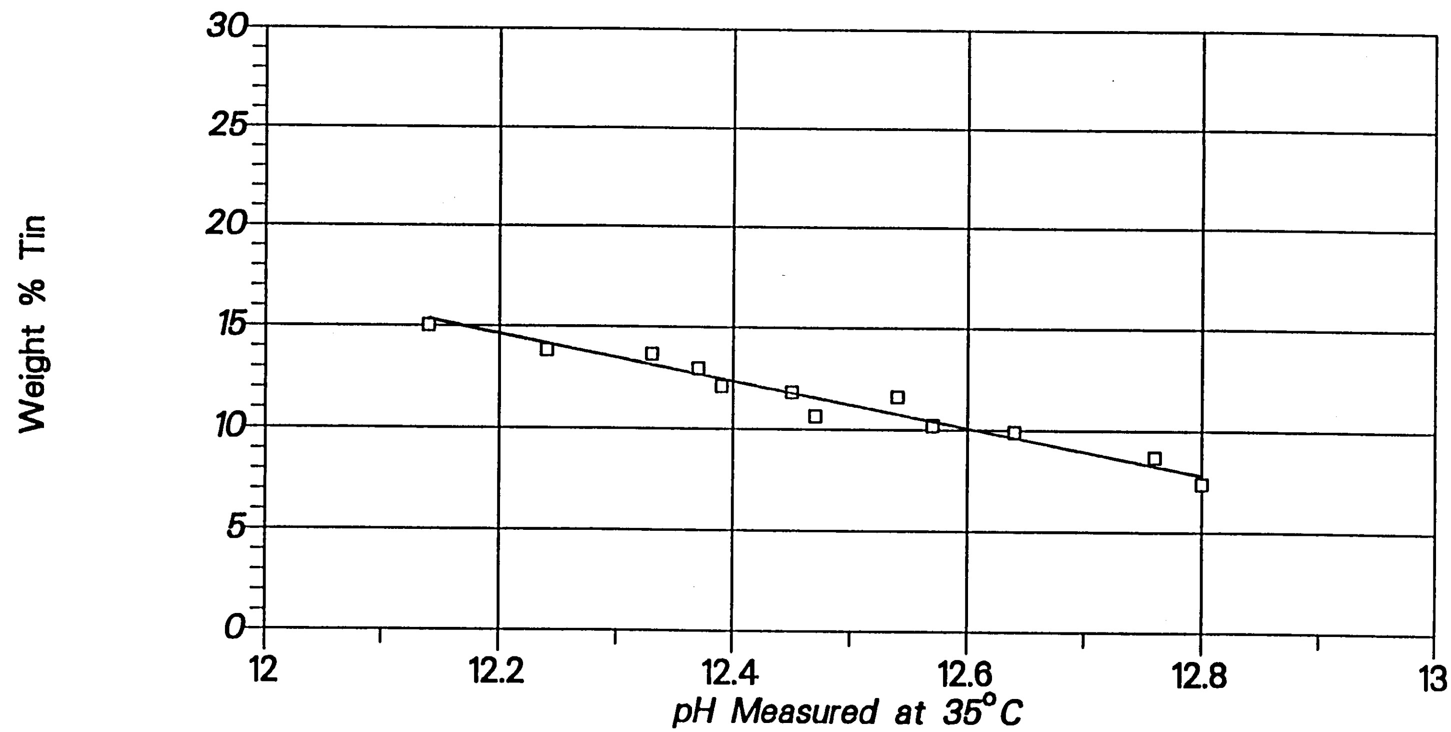

Figure 22

The effect of pH on the tin content of the bronze deposits obtained at a current density of 2 A dm^{-2}

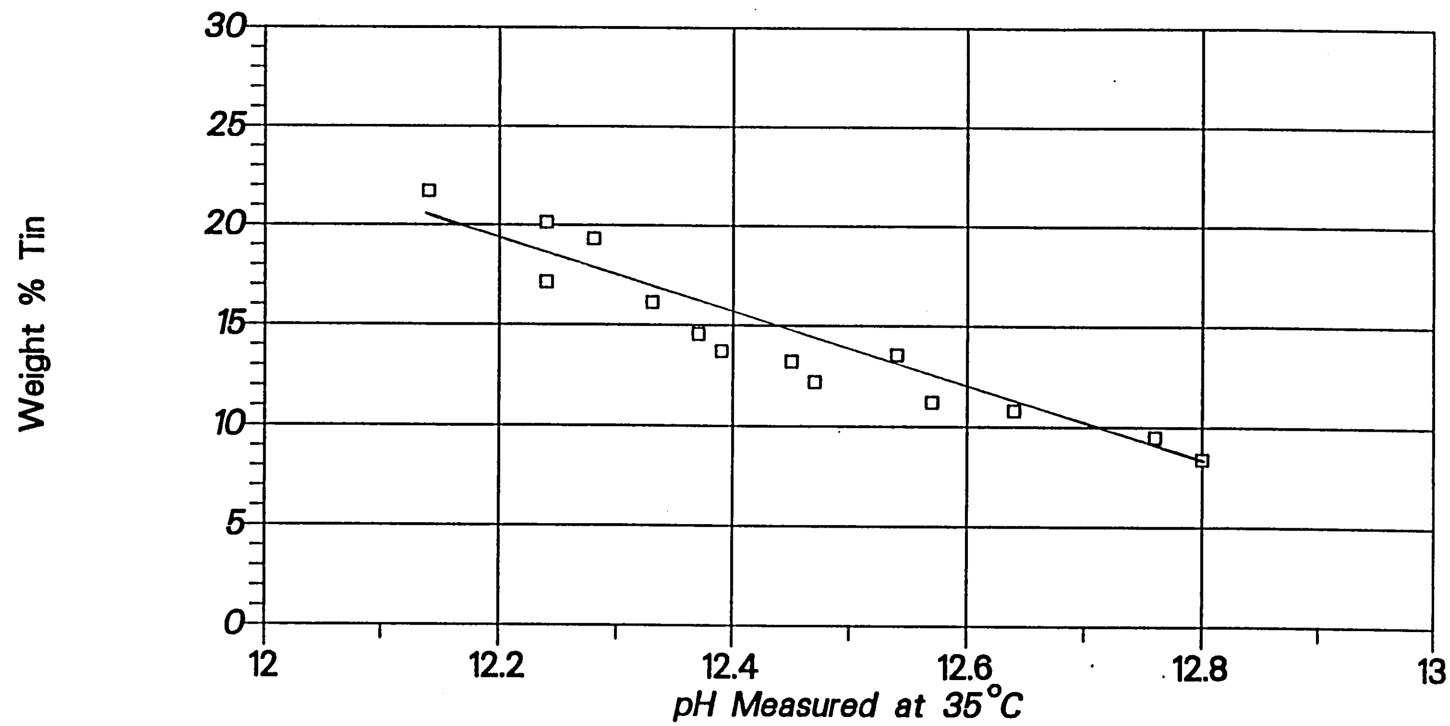

Figure 23

The effect of pH on the tin content of the bronze deposits obtained at a current density of 1 A dm^{-2}

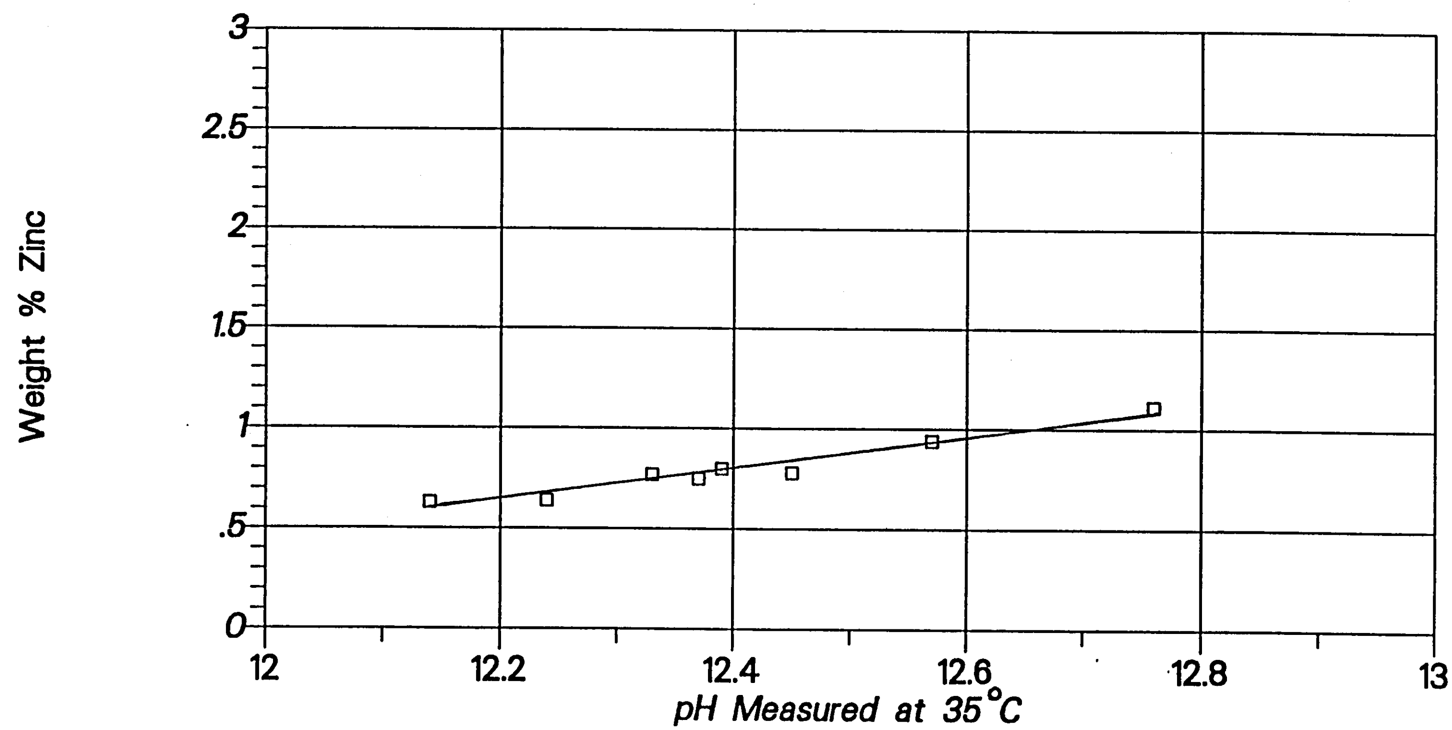

Figure 24

The effect of pH on the zinc content of the bronze deposits obtained at a current density of 2 A dm^{-2}

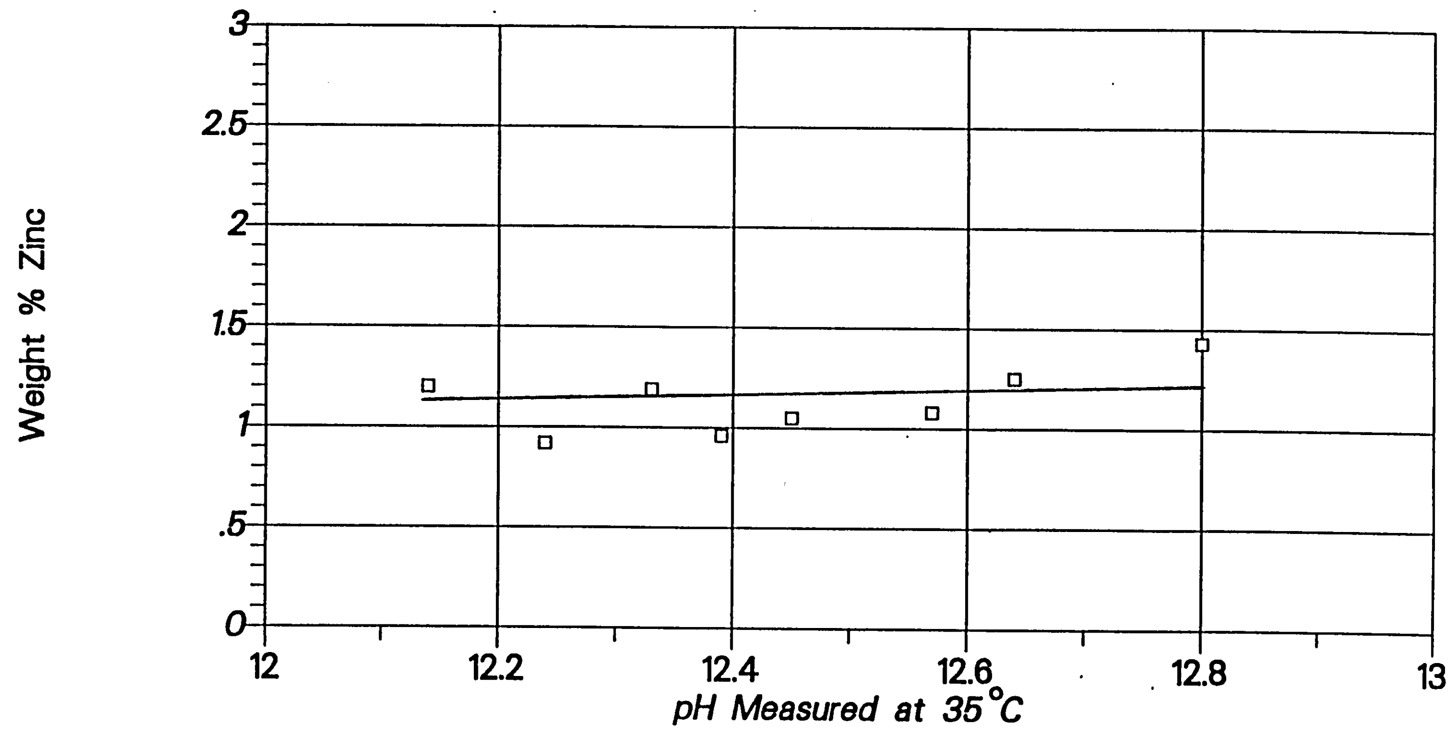

Figure 25

The effect of pH on the zinc content of the bronze deposits obtained at a current density of 1 A dm^{-2}

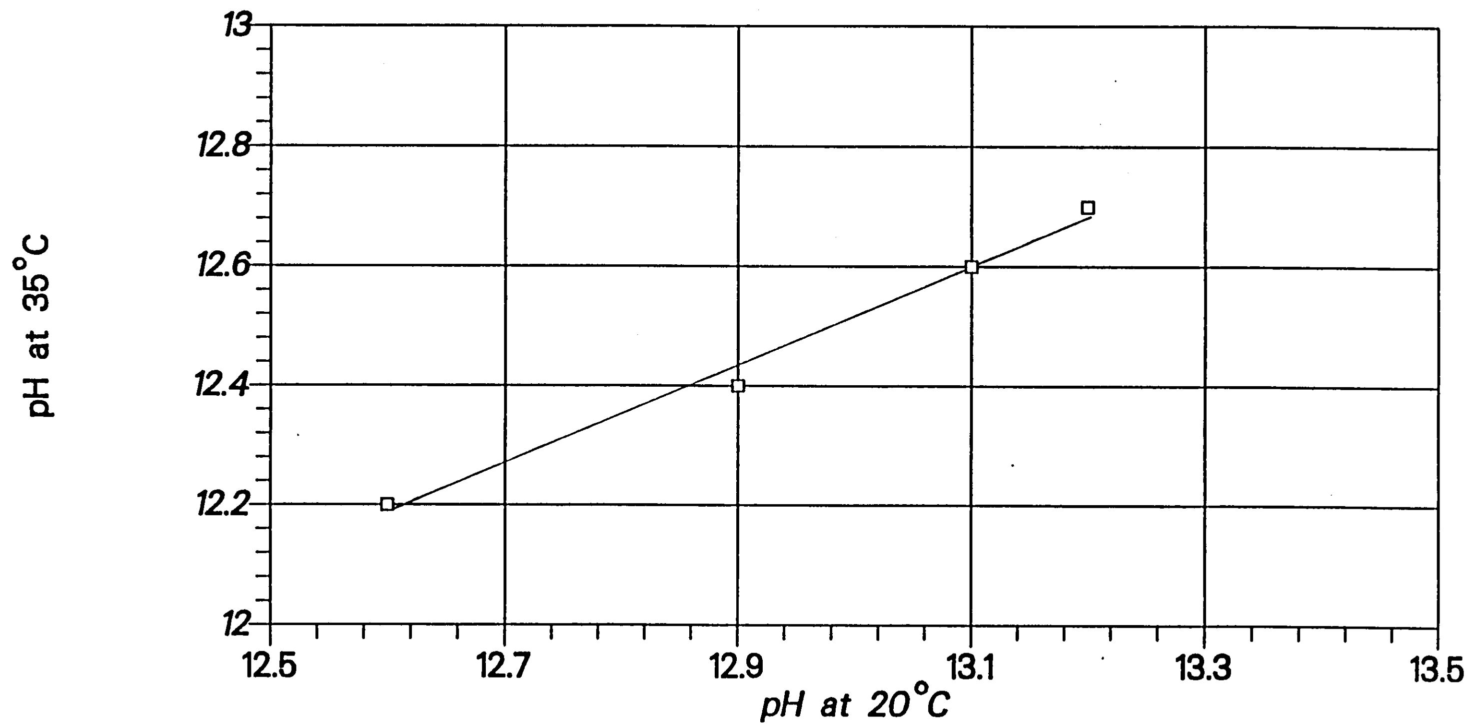

Figure 26

Temperature conversion chart for bath pH measurements made at 35 and 20°C respectively.

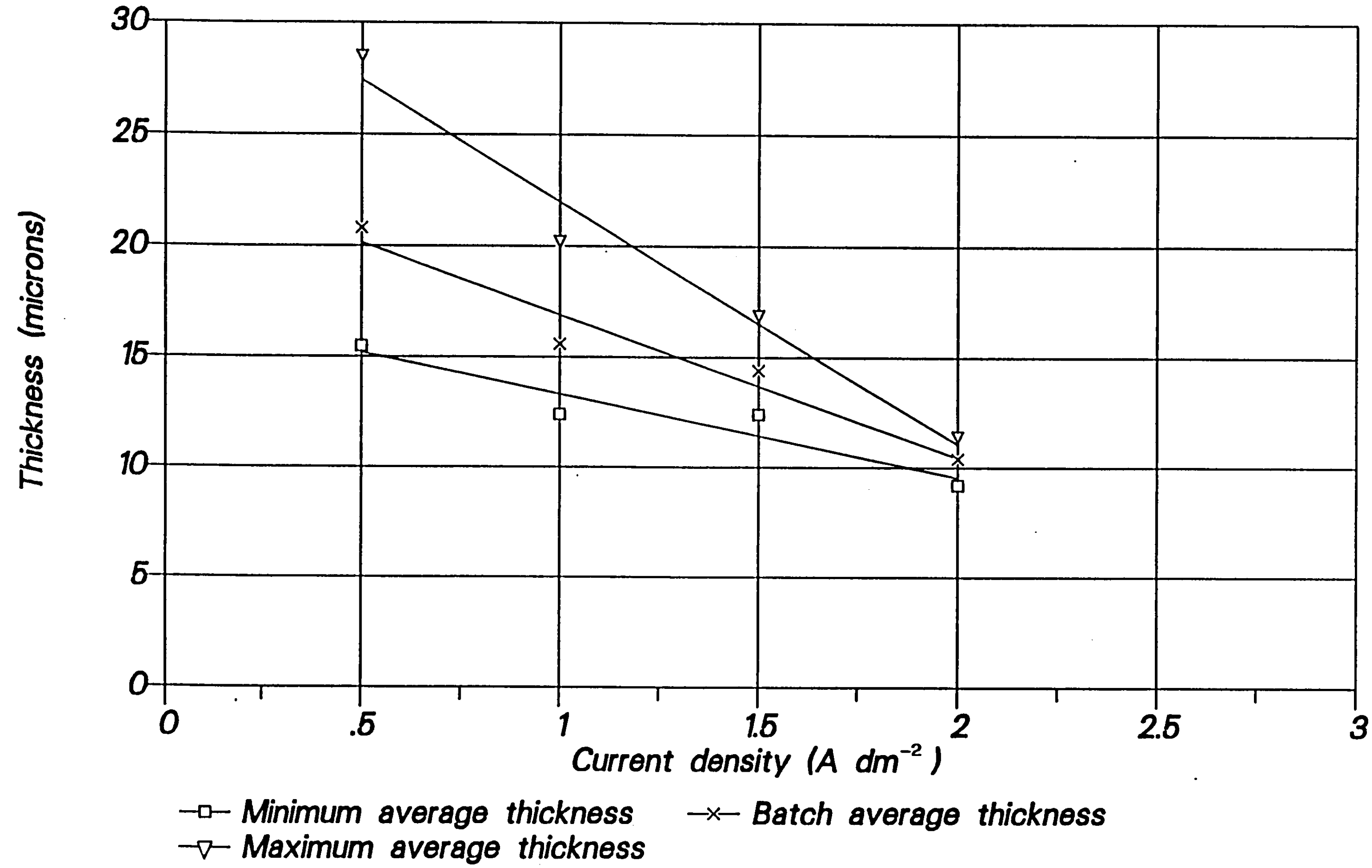

Figure 27

The effect of current density on the average thickness of bronze deposits, across a batch of 36 teaspoons, with an electrolyte pH of 12.4.

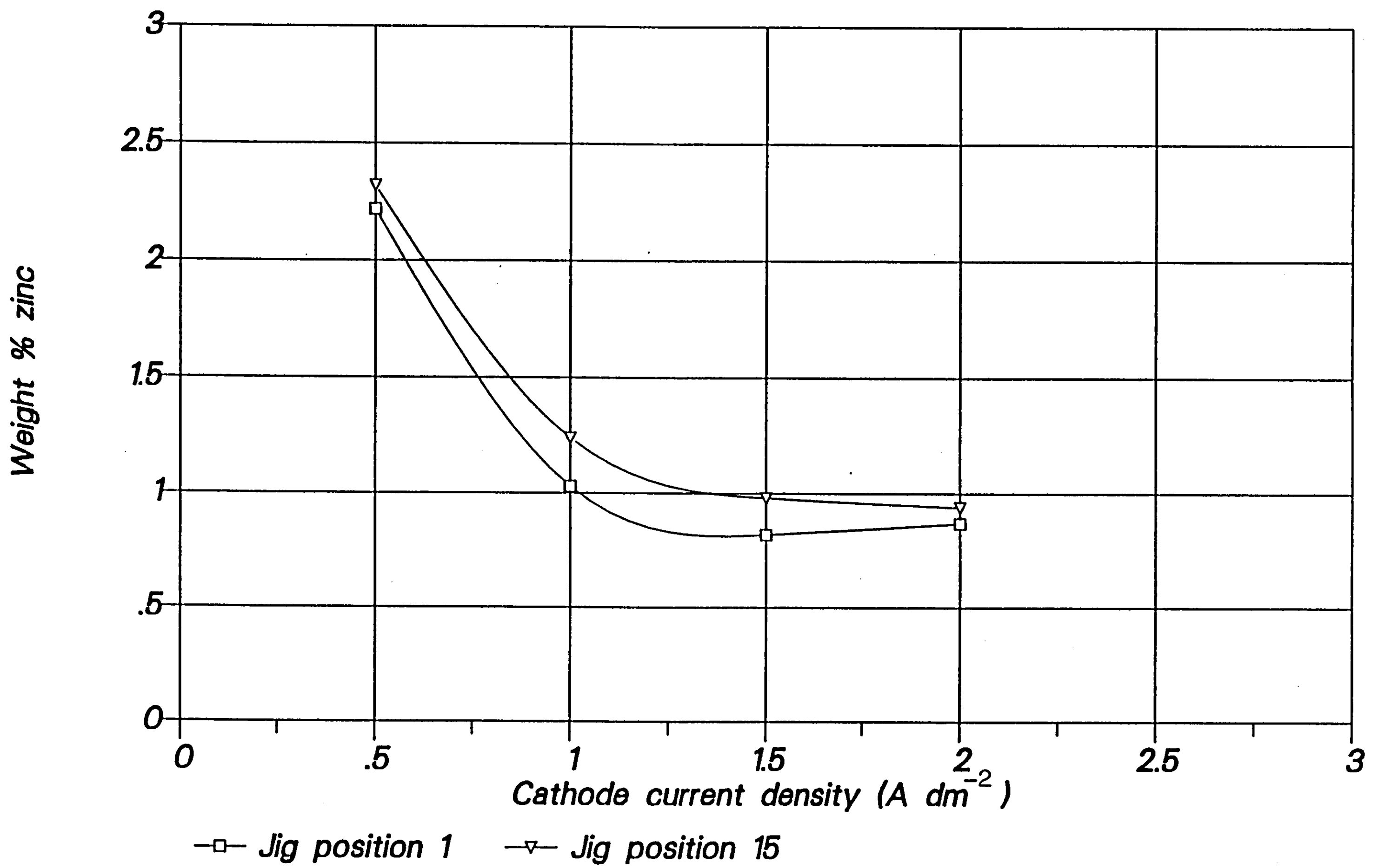

Figure 28

Effect of cathode current density on zinc content of bronze deposit with an electrolyte pH of 12.4.

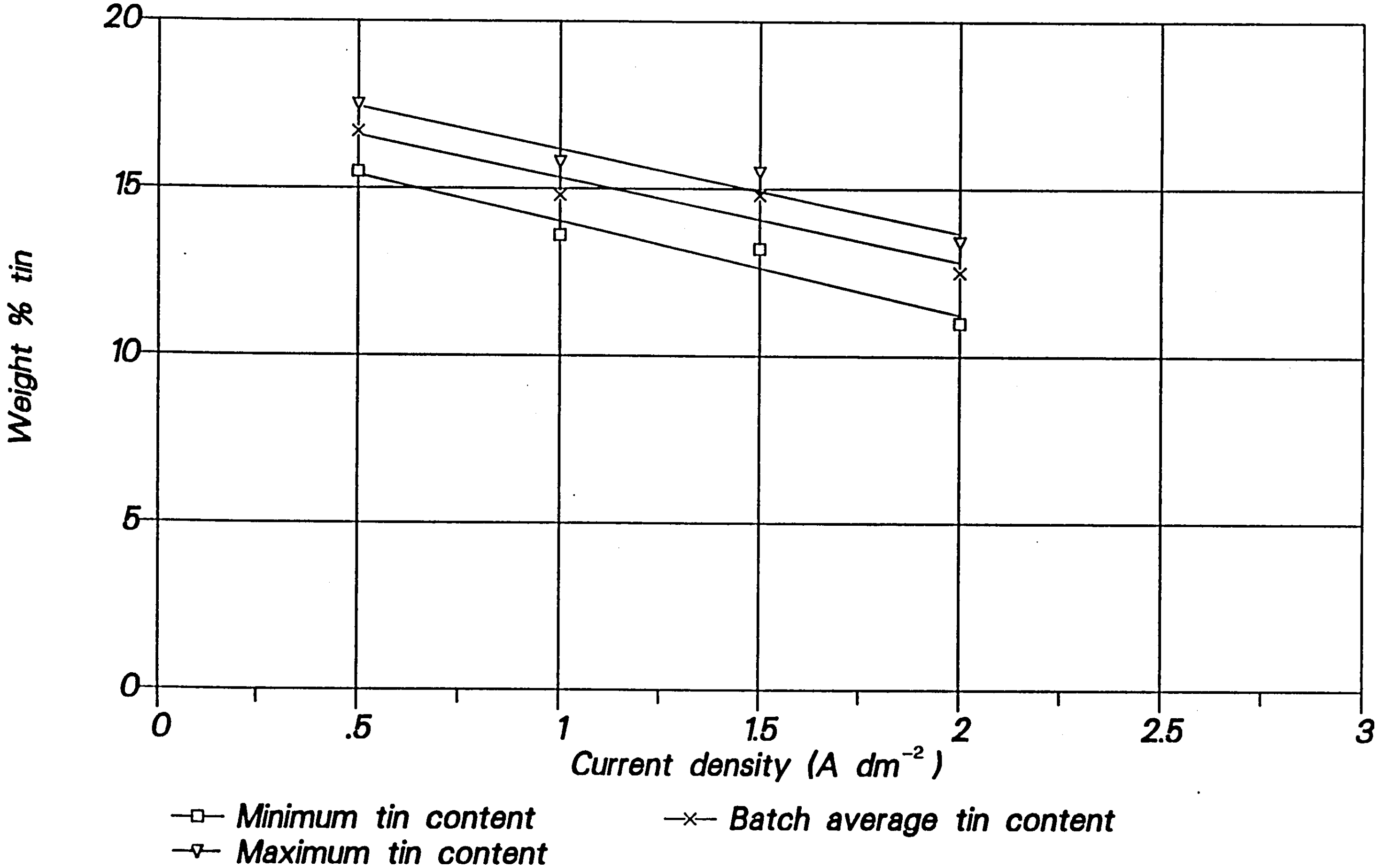

Figure 29

The effect of current density on the average tin content of bronze deposits across a batch of 36 teaspoons with an electrolyte pH of 12.4.

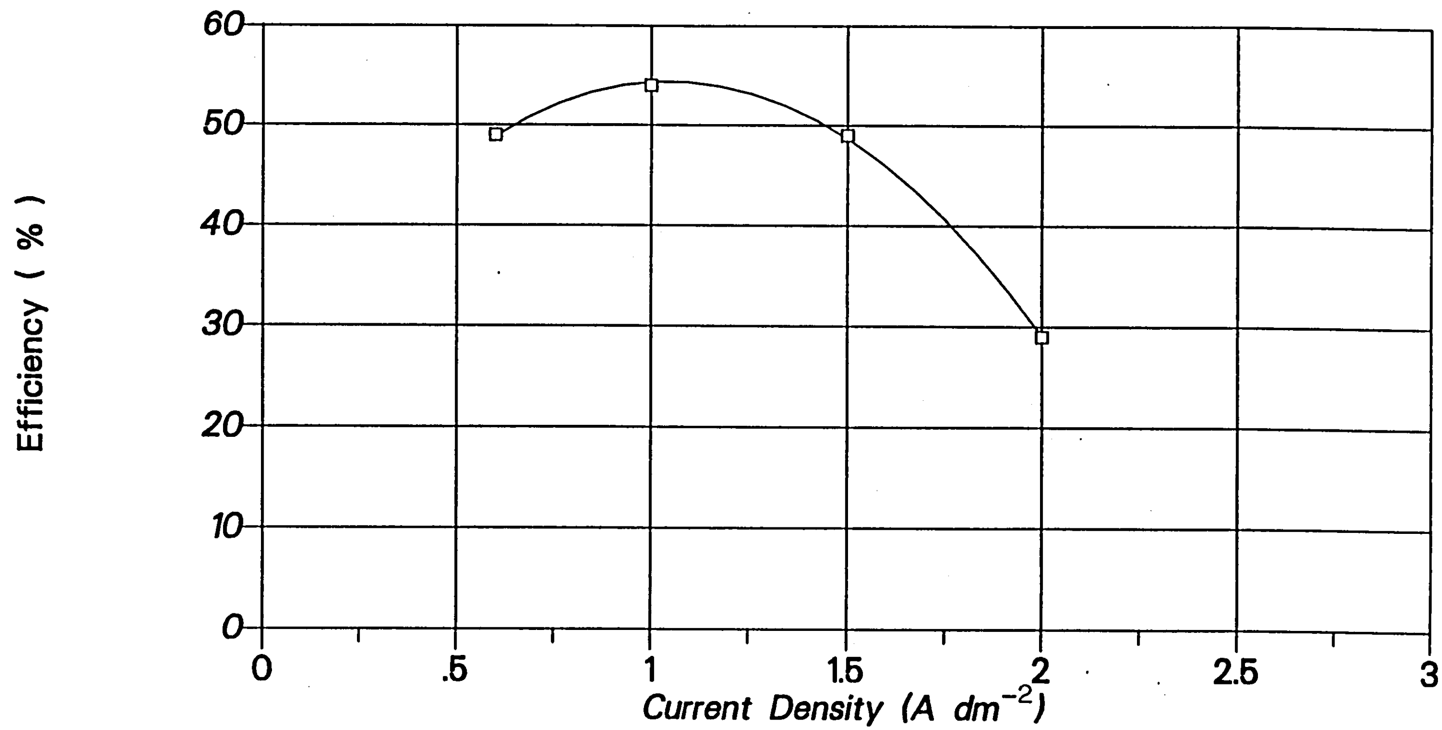

Figure 30

The effect of cathode current density on efficiency at an electrolyte pH of 12.4.

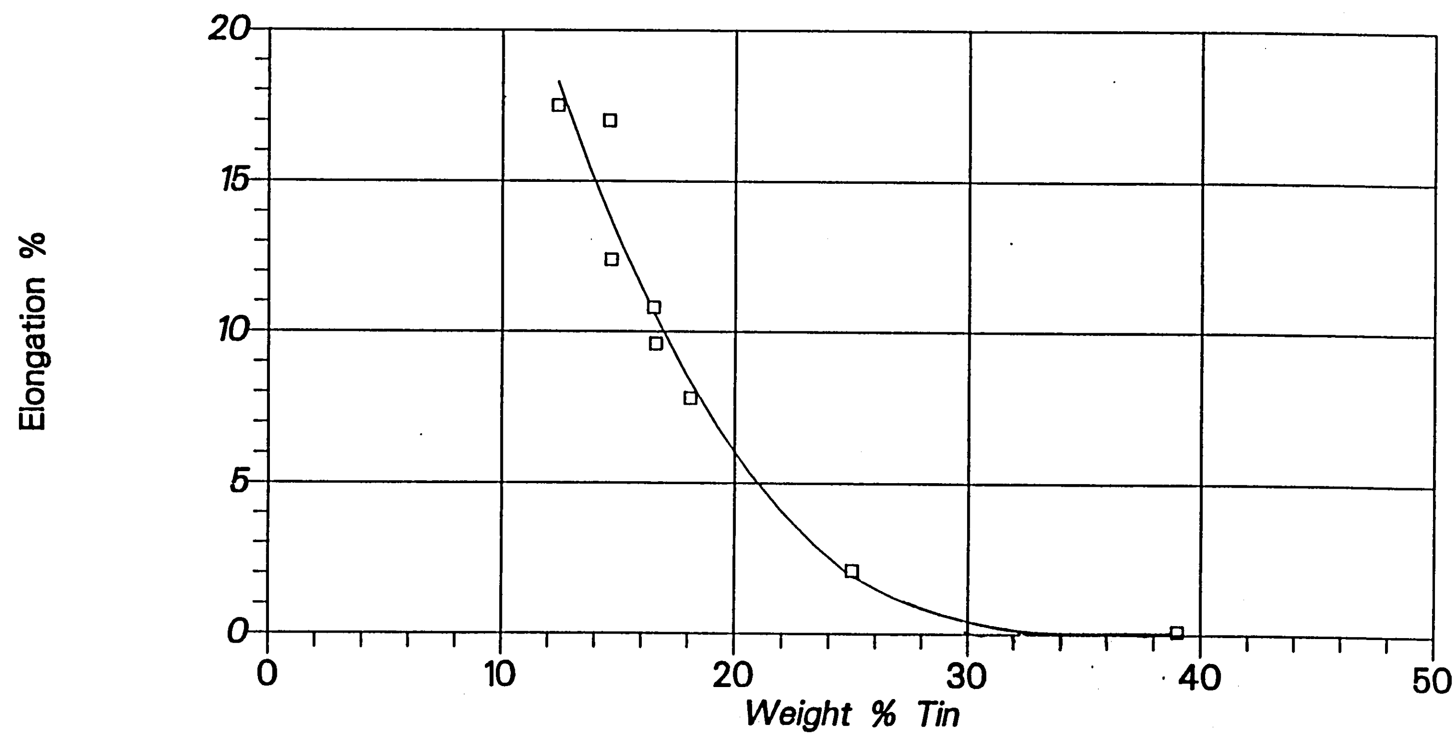

Figure 31

The effect of tin content on ductility of bronze deposits.

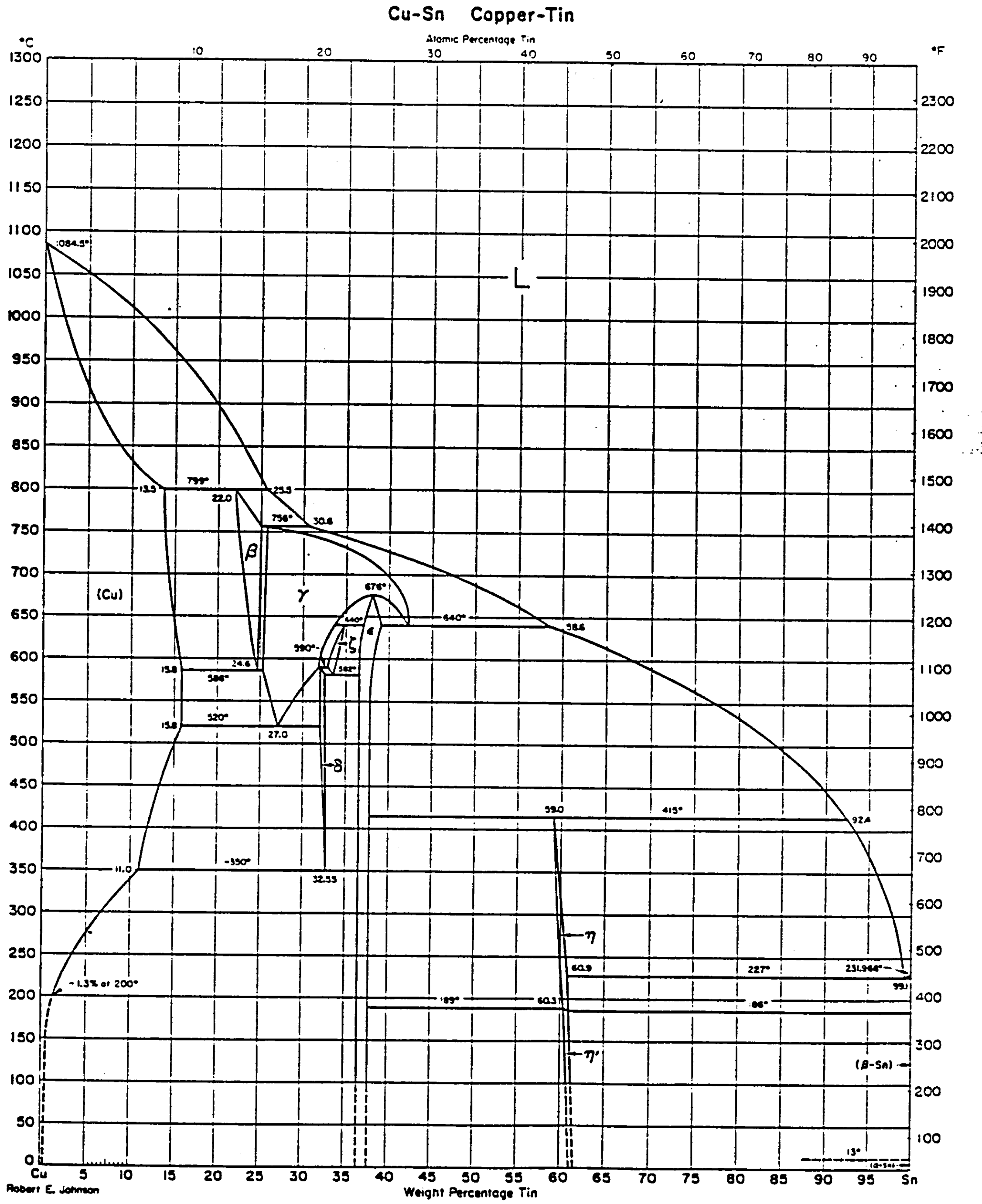

Figure 32

The copper-tin equilibrium diagram (Reproduced from American Society for Metals Handbook, 8th edition Volume 8).

Appendix 1.

Method of Calculating Cathode Current Efficiencies.

In the course of an experiment w grams of alloy is deposited in t seconds using a current of $i_{practical}$ amperes.

After analysis the composition of the alloy is A_{Cu}, B_{Sn} and C_{Zn} (Fraction).

Therefore the weight of metal deposited:

$w\ A_{Cu}$ grams

$w\ B_{Sn}$ grams

$w\ C_{Zn}$ grams

From Faradays law:

Weight of metal deposited, $w = \frac{i\ t\ A}{n\ F}$ (i)

where -
- i = current used (amperes)
- t = time (seconds)
- A = atomic mass
- n = valency of metal involved
- F = The Faraday = 96,500 Coulombs

The theoretical currents i_{Cu}, i_{Sn} and i_{Zn} are obtained by rearranging the equation (i) :

$$i = \frac{w\ n\ F}{t\ A} \qquad \text{(ii)}$$

Theoretical current required to deposit w grams of alloy is given by :

$$i_{theory} = i_{Cu} + i_{Sn} + i_{Zn}$$

Cathode current efficiency (for metal deposition) =

$$\frac{I_{theory} \text{ to deposit w grams}}{I_{practical} \text{ to deposit w grams}} \times 100\%$$