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Note

Precautions in preparing whisker-walled open tubular columns

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Previous reports demonstrated that the poor wettability of the smooth glass surface complicated the coating of open tubular columns. Roughening techniques, such as the whisker growth method were developed to alleviate the problems associated with coating polar liquid phases. Studies by Schieke *et al.*[1–3], using scanning electron micrographic techniques, revealed the nature of the whisker surface of the glass open tubular columns after treatment with 2-chloro-1,1,2-trifluoroethyl methyl ether. The conditions of etching ether concentration and treatment temperature were further studied by Sandra and Verzele[4] for preparation of this microcrystalline silica growth. Although capillary column technology has advanced considerably with the development of fused-silica columns, the whisker glass surface remains advantageous for coating polar liquid phases. In addition, this approach has utility for gas–solid chromatography applications[5]. When used for such applications, it was found necessary to make adjustment to the methods cited to optimize column characteristics. This report describes such modifications as well as the precautions that should be taken during the preparation of whisker-wall-coated open tubular (WWCOT) columns.

EXPERIMENTAL

Materials

All solvents were distilled in glass and purchased from Burdick and Jackson Labs. (Muskegan, MI, U.S.A.). 2-Chloro-1,1,2-trifluoroethylmethyl ether (etching ether) was purchased from PCR Research Chemicals (Gainesville, FL, U.S.A.). Corning Pyrex 7740 glass tubing, 10 mm O.D. × 2.5 mm I.D. and 8 mm O.D. × 4 mm I.D., which was purchased from A. H. Thomas (Philadelphia, PA, U.S.A.), was drawn into capillary tubing 1 mm O.D. × 0.25 mm I.D. and 1 mm O.D. × 0.5 mm

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I D., respectively, using a Model GDM-1 glass drawing machine manufactured by Shimadzu Scientific Instruments (Columbia, MD, U S A) A Packard Model 7400 gas chromatograph and nitrogen carrier gas (99.999" ,) were employed

RESULTS AND DISCUSSION

The whisker-growth technique originally attempted was that as outlined by Schieke *et al.*[1] In our laboratory, the resulting whisker growth was non-uniform

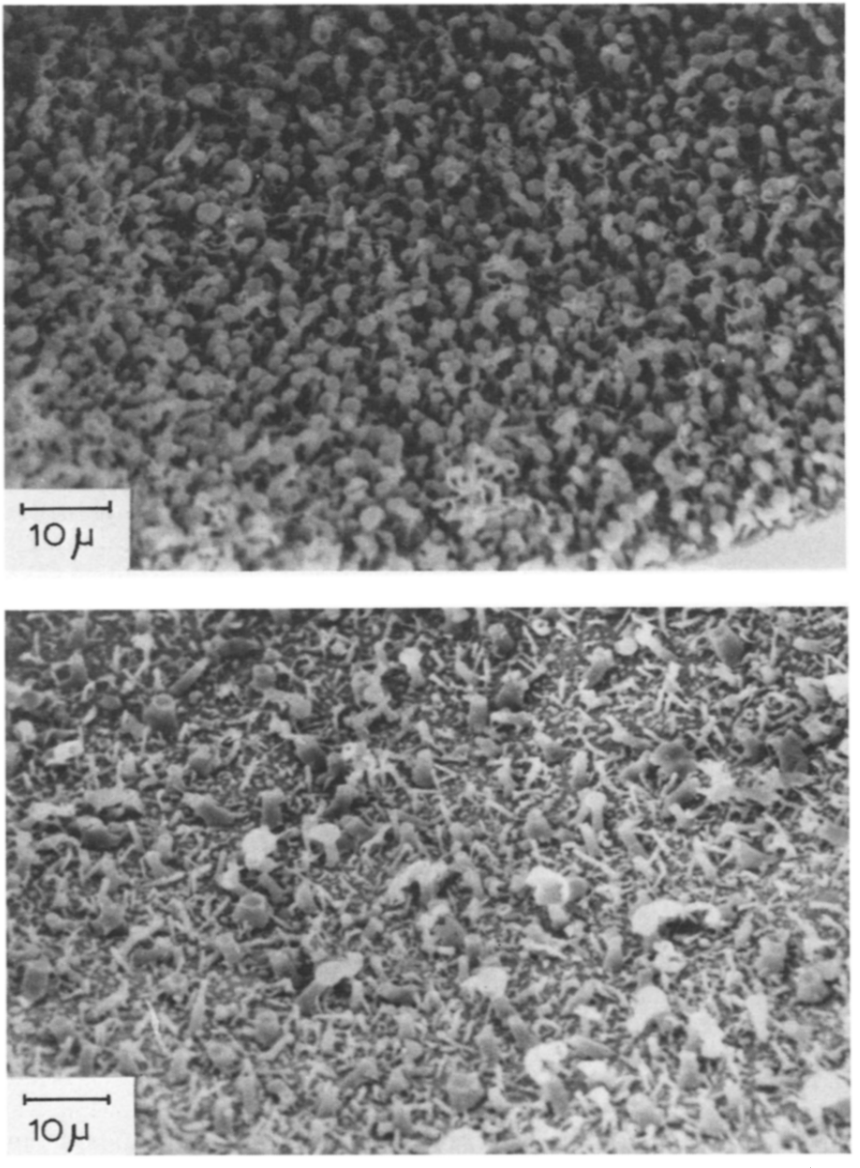

Fig 1 Scanning electron micrographs of the whisker surface resulting from the static vacuum etchin method (heated to 400 C, held there for 1 h and left to cool overnight) a = septum end b = vacuum end

throughout the column As illustrated in the scanning electron micrographs (Fig 1) the whisker density at the end where the etching ether was injected (septum end) was more dense than at the opposite end (vacuum side) Obviously the etching ether was not distributed evenly throughout the column The spherical caps on top of the whiskers obtained in this procedure were also reported by Schieke *et al*[1] These spheres which were removed after washing the column with ethanol were thought to result from the relatively short hold of 1 h at 400 C Another attempt to obtain a

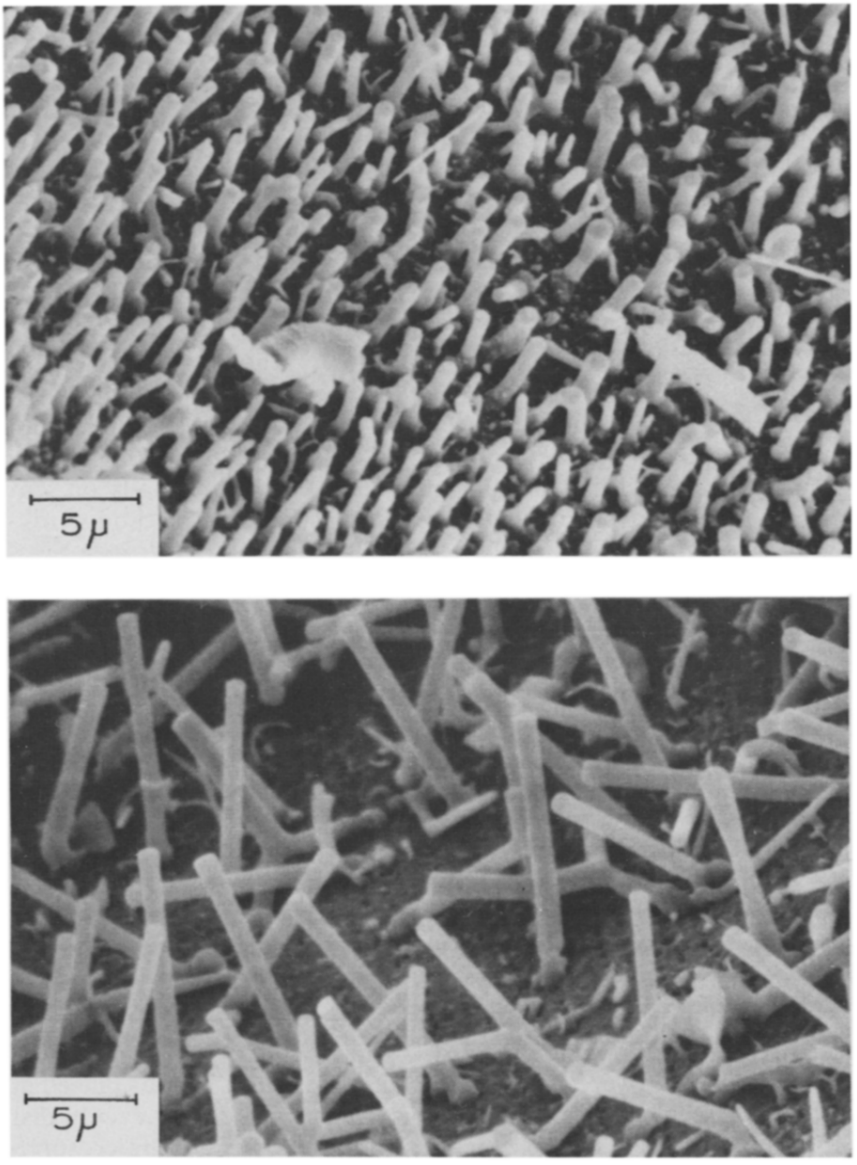

Fig 2 Scanning electron micrographs of the whisker surface resulting from the static vacuum etching method (temperature programmed to 400 C and held there for 12 h) a = septum end b = vacuum end

uniform whisker growth using their approach was made employing the modification described by Sandra and Verzele[4], namely temperature programming the column at 1 5 min to 400 C. The final temperature was maintained for 12 h as suggested by both groups. Although Sandra and Verzele[4] stated that the etching ether is more evenly distributed, scanning electron micrographs of the resulting surface (Fig. 2) still indicate that the whisker density was greater at the septum end. The whiskers at the vacuum end were approximately twice as tall as those at the septum end. It is noteworthy that the spherical caps were not present with this treatment.

In view of the lack of uniformity of whisker growth, the following modifications were made the vacuum remained attached to the glass capillary column while the etching ether was injected through the septum end in such a manner that bubbles were interspersed between small quantities of the etching ether. This end was microtorch sealed and evacuation was continued to distribute evenly the liquid dynamically throughout the column The end of the column, which was attached to the vacuum system was in contact with dry ice to prevent loss of the etching ether through vaporization This vacuum end was then microtorch sealed and the column was temperature treated for 12 h according to the previous procedure Scanning electron micrographs of the septum and vacuum ends of a 51-m glass capillary column treated in this fashion are presented in Fig. 3. As indicated, the whisker growth was of equal density and height at both ends of the column Unfortunately, the results from treating a 102-m glass capillary column with this procedure produced non-uniform whisker growth in a fashion opposite to that experienced previously (Fig 4) This phenomenon was rationalized to occur because the dynamic coating of the etching ether under vacuum proceeded so slowly that the concentration of ether originally present at the septum end continually moved toward the vacuum end. The method of dynamic coating the capillary with the etching ether was modified using nitrogen pressure as described by Clarke[6] Appropriate precautions were included to insure that the required amount of etching ether[4] remained in the column for proper and reproducible whisker formation The procedure used was as follows: the capillary tubing was washed with one column volume of methanol in each direction. Dry nitrogen, which was used at 50 p.s i. to push the methanol through the column, was allowed to pass through the column overnight. This column was then installed on a glass tube support in the gas chromatograph and connected to dry nitrogen at 50 p s i. The column oven temperature was programmed from 25 to 350°C at 5°/min with a final hold at 350 C for 12 h. One end of this capillary was then connected using heat-shrinkable Teflon® tubing to a 2 mm O D. end of a tapered 1/4 in O D standard glass tube. The appropriate amount of etching ether (0 3 mm^3/cm^2; 2.46 μl/m for a 0 25 mm I D. capillary or 4.9 μl m for an 0 5 mm I D. capillary), as determined optimal by Sandra and Verzele[4] to form whiskers 4–5 μm long, was inserted into this 1 4 in glass tube. This tube was secured with a Swagelok connection to a dry nitrogen supply at 50 p.s.i. The capillary was dynamically coated in this manner at constant linear velocity until the ether plug was exhausted within the last 5–10 coils of the column. Both ends of the capillary were attached to vacuum and dry ice was placed at both ends to restrict removal of the ether vapor. With the etching ether evenly distributed after 10–15 min, both ends of the capillary were sealed with a microtorch flame and the capillary was placed in the gas chromatograph. The column oven temperature was programmed from 25 to 400°C at 1.5°/min with a hold at 400°C for

12 h Under these conditions a unfirom whisker density was obtained throughout the entire column After cooling, the ends of the capillary were broken in a hood to release the generated hydrogen fluoride gas The column was then connected to dry nitrogen at 50 p s i in the gas chromatograph and the oven temperature was programmed from 25 to 200 C at 2°/min with a hold at 200°C for 6 h Upon cooling, the nitrogen was replaced with oxygen at 50 p s i and the column temperature pro-

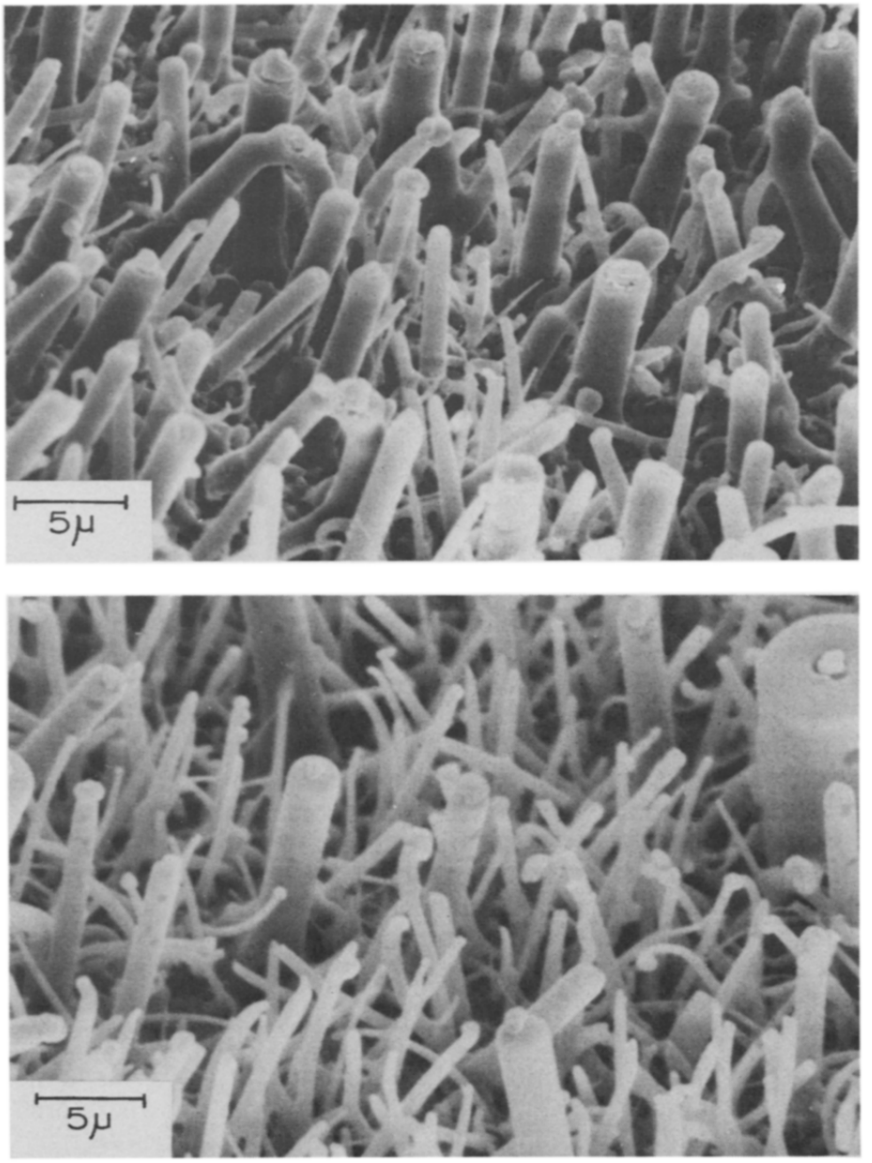

Fig 3 Scanning electron micrographs of the whisker surface resulting from the dynamic vacuum etching of a 51-m column (temperature programmed to 400 C and held there for 12 h) a = septum end b = vacuum end

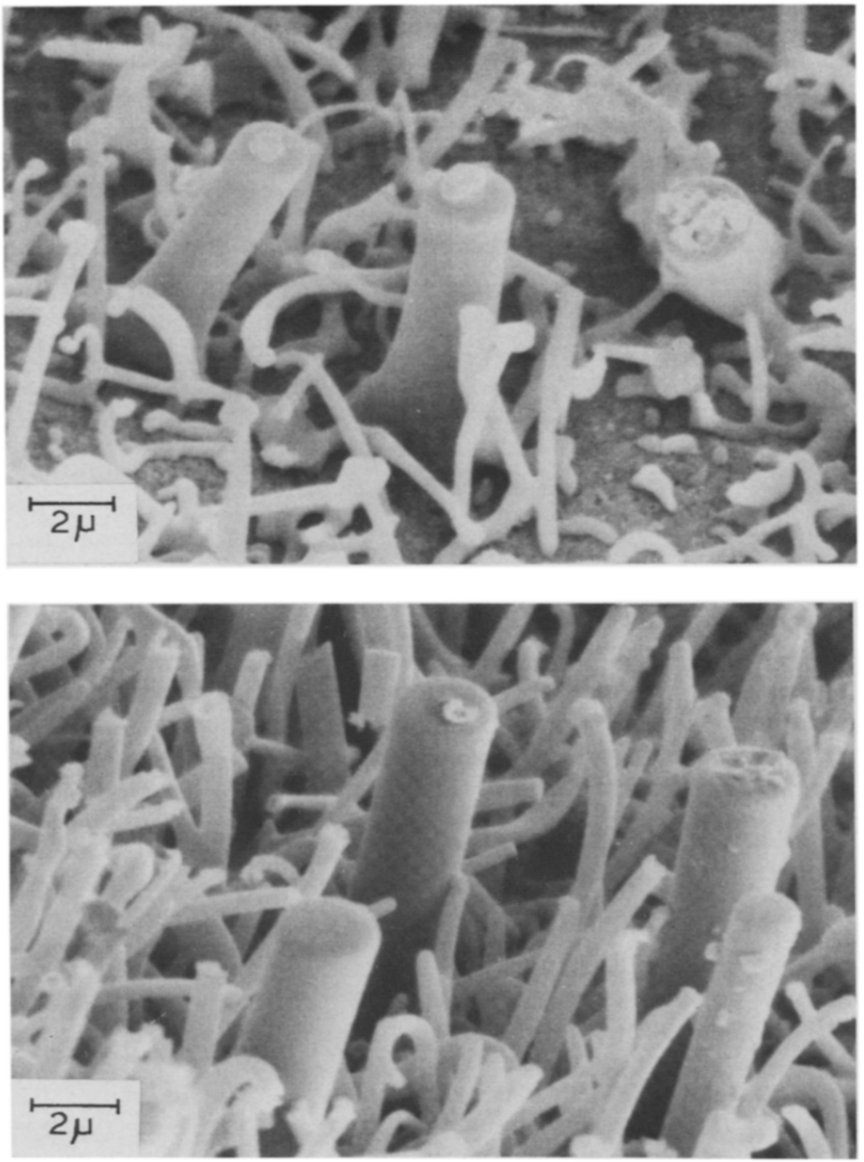

Fig 4 Scanning electron micrographs of the whisker surface resulting from the dynamic vacuum etching of a 102-m column (temperature programmed to 400°C and held there for 12 h) a = septum end, b = vacuum end

grammed from 25 to 450°C at 1°/min with a hold at 450°C for 12 h to remove the residual carbon deposit. After cooling, the whisker capillary column was microtorch sealed for storage if not immediately used

The means of supporting the capillary during the whisker-growing process was found to be very important to obtain uniform whisker growth in each coil of the column. Originally, a wire was used to suspend the capillary (horizontal coil axis) in

the gas chromatograph oven A slight irregular frosted look was observed where the capillary was touching the hanger wire This area became a bare spot after acid leaching with 20% hydrochloric acid A photomicrograph of this bare spot compared to that of an unexposed area for an 0 5 mm I D glass capillary column is presented in Fig 5 A large stainless steel support covering one quarter of the coil diameter was found to cause irregular whisker growth where the capillary touched this surface This was indicated by small bare blotches (after acid leaching) rather than a continuous bare area, as seen in the photomicrograph of an 0 25 mm I D glass capillary column in Fig 6 compared to a photomicrograph of an unexposed area Since the gas chromatograph oven was constructed of stainless steel, asbestos sheets were used to line as much of the oven as possible to eliminate its influence on the whisker growth process A glass tube support created bare spots at times where the capillary column touched the glass tubing Also, when the coils of the capillary column were too closely packed together during the whisker growth process, bare spots along the sides of the coils were observed A support method which did not create bare spots and provided undisturbed whisker formation employed a wire wrapped with asbestos tape upon which the coils of the column were evenly spaced

The vacuum method of introducing the etching ether into the glass capillary is suitable for preparing columns of less than 50 m in length However, the dynamic procedure taking care to distribute evenly an appropriate and reproducible concentration and of etching ether, provides uniform whisker growth in columns in excess of 100 m in length The bare spots in the whiskered columns were only visible as heavily frosted areas until the acid-leaching step of the deactivation method was found to remove the apparently unattached whiskers from the glass surface Taking care to line the oven walls and capillary support with a non-flaking asbestos material and

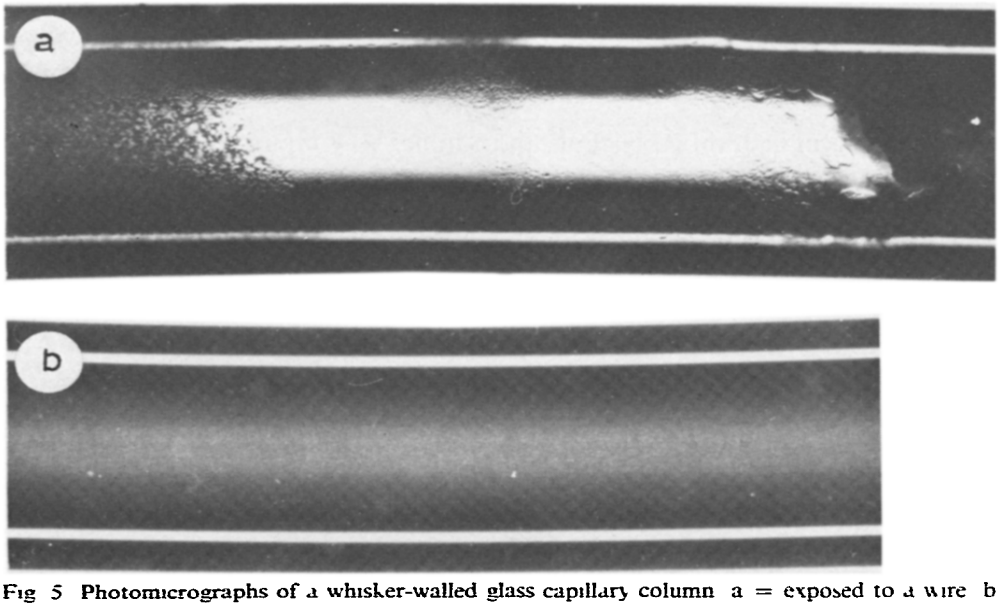

Fig 5 Photomicrographs of a whisker-walled glass capillary column a = exposed to a wire b = an unexposed area

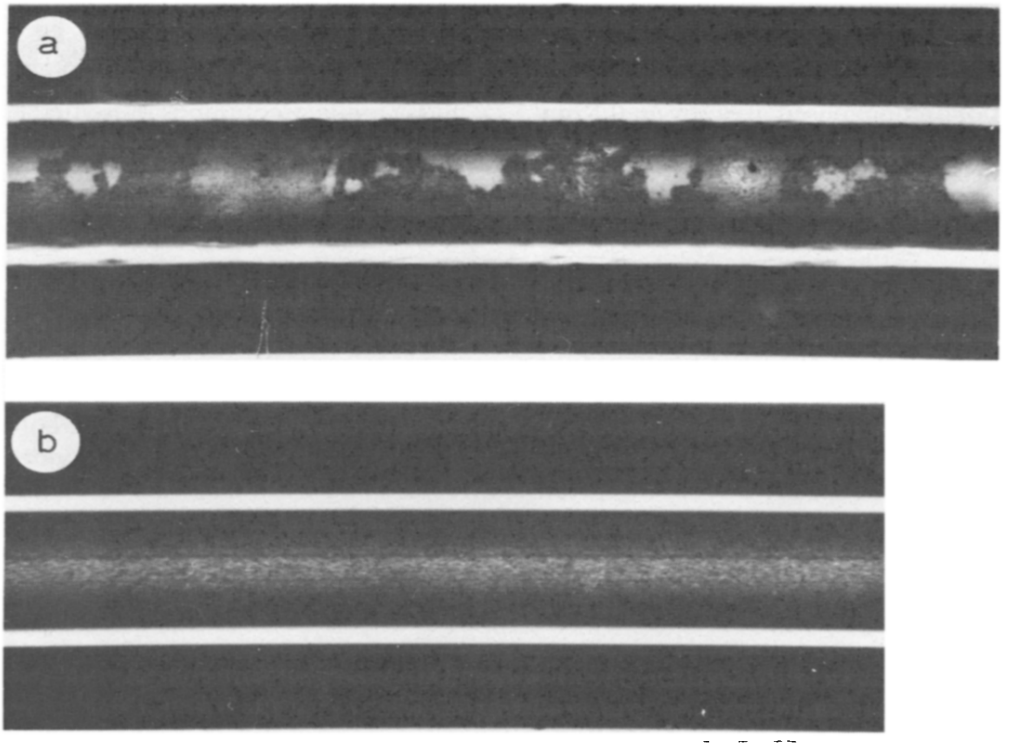

Fig. 6 Photomicrographs of a whisker walled glass capillary column. a = exposed to a sheet of stainless steel; b = an unexposed area

keeping the coils evenly spaced during the whisker-growth step eliminated this problem.

ACKNOWLEDGEMENTS

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