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# APPLICATIONS OF SURFACE-MODIFIED POROUS SILICAS TO GLASS CAPILLARY COLUMN PREPARATION

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## SUMMARY

Glass capillary columns, coated with porous, surface-modified silicas, have been evaluated for the separation of typical gasoline-range hydrocarbons. In this case, the separation is that of gas–solid chromatography. In addition, these silicas have been utilized to prepare PLOT columns with "polar" liquid phases such as the Silars and other cyanoalkyl materials. These "polar" columns do not require etching or other treatment of the glass surface. They are easy to prepare and yield stable, efficient, selective separations by gas–liquid chromatography. Further, because of the porous layer, they have higher sample capacities than wall-coated open-tubular columns.

## INTRODUCTION

The surface modification of micron-sized porous silica was described earlier[1]. When coated onto soft glass capillary columns, the silica provided efficient separations of complex hydrocarbon samples ($C_5$–$C_8$ range). The selectivity obtained with these columns was that of gas–solid adsorption chromatography.

This report describes, and discusses, two extensions of this work. Firstly, we evaluated these columns for the separation of typical gasolines ($C_5$–$C_{12}$ range). Also, utilizing the surface-modified, porous silicas, we developed a rapid dynamic technique for the preparation of stable PLOT (porous-layer open-tubular) columns containing "polar" liquid phases. These PLOT columns show the "selectivity" of the liquid phase and provide efficient separations by gas–liquid partition chromatography.

## EXPERIMENTAL

A GDM-1 glass-drawing machine (Shimadzu, Kyoto, Japan) was used to draw the glass capillaries (Kimble R-6 soda-lime glass).

A Sigma 3 gas chromatograph (Perkin-Elmer, Norwalk, CT, U.S.A.), equipped with a hydrogen flame-ionization detector, was utilized. Columns were connected with heat-shrinkable 30-gauge PTFE.

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A Model 3385A chromatographic automation system (Hewlett-Packard, Avondale, PA, U.S.A.) was employed to provide retention time and peak area data.

*Reagents*

Solvents used for column coating were methyl ethyl ketone and *n*-heptane from Burdick and Jackson Labs. (Muskegon, MI, U.S.A.). The hydrocarbons used to prepare standard blends were high-purity reagents from Philips Petroleum (Bartlesville, OK, U.S.A.) or the American Petroleum Institute.

Igepal RC-520 was obtained as a sample from GAF (Charlotte, NC, U.S.A.). Anhydrous sodium sulfate was procured from Matheson, Coleman and Bell (East Rutherford, NJ, U.S.A.). *p*-Toluenesulfonic acid monohydrate was obtained from Aldrich (Milwaukee, WI, U.S.A.). Methanol and xylene were Baker analyzed reagent-grade materials. Syloids, micron-sized amorphous silicas, were samples from W. R. Grace (Baltimore, MD, U.S.A.). Carbowax 350 was a sample from Union Carbide (New York, NY, U.S.A.). Silar 10C and CEF (cyanoethylformamide) were obtained from Applied Science Labs. (State College, PA, U.S.A.).

## RESULTS

All experiments were performed with 400 ft. × 0.02 in. I.D. columns prepared from Kimble R-6 soda-lime glass. Hydrogen was used as the carrier gas, at 10 p.s.i. in all tests.

Two samples, which are being cooperatively tested by Section L of Research and Development Division IV (ASTM D-2), were separated with a column similar to those described earlier. Chromatograms of an ASTM naphtha and an ASTM indolene are shown as Figs. 1 and 2. The temperature of the column, its programming rate, and other parameters are given in the figure captions. The column used for these separations was coated from a 7.5% suspension of PZ-240 (prepared from Syloid 244 and Igepal RC-520) in *n*-heptane.

In order to test the applicability of surface-modified porous silicas as addition agents for coating "polar" liquid phases onto soft glass columns, a column was prepared from a 2.5% suspension of PZ-250 (Syloid 244 reacted with Carbowax 350) containing 5.0% Silar 10C. Silar 10C is a "polar" cyanoethylated silicone. Ordinarily, it is a difficult phase to coat on to a glass column. Column etching, or the addition of solids, such as Cabosil or Chromosorb, is ordinarily used to prepare Silar columns of either the wall-coated open-tubular (WCOT) or PLOT type[2].

The PZ-250 plus Silar column was tested for the separation of a typical methyl ester mixture. The resulting chromatogram is shown in Fig. 3.

As "polar" liquid phases are useful for the separation of aromatic hydrocarbons from saturated hydrocarbons, the applicability of PZ-250 was further tested by preparing a glass column coated with a PZ-250 plus CEF mixture. As shown in Fig. 4, benzene is retarded very strongly on this column and elutes between *n*-dodecane and *n*-tridecane. The separations of the ASTM naphtha and the ASTM indolene with this column are shown in Figs. 5 and 6. Essentially, all of the saturated hydrocarbons are eluted prior to benzene in these cases.

Our experience with these "polar" columns has been that they are relatively easy to prepare, that they do not form beads and that they provide efficient separations for long periods of time when used at the temperatures specified.

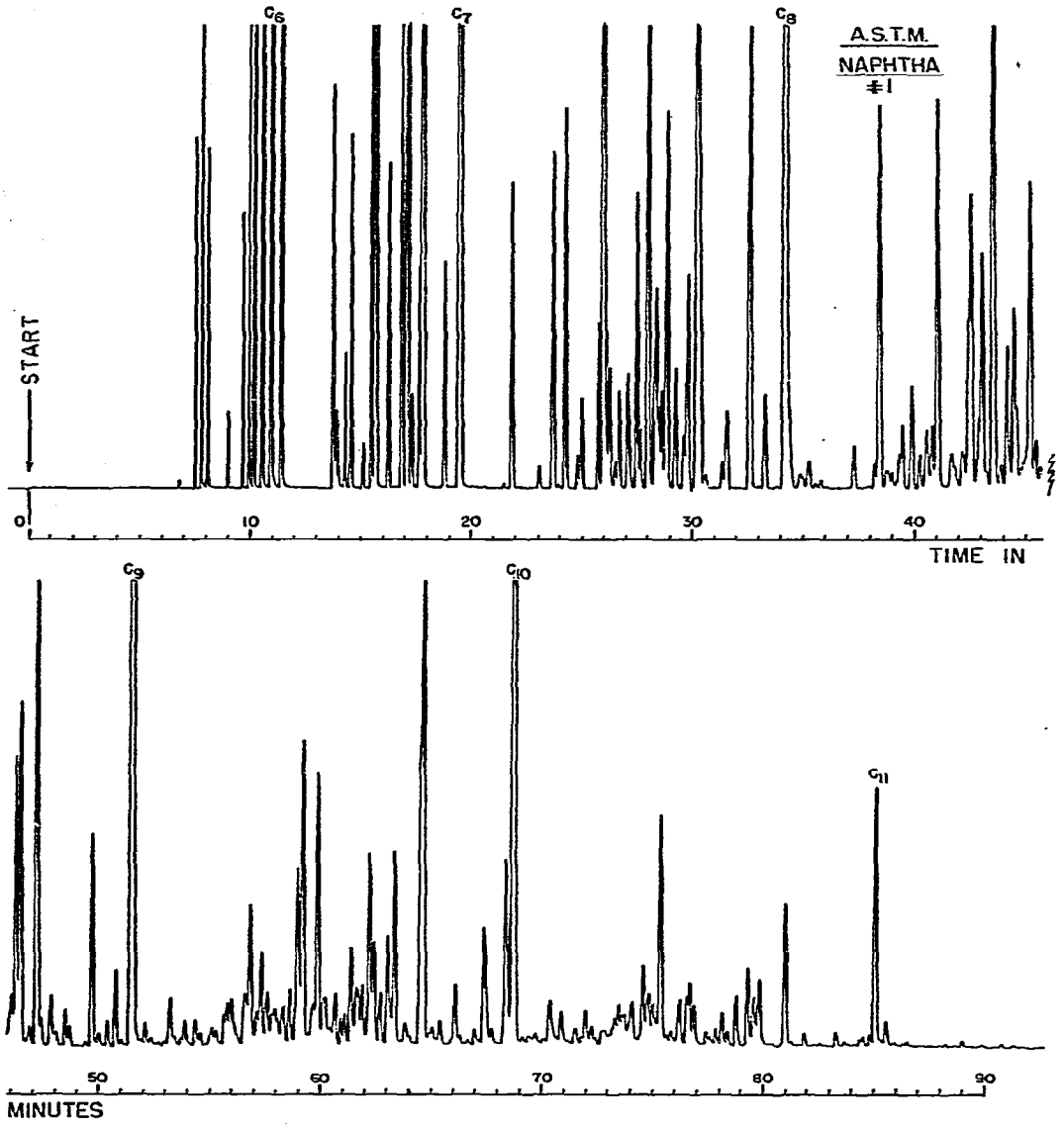



Fig. 1. Separation of ASTM naphtha. Column: 400 ft. × 0.02 in. I.D. glass coated with a 7.5% suspension of PZ-240. Conditions: 10 min isothermal at 25°C, then 1°C/min to 110°C.

## DISCUSSION AND CONCLUSIONS

The results obtained for the separation of the ASTM naphtha and the ASTM indolene, with a silica–Igepal RC-520 column (Figs. 1 and 2) indicate that this column, temperature-programmed as shown, provides an efficient separation of these complex hydrocarbon mixtures. $C_{11}$ hydrocarbons were eluted at about 110°C and $C_{12}$ hydrocarbons at about 130°C. Our tests indicate that silica–Igepal columns are

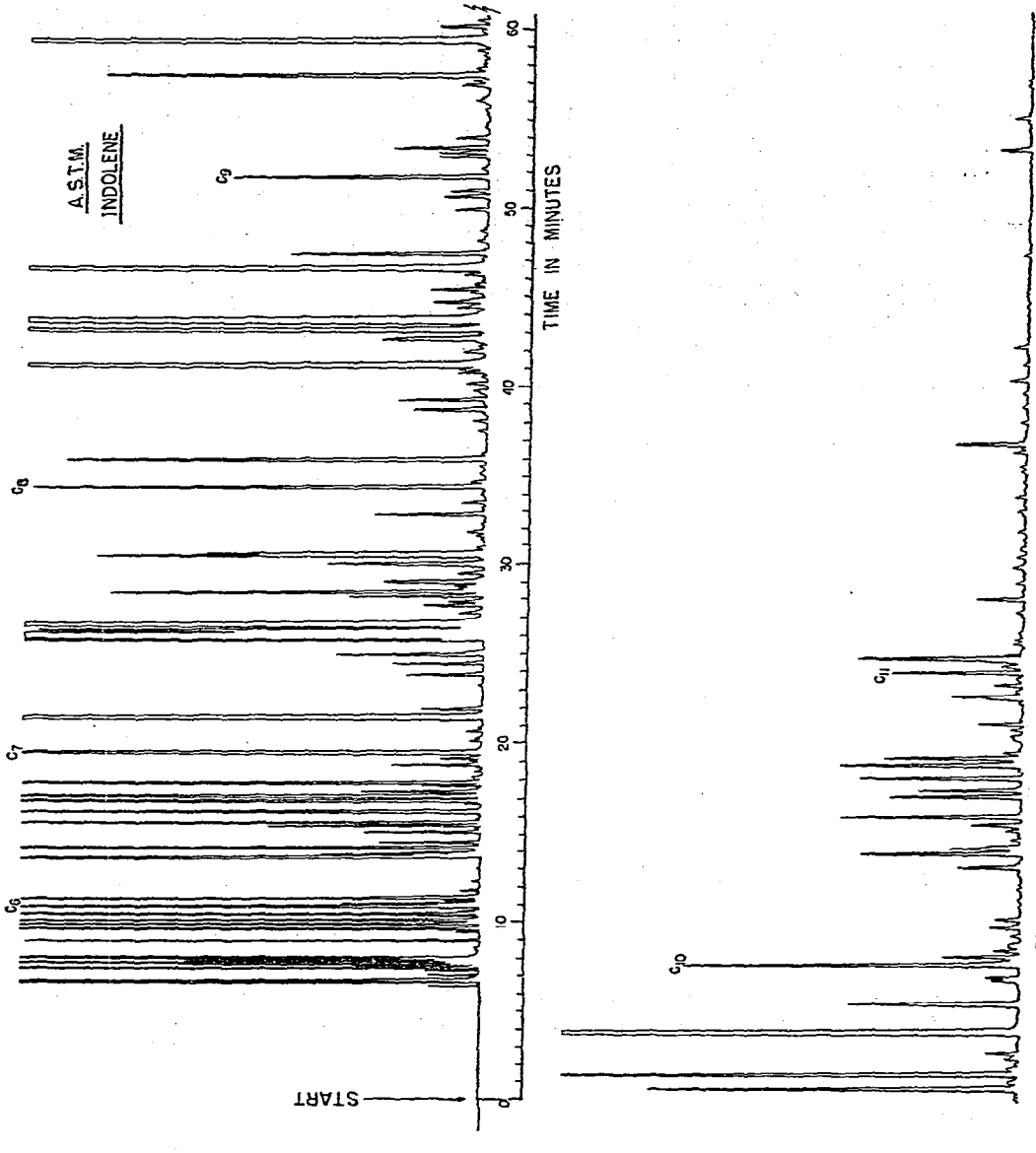



Fig. 2. Separation of ASTM indolene. Column: 400 ft. × 0.02 in. I.D. glass coated with 7.5% PZ-240. Conditions: 10 min isothermal at 25°C, then 1°C/min to 135°C.

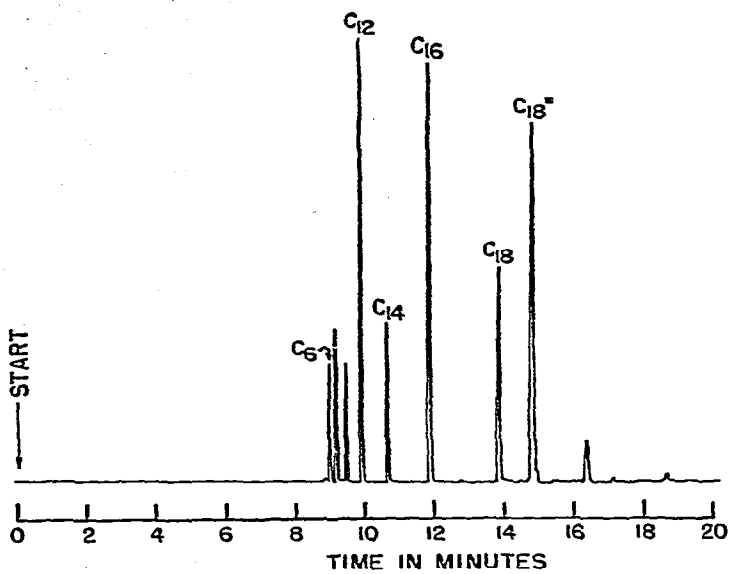



Fig. 3. Separation of fatty acid methyl esters. Column: 400 ft. × 0.02 in. I.D. glass coated with 2.5% PZ-250 plus 5.0% Silar 10C. Temperature, 200°C.

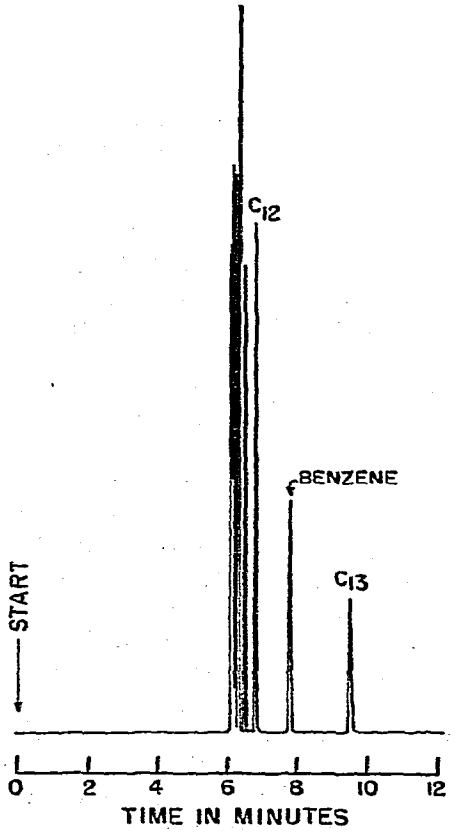



Fig. 4. *n*-Alkane–benzene standard. Column: 400 ft. × 0.02 in. I.D. glass coated with 2.5% PZ-250 plus 15.0% N,N-bis(2-cyanoethyl)formamide (CEF). Temperature, 90°C; pressure, 10 p.s.i. (hydrogen).

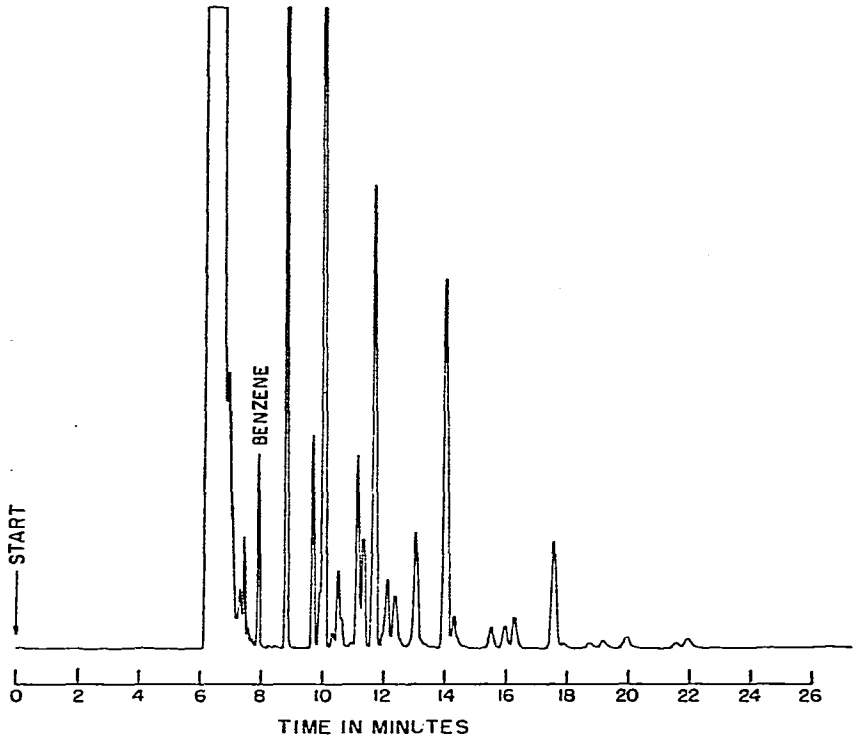



Fig. 5. Type separation of ASTM naphtha. Column: 400 ft. × 0.02 in. I.D. glass coated with 2.5% PZ-250 plus 15.0% N,N-bis(2-cyanoethyl)formamide (CEF). Temperature, 90°C; pressure, 10 p.s.i. (hydrogen).

stable for short periods of time at 200°C. However, for their best performance, they should not be used for long periods of time at temperatures above 175°C. With programming rates similar to those shown here, it should be possible to obtain efficient separations of hydrocarbons in the $C_{16}$ range at 175°C. In order to separate higher boiling hydrocarbons with surface-modified silicas, it will be necessary to develop more thermally stable silica–organic bonds. Obviously, an alternative is to utilize capillaries coated with thermally stable liquid phases recommended for use at 200–400°C.

Because of the large number of silicas which are available for chromatographic use, we studied the physical and chemical properties of a wide variety of silicas and feel that it is important to emphasize the particular properties of the surface-modified Syloids which enable them to perform as demonstrated. The particle size, pore volume, surface area and wettability of the silica particles determine how they will interact with the solvents used for coating capillary columns and with the column itself. Further, for a given silica and a given column surface, some solvents are better than others.

A thorough examination of all of the above factors was beyond the scope of this study. However, our experience indicates that "openness" or porosity of the silica is very important in order to prevent rapid settling and plugging of the capillaries during the coating procedure. The pore volume and/or the oil absorption values are convenient parameters to examine when evaluating silicas for these purposes.

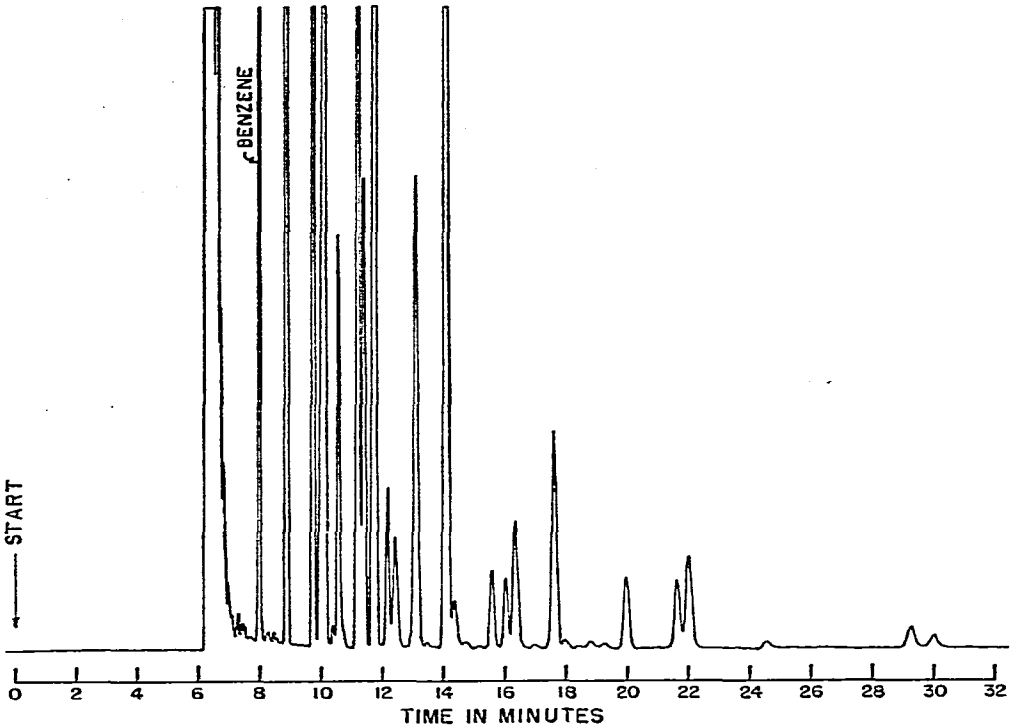
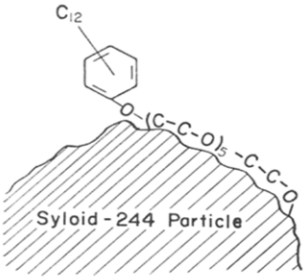



Fig. 6. Type separation of ASTM indolene. Column: 400 ft. × 0.02 in. I.D. glass coated with 2.5% PZ-250 plus 15.0% N,N-bis(2-cyanoethyl)formamide (CEF). Temperature, 90°C; pressure, 10 p.s.i (hydrogen).

Fig. 7. Photomicrograph (40×) of Syloid 244 4-$\mu$m amorphous silica.



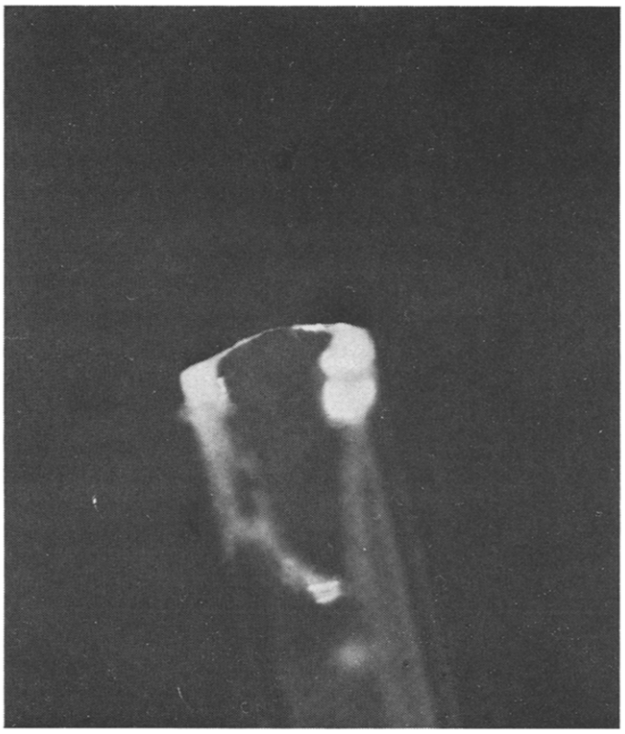



Fig. 8. Idealized structure of PZ-240, the reaction product of Syloid 244 with Igepal RC-520.

Fig. 9. Photomicrograph (40×) of end of 0.02-in. I.D. glass capillary column coated with a 7.5% suspension of PZ-240.

A photomicrograph (40×) of Syloid 244 is shown in Fig. 7. After reaction with Igepal RC-520, the reaction product (PZ-240) is hydrophobic and disperses readily in most organic solvents. A drawing of a proposed, idealized structure for PZ-240 is shown in Fig. 8. A photomicrograph (40×) of the end of an 0.02-in. I.D. column coated with a 7.5% suspension of PZ-240 is shown in Fig. 9.

Some recent tests indicate that PZ-240 or PZ-250 can also be used to prepare metal capillary columns (stainless steel) containing "polar" liquid phases.

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1 R. G. Mathews, J. Torres and R. D. Schwartz, *J. Chromatogr.*, 186 (1979) 183.
2 W. G. Jennings, *Gas Chromatography with Glass Capillary Columns*, Academic Press, New York, 1978.