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PERFORMANCE OF DIFFERENT TYPES OF CROSS-LINKED METHYL POLYSILOXANE STATIONARY PHASES ON FUSED-SILICA GLASS CAPILLARY COLUMNS

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SUMMARY

The chromatographic properties of two distinctly different types of silicone polymers, utilized as stationary phases and rendered insoluble on fused-silica glass capillary tubing by different methods involving the *in situ* cross-linking with either tetrachlorosilane or a variety of peroxides, were assessed. Columns showing excellent efficiency, thermal stability, and resistance to certain solvents were prepared from both classes of polymers having either Si–O–Si or Si–C–C–Si cross-linkages. The process of vulcanization of the silicone gums with certain of the peroxides frequently appeared to give rise to signs of renewed surface activity on fused silica columns previously rendered inert. This effect was either minimal or absent when reactive prepolymers were cross-linked with tetrachlorosilane.

INTRODUCTION

During the past six years, considerable progress has been made in the field of gas chromatography by Madini *et al.*[1-4] and Blomberg and Wännman[5,6] by pioneering the development of methods for the *in situ* production of efficient, thermally stable, insoluble silicone polymeric stationary phases from α,ω-hydroxypolymethylsiloxane type prepolymers on the treated surfaces of either sodalime or borosilicate glass capillary tubes. Film stability, the exceedingly low level of "bleeding" phenomena at elevated temperatures, the imperviousness of cross-linked stationary phases to exposure to large volumes of solvent, the ability to rinse away residual sample and film debris by appropriate solvents, and the relative ease by which thick films could be fabricated, were considered by these investigators to be the outstanding advantages of this technique.

More recently, in an attempt to achieve similar goals, Grob and co-workers[7,8] and Sandra *et al.*[9] utilizing methods well known in the field of silicone polymer chemistry used peroxides to insolubilize certain high-molecular-weight polydimethylsiloxane gums commonly employed as stationary phases for glass capillary columns. Both of these groups were impressed with the relative ease by which their preliminary attempts to cross-link these non-polar silicone phases succeeded in producing satis-

factory capillary columns. Interestingly, Grob and Grob[8] who carried out his cross-linking experiments on regular glass capillary column surfaces which were first subjected to persilanization[10], readily obtained well deactivated columns. In contrast, in a similar study, Sandra et al.[9], using fused-silica glass capillary tubing which was first deactivated either by octamethylcyclotetrasiloxane[11] or by the polysiloxane technique of Schomburg et al.[12], failed to offer results which could provide one with information concerning the status of activity or lack thereof on these surfaces after cross-linking under the conditions of their experiments.

When we sought to modify the methods of Madani and co-workers[1-4] and Blomberg and Wännman[5,6] as well as those of Grob and co-workers[7,8] and Sandra et al.[9], in early attempts[13,14] to insolubilize non-polar silicone polymers on fused-silica glass capillary surfaces, several problems were encountered.

These primarily centered around (a) the residual surface activity that remained following vulcanization and (b) the erratic wettability of these surfaces by polymeric solutions containing certain peroxides. In an effort to overcome these and other technical problems that developed under these circumstances, we then studied in detail the various factors that affected cross-linking, uniform film formation, thermal stability, and surface deactivartion. These on-going investigations, some of which are now described below, also extended into the utilization of other reactions which involved the use of one- or two-component systems in the presence of appropriate catalysts for the cross-linking of various types of silicone polymer at room or elevated temperatures.

At the outset, it was also recognized that the cross-linking reactions that occurred with the type of silicone polymer produced by the methods described by Madani and co-workers[1-4] and Blomberg and Wännman[5,6], differed significantly from that brought about by the action of free radicals formed during the thermal decomposition of various peroxides upon those silicone gum phases usually employed in gas chromatography.

As seen from the structure depicted in Fig. 1, in the former instance, mild cross-linking involves the silicon oxygen (Si–O–Si) bond in the polymer chain. This siloxane moiety, found also in the vitreous silica glasses and sand, is known to contribute to the outstanding high-temperature characteristics of certain of the silicones[15]. On the other hand, as noted frcm the structure seen in Fig. 2, when peroxides are heated to their decomposition ten:peratures in the presence of high-molecular-weight silicone gums or fluids, free radicals readily evolve which then react with and remove hydrogen atoms from the methyl groups of adjacent linear molecules, to form an elastic
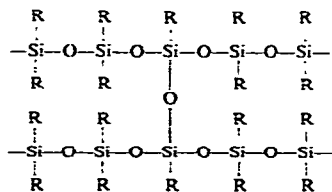

Fig. 1.   Room temperature cross-linking (mild) of polyxiloxane diol polymer by tetrachlorosilane. Note Si–O–Si linkage.
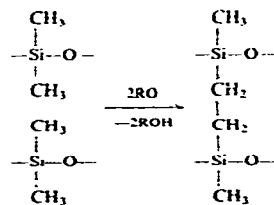
Fig. 2.   High temperature cross-linking of polysiloxane polymer by peroxides. Note Si–C–C–Si linkage.
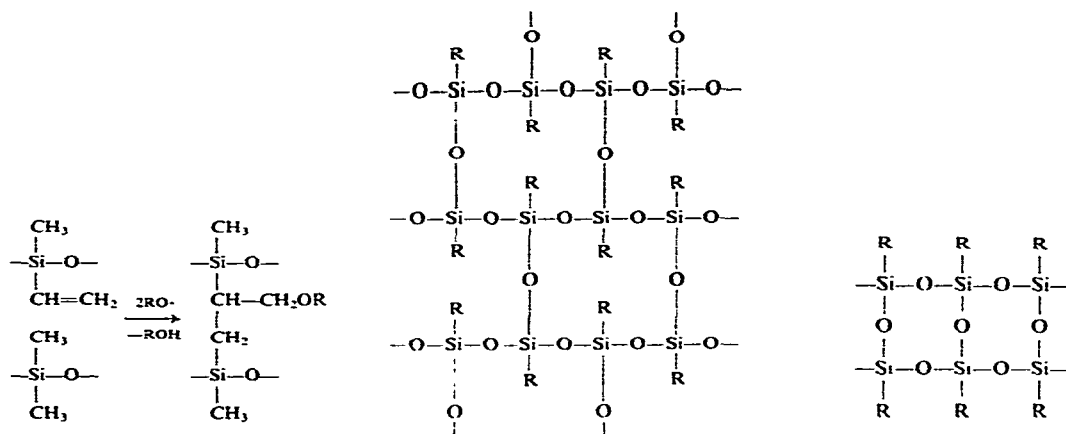
Fig. 3. High-temperature cross-linking of polysiloxane polymer containing vinyl side-chain. Note attack at the double bond and the Si–C–C–Si linkage.

Fig. 4. A "moderately" cross-linked polysiloxane polymer involving Si–O–Si linkages.

Fig. 5. A "highly" cross-linked polysiloxane polymer involving S—O–Si linkages.

(elastomeric) silicone rubber. In contrast to that observed in Fig. 1, the linkage here is of the Si–C–C–Si type. Similarly, when vinyl groups are present in the silicone polymer as in SE-54, the free radicals in this instance readily attack at the double bond (Fig. 3), permitting rapid and efficient cross-linking reactions to occur.

Under ordinary conditions, it is thought that silicone elastomers may have from 20 to 50 cross-links per polymer chain, spaced some 200–500 siloxy units apart[15]. If care is not taken to control the extent of the reactions, more extensive cross-linking induces physical and chemical changes which result in glassy, brittle polymers which are totally unsuitable for use as stationary phases in gas chromatography. Examples of moderate and extensive cross-linking involving Si–O–Si bonding are shown in Figs. 4 and 5.

From all of this, it was of great interest to also ascertain whether or not each of the two types of cross-linked polymer produced notable differences in chromatographic properties when used as insolubilized stationary phases on fused-silica glass capillary tubing.

EXPERIMENTAL

The fused-silica glass capillary tubing used in these studies had an outer polyimide coating capable of withstanding temperatures up to 400°C. All the surfaces were vigorously deactivated either by modifications of the procedure described by Stark et al.[11] utilizing octamethylcyclotetrasiloxane or by slight variations of the Schomburg et al.[12] polysiloxane method. In the latter instance, care was also taken to employ chemical moieties which bore a close structural relationship to the stationary phase used in the final preparation of the capillary column.

TABLE I*

DATA CONCERNING THE PEROXIDES USED

Peroxide	1 h $T_{\frac{1}{2}}$ (°C)**	10 h $T_{\frac{1}{2}}$ (°C)	Active oxygen (% by wt.)
Benzoyl peroxide (a)	91	73	6.5
Dicumyl peroxide (b)	135	115	5.8
tert.-Butyl peroxide (c)	149	126	10.8

Decomposition products: (a) benzoic acid derivatives: (b) methane, acetophenone, cumyl alcohol: (c) acetone, tert.-butyl alcohol

    * Data derived from Bulletins from Pennwalt Co., New York, NY, U.S.A.

    ** The half-life of a peroxide in a specific solvent (usually 0.2 M benzene) at any specified temperature is the time required at that temperature to affect a loss of 50 % of the active oxygen content of the peroxide. The reactivities of the various peroxides can be rated by comparing the temperature at which the half-lives are 1 h and 10 h.

Cross-linking with tetrachlorosilane

    The α,ω-hydroxypolymethylsiloxane prepolymers were obtained by slight modifications of the methods described by Blomburg and Wännman[5,6] and Lewis and Martin[16]. Those used in this study were relatively free-flowing liquids, readily soluble in pentane or methylene chloride. They provided one with remarkably uniform films when deposited by either the static or dynamic coating technique on previously deactivated fused-silica capillary tubing. Vulcanization with SiCl$_4$ in the vapor phase was then carried out at room temperature[5,6] on the prepared columns.

Cross-linking with peroxides

    Three different peroxides were used in this aspect of the study. These were benzoyl peroxide (BP). dicumyl peroxide (DCUP), and di-tert.-butyl peroxide (DTBP). Pertinent data concerning their relative reactivities at certain temperatures are given in Table I.

    (1) Benzoyl peroxide or dicumyl peroxide, in concentrations of 0.1–0.8 % (w/w) of the silicone polymer (SE-30 or SE-54), was added to the coating solution[8]. Film deposition was carried out by the static method. Following this, a gentle stream of nitrogen was passed through the columns for 3 h. At this point, with the flow of nitrogen reduced to 0.2–0.4 ml/min, the columns were placed for 1 h in an oven whose temperature was raised to 130°C (for BP) or to 150°C (for DCUP). After this, the columns were cooled down to room temperature with the low flow-rate of nitrogen being maintained for an additional 2 h. They were then placed in a gas chromatograph, where they were temperature programmed for 1–2 h at 225°C and then tested. If satisfactory results were obtained, the columns were slowly programmed to 280–300°C and then conditioned overnight at these temperatures and then retested in the morning. They were then removed from the instrument and then rinsed slowly with 4–6 column volumes of either pentane or methylene chloride. The solvent was then completely removed by a stream of nitrogen. The column was again placed in the gas chromatograph and slowly programmed to 300–325°C where it remained for 8–12 h.

    (2) Another set of fused-silica columns were similarly coated with solutions of stationary phase containing either BP or DCUP. However, after the coating pro-

cedure was finished, the column ends were sealed and the columns placed in an oven at 130°C (BP) or 150°C (DCUP) for 1 h. They were then allowed to cool down for an additional hour, after which time the ends were opened and the columns were flushed with nitrogen for an additional 2 h. They were then placed in gas chromatographs and conditioned, tested, and rinsed with solvents in a manner described above.

(3) A third set of deactivated fused-silica glass capillary columns were routinely coated with SE-30 without the addition of the individual peroxides to the coating solution. The columns were then conditioned and tested for efficiency and thermal stability. Following this, the columns were placed in an oven in a manner whereby 12–18 in. of the inlet and outlet ends of the column remained outside the oven proper. The inlet end of the column was placed through the silicone-teflon seal of a 25-ml vial which was filled with 3–5 ml of *tert.*-butyl peroxide. The outlet end was placed in a small flask containing vermiculite. The vial was then gently pressurized with nitrogen. Since the boiling point of this peroxide is 40°C at 55 mmHg, the peroxide vapor was very carefully allowed to flow slowly into the column for 30 min at room temperature. The temperature of the oven was then raised to 150°C and the flow of gaseous peroxide was allowed to continue for an additional 30 min. The column ends outside the oven were then sealed, and the column remained in the oven for an additional 30 min at 150°C. These columns were then processed as described in paragraph (2). Because of the high flammability of the DTBP vapors, this particular procedure should be carried out in a hood and approached with extreme caution! Only very small amounts of DTBP should be used at one time.

RESULTS AND DISCUSSION

Cross-linking with tetrachlorosilane (Si–O–Si linkages)

Excellent results were readily obtained with the reactive diol polymers produced by a modification of methods similar to that described either by Blomberg and Wännman[5,6] or Lewis and Martin[16]. The outstanding virtue of this procedure is the ability to pretest the column for uniformity of coating (*i.e.* efficiency), film thickness, and activity, prior to cross-linking. Moreover, it was noted that cross-linking with tetrachlorosilane (vapor phase) overnight at room temperature[6] was mild and effective. The columns obtained by this procedure (Fig. 6) were very inert, had excellent efficiencies (well over 3000 plates/m) and outstanding thermal stability in the 300–350°C range. After rinsing with solvent, the loss of phase, as measured by changes in the capacity factor (*k'*), averaged from 10–15%. Interestingly, in contrast to that usually noted with the cross-linking procedures carried out on the polysiloxane gums with the various peroxides, there was no discernible effect here on the deactivation procedures used to neutralize the residual silanol groups[14,17] found on the fused-silica glass capillary tubing.

Cross-linking with peroxides (Si–C–C–Si linkages)

Considerable differences in column quality were noted when the various peroxides were used in the *in situ* cross-linking of the non-polar silicone stationary phases on deactivated fused-silica capillary tubing.

Benzoyl peroxide. Droplet formation and all its consequences were occasionally seen following the application of the coating solutions containing this compound.
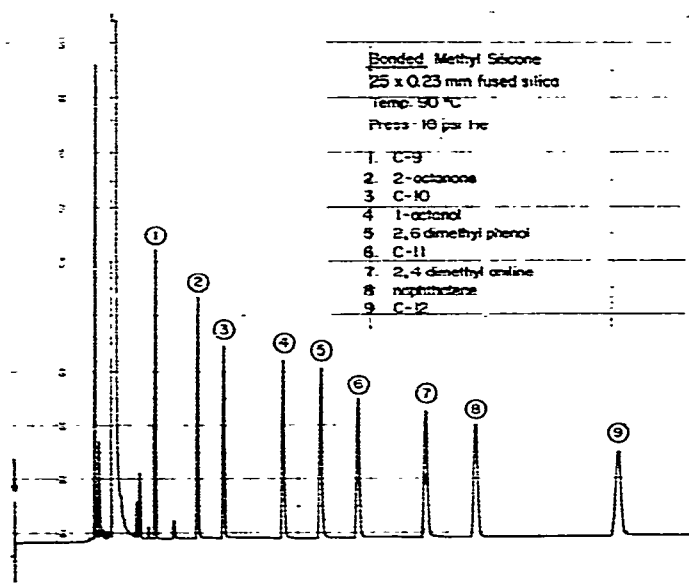
Fig. 6. Chromatogram obtained from fused-silica capillary column coated with a polysiloxane polymer cross-linked with tetrachlorosilane. Chart speed, 2 cm/min. Note complete absence of "tailing" of polar components.
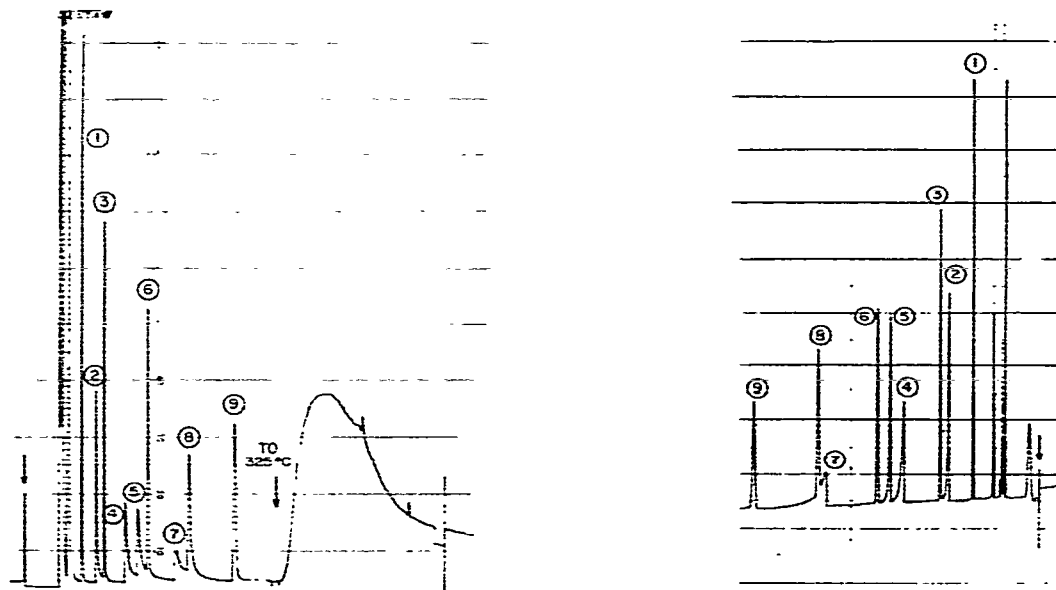
Fig. 7 Chromatogram obtained from a fused-silica capillary column (25 × 0.23 mm), coated with SE-30 cross-linked with benzoyl peroxide (closed system). Temperature, 90°C; pressure, 18, p.s.i. helium. Peaks: 1 = C_9 hydrocarbon; 2 = 2-octanone; 3 = C_{10} hydrocarbon; 4 = 1-octanol; 5 = 2,6-dimethylphenol; 6 = C_{11} hydrocarbon; 7 = 2,4-dimethylaniline; 8 = naphthalene; 9 = C_{12} hydrocarbon.

Fig. 8. As Fig. 7 except that cross-linking with benzoyl peroxide was carried out in an open system. Conditions and peaks as in Fig. 7.
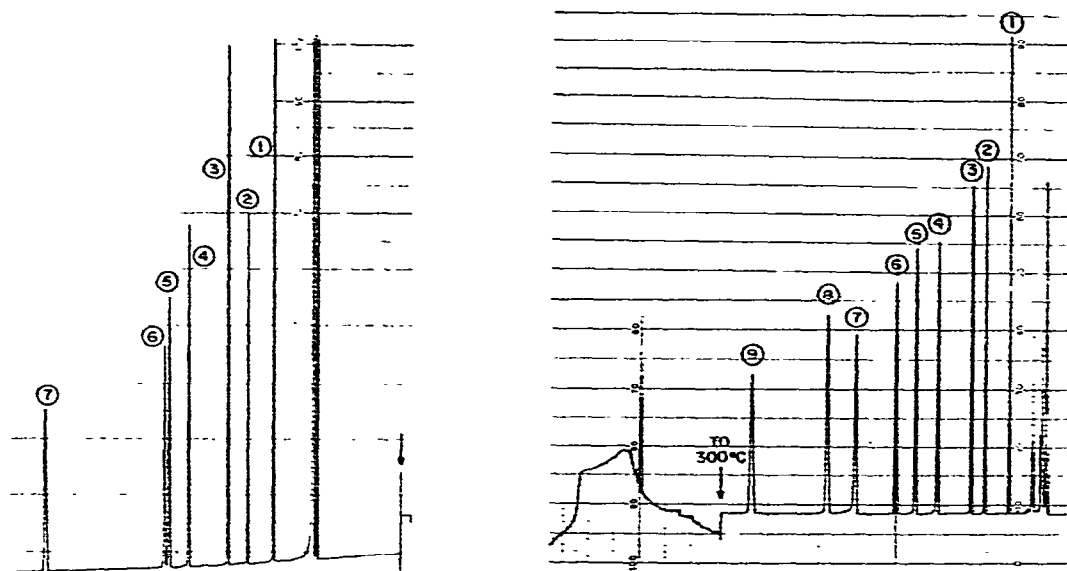
Fig. 9. Chromatogram obtained from a fused-silica capillary column (25 m × 0.009 in.) coated with 5 % SE-54 cross-linked with dicumyl peroxide. Temperature, 110°C; pressure 14 p.s.i. helium. Peak 7, 3835 theoretical plates/m at $k' = 4.8$. Peaks: 1 = 2-octanone; 2 = 1-octanol; 3 = 2,6-dimethylphenol; 4 = 2,4-dimethylaniline; 5 = naphthalene; 6 = C_{12} hydrocarbon; 7 = C_{13} hydrocarbon.

Fig. 10. Chromatogram obtained from a fused-silica capillary column coated with SE-30 cross-linked with dicumyl peroxide. Note very slight "tails" on peak 4 (octanol) and 7 (dimethylaniline). Conditions and peaks as in Fig. 7.

An increase in activity (Figs. 7 and 8) was frequently observed with both the open- and closed-column reaction techniques. It is difficult to determine at this time whether or not this is due to the persistance of by-products formed during the reaction or due to some chemical interaction with the particular surface deactivation procedure. Prolonged conditioning and/or solvent rinsing did not ameliorate the situation. The degree of cross-linking (90–95 %) was excellent as was the thermal stability. Different concentrations of the reagent maintained at slightly different temperatures did not significantly after the results here.

Dicumyl peroxide. Of all of the peroxides used in this study, on average, DCUP usually produced the most inert, efficient, cross-linked films, particularly when used in conjunction with the vinyl-containing SE-54 (Fig. 9). If SE-54 itself was initially employed in the polysiloxane deactivation procedure[12], surface activity was absent. Here too, the degree of cross-linking was high (> 90 %) and the thermal stability in the 300–350°C range was outstanding.

Similar results were seen when SE-30 was cross-linked with DCUP. On occasion, very small residual surface activity was noted here (Fig. 10).

Tert.-butyl peroxide. This compound provided us with very interesting results when it was used in its gaseous state to cross-link silicone stationary phase films that were previously coated onto the fused-silica glass capillary tubing. Under these circumstances, *prior to cross-linking,* as with the diol polymers[5,6,15], one had the opportunity here to test and condition the coated columns and select only those that
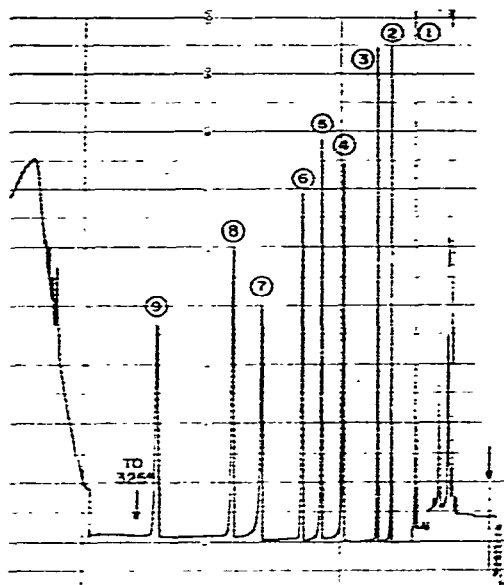
Fig. 11. Chromatogram obtained from a fused-silica capillary column coated with SE-30 cross-linked with di-*tert.*-butyl peroxide. Note slight "tails" on polar components 4 (octanol), 5 (dimethylphenol) and 7 (dimethylaniline). Conditions and peaks as in Fig. 7.

displayed very inert surfaces, appropriate film thicknesses, and very high efficiencies. Despite this outstanding advantage, in the beginning it was quite difficult to determine the optimal flow-rate, the time of exposure, and the optimal decomposition temperature for free radical formation, in order to achieve the required degree of cross-linking. Once these parameters were adequately determined, fewer failures were noted (insufficient vulcanization) and very efficient, thermally stable, cross-linked columns were produced (Fig. 11). Very slight surface activity was noted here since several of the polar components of the test mixture showed some signs of "tailing" (Fig. 11). Again, as mentioned previously, at this point it is difficult to determine the source of this activity since on pre-testing, prior to the institution of the cross-linking step, these columns appeared to be very inert. Accordingly, it has to be attributed to reactions occurring during the vulcanization procedure with peroxides which interfere directly or indirectly with the surface deactivation. The precise cause awaits further work in this area.

From the data thus far available from this study, it is difficult to discern any major chromatographic differences when cross-linked silicone polymers with either Si–O–Si or Si–C–C–Si linkages are properly prepared *in situ* on deactivated fused-silica glass capillary tubing. Obviously, vulcanization of the silicone gums, particularly the vinyl-containing SE-54, with peroxides is a much shorter and more straightforward procedure. However, once a significant amount of an appropriate molecular-weight, reactive linear polysiloxane-diol prepolymer is at hand, cross-linking of this material with tetrachlorosilane provided one with very efficient, thermally stable, capillary columns. The previously deactivated surfaces here usually remained totally unaffected by the procedure and continued to exhibit a very high degree of inertness.

Very good fused-silica glass capillary columns containing silicone stationary phases cross-linked by certain of the peroxides, in particular DCUP and *tert.*-butyl peroxide (in the gas phase), were also produced. However, difficulties were frequently encountered here in maintaining the well deactivated surfaces under conditions of the experiment. This is in contrast to the results obtained by Grob *et al.*[7] using borosilicate glass deactivated by persilanization[10], a process which we find to be not nearly as effective on fused-silica glass.

The maximum optimal temperatures for these columns appear to be in the range 300–325°C when operated isothermally, and 325–350°C when temperature programmed. Interestingly, when certain of the columns were heated for 18 h at 350°C, a considerable increase in surface activity was noted. However, the k' values and the efficiency essentially remained unaltered.

ACKNOWLEDGEMENT

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