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MANUFACTURE, BY ELECTROFORMING, OF THIN-WALLED NICKEL CAPILLARY COLUMNS FOR GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

A process is described for manufacturing nickel capillary tubing, in lengths up to 100 m, with an internal diameter between 100 and 500 μm and a wall thickness of 50 μm.

Steel wire is continuously plated in a bath, 5 m long, containing the plating solution. The wire is cathodic and a nickel anode is used. The nickel-coated wire is cut to suitable lengths, *e.g.*, 25–100 m, and the wire core is removed by stretching the wire.

The nickel capillary tubing is normally springy but may be softened by annealing at 450°C. In this state it may be bent or flattened to form a precise flow restrictor. End-sealing for deactivation, or static coating with stationary phase, is simply effected by crimping the tube.

The inner surface of the nickel tubing is smooth and lends itself to a variety of deactivation strategies.

INTRODUCTION

Although some of the earliest capillary columns in gas–liquid chromatography (GLC) were made of metal[1], and although they are still widely used for hydrocarbon separations, they have been superseded by glass[2] and, more recently, by flexible fused silica[3].

The advantages of flexible fused-silica capillary columns have been well documented[3]; their only apparent weakness is the thermal fragility of the outer protective sheath, which prevents the full exploitation of the potential of modern cross-linked silicone phases[4]. We believe that the objections to metal capillary columns, *i.e.*, rough inner surfaces (which lead to non-uniform stationary phase films), surface activity (which leads to peak tailing) and thick walls (which enhance thermal inertia and prevent fast temperature programming), can now be overcome. This paper describes the progress we have made.

CHOICE OF MANUFACTURING TECHNIQUE

After considering die-drawing[5] and continuous casting[6], it was decided that

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the deposition of a thin metal coating on a filament, which could be subsequently removed, offered the best chance of success. Metal deposition techniques which were investigated, included plasma spraying[7], vacuum coating[8], chemical vapour deposition[9], immersion plating[10] and electroplating[10].

ELECTROFORMING

This involves the deposition of the metal from an aqueous ionic solution on to a cathodic substrate by the passage of an electric current and the subsequent removal of the original substrate. Although many metals can be electroformed, nickel suited our purpose best.

Several substrates were investigated, *viz.*, (a) carbon-filled polythene tubing which could be removed by oxidation; (b) poly(vinyl chloride) (PVC) tubing made electrically conductive by the electroless deposition of silver and removed after plating by oxidation; (c) nylon filament, coated as in (b), which could be removed by stretching; and (d) metal wire that could be removed by stretching. After much experimentation, substrate (d) was chosen and in particular stainless-steel wire, which could be elongated by 30% before breaking.

The chosen plating technique requires that the electroformed tube should not adhere to the stainless-steel substrate (wire). Parting agents considered were silicone oil, albumin and an oxide layer. The last, which is formed by exposing the wire to air, was found to be the best.

The quality of the electroformed nickel tubing, *e.g.*, mechanical strength, hardness, porosity and pitting, depends on many factors, including the composition of the bath, the bath temperature, the density of the plating current, the voltage distribution on the cathode, the anode geometry and the electrical characteristics of the plating voltage. After much experimentation, the apparatus described below and the conditions under which it was operated gave excellent results.

APPARATUS FOR ELECTROFORMING NICKEL CAPILLARIES

The apparatus, shown schematically in Fig. 1 and overall in Fig. 2, has been designed for continuous operation. Basically it consists of a means of (a) supplying wire continuously (the feed mechanism); (b) cleaning the wire (the cleaning mechanism); (c) depositing a layer of nickel on the wire (the plating bath) and the electrical conditions; (d) drawing the wire through the plating bath (the drawing mechanism); (e) storing the plated wire (the take-up mechanism); and (f) removing the wire (the stretching mechanism).

Feed mechanism

The wire should be free from scratches and other surface defects, as these mar the inner surface of the electroformed capillary tubing. Good quality wire is widely available from primary sources, *e.g.*, West Japan Stainless Steel Wire Co. Alternatively, manufacturers of woven wire products can be approached. Generally the wire is supplied on spools containing up to 5 km lengths, depending on the diameter. The diameter of the wire determines the inner diameter of the electroformed nickel capillary. The range 0.1–0.5 mm can be handled without difficulty.

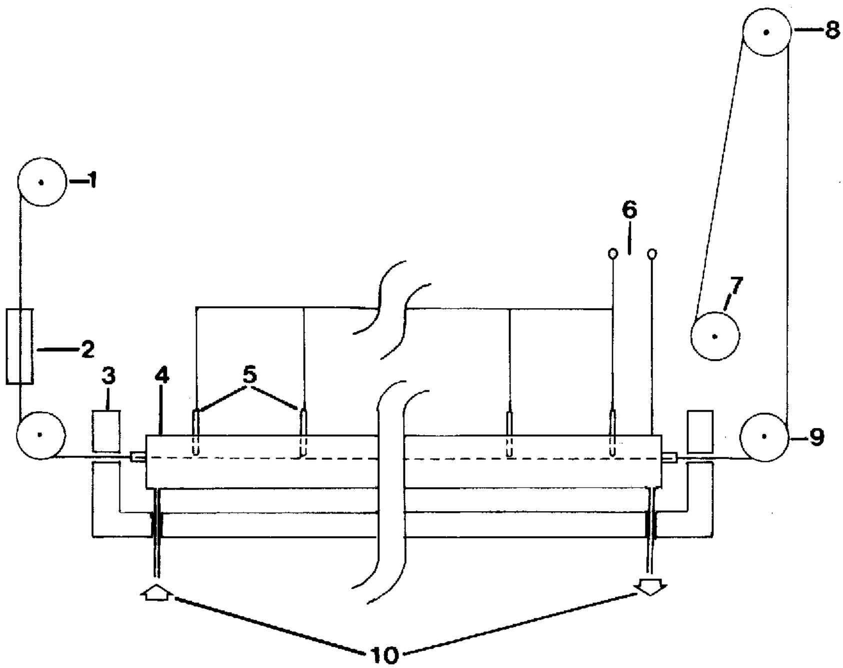

Fig. 1. Schematic elevation of plating system to show layout of main components. 1 = Feed spool; 2 = cleaner; 3 = lagged box; 4 = plating bath; 5 = sliding contacts; 6 = power supply; 7 = take-up spool; 8 = coiling guide; 9 = drawing mechanism; 10 = plating solution circulation.

Cleaning mechanism

The wire, as supplied, has an oxide surface contaminated with compounds used in the drawing process. The latter must be removed without destroying the oxide layer which functions as a parting agent. Of the many cleaning processes studied, the best results were obtained by passing the wire through the same detergent solution as used in the bath (see below). Details of the cleaning mechanism are shown in Fig. 3.

Plating bath (Fig. 4)

The bath is a high-density polypropylene tube (10 cm I.D. with a 6 mm wall thickness), 5 m long, which has been longitudinally sliced using a band saw (Fig. 4a). The ends of the bath are closed by welding on a flat polypropylene sheet using a hot air gun (Fig. 4b). In order to pass the wire into the bath, the ends are drilled and a length of 6 mm O.D. glass tubing is inserted (Fig. 4c). The outer end of the glass tube is fitted with a nylon Swagelock-type fitting containing a pre-drilled silicone-rubber septum[11].

The anode consists of electrolytically pure nickel balls (*ca.* 10 mm in diameter and available from supply houses specializing in equipment for nickel plating) held in place by a high-density polypropylene tube (7 cm O.D.) which has been slotted using a band saw as shown in Fig. 4d and e. The purpose of the slots is to provide electrical contact between the anode and cathode. The inner tube is covered with a woven Dacron cloth, which serves as a filter (Fig. 4f) to prevent fine particles of

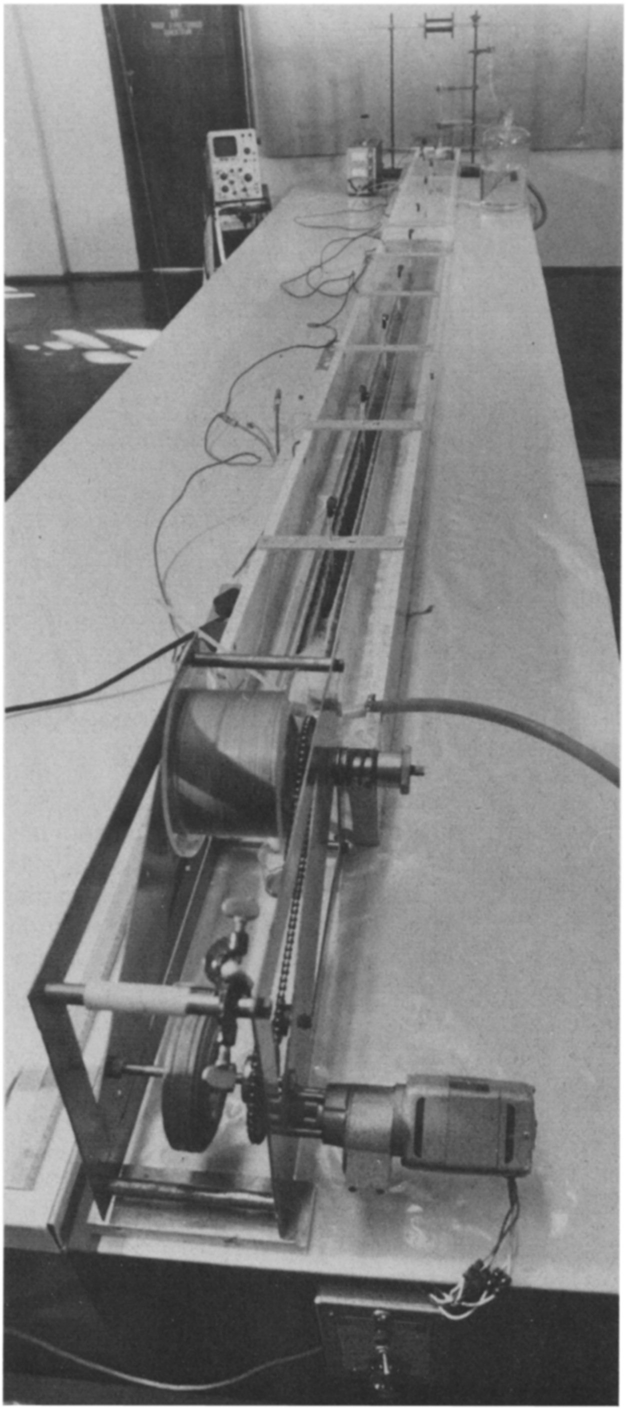

Fig. 2. Overall view of plating apparatus.

nickel from plating on to the wire and giving a rough surface. To ensure good electrical contact along the length of the anode, a titanium wire (3 mm O.D.) is inserted along the length of the bath (Fig. 4d), and this is connected to the power supply.

The resistance of the steel wire (17 Ω per metre) is sufficient to lead to a significant potential drop along the wire if the power supply is connected to the wire at the two ends of the bath. To prevent this, electrical contact is made at 0.5-m intervals along the wire. Details of the sliding contacts are shown in Fig. 4g. The contact region is sheathed in plasticized PVC tubing fitted over the glass tube guide and stoppered at the other end. The sheath contains two holes through which the wire passes. This arrangement causes a high resistance between the anode and the cathode in the region of the sliding contact and greatly decreases plating on the contact itself.

The plating solution consists of nickel sulphamate (350 g/l), boric acid (30 g/l) and detergent (5 g/l). It is stored in a 60-l polypropylene tank fitted with a 1.5-kW immersion heater, protected by a vitreous silica sheath (Jago Manufacturing, Kempton Park, South Africa) and a simple thermostat, of the type used in domestic water heaters, set at 55°C. A centrifugal pump with a high-density polypropylene impeller circulates the plating solution via a cartridge filter through the plating bath. Water loss by evaporation (*ca.* 3 l per day) is compensated for by a simple constant-level device attached to the tank.

Electrical circuit

Basically, a voltage of approximately 1–5 V at a current density of approximately 1–15 A dm^{-2} is used. Any ripple on the voltage should be less than 5%. The voltage may be fixed, which yields a direct current, or it may be alternated so that

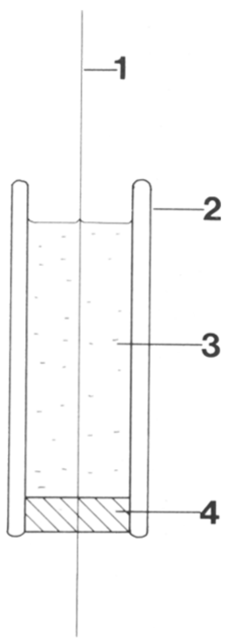

Fig. 3. Vertical section of wire cleaner. 1 = Stainless-steel wire; 2 = glass tube; 3 = detergent solution; 4 = rubber septum.

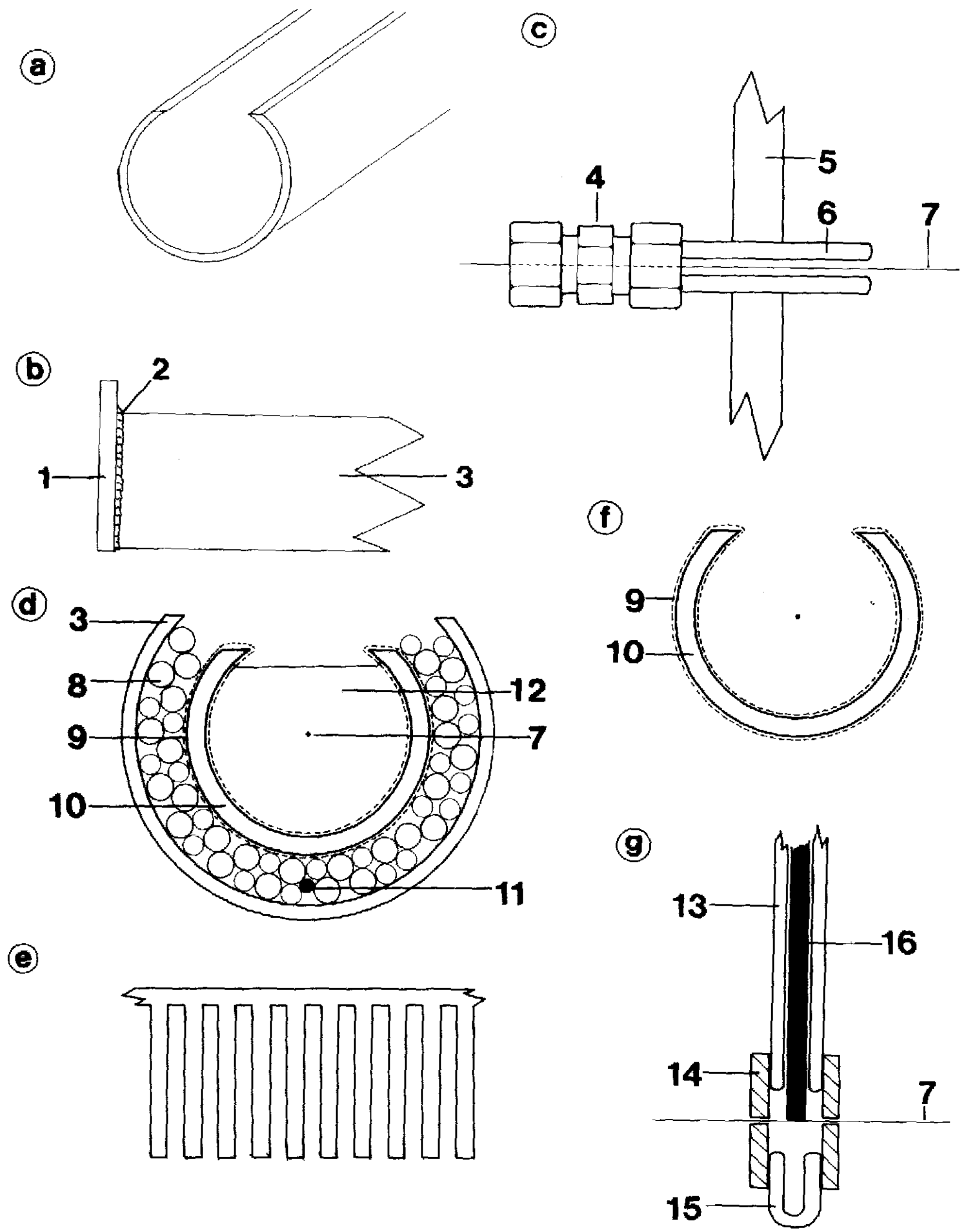

Fig. 4. (a) The main bath is made from pipe with a longitudinal slot; (b) flat plates are welded to the ends of the pipe; (c) the wire core is drawn into the plating bath through an adjustable seal; (d) transverse section of plating bath to show arrangement of anode elements; (e) elevation of inner, slotted tube; (f) arrangement of dacron filter sleeve around slotted tube; (g) sliding electrical contact. 1 = End plate; 2 = welding filler; 3 = pipe; 4 = nylon Swagelock compressing silicone-rubber septum; 5 = end plate; 6 = 6 mm O.D. glass tube; 7 = wire; 8 = nickel ball; 9 = Dacron filter; 10 = inner, slotted tube; 11 = titanium current carrier; 12 = plating solution; 13 = glass tube with close sliding fit to contact (16); 14 = PVC tube; 15 = glass stopper; 16 = polished stainless-steel rod.

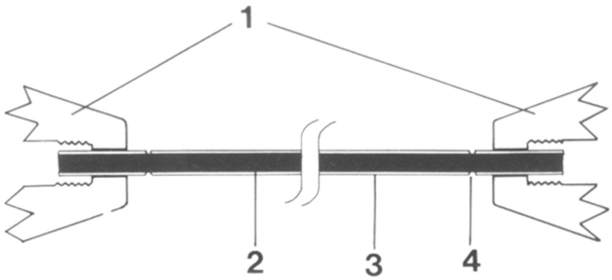

Fig. 5. Extraction of wire core from the nickel capillary. 1 = Pliers; 2 = wire core; 3 = nickel capillary; 4 = score mark through nickel.

a plating cycle is alternated with a stripping cycle. It may even be desirable to alternate the plating and stripping cycles. A great number of programmes are possible, and these form the body of the electroplater's lore. By these means the quality of the electroformed article is, to a large extent, determined and the many ailments, to which electroforming is prone, may sometimes be cured.

In our experience, a simple constant voltage of 1.5 V and a current density of 10 A dm^{-2} gives acceptable results.

Drawing mechanism

The electroplated wire from the plating bath passes over a grooved polypropylene wheel, which acts as a capstan. This wheel is connected to an electric motor fitted with a gear-box and variable-speed controller, which allow for wire speeds

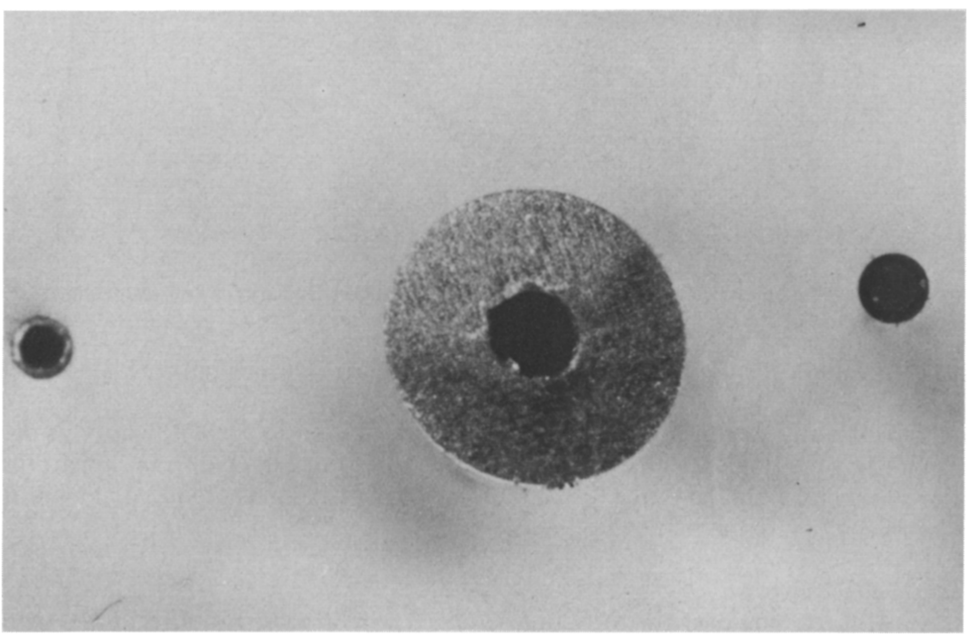

Fig. 6. Comparison between (from left to right) electroformed nickel capillary, drawn nickel tubing and flexible fused-silica capillary.

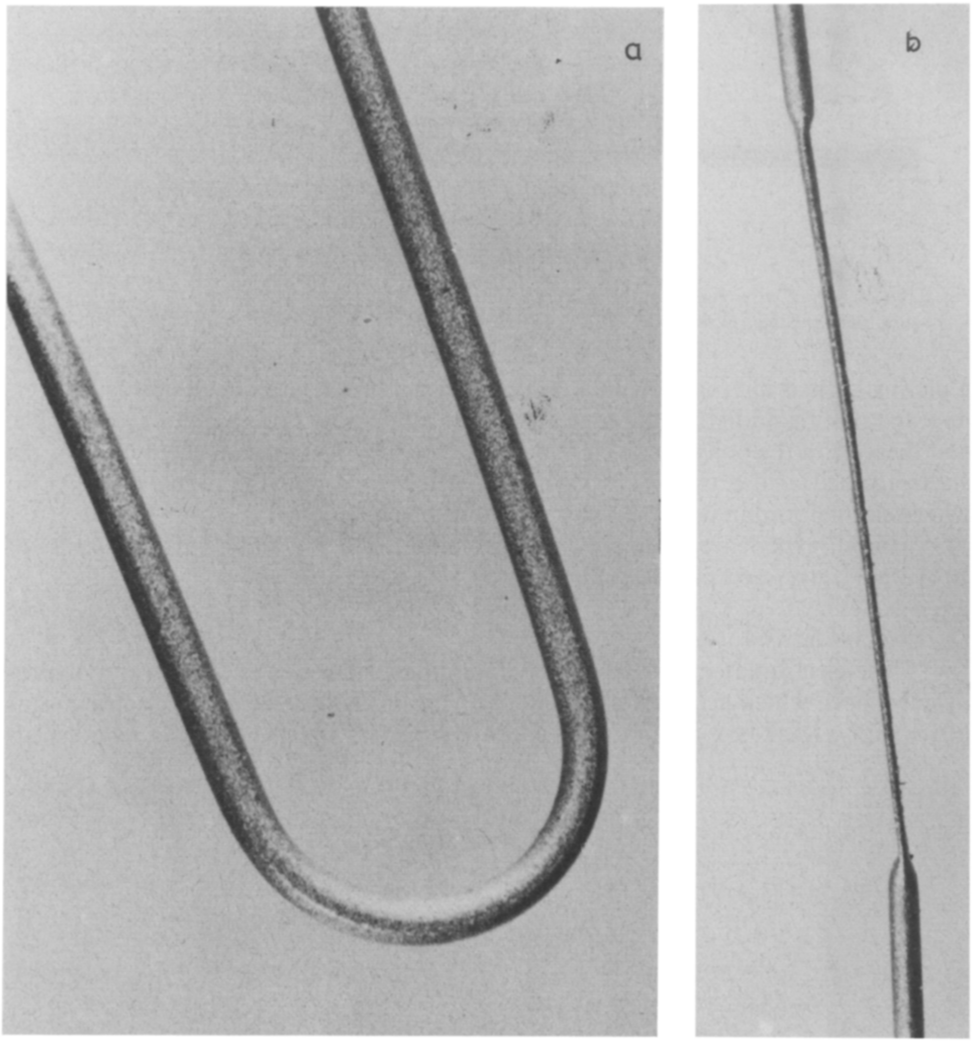

Fig. 7. (a) Bending properties of nickel capillary; (b) flattened nickel capillary for flow restriction.

between 5 and 60 cm min^{-1} (Parvalux Electric Motors, Bournemouth, U.K., Model SD I SIS).

Obviously the thickness of the plated layer, at a given current density, is determined by the residence time of the wire in the bath. For example, in the apparatus described here, a capillary tube with a wall thickness of 50 μm is produced at a linear wire velocity of 16 cm min^{-1}.

Take-up mechanism

After passing over the capstan, the plated wire is passed to a reel fitted with a slip-clutch and driven slightly faster than the capstan so that a constant tension is maintained on the wire.

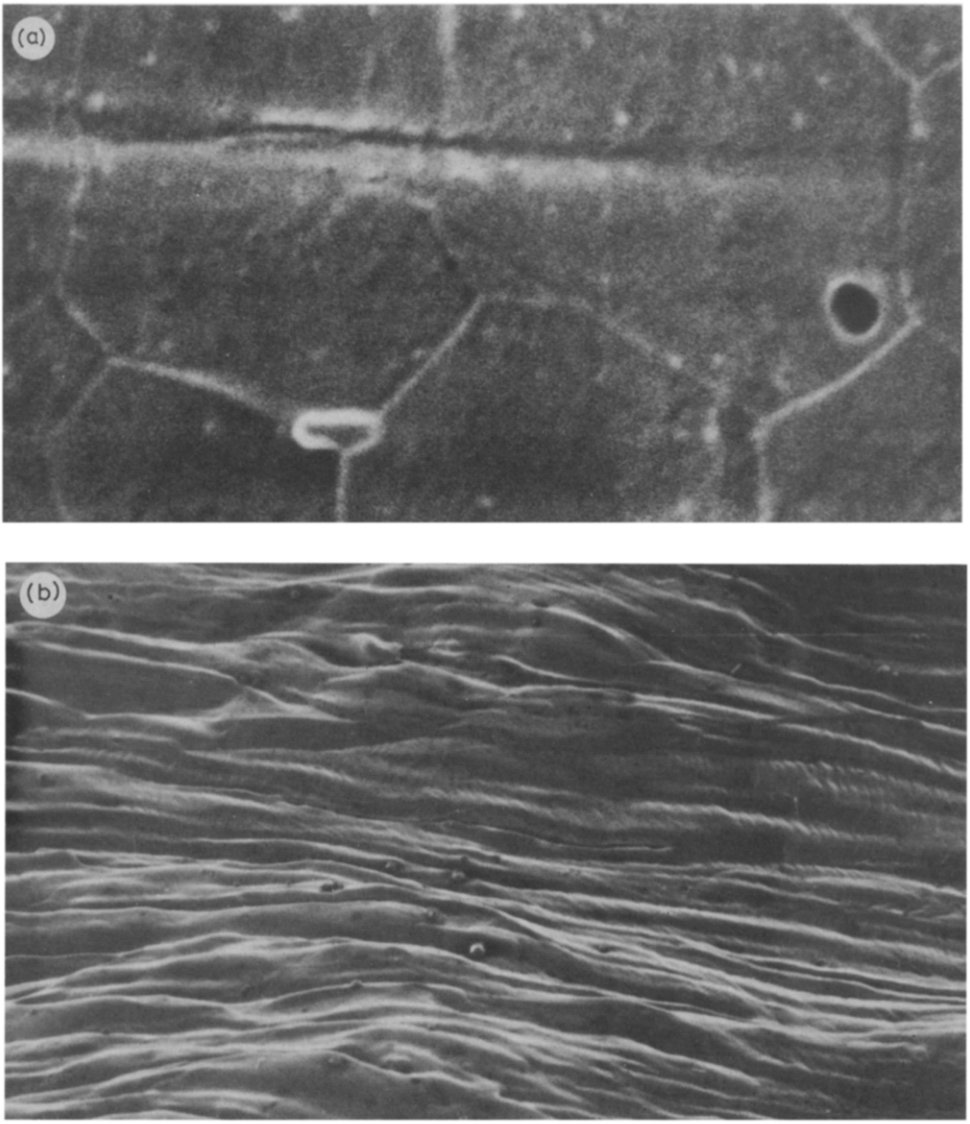

Fig. 8. (a) Inner surface of nickel capillary (× 13,620); (b) inner surface of drawn nickel tube (× 465).

Stretching mechanism

The spooled, electroplated wire is cut into lengths required for the capillary column, *e.g.*, 25 m. Rings are scored, using a file, through the plated nickel a few centimetres from both ends of the wire and the ends of the wire (Fig. 5) and the ends are gripped in hand-held pliers. The wire is then stretched. The extent of the stretching, before the wire breaks, is determined by the stretching speed and the smoothness with which it is carried out. Elongations of at least 30% are possible and this is more than adequate to reduce the wire diameter to a size at which it is readily withdrawn from the tube.

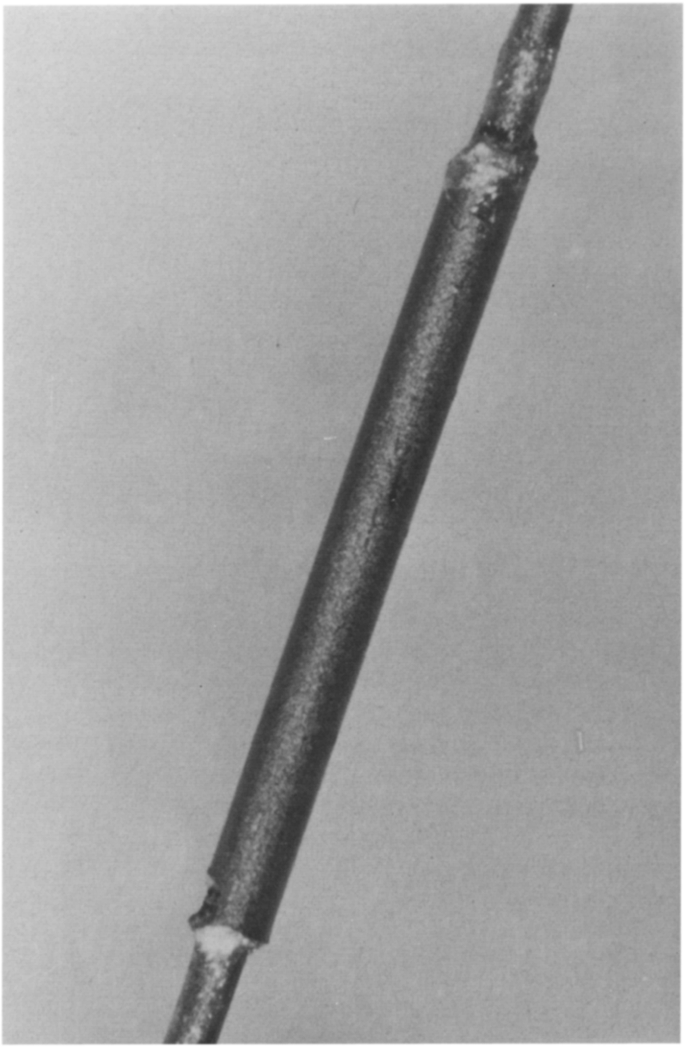

Fig. 9. Joining nickel capillary by means of soldering and a electroformed nickel sleeve.

FINAL COMMENTS

Capillary tubes of a wide range of inner diameters (*e.g.*, 0.1–0.5 mm) and wall thicknesses may be fabricated by the technique described here. If wider tubes are desired it would be advisable to consider another type of core. Fig. 6 shows a comparison between drawn nickel tubing, electroformed nickel tubing and flexible fused silica.

The mechanical properties of the nickel capillary tubing, *i.e.*, hardness and stiffness, may be varied considerably by changing the plating conditions or by subsequent heat-treatment. Annealing the nickel by heating it to 500°C softens it. This has several advantages in chromatographic practice. Firstly, relatively sharp bends can be made (Fig. 7a) and, secondly, the tubing can be precisely flattened to produce accurate restrictors for flow control (Fig. 7b). Both of these properties have been found to be important in the construction of a "universal" inlet[12].

Electroforming allows for very precise dimensional control. The wall thickness of the capillaries can be controlled to within 1 μm. This introduces the possibility of controlling the temperature of the capillary column by applying a voltage along its length as an alternative to the conventional air bath.

The inner surface of electroformed nickel columns, using the process described here, is as smooth as the surface of the wire core. Fig. 8a shows the inner surface under a magnification of 13,620 and may be compared with the inner surface of a drawn nickel tube at a magnification of 465 (Fig. 8b).

Methods of satisfactorily connecting fused-silica capillary columns to inlets, etc., present problems. Fig. 9 shows a simple and effective means of joining nickel capillaries using an electroformed sleeve and one of an extensive range of solders.

The surface of both nickel and fused silica are unsuitable, as such, for GLC; both require deactivation. Procedures for the latter are well described. We show elsewhere[12] that with nickel capillaries many more competitive options are open.

Electroforming is an art rather than a science. Fig. 10 shows the quality of capillary tubing that can be produced if the conditions are right, and examples of tubing produced if the conditions are wrong are shown in Fig. 11.

The apparatus described here can produce up to 400 m per 24 h. Higher production can readily be attained by devising a multi-channel apparatus.

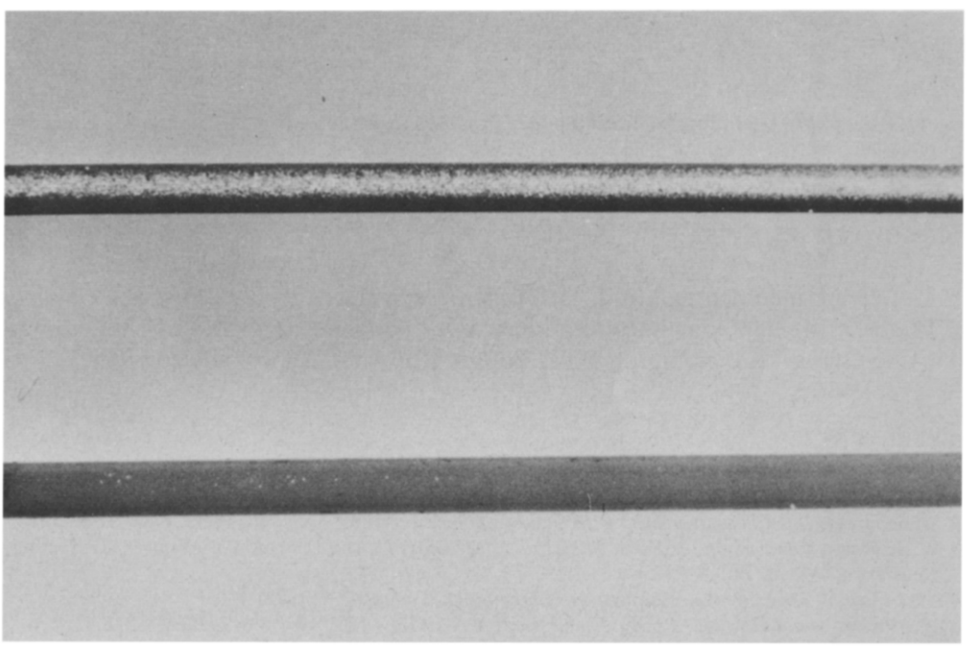

Fig. 10. Electroformed nickel capillary (above) and flexible fused silica (below).

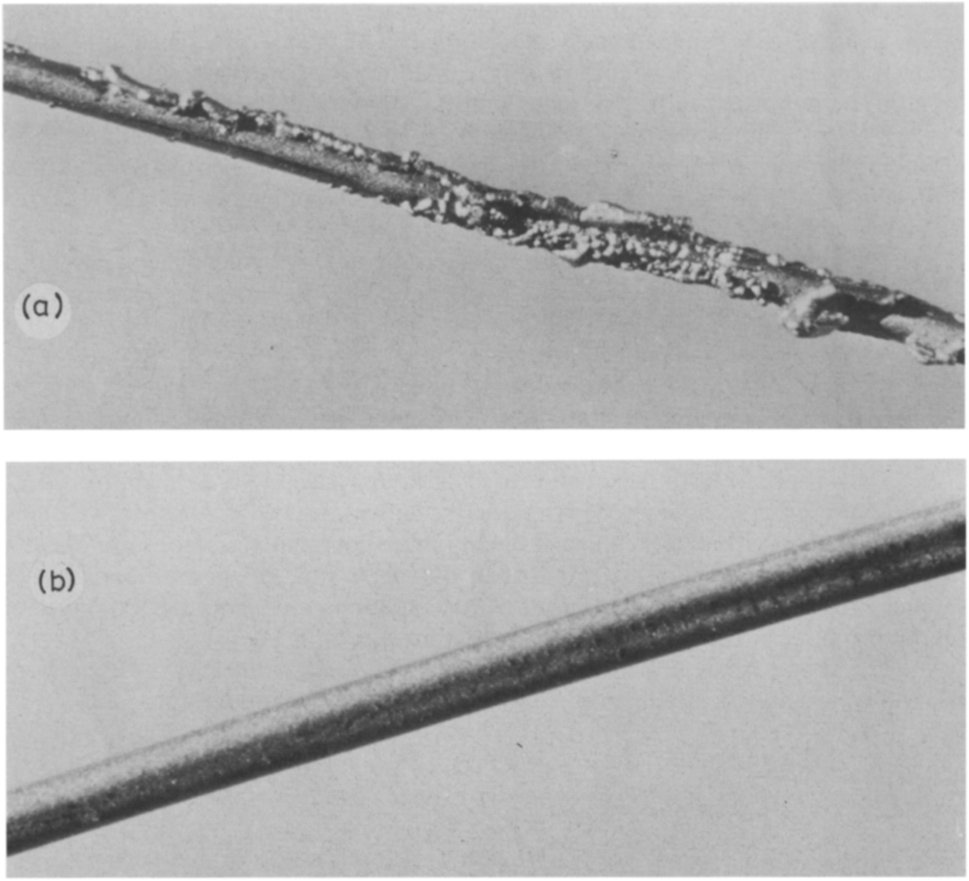

Fig. 11. Examples of electroformed nickel capillary produced under non-optimum conditions: (a) nodules; (b) pinholes.

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