*Journal of Chromatography*, 147 (1978) 111–117


CHROM. 10,265

# INVESTIGATION OF BARIUM CARBONATE LAYERS IN GLASS CAPILLARY COLUMNS BY SCANNING ELECTRON MICROSCOPY

K. GROB
*GC-Laboratory, ETH Zürich, EAWAG, 8600 Dübendorf (Switzerland)*
and
J. R. GUENTER and A. PORTMANN
*Department of Inorganic Chemistry, University of Zürich, Rämistrasse 76, 8001 Zürich (Switzerland)*
(Received June 1st, 1977)

## SUMMARY

The structure of barium carbonate layers produced on the inner surface of glass capillary columns may be influenced by a large number of experimental variables. The effect of some of these variables, namely crystallization temperature, type of detergent and pretreatment of the glass surface, has been studied by scanning electron microscopy. While crystallization at room temperature and appropriate selection of the detergent increase the density of the crystal layer, low temperature crystallization also avoids undesirable tower-shaped crystals. Almost unmodified layers are produced on glass that has been leached with 20% hydrochloric acid at 160° for 15 h.

## INTRODUCTION

Recently we described a procedure[1,2] for roughening the inner surface of glass capillaries before coating with polar phases, the necessary roughness being produced by barium carbonate crystals grown on the solid surface. Our first paper[1] included two scanning electron micrographs of the crystal layer. Subsequently we studied the influence of various parameters on the size, shape and distribution of the crystals primarily with the aim of producing finer and more closely packed particles[2]. This study has led to layers which differ considerably from those depicted previously, and we now present details of their structure and of their dependence on the experimental variables.

## EXPERIMENTAL AND RESULTS

### *Selection and preparation of samples*

A large number of experimental parameters were varied in order to determine their contribution to the structural differences between the crystal layers. The necessity of limiting the number of micrographs caused us to select parameters which either produced important differences or were of particular methodological interest.

One, apparently fundamental, variable, namely glass variety, was not studied since, after intense leaching of the raw glass surface[2], the crystal layers obtained on soft glass and borosilicate glass were very similar. For this study, we arbitrarily selected Pyrex glass. Our simplified rule[2] of using the same saturated solution of barium hydroxide whenever roughening (not covering) the glass surface prevented us from including the concentration of this salt as a variable.

Thus we selected three variables only: crystallization temperature (25 and 80°), the most important; detergent, namely Dehydrophen D[1], representing the nonylphenol polyglycol type, and Marlazin L 10 representing the dodecylamino type; and pretreatment of the glass surface (there is considerable interest in the influence of our intense acidic leaching treatment).

All of the treatments were carried out as described previously[1,2]. After crystallization, the remaining water was flushed out of the columns with acetone, and the columns were dried for 1 h at 220° under a low gas flow-rate. They were then ready for microscopy.

*Scanning electron microscopy*

Splinters of crushed capillaries with their internal surfaces exposed were mounted in various orientations on standard aluminium specimen supports by means of conducting glue. Sufficient surface conductivity was obtained by sputtering a 600–700 Å thick layer of gold on to the sample surfaces. Scanning electron micrographs were recorded with a Stereoscan S 4 microscope at an accelerating voltage of 30 kV, the specimens being tilted so that their surfaces either faced the secondary electron detector or were at grazing incidence to it. Original magnifications of the micrographs shown in this paper were $\times 1200$ and $\times 6000$. Three photographs are presented for each sample. Series a illustrates the distribution of the crystals, series b shows the structure of single particles and of their aggregations and series c is particularly indicative of particles in a upright position ("towers").

*Interpretation of micrographs*

*Sample 1.* The particles on the inner capillary walls are mostly in the shape of needles with poorly defined edges, probably owing to dendritic growth. Their average length is 3–4 $\mu$m; their diameter is 2000–3000 Å. Most of the needles are slightly bent. The smaller particles in Fig. 1a and b are in fact needles of about the same size as those described above, but aligned vertically to the image plane, as can be deduced from Fig. 1c which was taken at grazing incidence to the detector. Fig. 1c also illustrates that the individual particles seem to be firmly fixed to the glass substrate.

*Sample 2.* The particle size and shape of sample 2 are not characteristically different from those of sample 1. However, in this specimen, the aggregation of the needles to form bundles is somewhat more pronounced.

*Sample 3.* Sample 3 differs from the first two in having a clearly looser distribution of the individual crystallites, but with no change in their size and shape.

*Sample 4.* Sample 4 contains particles identical to those described for the 80° series, but this glass is also covered with much more finely divided material of diameter as low as 1000 Å, which cannot be considered as upright needles. Furthermore, the needles are thinner, and the interparticle distances are significantly lowered.

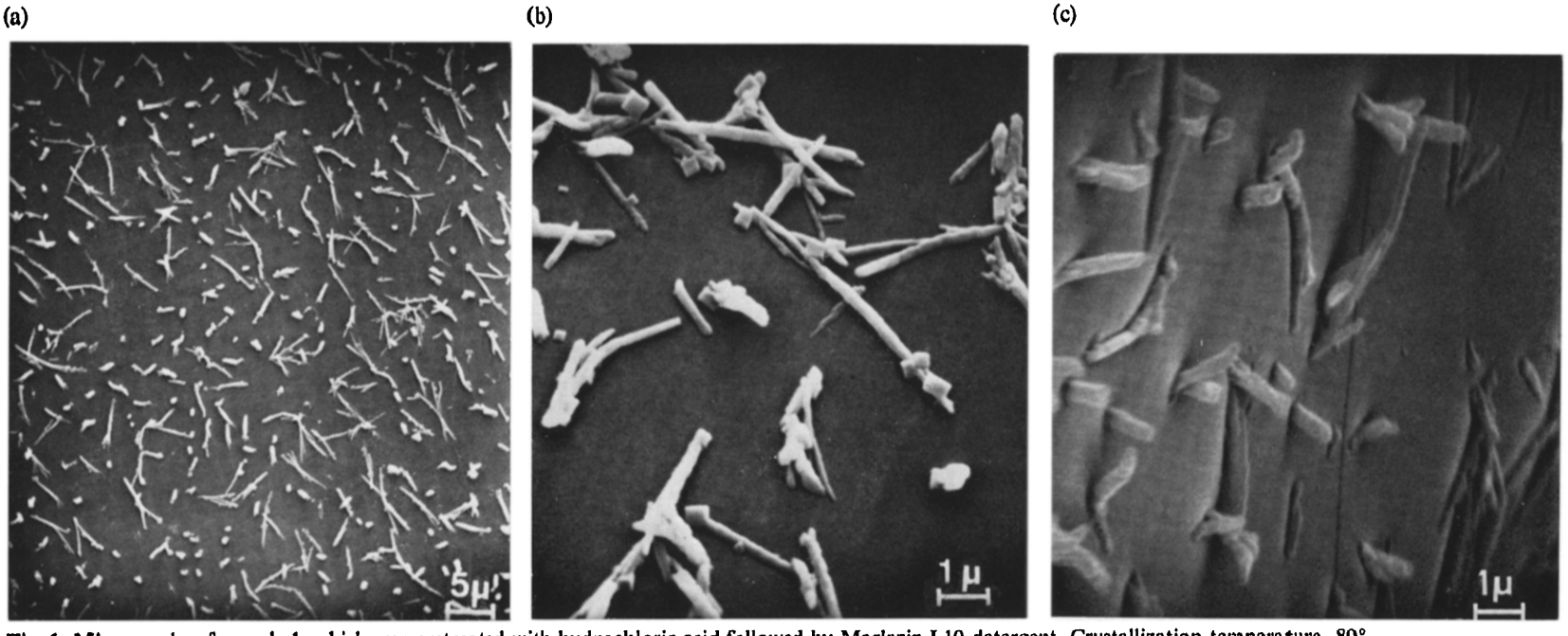


Fig. 1. Micrographs of sample 1, which was pretreated with hydrochloric acid followed by Marlazin L10 detergent. Crystallization temperature, 80°.
a, Distribution of the crystals; b, structure of single particles and their aggregations; c, particles in an upright position.

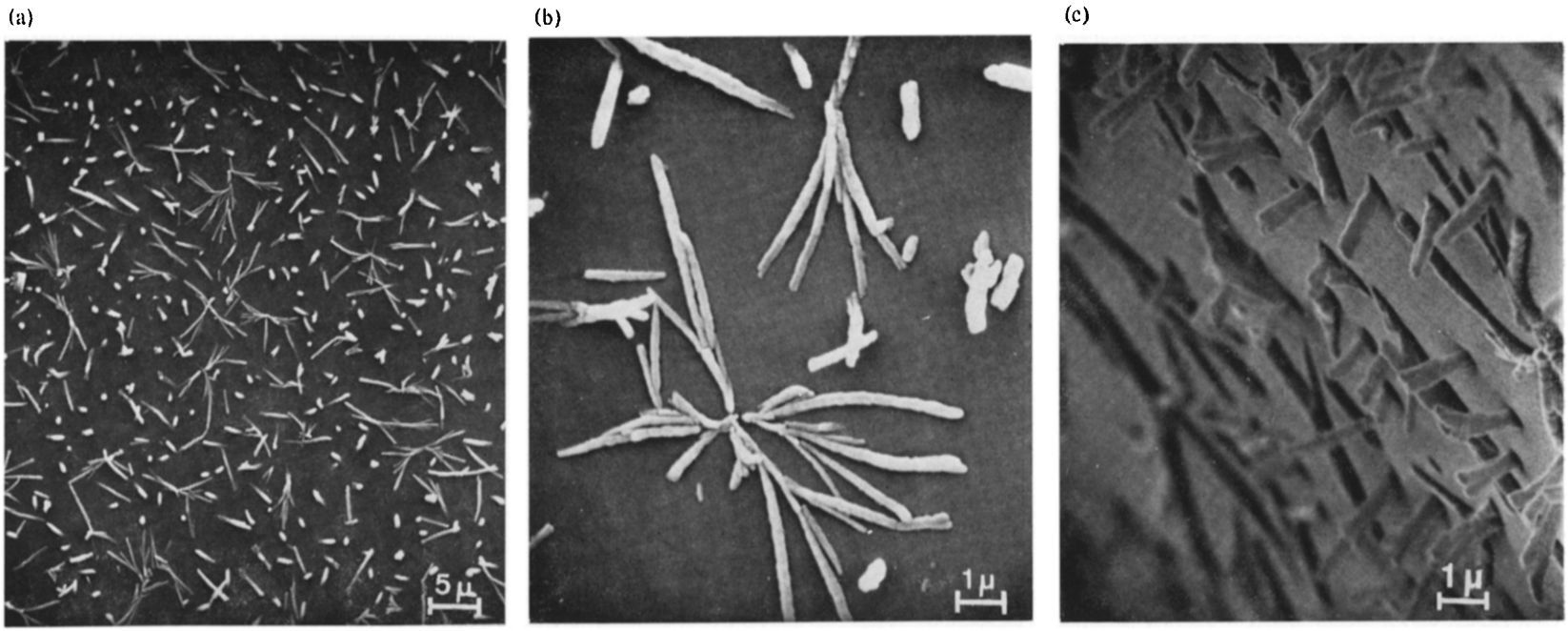


Fig. 2. Micrographs of sample 2, which was not pretreated with HCl. Other conditions as in Fig. 1.

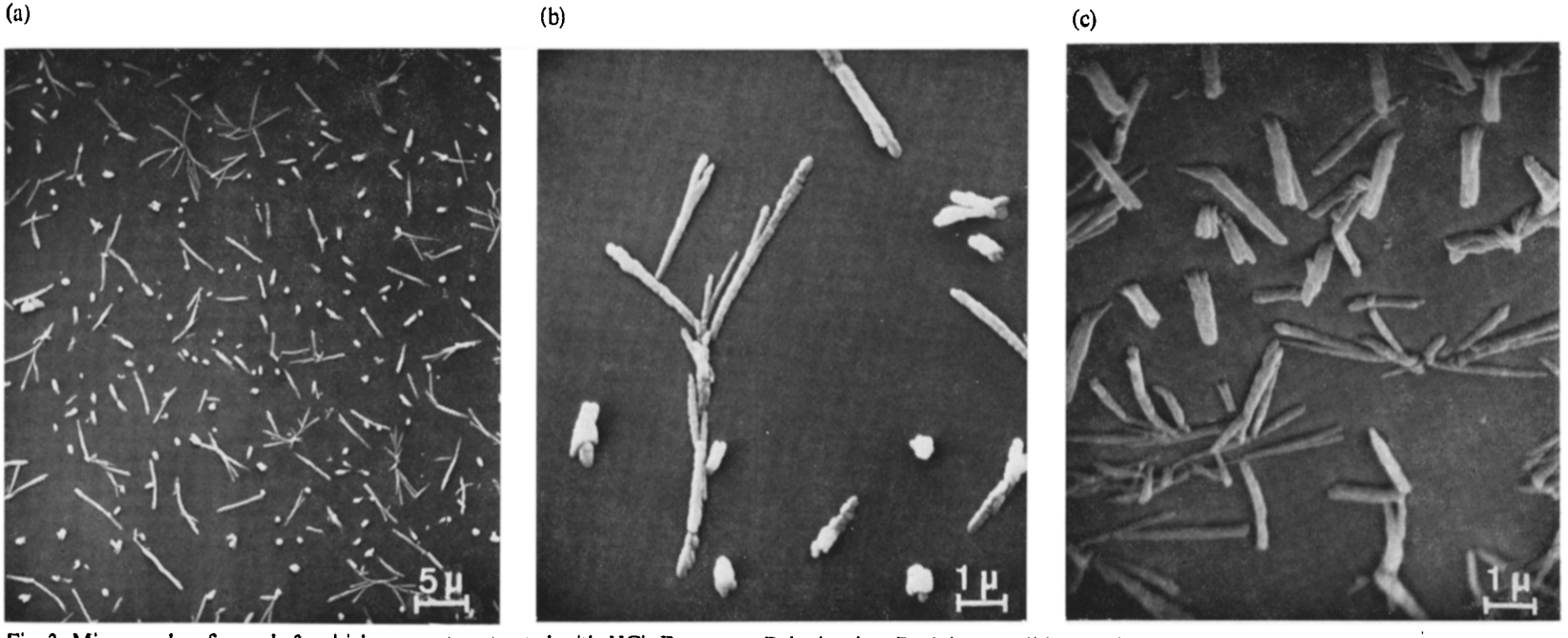


Fig. 3. Micrographs of sample 3, which was not pretreated with HCl. Detergent, Dehydrophen D. Other conditions as in Fig. 1.

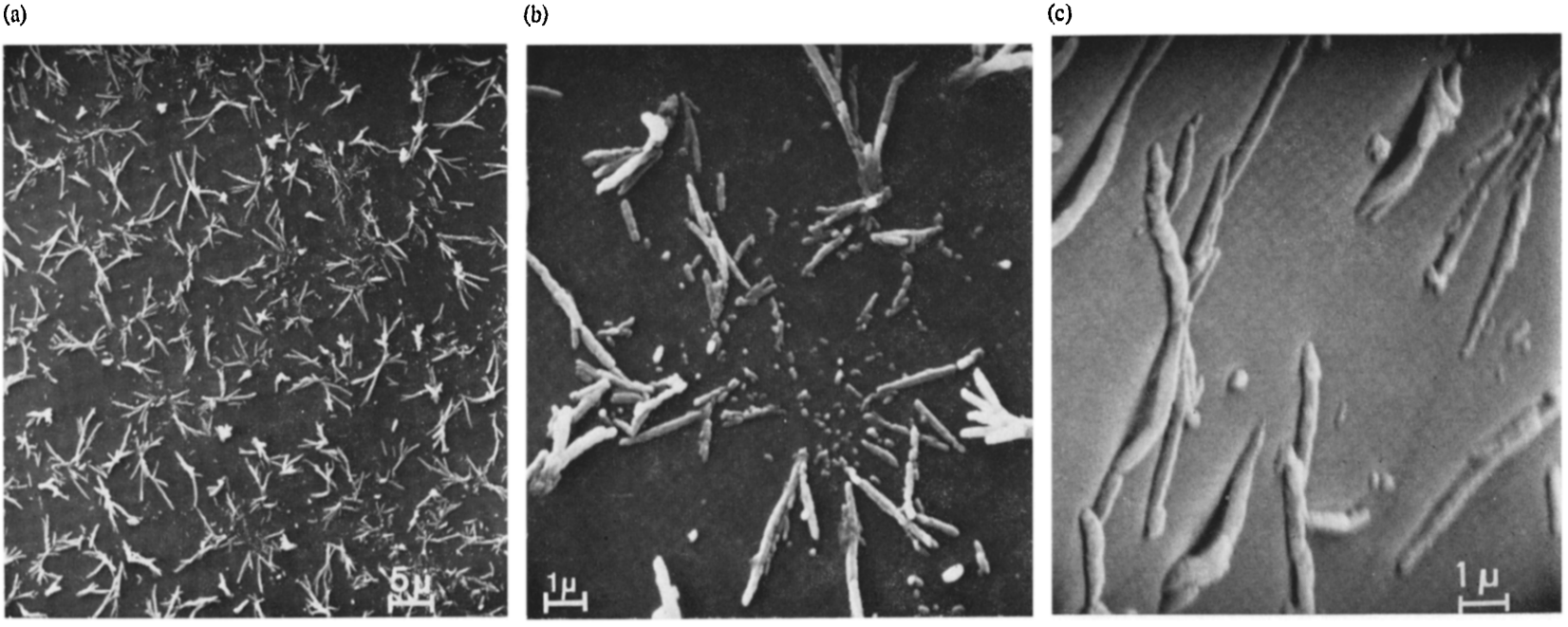


Fig. 4. Micrographs of sample 4, which was pretreated with HCl and detergent as in Fig. 1. Crystallization temperature, 25°.

## DISCUSSION

In terms of the column quality the influence of the variables may be discussed as follows.

Comparison of micrographs la and 2a with 3a shows that more closely packed particles are produced with the dodecylamine-type detergent than with the nonylphenol type.

The most important parameter is the crystallization temperature. A decrease in the crystallization temperature (samples 1–3 compared with sample 4) results in smaller and more closely packed particles, yielding coatings with 10–20% higher separation numbers. Moreover, there were no crystals in vertical alignment. These tower-like particles were predominant in our earlier work, as shown in ref. 1 by the micrographs obtained from a 3-fold diluted solution of barium hydroxide. According to Figs. 1c, 2c and 3c, the vertical particles still play an important role in the layers produced at 80°, while they are absent in Fig. 4c. We consider that the presence of such particles is undesirable since their position and shape prevents them from becoming immersed in or, at least, covered by even thick liquid films. It seems to be difficult or impossible to satisfactorily deactivate the uncovered portion. Thus, columns treated at 80° are generally more active than those roughened at room temperature, since the crystal layers of the latter consist exclusively of particles in horizontal positions (Fig. 4c).

It may be surprising that the very rough pretreatment of the glass surface has little effect on the crystal structure [compare Fig. 1a (HCl treated) with 2a (untreated)]. This optical result confirms our experience that intense leaching does not affect the separation efficiency, while it improves the inertness and eliminates the basicity of soft glass.

In relation to the greatly different conditions under which they were produced, the crystal layers in all of the four samples show surprisingly small differences. This is in accord with practical experience that perfectly constant structures and distributions of particles are easily obtained under approximately constant conditions.

## REFERENCES

1 K. Grob and G. Grob, *J. Chromatogr.*, 125 (1976) 471.
2 K. Grob, G. Grob and K. Grob, Jr., *Chromatographia*, 10 (1977) 181.