CHREV. 174

DEVELOPMENTS IN POLYSILOXANE STATIONARY PHASES IN GAS CHROMATOGRAPHY

J.K. HAKEN

Department of Polymer Science, The University of New South Wales, P.O. Box 1, Kensington, New South Wales 2033 (Australia)

CONTENTS

1. INTRODUCTION

Since the polysiloxane stationary phases were considered in a comprehensive review published in 1977[1] they have continued to be the dominant group of stationary phases used in gas chromatography (GC). With the passing of time the industrial products used by the earliest workers[2] have been almost completely superseded by refined products whose compositional variation is readily monitored by the use of arbitrary test substances such as those of McReynolds[3]. Although these replacement materials were prepared specifically for use in GC they corresponded to the major industrial groups of polysiloxanes.

Probably the first major initiative or deviation from simply adapting industrial

materials was shown in the work of Rotzsche[4,5] who in 1963 described a range of products with methyl, phenyl and cyanopropyl groups. While these phases found negigible acceptance they were followed a decade later by the introduction of specialty grades. During 1972[6] the first of the SILAR products were introduced and in 1974[7] the most polar cyanoalkyl siloxane (OV-275) available was introduced.

Also in 1962 Supina[8] developed a range of organosilicone polymers which were successfully offered as alternatives to polyesters largely for lipid separations. These materials have continued to find acceptance but their popularity is decreasing due to the availability of suitable cyanoalkyl products of greater thermal stability.

In the past attention has been drawn to the excessively large number of materials reported as stationary phases and lists of preferred stationary phases have appeared. The acceptance of such restrictions have been negligible[9] and interest in developing such schemes appears to have waned.

Preston[10], in a partial tabulation of stationary phases prepared from data extracted from papers abstracted from *Gas Chromatography Literature, Abstracts and Index* for the years 1968 and 1969, showed the dominant position of the polysiloxanes. Approximately 300 phases were reported and polysiloxanes cited in twenty or more reports are shown in the first columns of Table 1. Data extracted from the same source for 1970–1972[11], 1972–1976[1] and 1978–1982 are also shown in the table together with reports of the use of newer products that have been introduced.

The table indicates overall that fewer stationary phases are being reported, this being due to the lower number of papers being abstracted by the Preston service in recent years. It is clear that the dominant position of the dimethyl polysiloxanes continues while the older industrial products, *i.e.*, DC-200, SF-96, DC-11, JXR, W98, W982 and DC-550, are finally hopefully fading away. The popularity of polyphenylmethyl siloxane, mainly OV-17, continues although other specialty materials of the same composition are finding some acceptance.

Blomberg[12] has recently suggested that the use of the low-selectivity Dexsil phases may decrease due to the availability of methyl and phenyl siloxanes of higher thermal stability, a suggestion supported by figures reported in recent years as shown in Table 1. Similarly it is considered likely that the organosilicone polyester materials will find lower acceptance.

Siloxanes as stationary phases have previously been included in brief mainly Eastern European reviews on silicones by Wurst[13], Sladkov[14], Rotzsche and Hoffman[15,16], De Bruyn[17,18], Luskina and Turkeltaub[19], Reidmann[20], Bailescu and Ilie[21], Anvaer[22], Cermak[23], Kotsev[24], and Itsikson and co-workers[25,26], and also in part in an early work describing the development of chemically bonded chromatographic supports[27]. The importance of polysiloxanes as stationary phases is further evident by the examination of a recent fine review by Blomberg[12] on the current aspects of the stationary phase in gas chromatography. The majority of the work deals with recent developments in polysiloxanes.

The historical development of silicone materials as stationary phases has previously been detailed[1,11] and is not repeated here. Included are extensive tabulations of polysiloxanes that have been reported in the literature from the earliest reports. Details as available with regard to structure, chemical composition or polarity in terms of several arbitrary schemes that have variously been used are included to allow the selection of alternative materials as may be required. Soviet, Japanese and Dutch ma-

TABLE 1

POLYSILOXANE STATIONARY PHASES REPORTED IN *GAS CHROMATOGRAPHY ABSTRACTS* DURING 1968–1982

Phase	1968	1970	1972	1974	1976	1978	1980	1982
SE-30, E-301	569	302	302	260	295	184	157	115
DC-200	161	63	43	50	54	21	25	8
SF-96	61	29	25	16	16	10	7	5
JXR	-	24	15	11	12	1	2	1
DC-11	-	17	6	6	5	1	-	-
W98,W982	-	13	23	-	15	15	10	2
OV-1	40	92	64	64	186	104	83	40
OV-101	-	10	21	36	98	-	76	68
SE-52	100	37	28	20	21	11	15	18
OV-7	-	-	-	8	12	3	5	2
OV-17	51	92	126	115	302	175	201	104
OV-25	-	-	-	3	16	10	8	3
DC-550	41	18	13	11	5	6	5	5
QF-1	215	120	82	93	118	58	45	8
OV-210	-	6	17	19	34	28	34	14
OV-225	-	13	20	22	40	58	32	16
XE-60	118	53	46	39	35	32	26	11
SILARS	-	-	-	-	18	16	16	16
SP-2300	-	-	-	-	2	1	8	14
SP-2401	-	-	-	-	-	-	4	3
EGSS-X	-	23	22	15	12	9	5	8
Dexsils	-	-	1	14	36	60	4	14
OV-275	-	-	-	-	-	7	10	3
SP-2100	-	-	-	-	-	6	8	25
SP-2250	-	-	-	-	-	9	16	8
Russian	1388 }	90	122	87	74	41	10	
Other Siloxanes							26	14
Other Phases		1255	1067	1070	1381	892	738	446
Total	2744	2186	2053	2026	2518	1789	1576	971

terials have been reported in the literature but little compositional information has been available about the latter products.

The continued application of highly polar polysiloxane stationary phases has allowed increasing selectivity which in part has compensated for limited column efficiency. Over the last few years immobilized phases have allowed high column efficiency to be achieved, firstly with low-polarity columns and more recently with polar phases. It now seems that columns, particularly capillary columns, will soon be common which exhibit both high efficiency and selectivity.

Other developing areas concern the development of improved column materials for the separation of optically active compounds. While chiral stationary phases were well known the development of Frank et al.[28] in producing a chiral diamide utilising the high thermal stability of polysiloxanes and an established amide was a significant advance.

In the same way it is likely that the particular properties of liquid crystal materials will be further enhanced by their synthesis as polysiloxanes[29].

The presence of other metallic elements in polysiloxanes has been limited to boron with the carboranes possessing high thermal stability and poor selectivity. A recent report[30] has shown the preparation of a range of chemically bonded polymetallophenyl siloxanes as stationary phases. These exhibit some specific affinity toward olefins and may offer a further opportunity of increasing the application of polysiloxane stationary phases.

2. DIMETHYL POLYSILOXANES

The dimethyl polysiloxanes have since the early works continued to be the most widely reported of the polysiloxanes, the General Electric Company Gum Rubber SE-30 having been most widely used. A specialty grade SE-30 GC is produced and employs a different catalyst to the industrial product, the reduced catalyst residues possibly allowing it to compete more favourably with the specialty product of the Ohio Valley Company.

Dimethyl polysiloxanes fluids also found ready acceptance, the Dow Corning product DC-200 being used in many early reports. Unlike SE-30, DC-200 in common with other industrial products, i.e., SF-96, W98, W982, JXR and DC-11, now find little acceptance having been superseded by a few specialty products.

The chemistry, manufacture, purification and use of dimethyl polysiloxanes as stationary phases have been reported by Trash[31]. The stability is in part influenced by the presence of catalysts residues and during polymerisation catalyst selection and residue removal are important such that maximum resistance to thermal degradation is achieved.

The particular properties of polysiloxanes are due to their partly inorganic and partly organic structures. The characteristic thermal and chemical stability of the completely inorganic homologues are substantially retained while the organic pendant groups may be varied to provide compounds with greatly varying properties.

The bond energy of the Si–O is considerably greater than that of the C–C linkage while the Si–C bond is also strong, thus thermal stability and low vapour pressure have always been a feature of polysiloxane phases. The effective strength of the various bonds is, however, greatly influenced by the neighbouring atoms and the half-lives of substituent groups in air at 250°C calculated from weight loss and silicon content values determined before and after exposure for 100 h are shown in Table 2 where it is evident that the stability of phenyl and methyl substituents are vastly greater than those of the other substituents listed[32].

The stability of various polysiloxanes as stationary phases has been studied by Evans[33] who confirmed the superior behaviour of the methylphenyl siloxanes but established that in general the polysiloxanes were effected little by oxidation, even at 225°C

With dimethyl polysiloxanes oxidation can only occur at the methyl groups along the chain. Two reactions are possible depending on the severity of the conditions prevailing. The first is oxidation of the methyl groups to form carbonyl groups while the second is decomposition to form silica[34]. The first reaction would be expected to increase the retention of the more polar solutes whilst the latter could be expected to produce peak tailing as well as with gas–solid chromatography.

TABLE 2

THERMAL HALF-LIFE OF VARIOUS SUBSTITUENT GROUPS ON SILICON

Group covalently bonded to Si	Approximate half-life* at 250°C (h)
Phenyl	100,000
Methyl	10,000
Ethyl	6
Propyl	2
Butyl	2
Pentyl	4
Nonyl	8
Decyl	12
Dodecyl	8
Octadecyl	26
Cyclohexyl	40
Vinyl	101

* Time at which one-half of the groups are replaced by $O^{1/2}$.

The polydimethyl siloxanes have the general formula

$$R - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - O \left[- \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - O \right]_n - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - R$$
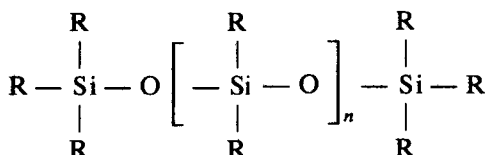
where R is a methyl group. Materials are available for industrial purposes as fluids with nominal viscosities in the range 0.65–1,000,000 cSt at 25°C and with chain length from 2 to over 2000 dimethyl polysiloxane units. Certain of the available viscosity grades are essentially pure compounds although most exhibit a molecular-weight distribution as is usual with polymers. The low-molecular-weight oligomers are shown in Table 3.

Several simple relationships between average molecular weight and viscosity at room temperature as shown in Fig. 1 are applicable. The relationship shown in eqn. 1 is applicable to fluids of average molecular weight (MW) greater than 2500[35].

$$\log \eta \text{ (cSt at 25°C)} = 1 + 0.0123 \text{ (MW)}^{\frac{1}{2}} \tag{1}$$

Higher-molecular-weight products are also available as gums or rubbers.

The relationship shown in eqn. 2 developed by Warrick et al.[36] was shown to be applicable to dimethyl polysiloxanes below a molecular weight of 40,000.

$$\log \eta \text{ (Poises at 40°C)} = 1.43 \log \text{ (MW)} - 5.4 \tag{2}$$

The viscosity of the dimethyl polysiloxane fluids greatly influences their usage. Materials of very low molecular weight are unsuitable for use at high operating temperatures due to excessive column bleed and in fact low-molecular-weight polysiloxane oligomers may be readily separated on methyl gum columns[37].

TABLE 3

PHYSICAL CONSTANTS OF LOW-MOLECULAR-WEIGHT DIMETHYL POLYSILOXANES

| Structure	Name	Number of Silicon Atoms	Boiling Point (°C)	Viscosity (cSt, 25°C)	Molecular weight
$(CH_3)_3Si-O-Si(CH_3)_3$	Hexamethyl disiloxane	2	100.5	0.65	162.37
$(CH_3)_3Si-O-\underset{CH_3}{Si}-O-Si(CH_3)_3$	Octamethyl trisiloxane	3	153	1.04	236.6
$(CH_3)_3Si-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_2 Si(CH_3)_3$	Decamethyl tetrasiloxane	4	194	1.53	310.70
$(CH_3)_3Si-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_3 Si(CH_3)_3$	Dodecamethyl pentasiloxane	5	229	2.97	384.86
$(CH_3)_3Si-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_4 Si(CH_3)_3$	Tetradecamethyl hexasiloxane	6	141.4 (20 mm Hg)	2.63	459.02
$(CH_3)_3Si-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_5 Si(CH_3)_3$	Hexadecamethyl heptasiloxane	7	165.2 (20 mm Hg)	3.24	533.17
$(CH_3)_3Si-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_6 Si(CH_3)_3$	Octadecamethyl octasiloxane	8	185.6 (20 mm Hg)	3.88	607.33
$(CH_3)_3Si-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_7 Si(CH_3)_3$	Eicosamethyl enneasiloxane	9	198.8 (16 mm Hg)	4.58	681.50
$(CH_3)_3Si-O-\left[\underset{CH_3}{\overset{(CH_3)_2}{Si}}-O\right]_8 Si(CH_3)_3$	Docosamethyl decasiloxane	10	202.8 (10 mm Hg)	—	755.65
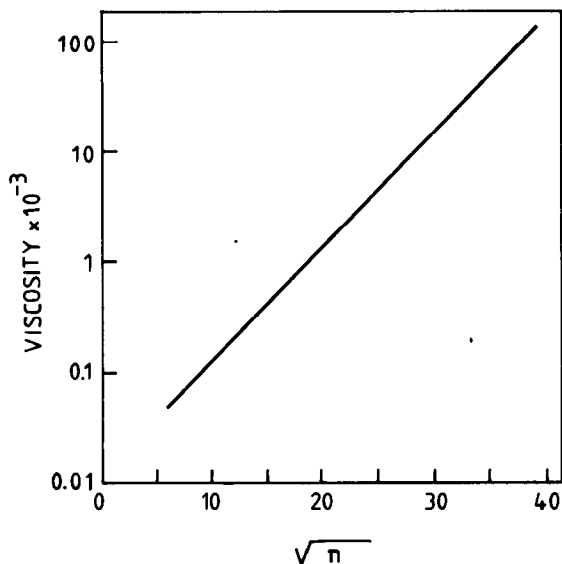
Fig. 1. Relationship between viscosity in centistokes at 25°C and molecular weight of dimethyl polysiloxanes, where n is the number of dimethyl polysiloxane units.

Fluids of 12,500 cSt have been extensively used although much lower viscosities can be tolerated in many applications, *i.e.*, 50–500 cSt. The viscosity of silicone oils is much less affected by variation in temperature than hydrocarbons and the property is of value for use at both elevated and reduced temperatures.

The property in part may be explained by the coiled helix structure of polysiloxanes with the alkyl groups protruding outwards[38]. This is a configuration producing low cohesive-energy density and accordingly low surface energy. With increasing temperature the molecules straighten and the intermolecular interaction increases with a resultant increase in viscosity. The usual decrease in viscosity with increasing temperature is minimized by the increases. While the temperature coefficient with methyl substituents is low, replacement with phenyl groups greatly increases the temperature dependence of the viscosity increases[39].

Baumann *et al.*[40] considered GC operation at sub-ambient temperatures and found siloxane polymers to be suitable as stationary phases. The materials considered are shown in Table 4 and no loss in resolution was observed with SF-96, *i.e.*, a 1000-cSt oil, at −60°C. Merritt *et al.*[41] have studied stationary-phase performance at cryogenic temperatures. Initial reports showed that a 5% tris(cyanoethyloxypropane) column was superior to a 5% SE-30 one when programmed from −170°C at 3°C/min. A subsequent publication[42] has shown that squalane is also more satisfactory than SE-30. It is known that the efficiency of separation is substantially reduced at temperatures below the melting point. The freezing point of SE-30 is − 50°C while squalane gradually freezes over the range of −60°C to −100°C and Carbowax 20M melts at 52°C. It is apparent that a silicone fluid rather than a gum may have proved more suitable[13].

The refractive index and specific gravity of dimethyl polysiloxanes both increase with molecular weight and these measurements make it possible to differentiate be-

TABLE 4

LOW TEMPERATURE OPERATING LIMITS[40]

Phase	Lower temperature limit (°C)
Polypropylene glycol 150	—20
Polyethylene glycol 200	No separation at —20
DC-550	—20
SE-30	Above 0
SF-96	—60
QF-1	—20
Nitrile Fluid XF-1112	—40

tween methyl- and phenyl-substituted fluids. The characteristics for various types of polysiloxanes are shown in Table 5[43,44].

The molecular-weight distributions of OV-101 and three grades of DC-200 have been determined by Trash[31] using gel permeation chromatography. The polydispersity of the OV-101 was considerably lower than for the higher viscosity grades of DC-200 and greater efficiency as a stationary phase was indicated, the problem of using polymeric materials having been previously discussed[45]. The analytical results of the molecular-weight determinations are shown in Table 6.

The importance in temperature-programmed GC of the exponentially changing diffusivity during the analysis where diffusion is slow and the column inefficient for much of the time has been considered by Hawkes and co-workers[46–49]. Diffusion[46] of n-alkanes was much faster with dimethyl polysiloxane gum (SE-30) than with a lower-molecular-weight oil (SF-96-200). The energy of diffusion was lower with dimethyl polysiloxanes than with polyethylene glycols making them more suitable for pro-

TABLE 5

PHYSICAL PROPERTIES OF SOME METHYL AND METHYLPHENYLSILICONE OILS

η (20°C)	d_4^{20}	n_D^{20}
Methylsilicone oils		
60	0.96	1.4041
140	0.97	1.4045
440	0.97	1.4053
680	0.97	1.4053
1440	0.97	1.4053
10,000	0.97	1.4058
50,000	0.97	1.4058
100,000	0.97	1.4058
Methylphenylsilicone oils (low phenyl content)		
200	1.03	1.465
1000	1.04	1.475
Methylphenylsilicone oils (high phenyl content)		
300	1.06	1.505
1000	1.09	1.515

TABLE 6

COMPARATIVE MOLECULAR-WEIGHT DISTRIBUTIONS FOR DIMETHYL POLYSILOXANE SAMPLES

M_w = Weight-average molecular weight; M_n = number-average molecular weight.

Sample	Viscosity (cSt)	M_w $(\times\ 10^4)$	M_n $(\times\ 10^4)$	M_w/M_n
DC-200	500	1.6	1.1	1.5
DC-200	1000	2.7	1.5	1.8
DC-200	60,000	6.7	3.9	1.7
OV-101	1500	2.9	2.2	1.3

grammed-temperature use. A subsequent study[47] considered dimethyl polysiloxanes of intermediate molecular weight and six other polysiloxane phases where diffusion was shown to be slower in diphenyl-substituted siloxanes in proportion to the exponent of the phenyl content and in all siloxanes is slower in proportion to the exponent of the density.

Although short-chain n-alkanes were shown to diffuse faster in SE-30 than in 200-cSt methyl fluid (SF-96), the opposite effect was later shown for longer-chain n-alkanes[48,49]. This effect was suggested to be due to competition between the effects of free volume and viscosity for dominance in the diffusion process.

The general utility of polydimethyl siloxanes in GC is evident by their use for a wide range of separations where, due to their low polarity, elution occurs in essentially a boiling-point sequence.

Over the last decade or so an increasing amount of information has become available concerning Russian-produced polysiloxanes supplied by the S. V. Lebedev VBIISK Institute, Leningrad. Some evaluations of the materials which are used in a small proportion of Russian works have appeared and are described in a subsequent section of this work. The information particularly concerning polarity comparisons has lagged many years behind Western reports but reasonable comparisons with Western products are now possible.

Several evaluations of dimethyl polysiloxanes with viscosities of 500–100,000 cSt and produced in India[50,51] have appeared. Performance equivalent to SE-30 was indicated but the equipment used was not sufficiently sensitive to allow vigorous testing. Recently, specialty polysiloxanes for chromatographic use were introduced by Chrompack in The Netherlands but reported use has been negligible.

It is widely recognized that the stability of polysiloxanes is enhanced when the polymer is endcapped with methyl groups and, while most phases are designed in this way, a study has used dimethylvinyl gum (SKTV) which contains hydroxy end groups. Aseeva et al.[52] showed that improved thermal and oxidation stability was achieved either by the addition of silica fillers which were found to deactivate the hydroxyl groups or by their conversion to trimethylsiloxy groups. The degradation of dimethyl polysiloxanes with various terminal groups and with metallic atoms was also studied by Lengyel et al.[53] using thermogravimetry and pyrolysis–GC.

The stability of dimethyl polysiloxanes and other industrially available polysiloxanes to acids and bases has been extensively studied[54], and more recently studies directed towards GC have appeared[55–59].

The degradation of diluted solutions of polysiloxane stationary phases during

TABLE 7

SPECIALITY POLYSILOXANES FOR GAS CHROMATOGRAPHY

The Ohio Valley Company have recently introduced a range of vinyl-modified phases, termed capillary OV-1, OV-17, OV-1701, OV-215 and OV-225, each with McReynolds constants of the parent material, with physical constants not available[327].

Phase	Substituent	Supplier*	Nominal viscosity at 25°C (cSt)	MW	Density	Ref. index	Rohrschneider constants					McReynolds constants					
							X	Y	Z	U	S	x'	y'	z'	u'	s'	h'
OV-101	100% Methyl	A	1200–1500	30,000	0.975	1.4038	0.16	0.20	0.50	0.85	0.48	17	57	45	67	43	33
SP-2100	100% Methyl	B	600									17	57	45	67	43	33
AS1-100 Methyl	100% Methyl	C	12,500									17	55	45	67	43	32
OV-1	100% Methyl	A	Gum	300,000–400,000	0.980	1.4040	0.16	0.20	0.50	0.85	0.48	16	55	44	66	42	32
SE-30 GC	100% Methyl	D	$9.47\cdot10^6$	1.0–$2.5\cdot10^6$	0.966 (30°C)		0.16	0.20	0.50	0.85	0.48	16	55	44	66	42	32
OD-1	100% Methyl	E	Gum									16	53	45	66	42	32
JXR	100% Methyl	C	Gum				0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32
OV-73	5.5% Phenyl	A	Gum	800,000	0.991	1.4245							40	86	76	114	85
OV-3	10% Phenyl	A	500	20,000	0.997	1.4436	0.42	0.81	0.85	1.52	0.89	44	86	81	124	88	55
OV-7	20% Phenyl	A	500	10,000	1.021	1.4766	0.70	1.12	1.19	1.98	1.34	69	113	111	171	128	77
OV-61	33% Phenyl	A	50,000	40,000	1.090	1.5279	0.98	1.30	1.57	2.38	1.85	101	143	142	213	174	99
OV-11	35% Phenyl	A	500	7000	1.057	1.5120	1.13	1.57	1.69	2.66	1.95	102	142	145	219	178	103
OV-17	50% Phenyl	A	1300–1500	4000	1.092	1.5397	1.30	1.60	1.79	2.83	2.47	119	158	162	243	202	112
SP-2250	50% Phenyl	B					1.30	1.60	1.79	2.83	2.47	119	158	162	243	202	112
ASI-50 methyl**	50% Phenyl	C					1.30	1.60	1.79	2.83	2.47	119	158	162	243	202	112
OV-22	60% Phenyl	A	50,000	8000	1.127	1.5656	1.58	1.80	2.04	3.27	2.59	160	188	191	283	253	133
OV-25	75% Phenyl	A	100,000	10,000	1.150 (25°C)	1.5825	1.76	2.00	2.15	3.34	2.81	178	204	208	305	280	144
SP-400	11% Chlorophenyl	B	500	10,000	1.252 (25°C)	1.3810	0.33	0.49	0.82	1.08	0.83	32	72	70	100	68	49
OV-202	50% Trifluoropropyl	A	Gum	200,000	1.252	1.3816							146	238	358	468	310
OV-215	50% Trifluoropropyl	A			1.284	1.3816							149	240	363	478	315
OV-210	50% Trifluoropropyl	A	10,000	18,600	1.284 (25°C)	1.3816	1.41	2.13	3.55	4.73	3.04	146	146	238	358	468	310
SP-2401	50% Trifluoropropyl	B	700	2600	1.30 (25°C)	1.558							238	358	468	310	206
ASI-50 methyl***	50% Trifluoropropyl				1.01 (25°C)							146	238	358	468	310	206
OV-105	5% Cyanoethyl	A	1500									36	108	93	139	86	74

Phase	Substituents	Supplier	Form	M.W.													
AN-600	25% Cyanoethyl	E	Gum	9000								202	369	332	482	408	—
OV-225	25% Cyanopropyl 25% phenyl	A		8000	1.096 (25°C)	1.5016	2.17	3.22	3.33	5.16	3.69	228	369	338	492	386	282
AS1-50 methyl[§]	25% Cyanopropyl 25% phenyl	C										228	369	338	492	386	282
SILAR 5CP	50% Cyanopropyl	F										319	495	446	637	530	379
SP-2300	50% Phenyl	B										319	495	446	637	530	379
ASI-50 phenyl[§§]	50% Cyanopropyl	C															
SILAR 7CP	75% Cyanopropyl 25% Phenyl	F										440	638	605	844	673	492
SP-2310		B															
SILAR 9C	90% Cyanopropyl/ 10% Phenyl	F										489	725	631	913	778	566
SP-2330		B										490	725	630	913	778	566
SILAR 10C	100% Cyanopropyl	F		5000								523	755	659	942	801	584
SP-2340		B		20,000								520	757	659	942	800	584
OV-275	100% Cyanoethyl	A										629	872	763	1106	849	686
Organosilicone Polymers																	
EGSS-X	Low methyl	C										484	710	585	831	778	566
EGSS-Y	Medium methyl	C										391	597	493	693	661	469
EGSP-A	Low phenyl	C										397	629	519	727	700	496
EGSP-Z	Medium phenyl	C										308	474	399	548	549	373
ECNSS-S	Low cyanoethyl	C										438	659	566	820	722	530
ECNSS-M	Medium cyanoethyl	C		500			3.96	6.01	5.39	—	6.50	421	690	581	803	732	548
OV-330	Phenyl–carbowax copolymer	A		5000								222	391	273	417	368	
Carborane–siloxane polymers																	
Dexsil 300 GC	Methyl	G	30–80°C	16,000–20,000			0.43	0.644	1.11	1.51	1.01	47	80	103	148	96	—
Dexsil 400 GC	Phenyl	G	Viscous	12,000–16,000								59	114	140	187	173	—
Dexsil 410 GC	2-Cyanoethyl	G	Viscous	9000								85	165	169	242	180	

* A = Ohio Valley Specialty Chem. Co., Marietta, OH, U.S.A.; B = Supelco Inc., Bellafonte, PA, U.S.A.; C = Applied Science Labs., State College, PA, U.S.A.; D = General Electric Co., New York, NY, U.S.A.; E = Analabs Inc., North Haven, CT, U.S.A.; F = manufactured by Silar Lab. Inc., distributed by Applied Science Labs.; G = manufactured by Olin Corp., distributed by Analabs Inc.

** ASI-50 Methyl 50 phenyl.

*** ASI-50 Methyl 25 cyanopropyl 25 phenyl.

§ ASI-50 Phenyl 50 cyanopropyl.

§§ ASI-50 Phenyl 50 cyanopropyl.

TABLE 8

INDUSTRIAL, MISCELLANEOUS AND OBSOLETE POLYSILOXANE STATIONARY PHASES

Phase	Substituent	Supp-lier*	Viscosity at 20% (cSt)	M.W.	Density	Refractive index	Rohrschneider constants					McReynolds constants					
							X	Y	Z	U	S	x'	y'	z'	u'	s'	h'
DC-200/MS200	Methyl	A,B	50,000–100,000		0.97 (25°C)		0.16	0.20	0.50	0.85	0.48	16	57	45	66	43	33
Perkin Elmer Column C	DC-200	C	packed column									16	57	45	66	43	33
SF-96	Methyl	D	50,000–100,000									14	53	42	61	37	31
SF-96-200	Methyl	D	200	11,000	0.972 (25°C)							14	53	42	61	37	31
SF-96-2000	Methyl	D	2000	34,975	0.974 (25°C)							14	53	42	61	37	31
Viscasil	Methyl	E	100,000	103,000	0.978 (25°C)							16	57	45	66	43	33
L-45	Methyl	D	50,000–100,000									16	57	45	65	43	33
Bayer M	Methyl	F	50,000–300,000									16	57	45	66	43	33
F-111	Methyl	G	50,000–100,000									16	57	45	66	43	33
L-46	Methyl	D	50,000–100,000									16	56	44	65	41	33
Embaphase Oil	Methyl	H	300–400		0.970–0.973 (20°C)							14	57	45	66	43	33
Silicone Oil 81705	Methyl	E															
DC-220	Methyl	A	44														
DC-330	Methyl	A	50														
NMI-50	Methyl	I	50														
NMI-200	Methyl	I	200		0.96–0.98 (20°C)							13	51	42	61	36	31
MO-50	Methyl	I	50		0.96–0.98 (20°C)												
MO-200	Methyl	I	200		0.96–0.98 (20°C)												
Lukooil M-50	Methyl	J	50														
Lukooil M-100	Methyl	J	100														
Lukooil M-200	Methyl	J	200														
Lukooil M-500	Methyl	J	500		0.973–0.977 (20°C)	1.403–1.407											
Silicone B	Methyl	I	100		1.03 (20°C)												
DMF-05	Methyl	K	500 (25°C)		0.972 (25°C)	1.4033											
DMF-1	Methyl	K	1000 (25°C)		0.972 (25°C)	1.4035											
DMF-12	Methyl	K	12,500 (25°C)		0.973 (25°C)	1.4035											
DMF-30	Methyl	K	30,000 (25°C)		0.973 (25°C)	1.4035											
DMF-100	Methyl	K	100,000 (25°C)		0.973 (25°C)	1.4035											
Silicone Vaseline	Methyl	U		3500													

Methyl Gums

Phase	Substituent	Code	MW	Range	Density											
SE-30	Methyl	E	9.47·10⁶	1.0–2.5·10⁶	0.966 (25°C)	0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32
SE-30 Ultraphase	Methyl	E	9.47·10⁶	1.0–2.5·10⁶	0.966 (25°C)											
Perkin Elmer Column Z (SE-30)	Methyl	C	9.47·10⁶	1.0–2.5·10⁶	0.966 (25°C)											
E-301	Methyl	G	Gum	1.0–2.5·10⁶		0.16	0.20	0.50	0.85	0.48	16	55	44	65	44	32
DC-410	Methyl	A	Gum								18	57	47	68	44	34
Silastic 401	Methyl	A	Gum								17	58	47	68	46	34
DC-401	Methyl	A	Gum								17	58	47	68	46	34
Silastic 132	Methyl	A	Gum													
Silastic 152	Methyl	D	Gum													
W95	Methyl	D	Gum		0.96											
W950	Methyl	D	10^{12}–10^{14}													
MS-2211	Methyl	B	10^{12}–10^{14}								15	56	44	66	40	32
DC-123	Methyl	A	10^{12}–10^{14}													
E-300	Methyl	G	10^{12}–10^{14}								15	56	44	66	40	32
DC-400	Methyl	A	Gum								15	56	44	66	40	32
SP-70	Methyl	R	Gum													
Silicone M-430	Methyl	G	Gum													
KS-1014	Methyl	D	Gum													
G-7100	Methyl	I	Gum													
NG-100	Methyl	I	Gum													
G1100F	Methyl	I	Gum													
GI 7000FF	Methyl	L	Gum													
MO 2,000,000	Methyl	L	Gum													
LC-1	Methyl	M	Gum													
Lukopren M50	Methyl	J	Gum													
Homacyan-410	Methyl	U,F	Gum	60,000–70,000												
SE-31	Methylvinyl (1%)	E	Gum								16	54	45	65	43	32
Silastic 430	Methylvinyl (1%)	A	Gum								16	54	45	65	43	32
LC-430	Methylvinyl (1%)	A	Gum								16	54	45	65	43	32
E-302	Methylvinyl (1%)	G	Gum								16	54	45	65	43	32

TABLE 8 (continued)

Phase	Substituent	Supplier*	Viscosity at 20% (cSt)	M.W.	Density	Refractive index	Rohrschneider constants					McReynolds constants					
							X	Y	Z	U	S	x'	y'	z'	u'	s'	h'
SE-33	Methylvinyl (1%)	E	Gum		0.98							17	54	45	67	42	33
E-303	Methylvinyl (1%)	G	Gum									17	54	45	67	42	33
W-96	Methylvinyl (1%)	D	Gum														
W-98	Methylvinyl (1%)	D	Gum														
W-960	Methylvinyl (1%)	D	Gum														
W-982	Methylvinyl (1%)	D	Gum									16	55	45	66	42	33
Rhodorsil Comme 785	Methylvinyl (0.15%)	N	Gum														
Silicone Rubber Polymer	Methylvinyl	O	Gum														
Lukopren G1000	Methylvinyl	J	Gum	3.5–$6.0 \cdot 10^5$													
Gi 7300 F	Methlvinyl	L	Gum														
NG 300	Methylvinyl	I	Gum														
DC-11	Methyl (10% silica)	A	Paste									17	86	48	69	56	33
Hi Vac Grease	Methyl (10% silica)	A	Paste				1.05	1.50	1.61	2.51	1.90						
Perkin Elmer Column O	Methyl (10% silica)	C	Paste									17	86	48	69	56	33
Hi Vac Grease extract	Fluid	A	12,500				0.16	0.20	0.50	0.85	0.48	16	57	45	66	43	33
DC-730	Ethyl	A	M.p. 62°C														
S-2116	30%	P					0.23	0.50	0.48	0.75	0.56						
DC-230	Stearoyl Stearyl	A	1200–1600														

Phase	Substituent	Code	Viscosity (cSt)	Density	(a)	(b)	(c)	(d)	(e)	(f)	(1)	(2)	(3)	(4)	(5)	(6)
F-157	Stearyl ester	A	M.p. 25°C 10 cSt (50°C)													
Phenyl Siloxanes																
DC-510	5% Phenyl	A	50–1000	1.00(25°C)							25	65	60	89	57	42
DC-556	10% Phenyl	A	15–30								37	77	80	118	79	53
DC-550	25% Phenyl	A	100–150	1.068(25°C)							74	116	117	178	135	81
DC-555	Low Phenyl (cyclic)	A	See text													
DC-701	Phenyl	A	10–15	1.03(25°C)												
DC-702	25% Phenyl (see text)	A	45								77	124	126	189	142	90
DC-703	25% Phenyl (see text)	A	55								76	123	126	189	140	89
DC-704	50% Phenyl (see text)	A	39													
OE-4008	50% Phenyl (see text)	L		1.066(20°C)												
DC-705	62.5% Phenyl (see text)	A	175													
OE-4007	62.5% Phenyl (see text)	L		1.095(20°C)												
DC-710	50% Phenyl	A	475–525	1.10(25°C)	2.660	1.05	1.50	1.61	2.51	1.90	107	149	153	228	190	170
OE-4006	75% Phenyl	L		1.04–1.11(20°C)												
OE-4011	35% Phenyl	L		0.99–1.04(20°C)												
OE-4130	33% Phenyl	L		0.99–1.04(20°C)												
NM3-200	33% Phenyl	I		0.99–1.04(20°C)												
NM4-500	25.0% Phenyl	I		1.04–1.07(20°C)												
NM5-500	35.0% Phenyl	I		1.04–1.11(20°C)												
PN-200	Med Phenyl	F	200	1.04(25°C)												
AR-20	25% Phenyl	O														
SE-52	5% Phenyl	E	Gum								32	72	65	98	67	44
E-350	5% Phenyl	G	Gum								32	72	65	98	67	44
SP-392	55% Phenyl	X									32	72	65	98	67	44
PHSi 191-43	40% Phenyl	E	B.p. 245–275°C (5·10⁵ mm Hg)													

TABLE 8 (continued)

Phase	Substituent	Supplier*	Viscosity at 20% (cSt)	M.W.	Density	Refractive index	Rohrschneider constants					McReynolds constants					
							X	Y	Z	U	S	x'	y'	z'	u'	s'	h'
287-149-2443	20% Phenyl	E															
287-149-244	35% Phenyl	E															
Lukooil MF	Diphenyl (see text)	J	100–200		1.0322–1.042	1.472–1.479											
Lukooil DF	50% Phenyl	J	500 min		1.08–1.10	1.52–1.55											
Supolimer 2	High phenyl	V															
SE-54	5% Phenyl 1% vinyl	E			0.98							33	72	66	98	67	46
E-351	5% Phenyl 1% vinyl	G										33	72	66	98	67	46
Gi 7500F	Phenyl vinyl	L															
X525	Unknown oilQ																
L-525	Unknown oilQ																
SR-119	Unknown resin	E										166	238	221	314	299	175
Chlorphenyl																	
F-61	11% p-Chlor-phenyl	A	500				0.31	0.49	0.82	1.08	0.83	32	72	70	100	68	49
F-60	11% p-Chlor-phenyl	A	63				0.33	0.49	0.82	1.08	0.83	32	72	70	100	68	49
DC-560	11% p-Chlor-phenyl	1	75				0.33	0.49	0.82	1.08	0.83	32	72	70	100	68	49
F-4050	3,5-Dichlor-phenyl	A															
Lukooil X-100	41% 3,4,5-Trichlor-phenyl	J		4.1% trimethylsilyl													
Lukooil X-200	5.5% 3,4,5-Trichlor-phenyl	J		5.5% trimethylsilyl													

Phase	Substitution		Density	Viscosity / Temp. range												
Lukoil X-600	8.3% 3,4,5-Trichlorphenyl	J		8.3% trimethylsilyl						19	57	48	69	47	36	
Versilube F-50	(see text)	E														
Wacker CR	Chlorphenyl	O	1.045 (25°C)	70 (25°C)												4280(25°C)
Chlorsilicone CHS-1	Chlorphenyl			20–1000												
Cyanoalkyl Substitution																
XF-1105	5% Cyanoethyl	E														
XE-60	25% Cyanoethyl	E			2.08	3.85	3.62	5.33	3.45	204	381	340	493	367	289	
XF-1125	25% Cyanoethyl	E			2.08	3.85	3.62	5.33	3.45	204	381	340	493	367	289	
OE-4910	12%	L														
XF-1112	Cyanoethyl	E														
XF-1150	50% Cyanoethyl	E			3.18	5.33	3.81	7.02	5.04	308	520	470	669	528	401	
238-149-99	50% Cyanoethyl	E														
238-149-239	50% Cyanoethyl	E														
287-149-251	8% Cyanoethyl	E														
287-149-203	20% Cyanoethyl	E														
287-149-300	65% Cyanoethyl	E														
XF-1165	65% Cyanoethyl	E														
QE-4178	37.5% Cyanopropyl															
Fluoralkyl Substitution																
QF-1	50% Trifluoropropyl	A	24,600	300–1000	1.41	2.13	3.55	4.73	3.01	144	233	355	463	305	203	

TABLE 8 (continued)

Phase	Substituent	Supplier*	Viscosity at 20% (cSt)	M.W.	Density	Refractive index	Rohrschneider constants					McReynolds constants					
							X	Y	Z	U	S	x'	y'	z'	u'	s'	h'
FS-1265																	
QF-1-10065			10,000														
LSX-3-0295	50% Trifluoro-propyl	A	Gum														
Silastic LS420	1% Vinyl	U										152	2441	366	4479	319	208
Fluorosilicone 88																	
Lukooil-X		J															
Lukooil-H		J															
Organosilicone Polymer																	
Copolymer 3	(see text)	V		2500													
Miscellaneous																	
DC-550/stearic acid																	
Silicone Grease c/ lithium capronate																	
Silicone Grease c/ sodium capronate																	
Hi Vac Grease/	45% Methyl																
Craig Polyester																	
Carbowax 20M/	42.8% Methyl																

SPMN/Cl silicone	V		
Silicone FM-1322	V	300	
Silicone MS-4	S		
Silicone KF-54	S		
Silicone 5	V		
Silicone M500	S		
Silicone KF-96	S		
Silicone Oil 2/300	V		
Silicone Siss	V		
Silicone Liquid	V		
139-15			
E Silicone			
Silicone MBL			0.97 (20°C)
Silicone A			1.03 (20°C)
Silicone B		100	
DOW-X24405	A	Low phenyl resin	

* A = Dow Corning, Midlands, MI, U.S.A.; B = Midlands Silicone, Barry, U.K.; C = Perkin-Elmer Corp., Norwalk, CT, U.S.A.; D = Union Carbide, New York, NY, U.S.A.; E = General Electric Co., New York, U.S.A.; F = Bayer Farbenfabriken AG, F.R.G.; G = Imperial Chemical Industries Ltd., U.K.; H = May and Baker, Dagenham, U.K.; I = VEB Chemiewerk, Nunchritz, G.D.R.; J = East Bohemian Chem. Co. "Synthesia", Kolin, Czechoslovakia; K = Metroark Private Ltd., Calcutta, India; L = Institute for Silicone and Fluorocarbon Chemistry, Radebeul, G.D.R.; M = Lachat. Chemical, IL., U.S.A.; N = Rhone-Poulenc, France; O = Wacker Chemie GmbH, F.R.G.; P = Bevaloid Pty, Ltd., Sydney, Australia; Q = Analabs, obsolete; R = Supelco Inc., Bellefonte, PA, U.S.A., obsolete; S = Japanese unknown; T = French unknown,; U = Czechoslovakian unknown; V = Russian unknown.

storage has been reported by Grob and Grob[55] and Venema et al.[56]. Solutions of SE-30 and SE-54 in chloroform containing a trace (0.01%) hydrochloric acid showed significant reductions in molecular weight over 24–48 h as indicated by gel permeation chromatography. The presence of about 0.001% of tetramethyl ammonium hydroxide, a material widely used as a catalyst during manufacture, showed a similar effect.

The stability at room temperature of some polysiloxane stock solutions against trace amounts of acids was subsequently studied[57] together with the effect of chemicals used or synthesized on glass surfaces during the preparation of capillary columns. Studies at 260°C of OV-101 and metal salts have shown considerable degradation indicated by reduced molecular weight such that it was recommended that chloroform be not used as a solvent for low- and medium-polarity stationary phases.

Solid cross-linked polymethyl siloxane materials have been described and are discussed in a subsequent section but there are many applicable to gas–solid chromatography although use has been limited. The major increase in use of dimethyl polysiloxane phases in recent years has been in capillary chromatography, especially in the development of immobilized or cross-linked columns.

The properties of dimethyl polysiloxanes, offered as chromatographic specialties are shown in Table 7 while other commercial products that have been reported as stationary phases are listed in Table 8.

3. POLYALKYL SILOXANES

Materials with alkyl groups other than methyl groups have found little acceptance, a probable reason being the reduced thermal stability as indicated in Table 1. While the polar character is reduced as compared with dimethyl polysiloxane and approaches that of the Apiezon materials, hydrogenated Apiezon[58], or the pure hydrocarbon $C_{87}H_{176}$ developed by Riedo et al.[59], the thermal stability is not comparable.

Several of the Russian produced polysiloxanes [SKTE(K) (ethyl substitution), SKT and SKSV(K)] have lower relative polarity values than imported dimethyl polysiloxanes, i.e., SE-30. The use of phases with other alkyl substituents has not been extensively reported although DC-730 and F-157 (ethyl substitution and stearyl ester, respectively) are available and Gensil S-2116 (30% stearoyl substitution) has been used in the separation of esters[60,61] and glycol ether derivatives[62]. The range of products of Petrarch Systems[63] include a variety of higher alkyl polysiloxanes.

4. METHYLVINYL SILOXANE GUMS

The products of this type that have been used are industrial materials that contain small amounts, i.e., less than 1.0%, of vinyl groups that are capable of undergoing cross-linking with peroxide catalysts. The low concentration of polar groups which are not thermally stable do not influence the phase constants (cf. OV-101 with SE-31 and SE-33). The materials do not possess any distinctive properties, are not offered as chromatographic grades and are for all practical purposes redundant. The Ohio Valley Company have recently introduced a vinyl-modified version of their OV-1 product, the material with 1% vinyl modification being developed for use in the preparation of bonded columns.

5. SILICA-FILLED SILOXANE COMPOUNDS

High-vacuum greases, elastomers, and compounds were used in many early works. The greases usually consist of a low-viscosity oil, *i.e.*, 300 cSt, with silica, often surface-treated, in concentrations of up to 10%. The effect of this addition is apparent in the Y and y' phase constants of Rohrschneider and McReynolds (*cf.* OV-1 and DC-11). Elastomers which are substantially dimethyl polysiloxanes, *i.e.*, Silastic 132 and 152, usually contain fillers, peroxides and other additives such as metal soaps and are less satisfactory than a pure gum such as OV-1 which is preferred.

6. PHENYL-SUBSTITUTED POLYSILOXANES

A wide variety of commercially available phenyl-substituted polysiloxanes have been used in GC since DC-550 (25% phenyl substitution) was reported in the pioneering work of James and Martin[2] in 1952. The majority of the products were produced by Dow Corning in the U.S.A., a company formed in 1942 to exploit the development of polysiloxanes and by its associated company and now subsidiary Midlands Silicones Ltd. in the U.K.

The low viscosity of the products tended to limit the temperature of operation and at the present time the specialty products have essentially replaced these older products. Higher-molecular-weight gums or elastomers with substantial phenyl substitution have not been extensively reported due largely to the high viscosities or solid nature of the products and the resulting difficulties in achieving good performance in gas–liquid chromatography.

The presence of phenyl groups with some electron-donating properties in a polysiloxane stationary phase tends to increase the general polarity and introduce an increasing measure of selectivity not apparent with dimethyl polysiloxane. The products are normally methyl-terminated with substitution from the 5-mole% level. Wurst[13] has reported that Lukooil MF consists of equal numbers of dimethyl and diphenyl units and Coleman[64] that SE-42 has 5% substitution as diphenyl groups. The manufacturers of Lukooil MF[65,66], however, reported the composition simply as 25% phenyl substitution.

Products of mixed cyclics are illustrated by DC-555 or MS-555 which is composed of (phenylmethyl siloxane)(dimethyl siloxane)$_3$, (dimethyl siloxane)$_2$(phenylmethyl siloxane), and (phenylmethyl siloxane)$_2$(dimethyl siloxane)$_2$. This product is not currently available and while DC-556 (10% phenyl) is recommended as a replacement for industrial purposes the phenyl contents of the two materials are similar but not identical.

The importance of using a stationary phase of known composition has been highlighted by Van Lenten and co-workers[67–69]. Kováts and McReynolds indices for a modified set of Rohrschneider solutes were examined using two different batches of Dow Corning DC-710 fluid, a 50% phenylmethyl siloxane of an approximate molecular weight of 2600. A significant difference between batches was due primarily to variation in the percentage of one oligomer, the cyclic pentamer. Five pure oligomers, *i.e.*, the cyclic tetramer, the linear tetramer, the cyclic pentamer, the linear pentamer and the linear heptamer, were separated and characterized by mass spectral analysis and examined with various solutes. The decreasing order of effect of oligomers on the range of solute

indices was *n*-propanol > ethyl acetate > dioxane > 2-pentanone ≈ benzene ≈ nitro-propane. The cyclic pentamer usually exhibited a larger index than the cyclic tetramer. The cyclic tetramer usually exhibited the smallest index for ethyl acetate, dioxane, 2-pentanone and nitropropane. The linear species fell between the two cyclic species. Of the linear species the linear tetramer generally exhibited the largest index value, while the pentamer and heptamer had about the same value.

Several low-molecular-weight phenyl siloxanes of known structure are shown below.

DC-703

$$
CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\left[\begin{array}{c}CH_3\\ |\\ Si\\ |\\ \end{array}-O\right]_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3
$$

Nonamethyl-triphenylpentasiloxane

DC-704
OE-4008

1,3,3,5-Tetramethyl-1,1,5,5-tetraphenyltrisiloxane

DC-705
OE-4007

1,3,5-Trimethyl-1,1,3,5,5-pentaphenyltrisiloxane

OE-4006

1,3-Dimethylhexaphenyltrisiloxane
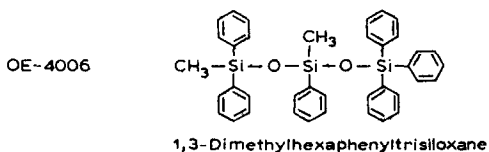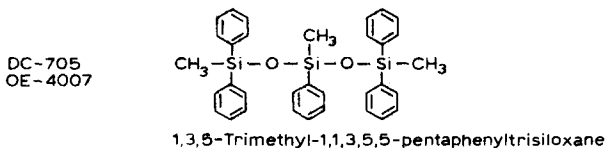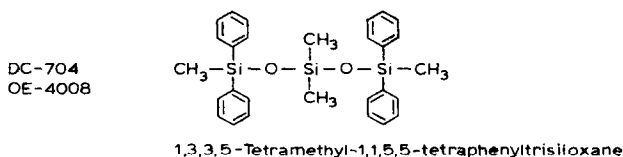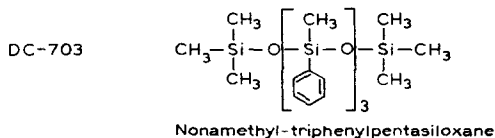
The Ohio Valley Company in the U.S.A. has for many years[70,71] offered a range of phenyl-substituted polysiloxanes of stated composition specifically for use as stationary phases. With higher molecular weights the considerable thermal stability of the phenyl siloxanes may be utilised and OV-17 (50% phenyl) is recommended for use at temperatures to 375°C while the other materials slightly lower recommended maximum operating temperatures.

Commercially available OV-17 was partitioned into a low- and higher-molecular-weight fraction by Barry et al.[71a] by supercritical fluid extraction with carbon dioxide. The higher-molecular-weight fraction was more thermally stable than commercial OV-17 due to its more viscous and gum-like nature. Molecular-weight studies were unfortunately not conducted although it is evident that the lower-molecular-weight fraction which formed approximately 30% of the material contained a very much greater amount of material capable of elution on a Dexsil column than the starting material.

The available phenyl siloxanes from Ohio Valley are of increasing polar character and range between 5.5 and 75% phenyl substitution, while the use of an 85% ex-

perimental material has been reported[60–62] and a 100% substituted material of low molecular weight has been prepared in this laboratory[72]. The Ohio Valley product range has been extended to include specialized materials previously available as industrial products. The product OV-61 is of the same composition as an experimental phenyl phase XE-61 (33% phenyl), which was described by Ikekawa *et al.*[73] for the separation of sterols with comparative studies using SE-30, SE-52, QF-1, XE-60 and NGS, and by Withers[74] in the analysis of glycol ethers as their trimethylsilyl ethers.

OV-73 was released as the first of a series of phenyl-substituted methyl siloxane gums. Containing 5.5% phenyl groups it has been treated to remove low-molecular-weight oligomers which cause column bleeding and is offered as a specialty version of SE-52[75] for use in capillary columns.

The use of a 44-m glass open tubular column coated with OV-73 has been reported by Spark and Ziervogel[76] for the separation of the methyl esters of a hydrogenated fish oil. Some overlap of $C_{22:1}$ esters was evident although on a 48-m column the *cis* and *trans* isomers of the $C_{22:1\Delta9}$ and $C_{22:1\Delta11}$ fatty esters were well resolved. In their work the authors question the need and use of polar capillary columns and indicate the high stability and easy preparation of non-polar columns.

Recently, vinylated grades of OV-17 and OV-1701 (a phase developed for capillary column use) but each containing 1% vinyl groups have become available. These exhibit the same McReynolds constants as the standard material and have been introduced for use in the preparation of bonded or immobilized capillary columns.

The Supelco organization have introduced SP-2250[77] which is chemically identical to OV-17 but for which higher column efficiency, lower bleed and extended life at elevated temperature are claimed.

McCloskey and Hawkes[78] in a study of the selection of standard phases reduced McReynolds' data[3] to a two-dimensional form and concluded that there was little advantage and significant disadvantage in phenyl contents in excess of 50%. However, they suggested that a lower-molecular-weight 75% phenylmethyl polysiloxane may be more satisfactory, a conclusion supported by studies with diphenyl polysiloxane[72].

Related polymers reported as stationary phases include methylphenyl- and dimethylsilyl-4'-dimethylsiloxy) phenyleneoxide[81].
units, methylphenyl siloxanes with diphenyloxide groups in the main chain[80] and poly(4-dimethylsilyl-4'-dimethylsiloxy) phenyleneoxide[81].

Cyclolinear siloxanes consisting of cyclic tetramer rings with pendant phenyl groups connected to a linear dimethyl polysiloxane chain as shown below have been reported as stationary phases[82].
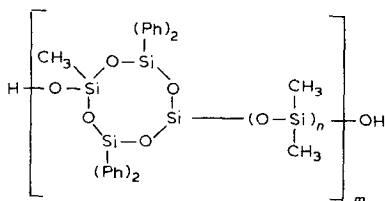
$n = 3$–20 and $m = 10$–100

The resistance to thermal and thermooxidative degradation of symmetrical and unsymmetrical phenyl-substituted polysiloxanes with varying numbers of methyl and

phenyl radicals has been described[83,84]. It was found that the resistance of disiloxanes increases with the increase in the number of phenyl radicals: hexaphenyl disiloxane was found to be resistant to thermooxidative degradation at 305°C. Unfortunately, phenyl groups increase the melting point and adversely affect the separation properties[85].

The effect of phenyl polysiloxanes on separation processes has been highlighted by advances in column technology where highly efficient, very inert and thermally stable capillary columns are coated with non-polar polysiloxane stationary phases. Due to their structure, the viscosity of the phenyl-substituted polysiloxanes change rapidly with temperature and thin-film coatings are unstable at elevated temperatures. The effect of viscosity on stability in capillary columns has been studied by Wright et al.[86]. The temperature viscosity relationship of methyl, phenyl and mineral oils is shown in Fig. 2[43]. The relative change in viscosity is less for the more viscous dimethyl polysiloxane than for the less viscous one. The change in viscosity increases with increased phenyl substitution and with OV-17 is little better than for a medium-viscosity mineral oil.

The low-temperature dependence of the viscosity of dimethyl polysiloxanes has been related to the chemical structure of the linear polysiloxane molecule[87]. The molecule is suggested to possess a helical conformation in the absence of solvents or diluents over a wide molecular-weight range. In the helix the siloxane bonds are orientated towards the screw axes while the methyl groups point outwards and shield the siloxane bond. Increased temperature has two effects on the molecule: it will increase the mean intermolecular distance and simultaneously it will expand the helices and thus diminish the distance. The increased intermolecular distance is opposed by the expansion of the helix and the viscosity appears to be little influenced by temperature. The presence of phenyl or other bulky substituents destroys the regular helical conformation and reduces the compensating effect of bond distance and helix expansion. The net
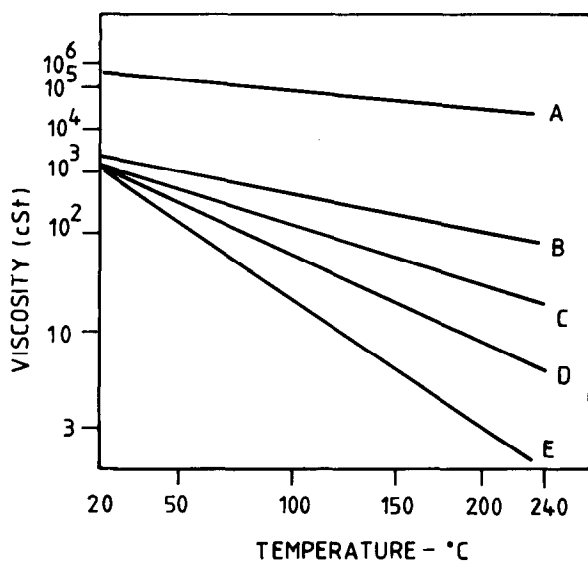
Fig. 2. Viscosity dependence on temperature for several polysiloxanes and a mineral oil: (A) high-viscosity methyl polysiloxane similar to OV-1, (B) medium-viscosity methyl polysiloxane similar to OV-101, (C) medium-viscosity and low-phenyl content methylphenyl polysiloxane, (D) medium-viscosity and high-phenyl content methylphenyl polysiloxane similar to OV-17, and (E) medium-viscosity mineral oil.

TABLE 9

SELECTED McREYNOLDS CONSTANTS

Phase	x'	y'	z'	a'	s'
MPHT (142°C)	135	145	142	324	227
OV-11 (120°C)	102	142	145	219	178
OV-17 (120°C)	119	158	162	243	202
DC-710 (120°C)	107	149	153	228	190

result is a greater temperature viscosity dependence. By using high-viscosity phenyl-substituted polysiloxanes[88] efficient and stable capillary columns have been prepared.

Komers and C Werný[89] attempted to overcome this problem by the synthesis of the related compound, 1,5-bis-(m-phenoxyphenyl)-1,1,3,3,5,5-hexaphenyl trisiloxane (MHPT) which has a temperature range of 40–360°C. The McReynolds constants are given in Table 9.

It is evident that MHPT possesses a selectivity similar to that of OV-17 and DC-710 and differs slightly from OV-11. It showed much less bleeding, however, than DC-710 and OV-17 at temperatures above 300°C. An obvious application of a stationary phase with such a high content of aromatic groups is the separation of polynuclear aromatic compounds and in drug analysis.

The effect of increased phenyl substitution and increasing polar character on the Rohrschneider constants is shown in Fig. 3. While it is evident that the plots are not linear but that the rate of polarity increase tends to decrease due to molecular hindrance, several workers have shown an approximate additivity with medium phenyl
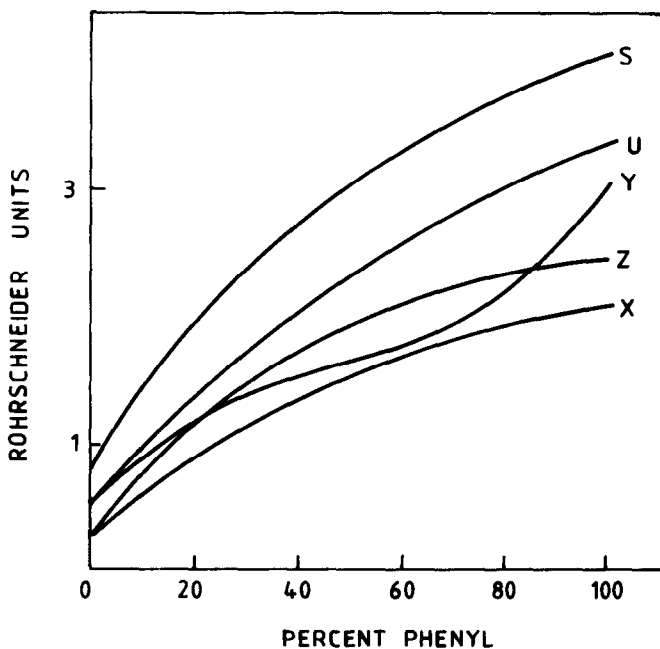
Fig. 3. Relationships between Rohrschneider constants and phenyl substitution.

substitution. Mann and Preston[90] showed that a 1:1 mixture of dimethyl polysiloxane and a 50% phenyl-substituted polymer were equivalent to a produce of 25% phenyl substitution while Lynch et al.[91] showed that mixtures of OV-17 and OV-101 would simulate OV-3, OV-7 and OV-11 with variation of McReynolds constants of less than 0.5%.

During a supply difficulty with the Dexsil carborane polymers, three phenyl polysiloxanes were offered as alternatives with slightly lower temperature limits by Alltech Associates. The materials Alltech PS-300, PS-400 and PS-410 approximate the general polarity of the Dexsil products and the McReynolds constants would suggest phenyl substitution of about 15%, 25% and 45% for the three products[92]. Recent use of the products would appear to be negligible.

The available phenyl-substituted polysiloxanes of industrial origin are shown in Table 8 while specialty products are shown in Table 7.

7. PHENYLVINYL SILOXANE GUMS

Analogous to the methylvinyl gums are several industrial products containing small amounts, i.e., 1% of vinyl groups and phenyl groups usually at the 5% level that have been used as stationary phases. The phenyl substitution in the material SE-54 is reported to be as diphenyl groups[64] but with products of this type the level of substitution is not sufficiently high to provide any worthwhile selectivity and the products are now largely redundant. OV-73 is a specialty gum product with 5.5% phenyl substitution developed for capillary column use[75].

8. CHLOROPHENYL-SUBSTITUTED POLYSILOXANES

Siloxanes containing chlorophenyl groups have been used as stationary phases, the materials DC-560, F-60, F-61 and SP-400 all being of similar composition with approximately 11% chlorophenyl substitution. The composition has been reported as containing p-chlorophenyl and phenyl groups but Coleman[64] has reported spectral bands due to dichlorophenyl groups. The Supelco product is the only material specifically offered as a stationary phase.

While the phases have been used in this laboratory[60,62], it is apparent that any specific contribution due to the halogen is trivial, this being in agreement with a study on phase selectivity by Weiner and Parcher[93]. Giles and Nahkiva[94] have reported hydrogen bonding with esters but this is apparently not evident with the materials available as phases due to the low degree of substitution.

The McReynolds constants equated to the basis of x' are shown below in Table 10 from which it is apparent that the above products are essentially identical to a phase containing 5% phenyl substitution. Any acceptor character u' due to the halogen would appear to be negated by the aromaticity, and the value of the class is doubtful. The similarity of behaviour in steroid analysis of F-60 and SE-30 has been previously noted by Horning et al.[95].

The composition of Versilube F-50 remains in doubt, it having been variously described as containing methyl-(p-chlorophenyl) groups[96], methyl, (10%) trichlorophenyl groups[97], methyl, trichlorophenyl and trisilyl ether groups[63] and tetrachlorophenyl groups[64]. The McReynolds values of the material, however, are in agreement with values for dimethyl polysiloxane.

TABLE 10

McREYNOLDS CONSTANTS FOR CHLOROPHENYL-SUBSTITUTED POLYSILOXANES EQUA-
TED TO BENZENE SOLUTE

Phase	x'	y'	z'	u'	s'	h'
DC-560,F-60,F-61,SP-400	1.00	2.25	2.18	3.12	2.12	1.53
OV-3	1.00	1.98	1.84	2.81	2.00	1.25
OV-1	1.00	3.43	2.75	4.00	2.62	2.00
SE-52	1.00	2.25	2.03	3.06	2.11	1.37
F-50	1.00	3.00	2.52	3.63	2.47	1.90

A further type of chlorophenyl substitution is illustrated by Dow Corning Fluid
F-4050. The material has been suggested as a stationary phase[98] and consists of a re-
latively short-chain dimethyl polysiloxane end-terminated with a 3,5-dichlorophenyl
group. A similar type of material has been described by Wurst[13] and its preparation
described by the chlorination of phenyltrichlorosilane[99] to form a mixture of trichlo-
rophenyl- (73.5%) and tetrachlorophenyltrichlorosilane (22.8%). The trichlorophenyl-
trichlorosilane reacted with dimethyldichlorosilane[100]. Details of the chlorophenyl-sub-
stituted products are shown in Tables 7 and 8.

9. FLUOROALKYL-SUBSTITUTED POLYSILOXANES

The currently available fluoroalkyl siloxanes are all homopolymers of 3,3,3-tri-
fluoropropylmethyl siloxane produced by base-catalysed polymerization of the cyclic
trimer. The preparation and properties of trifluoropropylmethyl siloxanes have been
described by Pierce and Kim[101].

The position of substitution of the fluorinated substituent affects the stability of
the Si–C bond. Substitution of the α- and β-carbon atoms weakens the bond although
γ-substitution stabilizes the bond and is normally utilized. The fluorosilocones are not
as heat-stable as methyl elastomers due to the susceptibility of the siloxane bond to
cleave and to undergo oxidative degradation[102]. Degradation of the 3,3,3-trifluoro-
propylmethyl siloxane at 400°C leads to the formation of both cyclic trimer and products
due to decomposition of the trifluoropropyl groups. The bond between the silicon and
fluoralkyl groups is related to an intramolecular transition of fluorine atoms from the
γ-position to the silicon atom[103].

The siloxane polymer QF-1 or FS-1265 fluid and first described as QF-1-0065 is
available in several viscosity grades and was introduced as a stable polar phase for GC
by VandenHeuvel et al.[104], for the analysis of steroids in 1961. The phase corresponds
to dimethyl polysiloxane with 50 mole% replacement of methyl groups with trifluo-
ropropyl groups and it thus possesses what is recognized as a marked acceptor charac-
ter.

Selective functional group retention effects were examined using a series of ste-
roids. The neopentylglycol succinate (NGS) values reflected polar properties leading
to a considerable increase in the retention of hydroxy and keto compounds, the effect
being of similar magnitude with both functional groups while a slightly smaller effect
was evident with esters. QF-1 indicated selective behaviour as increased retention was
apparent with oxygen-containing functional groups in the order ether, hydroxy, ester,

TABLE 11

COMPARATIVE McREYNOLDS CONSTANTS

Phase	x'	y'	z'	u'	s'	h
SE-30	16	55	44	65	42	32
NGS	272	469	366	539	474	371
QF-1	144	233	355	463	305	203
OV-17	119	158	162	243	202	112

TABLE 12

McREYNOLDS CONSTANTS FROM TABLE 10 EQUATED TO $x' = 1.0$

Phase	x'	y'	z'	u'	s'	h
SE-30	1.00	3.43	2.75	4.00	2.62	2.00
NGS	1.00	1.72	1.34	1.98	1.74	1.36
QF-1	1.00	1.61	2.46	3.21	2.11	1.41
OV-17	1.00	1.32	1.36	2.04	1.69	0.94

keto while the retention of hydroxy and keto steroids varied with structure to a greater degree than previously observed. From a consideration of McReynolds constants of the three phases significant acceptor characteristics of QF-1 are not readily apparent. Comparison with values for OV-17 indicates high values for z' and the related u' (Table 11). Simplification is possible by equating the phases to x' (Table 12).

With the low-polarity phase all the values tend to be high and selectivity is low, the low x' value being indicative of elimination of charge transfer forces by comparison with squalane. Comparison of QF-1 with NGS and OV-17 shows the significantly higher values of z' and u' and indicates the acceptor character of the phase. The same effect is evident by equating the McReynolds constant to the basis of z', where the lower values of the other constants, i.e., the difference, is significant (Table 13).

A number of specialty polymers are of the same composition as QF-1, i.e., OV-202, OV-210, OV-215 and SP-2401. Thermogravimetric analyses run from 200°C to 300°C at a heating rate of 2°C/min in a helium atmosphere show OV-210 and SP-2401 to possess greater thermal stability than QF-1 as indicated by the weight losses[105] presented in Table 14.

The column efficiencies of QF-1 and OV-210 are quite low, i.e., less than 500 theoretical plates per foot for a packed column and greater efficiency is reported for SP-2401. The manufacturers report values of 800 and 1040 theoretical plates per foot

TABLE 13

McREYNOLDS CONSTANTS FROM TABLE 11 EQUATED TO $z' = 1.0$

Phase	x'	y'	z'	u'	z'	h
SE-30	0.36	1.25	1.00	1.47	0.99	0.72
NGS	0.74	1.28	1.00	1.47	1.29	1.01
QF-1	0.40	0.65	1.00	1.30	0.85	0.57
OV-17	0.73	0.97	1.00	1.50	1.24	0.69

TABLE 14

WEIGHT LOSSES ON THERMOGRAVIMETRY OF FLUOROALKYL POLYSILOXANES

Phase	200°C	225°C	250°C	275°C	300°C
QF-1	0.5	0.9	1.3	1.8	2.3
OV-210	0.1	0.2	0.4	0.5	1.0
SP-2401	0.0	0.1	0.1	0.2	1.0

for a 6-ft. column for chloresterol and mannitol respectively[106]. Similar improved efficiency is obtained with the comparable product OV-202[75].

The variation in performance of fluoralkyl siloxane columns has been reported by Hanneman and Klimisch[107] to be due to decomposition of the polymer during column preparation. Acetone, a solvent widely recommended, has been shown to facilitate decomposition by reaction with residual catalyst and glass surfaces and ethyl acetate was recommended as a suitable solvent. Decomposition of the phases was shown by gel permeation chromatography where QF-1 was inferior to OV-210 and both were inferior to SP-2401. The molecular weights indicated were QF-1 (24,600), OV-210 (18,600) and SP-2401 (2,600). The molecular weights for the other specialty products are shown in Table 7.

The use of trifluoropropyl siloxanes in admixture with other polysiloxanes continues to be widely reported although it is doubtful if a single suitable polysiloxane is not available for use in most cases due to the wide variety of products offered. The use of QF-1 and dimethyl polysiloxane (SE-30) probably dates from a separation of chlorinated pesticides reported by Burke and Holswade[108]. Henly et al.[109] introduced the use of QF-1–OV-17 (9:7) to provide a superior separation of the same pesticides.

The GC of carbon dioxide, chlorine, hydrogen chloride, nitrosyl chloride, nitrogen dioxide and sulphur dioxide has been studied in various phases[110] and dialkyl phthalates, dialkyl adipates and fluorinated silicones were recommended as the most suitable stationary phases.

Soviet fluoroalkyl polysiloxanes have been reported for the separation of higher fatty alcohols and their performance compared against QF-1 and OV-210[111] together with Rohrschneider constants of the available products.

Schaal and McKinley[112] have reported that separation of anticonvulsant drugs can be better achieved by the use of DC-LSX-3-0295 (now known as DC-420 Silastic Gum) rather than the widely used stationary phase OV-17. This demonstrates that the fluoralkyl stationary phases may have a large potential for use with clinical serum samples. The Ohio Valley product OV-215 is comparable in performance to Silastic Gum DC-420. A vinyl-modified version of OV-215 (1% vinyl substitution) has recently been introduced which according to the manufacturers is a "gum verion of OV-210" which is thoroughly confusing as OV-215 is shown as a gum in the same report.

10. CYANOALKYL-SUBSTITUTED POLYSILOXANES

Silicone oils containing cyanopropyl groups were offered as a new class of polar stationary phases by Rotzsche in 1962[4,5]. A decade passed before specialty grades were offered to chromatographers by Silar Laboratories[113,114], while during the last decade these and competitive products have found acceptance for lipid separations.

TABLE 15

SEPARATION FACTORS ON CYANOPROPYL-SUBSTITUTED POLYSILOXANES[115]

Stationary phase	(% Methyl:% phenyl: % cyanopropyl)					
	100:0:0	75:25:0	75:0:25	50:15:35	62.5:9:37.5	50:0:50
Alkylbenzene/n-alkane	1.2	1.7	3.0	3.7	4.1	6.1
Alkylbenzene/cyclohexanes	1.1	1.5	1.9	1.9	2.4	3.0
Alkylbenzene/cycloolefins	-	-	-	1.6	2.0	2.2
Ketones/primary alcohols	2.1	2.6	1.5	1.5	1.3	1.3
Primary alcohols/ethers	0.4	0.4	1.5	1.4	1.7	2.1
Ketones/ethers	0.8	1.0	2.2	2.1	2.3	2.8
Alkylformates/ethers	0.9	1.3	1.8	1.8	1.8	2.1

Rotzsche[4,5] varied the number of cyanopropyl groups and produced phases of varying polarity and selectivity. Retention volumes for homologous hydrocarbons and oxygen-containing compounds were produced at 100°C and selectivity constants as described by Bayer[115] are shown in Table 15.

Table 15 shows how the selectivity coefficients are affected by the presence of polar groups in the siloxane. With increased polar character of the siloxane oil the selectivity is increased markedly for the separation of alkyl benzenes from n-alkanes or primary alcohols from ethers while it is decreased for the separation of ketones from primary alcohols.

Cyanoethyl siloxanes produced by General Electric appear to have been first described in detail by Litchfield et al.[116]. Using an experimental polymer 238-149-99 (i.e., equivalent to XF-1150) with 50% cyanoethyl substitution, XE-60 with 25% cyanoethyl substitution and a 1:1 mixture, the separation of some geometric isomers of C_{18} fatty esters was achieved. Some confusion has existed concerning the polarity of 238-149-99; Litchfield and Dutton[117] suggested polarity similar to diethylene glycol succinate although solute constants are much lower[64], while Supina[118] indicated performance similar to that achieved on the lower-polarity polyester, ethylene glycol adipate, which possesses similar constants. Another experimental material, XF-1105 with 5% cyanoethyl substitution, was offered for sale by Applied Science Labs. until supplies were exhausted. Subsequently[119] OV-105 has become available as a chromatographic speciality product of the same composition.

Bayer et al.[120] found nitrile phases effective in the resolution of aliphatic, olefinic and aromatic hydrocarbons of similar boiling point and suggested the selectivity to be due to the formation of a π-complex between the nitrile groups and the π-electrons of the olefins and aromatic compounds. Complex formation of this type was also suggested by Litchfield et al.[116] on the basis of stable π-complexes[121–123] and the similarity of elution behaviour in silver ion chromatography with Ag^+–olefin π-complexes of the same fatty esters[124–126].

The material OV-225, containing 25% each cyanopropyl and phenyl substitution, has been offered as a substitute for XE-60 but cannot be considered as an equivalent. While the u' values are the same and the s' value of OV-225 is higher, the other values of OV-225 are also increased and the general character of the phase becomes increasingly polar and the selectivity somewhat altered. The effect is shown in Table 16 by equating the contents to the basis of x'. The values of u' and s' both associated with

TABLE 16

COMPARATIVE McREYNOLDS CONSTANTS FOR OV-225 AND XE-60

Phase	x'	y'	z'	u'	s'	h
OV-225	1.00	1.62	1.59	2.11	1.25	1.23
XE-60	1.00	1.82	1.66	2.41	1.79	1.41

acceptor characteristics are higher with XE-60.

The (—)-methyloxime pertrifluoroacetyl chiral derivatives of carbohydrate enantiomers have been separated on capillary columns coated with OV-225. Each carbohydrate enantiomer produced two peaks corresponding to the syn(Z) and anti(E) alkoximes[127].

The position of substitution of the cyano group is of considerable importance. The cyano group on the α-carbon atom is of much reduced thermal stability as compared with substitution of the β- or γ-carbon atoms[103]. With a γ-cyanopropylmethyl polysiloxane the oxidative stability is equivalent to that of dimethyl polysiloxane[128]. The β-cyanoethyl group is approximately equivalent to the γ-cyanopropyl group while the γ-cyanoethyl group is much more inferior, the position weakening the silicon–carbon bond. The phenyl group on the same silicon atom as the γ-cyanopropyl group increases the thermal stability as shown with SILAR 5CP[64].

The high thermal stability of SILAR 5CP has been demonstrated by Myher et al.[129] who, with 3% phase, separated a series of natural glycerides based on unsaturation, positional placement of fatty acids and molecular weight. A useful column life of several months was possible with operation at 270°C.

β-Cyanoethylmethyl siloxane XF-1150 remained the most polar siloxane phase available for almost a decade, but possessed poor thermal stability. With the intro-

TABLE 17

RETENTION BEHAVIOUR OF METHYL ESTERS OF UNSATURATED FATTY ESTERS ON CYANOALKYL POLYSILOXANES

Phase	Methyl esters (relative retention)				
	18:0	18:1	18:2	18:3	20:0
10% Phase at 200[136]					
SP 2300	1.00	1.11	1.32	1.62	1.90
SP 2310	1.00	1.12	1.34	1.64	1.82
SP 2330	1.00	1.15	1.44	1.82	1.71
SP 2340	1.00	1.18	1.49	1.91	1.66
10% Phase at 180[133]					
SILAR-5CP	1.00	1.13	1.35	1.68	1.93
SILAR-7CP	1.00	1.17	1.46	1.88	1.80
SILAR-9CP	1.00	1.19	1.52	1.99	1.74
SILAR-10C	1.00	1.22	1.60	2.14	1.67
Separation at 175[133]					
BDS	1.00	1.11	1.36	1.75	1.90
EGA	1.00	1.12	1.34	1.72	1.89
DEGS	1.00	1.17	1.50	2.00	1.77
EGS	1.00	1.20	1.56	2.14	1.67

TABLE 18

McREYNOLDS CONSTANTS OF SOME POLAR STATIONARY PHASES

Phase	x'	y'	z'	u'	s'
OV-101	17	57	45	67	43
Carbowax 20M	322	536	368	572	510
FFAP	340	580	397	602	627
DEGS	499	751	593	840	860
SP-2340	520	757	659	942	800
SILAR 10C	523	775	659	942	801
OV-275	781	1006	885	1177	1089

duction of SILAR 5CP during 1972[6] a slightly more polar material (γ-cyanopropyl-phenyl siloxane) was introduced and became the forerunner of a variety of even more polar cyanoalkyl siloxanes. SILAR 10C (di-γ-cyanopropyl siloxane) later became available and both products have found use with fatty esters[129–131]. Phases of inter-mediate polarity were introduced and two equivalent series (SILARs[132–134] and the SP-2300 series[135–137]) are shown in Table 17. During a trademark difficulty SILAR 10C appeared as Apolar 10C[138], an absurd and confusing alternative name consider-ing the long established European use of the term to imply non-polar properties.

In 1974 a further more polar cyanoalkyl siloxane (OV-275) appeared and is re-ported to be stable at 275°C. This material is variously suggested to be di-α-cyanoethyl polysiloxane or a copolymer with γ-cyanopropyl groups. Use with fatty esters has been reported together with several varying reports of the McReynolds constants[119,138].

For many years polyester-type stationary phases have been used for GC sepa-ration of unsaturated fatty acid methyl esters. However, these phases have relatively poor thermal stability[139,140], and polar cyanoalkyl polysiloxanes have been found to have greater thermal stability and give enhanced cis–trans selectivity, the trans isomer being eluted earlier than the cis isomer[141,142].

The McReynolds constants for the most commonly used phases for methyl ester analysis are shown in Table 18[143]. The highly polar phases (SP-2340, SILAR 10C and OV-275) have been those most commonly used[143,144].

The intermediate-polarity cyanopropyl polysiloxanes have found some accep-tance. The x' values and "general polarity" of the SP-2300 series are listed in Table 19 although it is apparent that the materials are comparable with the SILAR range.

SP-2300 is slightly less polar than EGA while SP-2310 is slightly less polar than EGS and as might be expected on the basis of the polyesters, 18:3ω3 is eluted before 20:0. With SP-2330 and SP-2340, 18:3 eluted after 20:0, the value x' of 490 being similar

TABLE 19

Mc REYNOLDS CONSTANT x' AND GENERAL POLARITY OF SUPELCO CYANOALKYL POLY-SILOXANES

Phase	x'	General polarity
SP-2300	316	2424
SP-2310	440	3192
SP-2330	490	3536
SP-2340	520	3678

to DEGS while with SP-2340 the x' value of 520 is higher. Retention data for the series are shown in Table 18 and it would appear that the polyesters and cyanoalkyl siloxanes increase similarly in polarity with increased temperature.

Essentially similar data using the SILAR products and comparisons with behaviour on polyesters are shown in the same table. The separation of the *cis* and *trans* isomers, methyl oleate and methyl eladate have been separated using 15% of SP-2340 or OV-275 at 220°C[141]. To optimize the column parameters to facilitate the separation the amount of stationary phases, the type of support and the nature of the support surface must be considered. Increasing the loading of the stationary phase improves the separation factor for the pair of isomers, but reduces the efficiency of the column, while the use of a non-silanised support[136] offers greater column efficiencies with highly polar phases.

A comparison of the phases SILAR 10C, SILAR 9 CP, SP-2340 and OV-275 for the separation of methyl esters of fatty acids on packed columns has been reported by Heckers *et al.*[142]. The separation of seven pairs of *cis–trans* isomeric methyl esters were separated on 12% SILAR 10C and SP-2340; minimum overlap was observed with the C_{15} acids and maximum overlap with the C_{18} acids. Erucic and brassic acids were separated but with less resolution than oleic–elaidic acids. A comparison of the efficiency of the two phases showed that SP-2340 samples obtained over a period of two years had been of consistent chemical composition while SILAR 10C had been of very variable composition and accordingly SP-2340 was recommended.

Similar studies with OV-275 and SILAR 9CP showed very similar results with the same esters, the separation factors for all four phases for various separations being similar. Molecular-weight determinations estimated from nuclear magnetic resonance (NMR) signal ratios show SILAR 10C to vary between 4000 and 10,000, SP-2340, OV-275 and SILAR 9CP to be relatively stable at 2800, 2100 and 2080, respectively. Spectra would suggest that the SP-2340 and OV-275 are terminated with acetyl groups, the other with trimethylsilyl groups.
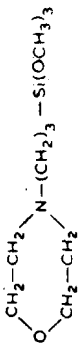
The use of SILAR 10C and SP-2340 for the estimation of the *trans* fatty acid content of food has been successfully reported[145,146]. The rapid analysis of *trans* fatty acids on SP-2340 glass capillary columns has been reported by Sampagna *et al.*[147]. Using a 15-m column incomplete resolution of *cis* and *trans* isomers was achieved, however, the use of correction factors allowed rapid quantitative analysis of fatty acids derived from partially hydrogenated food fats in less than 15 min.

Although the phases SP-2330 and SP-2340 will separate groups of *cis* isomers from *trans* isomers, a recently introduced cyanoalkyl phase SP-2560 available as a 100-m capillary column will resolve the components of *trans* isomer mixtures as demonstrated with a mixture of four $C_{18:1}$ isomers[328].

Recently, Walker[148] has suggested that caution should be used when using OV-275 as the stationary phase for analysis of samples containing polyunsaturated acids, since these compounds appeared to be underestimated in comparison with their analysis on a packed polyester column. As the column aged, decomposition of polyunsaturated compounds in the hot (220°C) stainless-steel column appeared to be the major reason for the poor recovery.

Yousef *et al.*[149] have shown that the introduction of phenyl residues into the cyanoalkylmethyl siloxane matrix results in superior resolution and improved recovery of the methyl ester acetates of the bile acids of rat and human bile.

TABLE 20

COMPOSITION AND McREYNOLDS CONSTANTS OF AMINOALKYLSILANE AND SILOXANE COMPOUNDS

Trade designation	Manufacturer[*]	Chemical composition	Formula	Viscosity at 25°C (cSt)	Specific gravity at 25°C	Boiling point (°C)	Refractive index at 25°C	McReynolds constants				
								x'	y'	z'	u'	s'
Z6020	1	N-β-Aminoethyl-γ-aminopropyl trimethoxysilane	$NH_2(CH_2)_2 NH(CH_2)_3 Si(OCH_3)_3$	10.0	1.01	146(15 mm Hg)	1.4418	247	700	393	454	433
A1120	2			6.5	1.038	259	1.448					
KBM-603	3			6.0	1.03	259	1.445					
A1100	1	γ-Aminopropyl triethoxysilane	$NH_2(CH_2)_3 Si(O_2CH_3)_3$	1.6	0.942	217	1.420	145	426	226	313	297
X12-563	3	N-Allyl-γ-aminopropyl trimethoxysilane	$CH_2=CH-CH_2- NH(CH_2)_3 Si(OCH_3)_3$	3.0	0.975	107(7.5 mm Hg)	1.434	323	653	441	593	555
X12-570	3	γ-Morphinylpropyl trimethoxysilane	$O{<}^{CH_2-CH_2}_{CH_2-CH_2}{>}N-(CH_2)_3-Si(OCH_3)_3$	4.1	1.05	122(5 mm Hg)	1.444	72	539	129	511	469
S4150/41	4	N,N-Dimethyl-γ-aminoethoxymethyl polysiloxane	$(H_3C)_2N-(CH_2)_2-O-(SiO)_x-CH_3$	106.0		—	1.462	-8	143	76	69	82
DC-530	1	Copolymer Z6020 and dimethyl polysiloxane						63	269	129	204	116
DC-531	1	50% solution DC-530 in 2-propanol and aliphatic solvents						30	155	119	84	62
DC-535	1	Low-molecular-weight dimethyl polysiloxane (DP=100) approx. 2% ethylenediamine moiety						24	159	70	93	70
MS-2560	5											
X-22-857	4	As DC-535 but approx. 2½% amine moiety						31	166	67	95	78

* = Dow Corning Corp., Midland, MI, U.S.A.; 2 = Union Carbide Corp., New York, NY, U.S.A.; 3 = Shin-Etsu Chemical Industries, Tokyo, Japan; 4 = Imperial Chemical Industries, Organics Division, Stevenston, Ayrshire, U.K.; 5 = Midlands Silicones Ltd., Barry, U.K.

The work of Zinkel and Engler[150] has shown that the phases SILAR 10C and OV-275 are of value in the GC of the methyl and *tert.*-butyl esters of diterpene resin acids, particularly in allowing for the first time simultaneous determination of levopimaric and palustric acid. No single stationary phase in a packed column, however, yet allows sufficient separation of all of the common pine resin acids and for a complete analysis several columns are necessary.

Takagi and co-workers[151,152] have reported the use of SILAR 10C for the separation of wax esters of chain length C_{28}–C_{44} and containing 0–7 double bonds. The equivalent chain length (ECL) values of the unsaturated wax esters are significantly dependent on the column temperature used and careful selection is necessary to allow separation of certain esters pairs differing in the degree or position of the unsaturation.

11. AMINOALKYL-SUBSTITUTED POLYSILOXANES

The use of simple aminoalkyl-substituted polysiloxanes as stationary phases in GC was reported by Ashes and Haken[153] and while a subsequent study[154] showed the relative reactivity of primary, secondary and tertiary amines, general use was restricted due to the chemical reactivity of the phases. During the last few years amino-substituted polysiloxanes have been widely reported as chiral stationary phases. The enantioselective phases allow separation of optical antipodes and the materials are described in section 16.

The simple phases were polymers containing an ethylene diamine moiety with both primary and secondary amino groups. On-column chemical reaction has been shown to occur with both aldehydes and ketones when the phases are used as short precolumns, *i.e.*, 6 in., or as the main column *i.e.*, 12 ft. With 10% phase on Celatom, isothermal operation at 100°C and 130°C effectively abstracted aldehydes, lactones and most ketones. Partial removal of ketones that are sterically hindered occurs as with other reported abstraction columns. Epoxides were largely unaffected and a specificity superior to simple aromatic amine abstractors was observed.

To determine the relative reactivity of primary, secondary and tertiary amino groups and the possibility of more selective chemical reactions a series of support bonded aminoalkyl silanes were prepared from silicones of similar molecular weight and contained individually each type of amino group[154]. Chemical reaction occurred with both primary and secondary amino groups. The reactivity with ketones, which are generally less reactive than aldehydes, was shown to be dependent of molecular shape, with branched chain compounds shielding the carbonyl and exhibiting reduced reactivity. The primary aminon groups are more reactive than the secondary amino groups but the compound containing both groups was most reactive due simply to a concentration effort. While reaction with tertiary amino groups might be expected on theoretical grounds, this did not occur. The composition and McReynolds constants of the compounds studied are shown in Table 20.

A convenient method for the synthesis of thermally stable aminoalkyl polysiloxanes has been developed with the amino functionality being suitable for side-chain reaction to incorporate the desired selectivity. Two chiral and three achiral phases have been described by Fisk[155] using OV-105 as starting material. Reduction of the nitrile was achieved with diborane with the chiral phases using derivatives of 1-valine and the achiral phases trifluoroacetic anhydride and methyl iodide. The work is a continuation of earlier studies by Lochmüller and Hinshaw[156,157].

12. ORGANOSILICONE POLYMERS

Supina[8] developed a range of organosilicone polymers which are commercially available from Applied Science Lab., and are prepared by the reaction of a polyester adduct of ethylene glycol succinate and an organosilane. The products were largely offered as substitutes for polyester phases but improved thermal stability is claimed. Use in recent years would appear to have decreased markedly due both to the availability of polar siloxanes which have superior thermal properties to the polyesters and to the more reproducible composition of the polysiloxanes.

The polymers are prepared by the reaction of organosilanes with the hydroxyl groups of the glycol and products are available which incorporate the dimethyl siloxane, methylphenyl siloxane and methylcyanoethyl siloxane structures.

Few data are available concerning the siloxane content of the polymers, analyses that have been conducted show large variations in composition and it is difficult to believe that reproducible results could be obtained with the various samples that have been examined[158].

The compositions of the three types described[20] are shown below.

$$-\left[(CH_2)_2 - O - \overset{\overset{\displaystyle O}{\|}}{C} - O - (CH_2)_2\right]_x \left[\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}} O\right]_y-$$

EGSS-X $y/x < 1$ EGSS-Y $y/x > 1$

$$-\left[(CH_2)_2 - O - \overset{\overset{\displaystyle O}{\|}}{C} - O - (CH_2)_2\right]_x \left[\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{Si}} O\right]_y-$$

EGSP-A $y/x < 1$ EGSP-Z $y/x > 1$

$$-\left[(CH_2)_2 - O - \overset{\overset{\displaystyle O}{\|}}{C} - O - (CH_2)\right]_x \left[\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_2-CH_2-CN}{|}}{Si}} O\right]_y$$
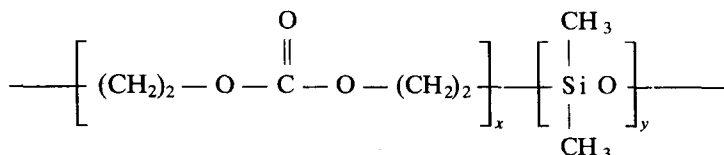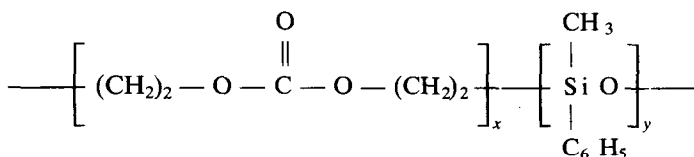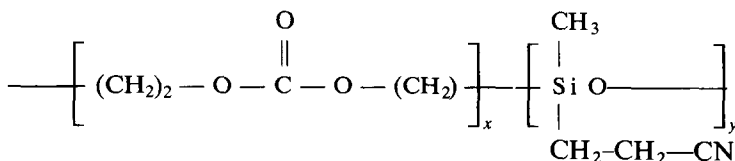
ECNSS-S $y/x < 1$ ECNSS-M $y/x > 1$

The variability of composition is probably not unexpected as possibly the only work that has considered multiple samples of these materials shows variable retention performance[159]. It has been observed that significant variations in the polarity of the columns occur with variation of the stationary-phase loading. The effect has been demonstrated with EGSS-X[159] and by Ackman[160] with fatty esters using representatives of each type of the polymers.

The separations that have been reported include fatty esters[161], glyceryl ethers[162] and trimethylsilyl derivatives of carbohydrates[163] on EGSS-X, catecholamines[164] and sterol sulphonates[165] on EGSP-Z and fatty esters[166], fatty amines[167] and monosaccharides[168] on ECNSS-M.

McReynolds constants for the phases are shown in Table 7 and as expected a decrease in the polar character of the phases is experienced as the ester content is reduced.

A material that has been used in several Russian works is copolymer 3, the co-polymerization product of liquid polymethylphenyl disiloxane and hexamethyl disiloxane[169].

A phenyl siloxane–Carbowax copolymer (OV-330) has been introduced by the Ohio Valley Company. The McReynolds constants shown in Table 7 are much lower than the Applied Science Labs. products while no reports of use have been observed.

13. SILOXANE-TERMINATED POLYESTER PHASES

In addition to the siloxane ester copolymers previously described certain of the conventional polyesters offered as stationary phases have been terminated with groups which tend to inhibit thermal decomposition and thus some increase in working temperature or an extension of the useful life is claimed.

Polyester end-groups have been reacted with methyl silanes to achieve a terminal trimethylsilyl ether group. The siloxane content of these materials is minimal and the column characteristics are effectively those of the reactant polyester.

14. CARBORANE–SILOXANE POLYMERS

The Olin Corp. have developed a variety of linear polymers that incorporate both carborane and siloxane units within the chain[170–173] and various applications have been reviewed[174]. Three materials have been marketed by Analabs as high-temperature stationary phases and while Olin Corp. have discontinued manufacture an alternate supplier has been obtained. The carborane group is dicarbaclosododecaborane ($B_{10}H_{10}C_2$), which has silicone chains bonded to the carbon atoms. The carboranes are unusual both from their structure with 6-coordinate carbons and their thermal stability. The m-borane is considered quasi-aromatic and capable of assuming many resonance states and stabilizing adjoining groups against thermal degradation.

The boron contents of the available polymers are quite high, the carborane groups consisting of 75.8% boron. The product Dexsil 300 GC consists of one carborane group with *meta* attachment in a chain with four dimethyl siloxane units as the repeating unit, the boron content of the polymer being 25.5%. The other polymers Dexsil 400 GC and Dexsil 410 GC have as the repeating unit one carborane group and five dimethyl poly-siloxane units, the central silicone atom having one phenyl and one 2-cyanoethyl group, respectively.

Thermal gravimetric analyses showed XE-60 to lose weight at about 228°C, SE-30 at about 350°C and Dexsil 300 GC at about 625°C[175]. Although the recommended maximum temperature limits are 450°C for extended periods and 500°C for limited periods, the materials offer a major advance in stationary phases for high-temperature operation and the usage is apparently increasing.

The McReynolds constants of the three phases are shown in Table 7 where it is apparent that Dexsil 300 GC is of modest polarity, being somewhat similar to that of OV-3, *i.e.*, 10% phenyl substitution, that Dexsil 400 GC is similar to OV-7, *i.e.*, 20% phenyl substitution and Dexsil 410 GC slightly more polar than OV-17, *i.e.*, 50% phenyl substitution. A substantial bibliography[176] and later supplement[177] have been prepared showing reported uses of Dexsil 300 GC for high-temperature applications, including methyl esters, aromatic amines, halogenated alcohols, polyphenyl ethers, low-molecular-weight dimethyl siloxane oligomers and butter triglycerides. Due to low polarity as indicated by McReynolds constants the phase has little selectivity and its utility is due solely to the increased operating temperature that is possible.

The use of Dexsil 400 GC, a low-phenyl-containing product, has been reported[178,179] with the butyl esters of some trifluoroacetyl amino acids. A 150-ft. capillary column was temperature-programmed to 300°C and used Dexsil 400 GC with hydroxyl end-groups and also as commercially offered, *i.e.*, end-capped with trimethylsilyl groups. The use of Dexsil 410 GC appears to have been reported only in the supplier's literature.

Two other carborane–siloxane polymers similar to Dexsil 300 GC have been reported[180] for the capillary column separation at 360°C of cholestrol esters, triglycerides and high-boiling hydrocarbons. The materials experimental carborane polymers 7001-8-73 and 7001-8-95C are available from Chemical Systems[181] as 5-SiB-1 and 5-SiB-1.5 with 2.0 and 2.5 dimethyl polysiloxane groups per carborane nucleus, respectively. Both are reported[181] to perform indefinitely at 270°C and for short periods at 400°C. For GC–mass spectrometry (MS) the first product is preferred as hydrogen is reported to be the sole decomposition product.

Several carborane materials have been briefly described in Soviet publications although compositional details are brief[182,183].

15. BONDED SILOXANE STATIONARY PHASES

The utility of many polysiloxane phases is greatly enhanced, particularly in capillary-column applications, by their presence in the column in a bonded or actually a cross-linked form with improved performance both with regard to column efficiency and stability.

The silicone intermediates, by their very nature, are available in a huge number of forms and may be polymerized to form a much greater range of siloxane products.

Recent years have seen many claims of new developments in siloxane technology as applied to chromatography. However, it is doubtful if any of these developments are new. Rather virtually all of these endeavours are applications of established technology. The general basis of bonded columns relies on disclosures of now defunct patents issued decades ago and which have become established for various industrial purposes[184].

Cross-linking is effected by two major types of chemical reaction both well known in silicone elastomer and rubber technology, as shown below, and which differ fundamentally in the type of atom adjacent to the silicone atom although it should be recorded that the first bonded phases were not cross-linked but simply *in situ* formation of a linear polymer material.

The preparation of polysiloxanes from silanes is the simplest type of reaction

where two processes occur: firstly hydrolysis to a silanol of appropriate functionality and then condensation to a polymer with elimination of a molecule water at each reaction site. In practice, however, the reactions are frequently conducted simultaneously, almost always in the presence of a suitable catalyst. The silanes are available with functionalities of 1 to 4 and depending on this condition various products are formed.

In the simplest case the monofunctional silane trimethyl chlorosilane is considered. On hydrolysis a silanol is formed which on condensation yields hexamethyl disiloxane according to eqns. 3 and 4.

$$
\begin{array}{c}
\quad\ \ CH_3 \qquad\qquad\qquad\ \ CH_3 \\
\quad\ \ | \qquad\qquad\qquad\qquad\ | \\
CH_3 - Si\ \ - Cl + H_2O \rightarrow CH_3 - Si\ \ - OH + HCl \qquad\qquad (3)\\
\quad\ \ | \qquad\qquad\qquad\qquad\ | \\
\quad\ \ CH_3 \qquad\qquad\qquad\ \ CH_3
\end{array}
$$

$$
\begin{array}{c}
\qquad\quad CH_3 \qquad\qquad\qquad CH_3 \qquad CH_3 \\
\qquad\quad | \qquad\qquad\qquad\qquad | \qquad\quad | \\
2\left[CH_3 - Si\ \ - OH \right] \rightarrow CH_3 - Si\ \ - O - Si\ \ - CH_3 + H_2O \qquad (4)\\
\qquad\quad | \qquad\qquad\qquad\qquad | \qquad\quad | \\
\qquad\quad CH_3 \qquad\qquad\qquad CH_3 \qquad CH_3
\end{array}
$$
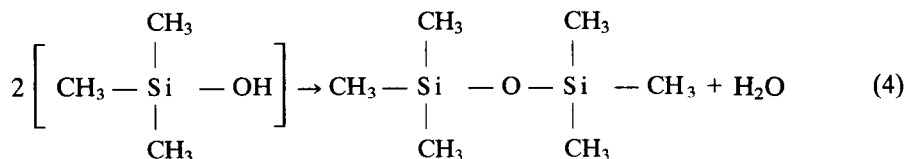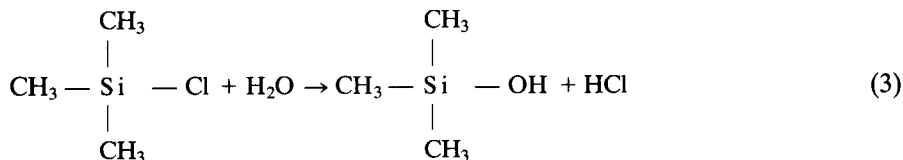
Effectively the dimer is formed and the monofunctional silane finds extensive use as a chain termination. To form a linear polymer condensation of the disilanol produced by hydrolysis of dimethyl dichlorosilane is necessary as shown in eqn. 5.

$$
\begin{array}{c}
\qquad\quad CH_3 \qquad\qquad\qquad CH_3 \\
\qquad\quad | \qquad\qquad\qquad\qquad | \\
n\left[HO - Si\ \ - OH \right] \rightarrow HO\left[- Si\ \ - O \right]_n H + nH_2O \qquad (5)\\
\qquad\quad | \qquad\qquad\qquad\qquad | \\
\qquad\quad CH_3 \qquad\qquad\qquad CH_3
\end{array}
$$
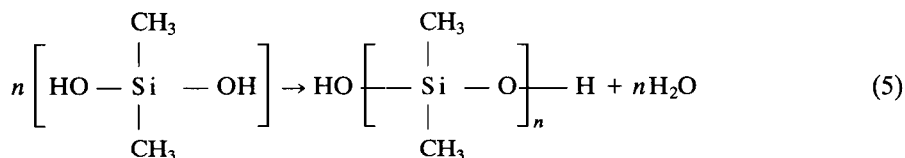
To introduce a measure of cross-linking inclusion of some trichloro- or tetrachlorosilane, usually the trichlorosilane is required. The product formed in eqn. 6 results from reaction of the dichloro- and trichlorosilane.

$$
\begin{array}{c}
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3 \qquad CH_3 \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \qquad\qquad | \\
\qquad\qquad\qquad\qquad\qquad\qquad\ - Si\ - O - Si\ - \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad | \qquad\qquad | \\
\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\ CH_3 \\
\\
\quad OH \qquad\qquad\qquad CH_3 \qquad\qquad\quad O \qquad\quad CH_3 \\
\quad | \qquad\qquad\qquad\qquad | \qquad\qquad\qquad\ | \qquad\qquad | \\
CH_3 - Si\ - OH + HO - Si\ \ - OH \rightarrow HO - Si - O\left[- Si\ \ - O \right]_x H \quad (6)\\
\quad | \qquad\qquad\qquad\qquad | \qquad\qquad\qquad\ | \\
\quad OH \qquad\qquad\qquad CH_3 \qquad\qquad\quad O
\end{array}
$$
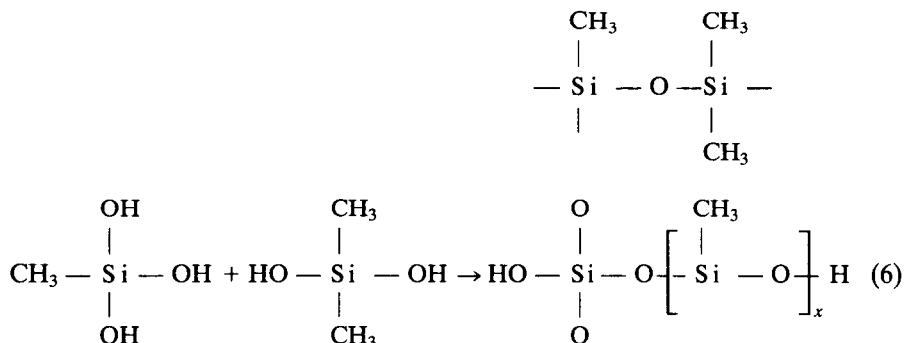
With the tetrachlorosilane a solid thermoset mass is formed:

$$
\begin{array}{cccc}
 & | & & | \\
-\mathrm{Si}- & \mathrm{O}- & \mathrm{Si}- & \mathrm{O}- \\
 & | & & | \\
 & \mathrm{O} & & \mathrm{O} \\
 & | & & | \\
-\mathrm{Si}- & \mathrm{O}- & \mathrm{Si}- & \mathrm{O}- \\
 & | & & | \\
 & \mathrm{O} & & \mathrm{O} \\
 & | & & | \\
-\mathrm{Si}- & \mathrm{O}- & \mathrm{Si}- & \mathrm{O}- \\
 & | & & |
\end{array}
$$
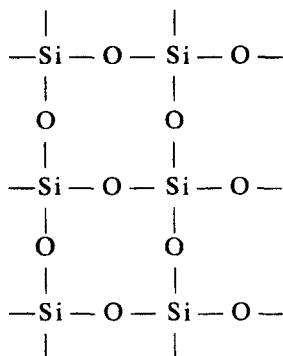
The second type of cross-linked products considers attachment of a linear polysiloxane chain by a free radical usually generated by decomposition of an organic peroxide or alternatively by the use of ionizing radiation. Termination occurs by collision of free radical sites with resulting cross-linking depending on chlorine with a free radical resulting from a methyl group or a more amenable vinyl group. The linking may be of the type Si–C–C–Si– or –Si–C–C–C–Si– as shown in eqn. 7a and b.

$$
2\left[-\underset{\overset{|}{\mathrm{CH_3}}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{Si}}}-\mathrm{O}-\right] \xrightarrow{2\,\mathbf{R}^{\bullet}} -\underset{\overset{|}{\mathrm{CH_2}}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{Si}}}-\mathrm{O}- + 2\,\mathrm{RH}
\tag{7a}
$$

$$
\begin{array}{c}
\mathrm{CH_2} \\
| \\
\mathrm{CH_2} \\
| \\
-\mathrm{Si}-\mathrm{O}- \\
| \\
\mathrm{CH_3}
\end{array}
$$

$$
\begin{array}{c}
\overset{\mathrm{CH_3}}{\underset{\mathrm{CH=CH_2}}{-\mathrm{Si}-\mathrm{O}-}} \\[2em]
\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}
\end{array}
\xrightarrow{\mathbf{R}^{\bullet}}
\begin{array}{c}
\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_2}}{-\mathrm{Si}-\mathrm{O}-}} \\
| \\
\mathrm{CH_2} \\
| \\
\mathrm{CH_2} + \mathbf{R}^{\bullet} \\
| \\
\overset{}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}
\end{array}
\tag{7b}
$$
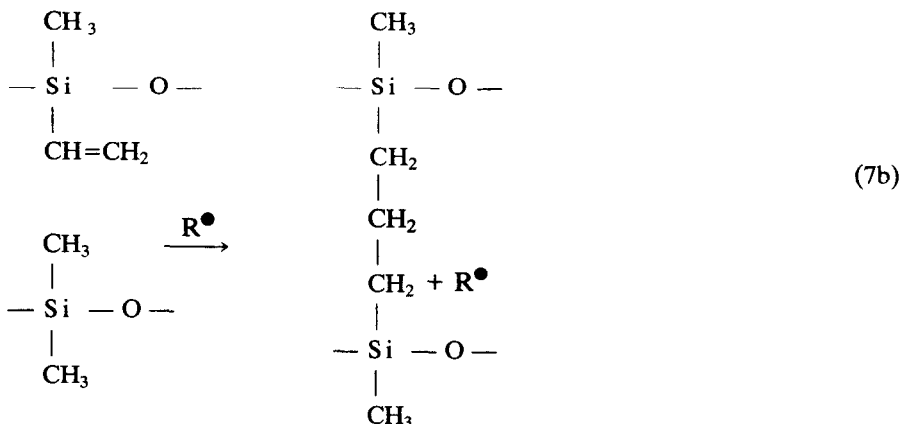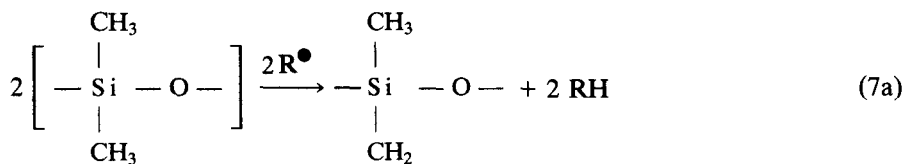
Probably the earliest attempt to produce a polysiloxane-bonded phase was that of Bossart[185,186] in 1968. Another early attempt to achieve bonding to the support surface to produce a cross-linked film was conducted by Grob[187] who in 1966–1967 achieved a polybutadiene layer. Bonding of terminal hydroxyl and of organo–lithium groups on the Si-Cl groups was carried out by treatment of the glass surface with thionyl chloride. Immobilized coatings were achieved by *in situ* polymerization of polyolefins using borontrifluoride catalysis. The coatings were not sufficiently thermostable because the use was restricted to untreated glass surfaces. The leaching of glass surfaces is now known to be an integral part of successful bonded columns[188].

The first real attempt to produce a capillary column coated with an immobilized polysiloxane was reported by Madani and co-workers[189,190] who used a polymer produced by prior hydrolysis of dimethyl dichlorosilane. The partially polymerized product was then made to react *in situ* under basic conditions[191] to provide a high-stability coating. It was suggested that the stability might be due to chemical bonding to the glass although this is unlikely. The polymer is linear and cross-linking is thus unlikely to be a reason for any increased stability. The method of polymerization[31] could be expected to yield a mixture of cyclic products of the type

$$-\text{O}-\left[\begin{array}{c}\text{CH}_3 \\ | \\ \text{Si}-\text{O}- \\ | \\ \text{CH}_3\end{array}\right]_n$$
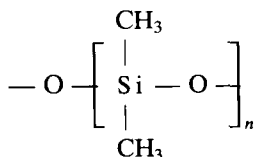
where n might be expected to vary between 5 and 10, and linear polymers terminated by hydroxyl groups. The final step of heating to 320°C might be expected to cause some rearrangement of the cyclic oligomers. Infrared (IR) spectroscopy showed a typical spectrum of dimethyl polysiloxane with hydroxyl absorption at approximately 3600 cm^{-1}, typical of α,ω-hydroxy polydimethyl siloxane. Comparison of an *in situ* polymerized column with OV-1 with steroid metabolites in the range 190–280°C showed essentially identical behaviour.

Cross-linked polymethyl siloxane glass capillary columns[192-195] were prepared and compared with linear polysiloxane-coated columns by Blomberg and Wännman[196] following the report of Grob[197] that increased film stability is achieved by using polysiloxanes that employ a degree of cross-linking. The procedure employed was basically that of Madani and co-workers[189,190] where a prepolymer was prepared by hydrolysis of a mixture of silanes of suitable functionality, which was then coated onto a glass capillary with final cross-linking being achieved *in situ*. While the columns of Madani and co-workers[192–194] were prepared using ammonia as a catalyst, the cross-linked system was considered to be more successfully achieved using a less reactive system[198].

The chlorosilanes were treated with *n*-butanol and after reaction water was added. This procedure was suggested to prevent cyclization and precipitation of polymer in the prepolymer formation[198]. The purity of the reactants is important as monochlorosilanes in the reactants will act as chain terminators. Linear polymers have a CH$_3$/Si ratio of 2 and are prepared from dichlorodimethyl silane. The highly cross-linked polymer has a CH$_3$/Si ratio > 1.2 and is a hard brittle material such that the cross-linked product of value has a CH$_3$/Si ratio much closer to 2. The polarity of the

phase as indicated by retention indices, is as expected increased as the methyl content, *i.e.*, the CH$_3$/Si ratio is increased. Reaction with ammonia has also been reported by Diez-Masa *et al.*[199] for the preparation of low-polarity capillary columns.

The uniformity of the film is important and the best results were achieved when the borosilicate glass was treated with tetrachlorosilane. The final *in situ* cross-linking was achieved by heating and conditioning for 48 h at 300°C. This was required to get the desired cross-linking and reduction of bleeding to an acceptable level.

An estimate of the thickness of the polysiloxane layer was obtained using the equation of Fairbrother and Stubbs[200] shown in eqn. 8:

$$dT = CR \left(\mu + \eta/\gamma \right)^{1/2} \tag{8}$$

where dT = film thickness (μm), C = concentration (%), R = column radius (mm), μ = coating velocity (mm/sec), η = viscosity of coating solution (10^{-3} kg/msec), and γ = surface tension of coating solution (10^{-2} N/m).

With the polymer where the CH$_3$/Si ratio is 1.6 the average film thickness of columns from solutions of 20 and 30% concentration were 0.34 and 0.63 μm, respectively.

The capillary columns produced were principally designed for routine analysis of polyaromatic hydrocarbons and separations in excess of 300°C were made with the normal limitations of selectivity of a low-polarity stationary phase.

The cross-linked polymethyl siloxane column[201] was successfully used for the routine separation of polyaromatic hydrocarbons, the film stability of the column being increased by using gums with a high degree of cross-linking. Measurements of heights equivalent to theoretical plates (HETP) for n-C$_{24}$ alkanes were determined. The best columns were produced using Pyrex glass that had been leached with hydrochloric acid and etched with tetrachlorosilane, the final *in situ* polymerization being performed in the presence of ammonia. Columns coated with commercial α,ω-hydroxypolymethyl siloxane of MW 1.2 · 10^6 (Polastoil 1600 POCH Gliwice, Poland) and 15,000 (Polastoil 200) were also examined, the lower-molecular-weight product behaving similarly to the laboratory-prepared material such that similar molecular weights were assumed.

The same procedure employing a measure of phase cross-linking as occurs in a rubber was extended to the preparation of thermostable cyanosiloxane-coated capillary columns[202]. Two types of α,ω-hydroxypolycyanosiloxanes were prepared[203]. The first prepolymer with 25‰ cyanoethyl substitution was prepared from an equimolar ratio of β-cyanoethylmethyl dichlorosilane and dimethyl dichlorosilane. Bis-γ-cyanopropyl dichlorosilane was used for the fully substituted polymer. The silanes in ethereal solution were polymerized by the addition of ice. The prepolymers formed were applied in ethyl acetate to the columns by the dynamic method. The columns were allowed to stand for 12 h in the presence of ammonia and tetrachlorosilane. The columns on extraction were essentially unaffected, the polymer apparently being of low solubility due to its high molecular weight or to bonding of the tetrafunctional silane and the glass surface as otherwise the polymer is linear and not cross-linked.

Both β-cyanoethyl and γ-cyanopropyl groups produce a strong silicon–carbon bond, whereas α-cyanoethyl substitution produces a weak temperature-sensitive bond. The utility of the columns was demonstrated as before[194] by the examination of poly-

nuclear aromatic compounds and also by the analysis of aldonitrile derivatives prepared from sugars.

The polymethyl siloxane coating procedure on a further study[204] was shown to be extremely susceptible to the column leaching procedure. An essentially smooth capillary surface was necessary thus requiring a mild leaching. Also excessive drying of the column is detrimental to the subsequent treatment with tetrachlorosilane. The average chain length of the prepolymer was determined by gel permeation chromatography to be 44 units. An infrared spectrum of the α,ω-hydroxypolymethyl siloxane showed the absence of any hydroxyl absorption which even at this chain length is considered unusual.

When a column is used further polymerization should not occur. Such effects may happen with cross-linked polysiloxane phases. However, it was found that stable polymers are produced when cross-linking is achieved using either a small amount of methyl trichlorosilane[193,196] or a small amount of silicon tetrachloride[201,202], the small amount of cross-linking that can occur being due to reaction of the α,ω-hydroxy groups of the chain and less likely, bonding to hydroxyl groups on the surface on the glass. The elution at 300°C of an n-alkane, n-dotriacontane, and an aromatic hydrocarbon $i.e.$, anthathrene, were examined on columns with silicone rubber and gum. Both columns are more suitable for polynuclear aromatics than n-alkanes despite the extensive use of these columns with the latter compounds. This result is in accordance with the conclusions of Hawkes and co-workers[47,49] who found that diffusion of the n-alkanes was restricted.

A study of the column film thickness shows that relatively thick films are selected to obtain sufficient activation but such films cause an increase in retention. The silicone rubbers as produced here show less retention than the silicone gums. Hydrocarbon retention on a silicone rubber column of approximately 0.7 μm is equivalent to that of a gum column of approximately 0.3 μm and thus a thickness of 0.7 μm was considered acceptable.

Column bleed is accentuated by film thickness. However, the cross-linking reduces the bleed and the 0.7-μm column showed acceptable bleed to 380°C. Comparatively, a thickness of 0.12 μm of SE-30 produced a column with a maximum allowable temperature of 350°C. Of the rubber columns least bleed was apparent where the cross-linking had been achieved and where methyl trichlorosilane had been used[196].

Grob et al.[205] reported the use of silicone rubber-immobilized phases by free radical reaction. Conversion of a polydimethyl siloxane methyl group to a free radical by a thermally produced benzoyl free radical with reaction with an adjacent methyl group was achieved to form a covalent linkage. The phase used, $i.e.$, OV-1 was diluted to form an 0.2% w/w solution, and a 2% (w/w) solution of benzoylperoxide in benzene was added such that the catalyst concentration was 0.1–1.0% (w/w) on the polysiloxane. The capillary column was coated by static or dynamic methods with a gas flow-rate of 2–4 ml/min applied for 15–20 min. The flow-rate was then reduced to 0.1–0.2 ml/min to reduce premature evaporation of peroxide and heated to 100°C after which it was programmed to 130°C at 0.2°C/min. With the thick films (0.8 μm) it was observed that prolonged rinsing with methylene chloride produced a slight apparent increase in film thickness.

An extension of the work of Grob and Grob[206] studied the effect of thermal rearrangement where it is known that the separation efficiency of newly prepared col-

umns may decrease during the first conditioning, even when the support is sufficiently wet by the stationary phase. The decrease is accentuated during the first few hours and then tends to stabilize. The decrease appears to be least on smooth support surfaces and increases with increasing roughness. It is also least with stationary phase gums and increases as the viscosity of the phase is reduced[197].

Stationary phase gums were considered to produce films of intermediate thickness between fluids and immobilized phases. The use of lower-viscosity phases was shown to offer an advantage in that thicker films may be produced because of the lower solution viscosities. The time between static deposition and cross-linking is very important, a compromise existing between cross-linking or irregular distibution due to film collapse. Various peroxides exhibit different decay temperatures and while a low-decay temperature peroxide may be used blocking of the capillary during coating is more likely to occur.

These authors[206] were successful in preparing thick films from fluid phases by modification of several aspects of the earlier procedure[205]; firstly premature film collapse was avoided by the addition of some gum to the fluid. Alternatively a higher-molecular-weight fluid might have been used while a 3% coating solution of a gum, *i.e.*, OV-1, is difficult to manipulate a mixture of 2% OV-101 and 1% OV-1 is satisfactory.

The most readily induced free radical cross-linking reaction occurs between methyl groups of adjacent siloxane chains. It is also possible that cross-linking occurs between methyl groups of siloxanes and those of the persilylated support surface.

Substituent phenyl groups hinder cross-linking of methyl groups on adjacent chains. While cyanoalkyl groups behave similar vinyl substituents are more reactive.

A 5% phenyl substitution as occurs in SE-52 and OV-73 hinders cross-linking to the extent that the catalyst content must be increased from 0.4% to 1.0% (w/w) to produce an immobilized non-extractable column. The presence of 2% vinyl groups in addition to 5% phenyl groups requires a comparable level of catalyst to that required with polydimethyl siloxane.

With increasing phenyl substitution, cross-linking becomes difficult or impracticable. As indicated in earlier work[205] the limit was represented by OV-61 (33% phenyl substitution) where an 0.2-μm film of OV-61 contained 4% peroxide (*i.e.*, twenty times that of OV-1). While this was an unreasonably high level of catalyst it was also fairly ineffective as on solvent washing 60% of the film thickness was lost.

The work of Grob *et al.*[205] evaluated four catalysts with different decay temper-

TABLE 21

DECAY TEMPERATURES OF ORANIC PEROXIDES

Peroxide*	Active oxygen (%)	Decay temperature (°C)
Bis(2,4-dichlorobenzoyl)	4.2	72
Benzoyl	6.4	91
Dicumyl	5.7	136
Di-*tert.*-butyl	19.7	146

* ELFA-Oxychemie, Zurich, Switzerland.

atures from the wide range of industrially available products. Table 21 shows the temperatures at which half of the peroxide was decomposed for 1 h.

The decomposition of peroxides yields varying residual products which are known in some industrial applications to be undesirable.. The dialkyl peroxides produce alcohols and ketones while the diacyl peroxides yield mainly benzoic acid derivatives.

The dialkyl peroxide dicumyl peroxide decomposition is shown in eqn. (9) where firstly cumyloxy radicals are produced.

$$\tag{9}$$
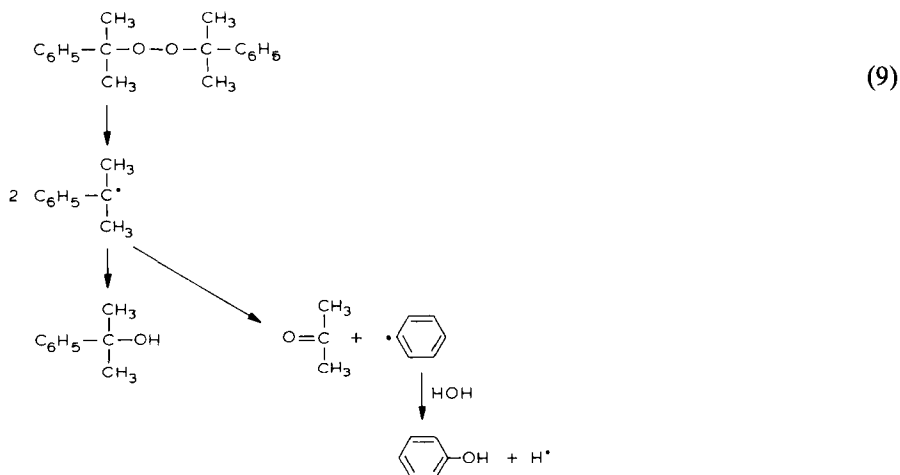
The same type of reaction scheme is applicable to the diacyl peroxides, benzoyl peroxide producting benzoyl and phenyl radicals with benzoic acid formed.

This acid formation may prove to be undesirable as it is well known that decomposition of polysiloxanes may be accentuated by the presence of free acid[207] and for some high-temperature applications this catalyst is not used.

The cross-linking procedure previously indicated[206] was simplified such that the static coated column was flushed for 5–10 min with twice the normal gas flow-rate, then the rate was reduced to the minimum that could be reliably maintained (0.02–0.1 ml/min). The oven was heated rapidly to 160°C and after 1 h heated to 180°C with the same glass flow-rate, the rate was then increased to the normal level and heating continued for 1–2 h.

The importance of vinyl groups was further investigated[208] with the result that persilylation of the glass with divinyltetramethyl disilazane rather than hexamethyl disilazane caused a marked reduction in the amount of stationary phase which could be leached out after cross-linking.

The production of the more polar column OV-1701 (7% phenyl, 7% cyanopropyl and 86% methyl substitution) was achieved[209] using basically a modification of the pretreatment. Two schemes were reported with only minor differences in performance. Persilylation of the column was achieved using either dimethyltetraphenyl disilazane (4 volumes) with subsequent heating overnight at 370°C. The coating and immobilization was carried out in the first case with a solution of 0.1–3.0% OV-1701 in diethyl ether. Dicumyl peroxide was used as catalyst at a concentration of 0.5–3.0% (w/w) of the OV-1701. After flushing the column was heated for a variable period with a low gas flow-rate at 150°C. The second procedure used a 1% OV-1701 solution in toluene with the

same catalyst as 0.5% (w/w) of the OV-1701. The column was conditioned for 2 h, the first at 150°C, the second at 170°C.

Grob and Grob[210] have recently described the use of the vinylated versions of OV-17 and OV-1701 in capillary columns and indicated that the presence of vinyl groups may not necessarily produce a non-extractable column. The conclusion was that immobilization required both cross-linking and covalent bonds to the glass support surface.

An evaluation of the columns produced by Madani[190,192,193] and by Blomberg and co-workers[195,196,201,202,204] was conducted by Sandra et al.[211] against high-temperature-stable OV-1 columns prepared by Grob et al.[212] and by Godefroot et al.[213], and was encouraging but disappointing results were achieved in the drop in efficiency to a value of approximately two-third that of the high-temperature-stable OV-1 columns.

Chemical bonding of the siloxane to the glass as may be achieved with silanes and glass pretreatment was recognised by Sandra et al.[211] to be not essential for producing a non-extractable column coating. The solubility of polymers is influenced by the degree of cross-linking and this reaction alone was considered to be likely to provide a suitable film. The work as demonstrated by Grob and co-workers[205,206,208,209] reported that SE-54 was readily cross-linked by the addition of benzoyl peroxide.

The SE-54 (4 mg/ml) in n-hexane was catalyzed by the addition of 0.02 mg/ml benzoyl peroxide in toluene, i.e., 0.5% benzoyl peroxide w/w. The columns were statically coated and cross-linked by heating. The sealed nitrogen-filled columns were heated at 85°C for 4 h. The first washing gave a 10% reduction in the k' value indicating some loss of polysiloxane, however, no further reductions were experienced on subsequent washings.

Peroxide-initiated cross-linking was also examined by Blomberg et al.[214] who prepared columns using five polysiloxane gums, i.e., SE-30, SE-33, SE-52, SE-54 and OV-215, with polymerization initiated by dicumyl peroxide. The glass capillaries were leached with hydrochloric acid as reported by Grob et al.[215] and then silanized with cyclic silanes[216,217] such as a mixture of trimer and tetramer of (3,3,3-trifluoropropyl)methyl siloxane synthesized according to Tarrant et al.[218] or purchased from Petrarch Systems, Levittown, PA, U.S.A.

The capillaries were coated statically with 0.5% (w/v) solutions of the polysiloxanes in methylene chloride or in diethyl ether–ethyl acetate (4:1) for OV-215 containing dicumyl peroxide as 1–4% (w/w) of the polysiloxane. The capillaries were flushed for 1 h with dry nitrogen at room temperature after coating.

Cross-linking was achieved dynamically or statically. In the first case the capillary was mounted in the chromatograph and a slow nitrogen flow-rate (0.1 ml/min) was applied. The temperature was rapidly increased to 140°C and maintained there for 10 min. The carrier gas flow-rate was increased to 3 ml/min and the temperature programmed to 230°C at 5°C/min, the final temperature being held for 1 h.

With static polymerization the flushed capillary was evacuated and then sealed. The column was then heated and maintained at 140°C for 5–30 min. Rinsing the columns with methylene chloride reduced the capacity ratios (k') by less than 5%. Column bleed was low in all cases to 300°C for SE-30, SE-33, SE-52 and SE-54 and to 275°C for OV-215, but was somewhat higher than columns produced by condensation and

TABLE 22

CHARACTERISTICS OF SOME AR-GLASS CAPILLARY COLUMNS COATED WITH CROSS-LIN-KED SILOXANES[33]

Stationary phase	Coating efficiency (%)	HETP for naphthalene (mm)	Kovats retention index		df (μm)	Column diameter (mm)
			Octanol	Naphthalene		
SE-30	96	0.22	1051	1153	0.34	0.28
SE-33	107	0.22	1051	1154	—	—
SE-52	99	0.24	1068	1184	0.34	0.28
SE-54	94	0.21	1067	1183	0.32	0.26
OV-215	86	0.28	1243	1436	0.32	0.26
OV-215*	87	0.25	1242	1429	0.32	0.26

* Not cross-linked.

cross-linking of silanes, the difference being attributed to the lower bond strength of the Si–C linkage[43].

The characteristics of the columns produced are shown in Table 22 and chromatograms of test mixtures on SE-54 and OV-215 columns were reported.

A subsequent work[219] reviewed the study[214] and provided some data on fused-silica columns as shown in Table 23 and showed separations of amine test mixtures, barbiturate drugs and tricylic antidepressants. The work concluded that the two types of columns, i.e., Si–O–Si or Si–C–C–Si bonded, were complementary; the former type has been shown to have a lower bleed rate and to be more suitable for the separation of polycyclic aromatic compounds due, it is suggested, to a slight residual silanol content, while the latter is suggested to be more suitable for use with aqueous samples.

Comparisons of the two types of bonded columns were presented by Lipsky and Murray[220,331] and indicated their difficulties in early attempts to insolubilise non-polar polysiloxanes on fused-silica capillary columns. Initially the problems were associated with (a) residual surface activity that remained after the in situ cross-linking, and (b) the erratic wettability of the glass surfaces by polymeric solutions containing small amounts of free radical initiators.

The α,ω-hydroxypolymethyl siloxane prepolymers were produced similarly to those of Blomberg and Wännman[196,201] and Lewis and Martin[221]. The polymers were readily soluble in n-pentane or methylene chloride and the condensation was limited such that free-flowing liquids were produced. Static or dynamic coating was readily achieved with the formation of uniform films on deactivated fused-silica columns. Curing with silicon tetrachloride was conducted in the vapour phase at ambient temperatures[196,201].

TABLE 23

CHARACTERISTICS OF SOME FUSED-SILICA COLUMNS[39]

Stationary phase	Coating efficiency (%)	HETP for naphthalene (mm)	Kovats retention index		df (μm)	Column diameter (mm)
			Octanol	Naphthalene		
SE-30	93	0.19	1054	1156	0.25	0.20
SE-54	96	0.19	1069	1184	0.25	0.20

Excellent results were achieved with the reaction with disilanol polymers produced. The outstanding advantage of the procedure was indicated to be the ability to pretest the column for efficiency, *i.e.*, uniformity of coating, film thickness and activity, before cross-linking. The vapour-phase cross-linking with silicon tetrachloride was carried out overnight and was found to be mild and effective such that the columns were inert and of high efficiency, *i.e.*, over 3000 plates/m.

Free-radical-initiated cross-linking was examined with three peroxides *i.e.*, benzoyl peroxide (BP), dicumyl peroxide (DCUP) and di-*tert.*-butyl peroxide (DTBP). The BP or DCUP in concentrations of 0.1–0.8% (w/w) of polymer (SE-30 or SE-54) solution was applied to the columns by a static method. After coating a gentle stream of nitrogen was passed through the column for 3 h. The nitrogen flow-rate was then reduced to 0.2–0.4 ml/min and the column was heated to 130°C (BP) or 150°C (DCUP) for 1 h. After cooling to ambient temperature with the gas flowing for 2 h, temperature programming was carried out for 1–2 h at 225°C. The cooled columns were washed with *n*-pentane or methylene chloride and again slowly programmed to 300–325°C, the final temperature being maintained for 8–12 h.

The second set of columns were coated using the same catalyzed polymers. After coating, however, the columns were sealed and placed in an oven at 130°C (BP) or 150°C (DCUP) for 1 h. After cooling the columns were opened and flushed with nitrogen for 2 h after which they were conditioned and tested as above.

Columns were coated as above with SE-30 solutions without added initiator after which they were conditioned and evaluated. Subsequently the columns were placed in an oven with the inlet and outlets accessible. The inlet of the column was attached to a small vial containing 3–5 ml DTBP which was pressurized with nitrogen to expel the initiator evenly through the column for 30 min at room temperature. The DTBP boils at 40°C at 55 mmHg and is highly inflammable and must be handled with extreme care. After the room temperature treatment the oven was heated to 150°C and the peroxide vapour allowed to flow for another 30 min. Finally the column ends were sealed and heating continued for a further 30 min at 150°C and then washed and conditioned as previously outlined.

As indicated by the other groups of investigators the particular peroxide used produced different results. The BP formed droplets during coating while increased activity was also noted. A high degree of cross-linking (90–95%) and thermal stability was achieved with the use of BP.

Generally the most inert, efficient cross-linked films were achieved with DCUP, particularly when used with SE-54 containing vinyl unsaturation. If SE-54 was used in the deactivation step reported by Schomburg *et al.*[222] surface activity was absent while with SE-30 minor activity was occasionally observed. Cross-linking was high (> 90%) and thermal stability outstanding in the 300–350°C region.

Gaseous initiation with DTBP provided columns which could be examined before reaction as with silanol prepolymers[196,201,223]. Very slight activity was noticed as some boiling of polar components of test mixtures. As noted previously this activity developed during the free-radical initiation.

In summary Lipsky and McMurray[220] were unable to determine any major chromatographic differences between either type of cross-linked polysiloxane coated but rather confirmed observations of other groups of workers.

It is evident that none of the groups of investigators are polymer chemists or

experienced in silicone elastomer technology which has continued to develop from patents issued decades ago. The industrial procedures are very largely dependent on technique and it is likely that even superior columns would become available if a major siloxane producer were interested in the small market concerned.

Free-radical cross-linking of synthesized methylphenyl siloxanes for use in fused-silica capillary columns was reported by Peaden et al.[224]. While it has been shown that phenyl groups inhibit cross-linking and Grob et al.[205] had indicated a 33% substitution, i.e., OV-61, to be the highest level attainable with reasonable insolubility columns have now been prepared with 70% phenyl substitution. Four phenyl-substituted polysiloxanes were prepared: (1) 50% phenyl substitution with a phenyl group and a methyl group attached to each silicon atom; (2) as (1) but with 1% vinyl substitution; (3) 50% phenyl substitution but a copolymer of dimethyl and diphenyl polysiloxane groups; (4) 70% phenyl substitution with 5% vinyl substitution.

The syntheses were achieved using mixtures of appropriate silanes. Hydrolysis of the mixtures was accomplished in an equal concentration mixture of acetonitrile, water and methylene chloride to form 25% (w/v) silane. The polymerization employed 0.05% (w/w) cesium hydroxide or tetramethyl ammonium hydroxide as catalyst and heating at 110–130°C until the viscosity ceased to increase. The catalyst was destroyed by the addition of chlorotrimethyl silane.

The polymer product contained both high- and low-molecular-weight polymers. The low-molecular-weight polymers were removed by fractional precipitation. The polymer was dissolved in methylene chloride and precipitated with methanol. The low-molecular-weight species remained in solution and were essentially removed after four precipitations. The polymers were prepared in the laboratory such that higher-viscosity products were produced than are commercially available, this being necessary to achieve efficient coating.

Capillary columns were prepared by statically coating untreated and non-deactivated fused-silica capillary tubing. Coating solutions contained 3.20 mg/ml polymer in methylene chloride, this concentration having been determined experimentally to produce a film thickness of 0.25 μm. Benzoyl peroxide or dichlorobenzoyl peroxide (3.10%) was added to the polymer solutions 30 min before use. The coated columns were purged with nitrogen, their ends sealed after which they were thermally cured BP (150°C) or bis (2,4-dichlorobenzoyl)peroxide (DCBP) (125°C) for 30 min by programming an oven from 40°C at 4°C/min. The cured columns were washed with methylene chloride and conditioned for 8 h at 260°C by programming from 40°C at 0.5°C/min.

Tetramethyl ammonium hydroxide was the preferred catalyst due to the absence of residues while any cesium hydroxide not removed from the film caused considerable column bleed[225]. The level of catalyst[42] depended on the polymer and here 50% phenyl substitution required 3% benzoyl peroxide while with the addition of 1% vinyl groups 2% BP yielded a 70% non-extractable polymer. A 70% phenyl polymer with 8% BP yielded a 40% insoluble product while with the presence of 2% vinyl substitution a 70% insoluble polymer resulted.

The k' value of dodecane on washed 50% phenyl-substituted columns was 4.9, the efficiency being 3200 plates/m. The authors indicated the extremely high intrinsic thermal stability of phenyl siloxanes[226]. With the 70% phenyl-substituted polymer a polycyclic aromatic mixture was separated by temperature programming from 80°C to 400°C at 4°C/min with the elution of compounds of molecular weight greater than 400.

Free-radical cross-linking of available polysiloxane phases has also been studied by the same workers[227]. Various peroxide and free-radical initiators were evaluated together with the effect of chain length and functional group of the polysiloxane. Capillary columns were prepared from fused silica initially rinsed with methanol, dried and dynamically coated using octamethylcyclosiloxane[228] which after purging was heated for 2 h at 240°C with the column ends closed to achieve deactivation. The stationary phases, i.e., OV-101, OV-3, OV-17, OV-22, SP-2340, SILAR 10C, SE-30, SE-52 and SE-54 were used as a 4% (v/v) solution in methylene chloride with the free-radical initiators, i.e., benzoyl peroxide, dicumyl peroxide, 2,2'-azobis-(2-methylpropionitrile) (AIBN) added in the appropriate amounts as 1% (w/v) solutions in methylene chloride.

Depending on the initiator used the coating and cross-linking procedures varied. The solid peroxides, i.e., BP, DCBP and DCUP, were added directly to the siloxane solution while the liquid initiators DTBP and azo-tert.-butane (ATB), were applied after the columns were coated. Saturation with the vapour was achieved by bubbling nitrogen through the initiators and then purging the coated column at 40°C for 2 h.

The same workers[329] have shown that DCUP causes oxidation during cross-linking of susceptible functional groups such as tolyl and cyanopropyl substituents and have indicated a preference for ATP as an initiator that has little effect on the phase polarity and the column efficiency while maintaining a high level of non-extractability. In addition to the azo compounds ATB[227,329] and AIBN[227] described above a number of non-commercial azo compounds, i.e. azocumene (AZC), 1,1-diphenylazoethane, azocyclohexane, azo-tert.-octane (ATO) and azo-tert.-dodecane (ATD) have been examined[330]. The azo analogue of DCUP, i.e. ATO, was found to be relatively unstable and not suitable for use. Both ATO and ATB generally provided acceptable columns with adequate levels of cross-linking. It was concluded that ATO had little or no effect on activity with SE-54 which is consistent with results obtained with ATB[227]. It is however unlikely that commercial eploitation of a polymer product based on a laboratory-prepared initiator would be considered.

Cross-linking was achieved using both static and dynamic procedures. Static coating was achieved with the coated columns containing peroxide after purging and sealing. The columns were temperature-programmed from 40°C to the curing temperature at 4°C/min and held at this temperature. The cross-linked columns were worked with methylene chloride and conditioned with a slow gas flow-rate for 1 h at 40°C to remove any residual solvent. Temperature programming to 260°C at 0.5°C/min was carried out with the maximum temperature maintained for 8 h.

Dynamic curing was achieved by connecting the columns to a gas manifold and heating in an oven at 5–10°C/min. Typical curing conditions used a gas flow-rate of 10 ml/sec with a final temperature of 250°C being maintained for 15–30 min. The columns were washed with methylene chloride and conditioned with a fast gas flow-rate (25–30 ml/sec) at 5°C/min to 350°C and held for 4 h.

Preliminary polymerization trials extended earlier reports and showed that SE-30, SE-52 and SE-54 produced insoluble films with 2% or less initiator. The benzoyl peroxide proportions required with these three siloxanes were 0.2%, 0.5% and 1% (w/w), respectively. Higher concentrations of AIBN were required with OV-101 and together with discolouration of the siloxane the results were considered to be unsatisfactory. OV-101 required considerably more benzoyl peroxide, i.e., 4%, than SE-30 to produce insolubilization. SE-30 has an MW about 25 times that of the fluid OV-101

and requires about the same excess of initiator. SE-30 with very long chains clearly requires relatively few cross-links as compared with OV-101 to provide insolubility.

The method of cross-linking has been previously shown by free-radical mechanisms with vinyl groups linkages between methyl and vinyl groups occurring (eqn. 7b) and lower catalyst levels are required as shown by earlier workers[205,206].

While the difficulties of cross-linking phenyl-containing polysiloxanes are well known[43,205], Peaden et al.[225] have shown that polysiloxanes containing up to 70% phenyl substituents were readily cross-linked although peroxide levels greater than required for the polysiloxanes were used.

Variations in polarity of cross-linked SE-54 due to the incorporation of initiator decomposition products were examined by retention measurements. The decomposition products of ATB, i.e., nitrogen, isobutane and isobutene, are non-polar while those of BP, i.e., benzoic acid and benzene, are polar and decreased and increased polarity as expected occurred. The greatest polarity changes were observed with DTBP, the decomposition products, i.e., acetone and methane, being, somewhat surprisingly, suggested as being incorporated into the SE-54 to a significant extent.

A further problem encountered with free-radical-induced polymerization is increased column activity from initiator decomposition products. The inertness of the cross-linked columns was examined in two ways. Both irreversible and reversible adsorption mechanisms were monitored. Reversible adsorption was quantified using peak asymmetry figures[229]. Peaks tailing on the trailing edge (adsorption) have asymmetry factors greater than 1.0 while leading-edge tailing (overloading) has peak asymmetry figures less than 1.0. Except for the alkyl amines the peaks exhibited excellent symmetry. The BP initiation caused the greatest increase in peak asymmetry while DCBP, DTBP, DCUP and ATB had minimal effects.

Irreversible adsorption is also of importance and while symmetric peak shapes are observed reduced peak areas or heights are experienced. The phenomenon was evaluated by comparing ratio of test compounds to that of an alkane standard in the test mixture. The most significant effects were again observed with the alkyl amines. The BP-initiated columns showed 80% irreversibly adsorbed octylamine while DCUP with symmetric peaks showed 70% adsorption. While variations occurred with all test compounds, ATB had few overall deleterious effects on the activity and polarity of the cross-linked SE-54 columns.

The bleed rate of capillary columns is a major factor in their utilization in GC–MS. A method for the determination of bleed rate of low-polarity bonded siloxane columns has been developed by Grob and Grob[230], together with a re-silylation procedure to minimize the problem.

Several workers have studied the degradation processes that occur with polysiloxanes at elevated temperatures[222,231] and the most prominent degradation reaction with polysiloxanes is attack by a terminal silanol group on a neighbouring silicon atom. The reaction leads to the formation of cyclic oligomers, the trimer being most abundant, with the tetramer, pentamer etc. being present in rapidly decreasing amounts. The reaction is shown in eqn. 10.

$$\begin{array}{ccc}
\underset{\substack{(CH_3)_2 \ (CH_3)_2 \ (CH_3)_2 \\ \sim Si-O-Si-O-Si \\ H-O-Si-O \\ (CH_3)_2}}{} & \longrightarrow & \sim Si-OH \ + \ \underset{\substack{(CH_3)_2-Si \quad Si-(CH_3)_2 \\ O \qquad O \\ Si \\ (CH_3)_2}}{\overset{O}{}}
\end{array} \qquad (10)$$
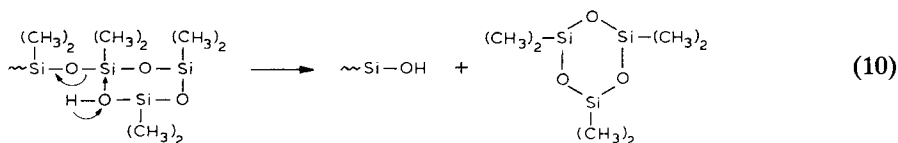
This reaction with formation of low-molecular-weight oligomers which are of appreciable volatility is as experienced with GC–MS where a typical siloxane background is observed. While this reaction is suppressed by elimination of the silanol group through silyl ether chain termination a much lesser degradation reaction occurs with the same oligomer formation as shown in eqn. 11.

$$\tag{11}$$
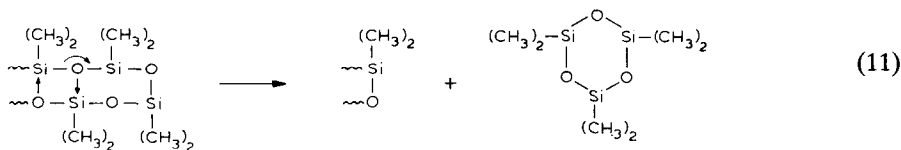
The bleeding test developed was an isothermal technique, the characteristic altered to provide conditions conducive to bleeding being the flow-rate, this being different to the procedure of Schomburg et al.[222] who compared baseline levels at different column temperatures.

Re-silylation, an established procedure for column rejuvenation, employed bis(trimethylsilyl)acetamide (BSA), hexamethyl disilazane (HMDS) and diphenyltetramethyl disilazane (DPTMDS) with equivalent results. The latter reagent was preferred due to its lower volatility flushing to remove the solvent was possible without loss or displacement of the DPTMDS. A 10% solution of DPTMDS in n-pentane was sucked into the column in sufficient quantity to fill 5–10% of the column volume. The solution was admitted at the detector end to achieve some backflushing effect of contaminants admitted during use and also to provide an accumulation at the inlet end where losses due to a washing effect may occur. The column on removal of the solution was mounted in the chromatograph with connection at the inlet end. Flushing was effected with normal gas flow for several minutes at ambient temperature after which it was reduced to 1% of the normal flow and heated to 200°C for 15 min and then at 300°C for 300 min. After this treatment the column was washed with methylene chloride and briefly conditioned prior to reuse. Re-silylation of freshly prepared columns of low-polarity phases reduced the bleed rate to 20–30% of the original bleed while with used columns the results were widely variable with reductions being in the order of 5 to 40%. The authors concluded that the testing indicated that the re-silylation influenced the liquid phase, rather than the support surface. While this might be a reasonable assumption, particularly with the used columns where established degradation reactions indicate the formation of silanol groups, any considerable change with new columns is unlikely. It is doubtful if the peroxide-catalysed siloxane gums have any significant silanol groups. It is possible of course that the silylation reagent may react with protonic impurities, i.e., catalyst residues whose volatility is increased and thus are more readily lost during the heating operations. This, however, is not a very realistic hypothesis as any such impurities would have been expected to have been removed during the initial cross-linking. If the initial column temperature did not reach these temperatures employed the hypothesis may have some credence but the same result would be achieved by simply altering the final step of the initial preparative procedure.

The preparation of highly efficient capillary columns has developed with much greater success using low- rather than high-polarity phases. A property which has remained largely unstudied is the viscosity of the stationary phase, a situation recently considered by Wright et al.[232]. Capillary columns coated with commercially available

TABLE 24

SELECTED COMMERCIALLY AVAILABLE METHYL POLYSILOXANE AND METHYLPHENYL POLYSILOXANE STATIONARY PHASES

Phase	% Phenyl	Number of siloxane units	Viscosity (cP)
OV-1	0	> 14,000	Gum
OV-101	0	400	1,500
OV-61	33	380	> 50,000
OV-17	50	29	1,300
OV-22	65	50	> 50,000

high phenyl siloxanes, *i.e.*, 10% phenyl substitution, have tended to demonstrate low efficiencies and poor thermal stabilities. While inadequate wettability has been suggested to be the major problem, surface tension measurements with column materials and stationary phases do not support the assumption. Columns prepared after deactivation and treatment to surfaces that could be readily wetted with OV-17 and OV-25 still exhibit poor efficiencies[233]. Cross-linked capillary columns were preferred by the authors[224] using laboratory-prepared siloxane gums, *i.e.*, 50–70% phenyl substitution, of much greater viscosity than available materials of comparable phenyl contents, and examination of these polymers was carried out.

Static coating of undeactivated fusing silica was carried out using OV-101, OV-61, OV-17, OV-25 and 50% and 75% phenyl-substituted polysiloxane gums to produce 0.25 μm film thickness.

The viscosity dependence of several phases is shown in Fig. 2 where it is evident that the viscosity of the dimethyl polysiloxane gum is least affected by increasing temperature and that changes in viscosity become greater with increased phenyl substitution. The phenyl content, number of siloxane units and viscosity are shown in Table 24 while relative efficiency dependence on temperature is shown in Fig. 4 where the increased performance of the higher-viscosity polymers is evident.
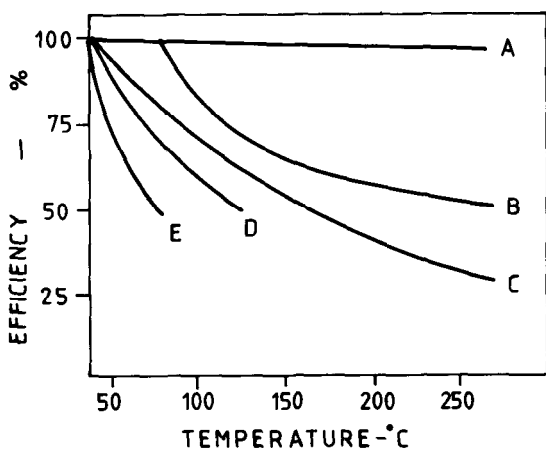
Fig. 4. Relative efficiency dependence on temperature for several stationary phases coated on untreated fused-silica capillary columns: (A) OV-101, (B) 70% phenylmethylphenyl polysiloxane gum phase, (C) 50% phenyl methylphenyl polysiloxane gum phase, (D) OV-17, and (E) Apolane-87 (C_{87} hydrocarbon phase).

TABLE 25

McREYNOLDS CONSTANTS FOR OV-1701 AND OV-17 AT 80°C[234]

Phase	x'	y'	z'	u'	s'
OV-1701	723	783	800	883	465
OV-17	759	773	788	894	926

Other studies[209] using gum phases rather than lower-viscosity analogies support the observations of the authors.

The composition of the gum-like phase OV-1701, a moderately polar cyanopropylphenyldimethyl siloxane introduced as a substitute for OV-17 has been studied by Sandra et al.[234]. Gel permeation chromatography indicates a molecular-weight distribution from 10^4 to 10^6 with a peak maximum of $2 \cdot 10^3$, this being in agreement with manufacturers' data. Analysis using NMR and IR spectrophotometry showed the phenyl, cyanopropyl and the methyl substitution to be 6.8, 6.8 and 86.4%, respectively. Analysis showed the polar groups to be attached to the same silicon atom while methylcyano or methylphenyl substitution to silicon was absent, thus indicating the silanes used in the syntheses. The McReynolds constants at 80°C are shown in Table 25. The polarity of OV-1701 is significantly lower than that of OV-17. Retention of alcohols is higher and with lower phenyl substitution lower aromatic retention is evident, i.e., benzene and pyridine. The temperature stability of OV-1701 is lower than that of OV-17 as determined by thermogravimetry which differs from some claims for capillary column use. However, droplet formation does not occur upon coating on fused silica and heating to 300–320°C. The phase has been used by the same authors[235] successfully for the analysis of pesticides.

Cross-linked capillary columns with high phenyl substitution have recently been described by Buijten et al.[236]. Siloxanes (1) containing 50% phenyl substitution, 46.7% methyl substitution and 3.3% vinyl substitution; (2) containing 50% tolyl, 50% methyl substitution; and (3) OV-1701 were used for the preparation of capillary columns.

The first polymer prepared was via a two-stage reaction. A mixture of 0.38 and 0.33 moles of diphenyl dichlorosilane and dimethyl dichlorosilane was replaced with 1 mole n-butanol until evolution of hydrogen chloride gas had ceased. Penta(methylvinyl)cyclopentasiloxane was also refluxed for 12 h with 0.5 moles of n-butanol. The two reaction products were mixed and refluxed with 2 moles of distilled water for 9 h[198]. The oil-like product was recovered for use.

The tolyl polymer was prepared by the slow addition with stirring of methyltolyl dichlorosilane into 30 ml of 12% aqueous ammonia, the temperature being maintained at 2°C[191] with subsequent recovery of the oily product. The two siloxanes were further polymerized with sodium trimethylsilanoate as catalyst[237]. Catalyst was removed by diluted hydrochloric acid washing (pH 1) and continued washing to neutrality. The hydroxyl-terminated siloxanes were endcapped with trimethylchlorosilane. Both soda-glass and fused-silica capillaries were leached with 20% hydrochloric acid for 15 h at 260°C and 140°C, respectively[215]. Deactivation used hexaphenyl cyclotrisiloxane[233].

Static coating used the stationary phases 0.5% (w/v) in methylene chloride with DCUP (3% on phase) for the phenyl siloxanes and 0.5% for the tolylsiloxane. The sealed columns were heated from ambient temperature to 170°C at 15°C/min and held at 170°C for 3 min. It was found that the column activity increased with increased curing

TABLE 26

PROPERTIES OF 20-m AR-GLASS AND FUSED-SILICA CAPILLARY COLUMNS, DEACTIVATED WITH HEXAPHENYL CYCLOTRISILOXANE AND COATED WITH METHYLPHENYL SILICONES[233]

Efficiency measured for naphthalene at 90°C.

Stationary phase	Column diameter (mm)	Film thickness (μm)	Capacity ratio, k' (naphtha-lene)	HETP (mm))	UTE* (%)	Kováts retention index	
						n-Octanol	Naphthalene
50% Phenyl	0.25	0.25	20.0	0.28	83	1175	1379
OV-1701	0.25	0.30	19.1	0.24	95	1189	1286
OV-1701	0.21**	0.26	16.0	0.22	87	1189	1282
50% Tolyl	0.25	0.31	12.4	0.28	81	1150	1359
OV-17	0.24	0.30	13.7	0.46	47	1155	1373

* = Utilization of theoretical best efficiency.
** = Fused silica, others AR-glass.

times, this being the reversed behaviour as recently reported by Moseley and Pellizzara[238]. The properties of the columns are shown in Table 26.

The preparation of cyanopropyl polysiloxane columns using both soda-glass and fused-silica capillary columns was achieved[239,240] with high efficiency and deactivation. Leaching of the column followed by high-temperature silanization with cyanopropyl cyclotetrasiloxane was employed with *in situ* cross-linking by peroxide. Three phases were prepared having 33, 50 and 95% cyano substitution with some vinyl and tolyl substitution used as before. The column with 33% cyanopropyl substitution was cross-linked using radiation from a high-voltage electron source. A radiation dose of 25 Mrad was used from a Van der Graaf generator.

In a study which largely studied a general examination of OV-1701 Sandra *et al.*[234] prepared cross-linked fused-silica capillary columns. Deactivated columns were statically coated with OV-1701 (0.1–0.5%) in dichloromethane. Cross-linking was achieved using DCUP (0.5–5% of OV-1701) in toluene with reaction statically at 150°C or dynamically as described by Grob and Grob[209].

Columns showed high efficiencies and low activity. Columns coated with OV-1701 were used isothermally at 320°C with occasional conditioning at 350°C although some bleed was evident at high temperature.

Moseley and Pellizzara[238] have also prepared non-polar immobilized stationary phases by a modification of the peroxide treatment of Grob and Grob[206] this being an extension of work on deactivation of fused-silica columns by polysiloxane deactivation methods.

The fused-silica capillaries were acid-treated, a process frequently omitted with the preparation of fused-silica capillary columns due to small amounts of metallic ions present. The authors, however, consider that at the high temperature, *i.e.*, 2000°C, necessary to draw the capillaries dehydroylation of surface silanol groups may occur to form silyl ether bridges[241]. Hydrothermal treatment of the silica, rinsing and dehydration within the convention of Unger[241] and Grob[242] was conducted using the polysiloxane deactivation method[238].

The capillary was purged with dry nitrogen filled with SE-52 in pentane (0.2%), sealed and allowed to stand overnight before static coating with SE-54[26]. The columns

TABLE 27

PROPERTIES OF NON-POLAR IMMOBILIZED CAPILLARY COLUMNS[238]

	Heat treatment at 320°C (h)	Efficiency	Activity	Film thickness (μm)
1	24	High	Moderate	0.11
2	48	Higher	Lower	0.075
3	110	Highest	Almost neutral	0.07

were purged, flame-sealed and programmed to 320°C at 1°C/min. The columns were held at 320°C for 48–110 h.

The columns prepared were evaluated for activity and separation with results shown in Table 27. The method was shown to produce acceptable thin film thicknesses, thicker films being produced using the same technique of Grob[206] but with the reported temperature at 160°C.

Ozone has found limited industrial use as a cross-linking agent. Due to its slow rate of diffusion in the silicone, only relatively thin sheets of elastomers may be cured[332]. However, thin films are the requirement in gas chromatographic columns and Buijten et al.[333] have described a technique for the preparation of low-polarity columns using SE-30, SE-33, SE-52 and SE-54. The fused-silica columns were deactivated with octa-methylcyclotetrasilane and then statically coaed with 0.4% w/v stationary phase in methylene chloride. After flushing with dry nitrogen, the columns were conditioned by heating at a rate of 2°C/min to 200°C and then maintained isothermally for 5 h. After preliminary testing the columns were flushed with ozone generated by an ozonizator (3% ozone in oxygen) for up to 3 h, sealed and conditioned at 150°C for 15 min.

More polar phases, i.e. OV-1201, OV-215, tolylmethyl and cyanopropyl (33%) metyl tolyl polysiloxane gums were subsequently reported[334]. The coating efficiency and deactivation were good with maximum operating temperatures being at least 300°C except for the cyano and fluoro derivatives where 275°C was the maximum.

The cross-linking of polysiloxanes by γ-irradiation has been reported by Bertsch et al.[243], as an alternative to the use of organic peroxides.

The stability of films on surfaces on which they are barely wettable decreases with temperature and thus a sufficient polymerization rate is necessary to prevent film collapse. The peroxide also leaves residues and by-products.

The process employed leached and HMDS-deactivated borosilicate columns as reported by Grob et al.[212] statically coated with a 0.4-μm film of SE-30. Polymerization was achieved using a cobalt-60 γ source at a dose rate of 0.48 Mrad h⁻¹. The columns were exposed to doses of 0.1 to 50.0 Mrad. After irradiation the columns were briefly conditioned and then washed with dichloromethane and n-hexane. It was indicated that excessive cross-linking produces brittle films with poor chromatographic properties and thus the radiation dose requires optimization.

While radiation-induced polymerization has been extensively studied it is now apparent that many applications are most successfully carried out using chemical initiation. It is well known that while free radicals are generated, cleavage of the polymer chain is also likely and it is believed that the utility of this procedure is low.

The whole rapidly developing situation with bonded capillary columns is further illustrated by the almost simultaneous publication of a second work also using γ-

radiation[244]. Deactivated and undeactivated alkali-glass and fused-silica capillaries were coated by the dynamic or preferably the static procedure and then exposed to γ-radiation from a cobalt-60 source for 2–3 h. Three Mrad of γ-irradiation were employed after which the columns were evaluated for (1) tailing behaviour, (2) separation efficiency (determination of number of theoretical plates; k' of homologous alkanes), (3) insolubility (determination of k' value of n-nonane at 80°C before and after solvent washing), (4) bleeding.

The following stationary phases were successfully bonded using ionizing radiation: OV-1, SE-30, SE-52, SE-54, OV-1701, PS 286 (methyl-3,3,3-trifluoropropylmethylvinyl polysiloxane gum, Petrach Systems); phases not successfully insolubilized were OV-101, OV-215, OV-17, OV-330 and OV-210.

With all columns successfully cross-linked chromatograms and data were shown to indicate that the results compared favourably with benzoyl peroxide or dicumyl peroxide columns that were evaluated simultaneously as controls.

Low-temperature plasma techniques have been used for the preparation of stable capillary columns including etching and formation of a methyl siloxane film[245]. Under the influence of a radio frequency discharge, low-pressure gaseous fluorocarbons, i.e., 2-chloro-1,1,2-trifluoroethylmethyl ether and difluorochloromethane, introduced into the glass capillary, generate excited fluorine radicals which etch the glass surface.

A third report of immobilization using γ-radiation has been reported by Hubball et al.[335] who studied OV-1 on fused-silica capillary columns. Using cobalt-60 sources, a 3 Mrad irradiation produced superior results to 7 and 10 Mrad, the column being deactivated using octamethyl-cyclotetrasilane according to the work of Stark et al.[228].

The plasma polymerization was achieved using dimethyl dichlorosilane (DMCS) with oxygen as co-gas. The reagent mixture being prepared by bubbling dry oxygen into heated DMCS. Scanning electron micrographs showed a substantial etching effect after plasma treatment. The plasma polymerization conditions were based on the work of Thompson and Smolinsky[246] with DMCS and oxygen. The exposure times varied between 1 and 10 h and were conducted under a high vacuum, i.e., 1.5 Torr. The bleed characteristics of the methyl siloxane-coated columns were examined by GC–MS at 200–300°C. The mass spectra revealed a small fragment ion arising from DMCS. Comparisons with other bonded columns were not reported nor were chromatograms shown or indications of the efficiency of the columns produced.

Commercially manufactured bonded columns are available from several specialty companies: "Durabond" columns, the product of J. & W. Scientific[247] being offered in 15, 30 and 60 m lengths, the columns DB-1 (replacing SE-30) and DB-5 (replacing SE-52 and SE-54) being provided with film thicknesses of 0.1, 0.25 and 1.0 μm.

Scientific Glass Engineering[248] offer a wider range of bonded siloxane columns in both small-bore (film thickness 0.25 μm) and wide-bore (film thickness 0.5 μm) varieties. The available columns are BP-1 (dimethyl polysiloxane), BP-5 (methyl-(5%)phenyl siloxane), BP-10 (OV-1701), BP-15 (OV-225) and BP-75 (OV-275).

The most polar of the commercially available bonded capillary columns is BP-75, produced by bonding OV-275 on vitreous silica. The column has recently been reported for the separation of alditol acetates[249] prepared from monosaccharides by the method of Blakeney et al.[250]. Chromatography was carried out on a 6 m × 0.2 mm I.D. column which was held at 170°C for 4 min and the temperature programmed to 230°C at 4°C/min. The resolution of thirteen alditol acetates was comparable to that
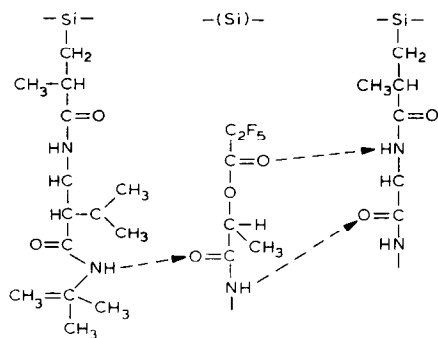
Fig. 5. Complex formation with Chirasil-Val.

obtained on a 28 m × 0.5 mm I.D. Support-coated open tubular (SCOT) column coated with SILAR 10C[251]. Other separations reported have also used OV-275 and SILAR 10C[252].

16. CHIRAL POLYSILOXANE STATIONARY PHASES

The separation of optically active compounds is of considerable importance and has been the subject of several recent reviews[253,254,338]. The separations have been greatly facilitated by the use of GC and chiral polysiloxane stationary phases which have become established during the last few years. Enantiomers may be separated in GC by three major groups of methods as indicated below. (1) Conversion of enantiomers into diastereoisomeric derivatives followed by separation on a conventional stationary phase[255–258]. (2) Direct separation of the enantiomers on an optically active stationary phase[259–261]. (3) A combination of both methods, with separation of the diastereoisomeric derivatives on an optically active stationary phase[262].

The basic procedures were introduced by Gil-Av and co-workers[255,259] although direct separations of the enantiomers have proved to be most successful. The peptide phase N-trifluoroacetyl-L-valyl-L-valinecyclohexyl ester[259] was first produced and was followed by other peptide and polyamide phases. The diamide phase, N-n-decosanoyl-L-valine-tert.-butyramide[263] proved to be more satisfactory than the other materials due to its higher resolution factors and generally lower polarity which reduced the retention times.

Frank et al.[28] poduced a chiral diamide utilizing the high thermal stability of

TABLE 28

RETENTION INDEX INCREMENTS OF CHIRASIL-VAL AT 50°C USING THE McREYNOLDS PROBES[266]

Probe	ΔI
Benzene	24
n-Butanol	264
2-Pentanone	102
2-Nitropropane	130
Pyridine	107
1,4-Dioxan	82

polysiloxanes with the active centre L-valine-*tert.*-butylamide (developed by Charles *et al.*[263] in the side chain, by the reaction of a copolymer of 2-carboxypropylmethyl siloxane and dimethyl polysiloxane with the amide. The dimethyl polysiloxane was used in the siloxane backbone to regulate the distance between the chiral centres to optimize the separations possible.

The phase has been aptly named Chirasil-Val® by its inventors[28] and since its introduction has been available as 25-m coated capillary columns from Applied Science Labs.[264].

D- and L-amino acids, or the peptides, are covalently bound to the polysiloxane backbone by reaction with the carboxyl group. The material as shown in Fig. 5 is presumably produced by condensation of the appropriate mixture of silanes with reaction after end-capping with trimethyl chlorosilane of the resulting polysiloxane with the optically active amide. The ratio of dimethyl polysiloxane units to chiral siloxane units is shown variously as 5[265], approximately 7[266,267] or 0.86 nmoles L-amino acid per gram of polymer[265]. The percentage substitution of the active groups is thus approximately 6.25% (in terms of the nomenclature frequently used with siloxane phases).

The polarity of Chirasil-Val as indicated both by the above degree of substitution and the McReynolds constants shown in Table 28 is relatively low, although the values are not directly comparable due to their determination at 50°C[266] which was necessary because of the low capacity factor of the capillary column employed.

The high value for the *n*-butanol probe indicates its capacity to form a hydrogen bond. The structure of the diastereomer complex formed with N-cyclohexyl-O-pentafluoropropionyl-L-lactimide is shown in Fig. 5. This enantiomer produces a more stable complex than the D-enantiomer which is eluted first. The figure shows the space filling isopropyl and methyl groups of the receptor and substrate respectively, and that the C-terminal alkylamide groups fit together as stacked layers and stabilize the structure by Van der Waals forces. This stacking is not possible when the substrate has the D-configuration as mutual hindrance of the two alkyl groups leads to a less stable complex which is eluted earlier. The figure also shows the importance of the dimethyl polysiloxane units which separate the L-valineamide groups and prevents the formation of intramolecular hydrogen bonds which would give the polymers a quasi-crystalline structure as occurs with nitrile polymers such as polyacrylonitrile.

D- and L-isomer separation is largely attributed to this formation of these hydrogen bonds of various strength between the solvent and solute[268], although other interactions must also be considered[262].

The high thermal stability of the stationary phase was shown by its continual use at 175°C[28] while later testing was at 200°C[266] with use for short periods at 240°C while the advertising literature indicates use up to 260°C[264]. Chirasil-Val has allowed the enantiomers of all of the protein amino acids to be estimated for the past time. The early work used an 18-m column and with a mixture of seventeen amino acids overlapping occurred only in the case of D- and L-proline, D-isoleucine and L-*allo*-isoleucine and L-threonine and D-*allo*-isoleucine[265]. The acids being examined as the N-pentafluoropropionyl-D,L-amino acid isopropyl esters. A superior separation was achieved by the same workers[266] in a study which indicated the dependency on the chemical nature of the capillary column wall such that it is necessary to employ a surface pretreatment if all the amino acids are to be resolved. Of the various methods of pretreatment evaluated, etching of borosilicate glass with gaseous hydrogen chloride followed
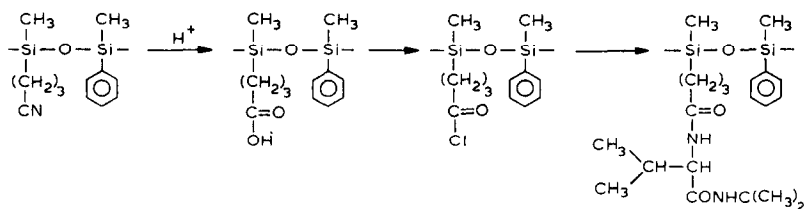
Fig. 6. Conversion of OV-225 to a chiral siloxane via hydrolysis and acid chloride reaction.

by the deposition of colloidal silicic acid was found to be most suitable.

Subsequent work[269] developed enantiomer labelling as a method for the quantitative determination of optically active species and is based on the valid assumption that optical antipodes exhibit identical chemical and physical properties in a non-chiral environment. The analysis of derivatized amino acids involved use of the unnatural enantiomer with separation on a 20-m Chirasil-Val column (film thickness approximately 0.1 μm) programmed to 200°C. Other works reported racemization studies[270,271].

Abe et al.[272] examined the resolution behaviour of N(O)-perfluoroacyl-D,L-amino acid alkyl esters on Chirasil-Val. The effects of the alcohol used for the esterification varied as steric hindrance increased with bulky alkyl groups and the influence of perfluoroacyl substitution on the retention times together with D- and L-resolution and elution order were considered.

The determination of S-methyl-I-cysteine in haemoglobin[273] has been carried out using a Chirasil-Val coated capillary column. The initial column temperature of 80°C being held for 3 min, followed by temperature programming to 180°C at 5°C/min, the enantiomers are separated as the alkyl-N-trifluoroacetyl (N-TFA), N-pentafluoropropionyl (N-PFP) and N-heptafluorobutyl (N-HFB) derivatives.

Fifteen D-amino acids in protein/peptide samples have also been separated as the N(O,S)-trifluoroacetylisopropyl esters on a Chirasil-Val coated capillary column programmed from 70 to 200°C at 4°C/min[274]. Other separations include the 2-amino-1-phenylethanols[28], amino alcohols (sympathomimetic drugs)[269], sugars[275,276] and for the configurational determination of myo-inositol in rat brain[277].

While much attention with chiral phases has been directed towards the separation of racemic mixtures, a recent work has shown the quantitative analysis of one enantiomer in small proportions in the presence of the other. The analysis of small amounts, i.e. 0.3–1.75%, of the D-enantiomer of monosodium glutamate in the L-enantiomer was determined as the trifluoroacetyl derivative on a 25-m glass capillary column packed with Chirasil-Val operated isothermally at 150°C[336].
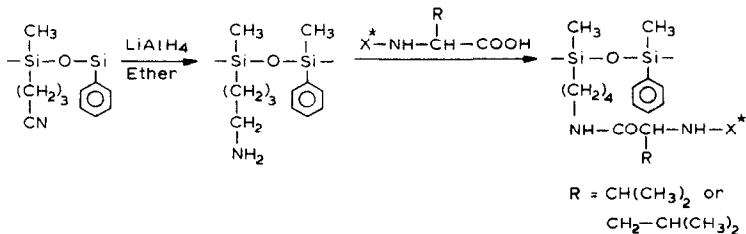
Fig. 7. Conversion of OV-225 to a chiral siloxane via reduction and coupling.

A modified version of Chirasil-Val employing 15% phenyl substitution has been reported[278] to provide improved resolution.

This material has recently become commercially available[264] as Heliflex Chirasil-Val in the form of 25 m × 0.31 mm I.D. fused-silica capillary columns with a film thickness of 0.23 μm. The column has been used by Abe *et al.*[337] for GC of amino acid enantiomers. Some 19 amino acids were examined as alkyl esters n-C_{1-4}, iso-C_{1-4}, neo and 3-methyl-C_5 grouped together as tri-, penta- and heptafluoroacetyl derivatives. Not unexpectedly, elution of the derivatives was dictated by the structure of the alkyl groups. The best results were obtained with the TFA-ethyl derivative, the separations being achieved with an initial isothermal period of 4 min at 80°C and then programmed at 3°/min to 200°C.

An alternative approach to produce a similar chiral polysiloxane[279,280] was based on incorporation of the same optically active amide into a polysiloxane backbone containing pendant phenyl groups. The stationary phase OV-225 was used to form the backbone, the mobile groups being hydrolyzed and the acid formed converted to the acid chloride to allow reaction with the optically active amide[279]. The reaction is shown in Fig. 6. This material has several differences to the Chirasil-Val, *i.e.*, a propyl rather than an ethyl group links the backbone and the chiral centre, the backbone contains phenyl groups and the chiral groups are closer. Due to the phenyl groups the polarity is higher than Chirasil-Val and some difference in elution order of N-pentafluoropropionyl-D,L-amino acid alkyl esters was observed. With the phenyl-containing phase glycine elutes after the isoleucines, proline after serine, and cysteine before aspartic acid, the elution of amino acids after methionine being the same on both phases. This material did not resolve D,L-proline and D,L-ephedrine, both secondary amines, where only two hydrogen bonding sites are available. As the chiral phase has approximately nine siloxane units between the active centres, it was believed that inadequate chiral centres were available to allow baseline separation of secondary amines.

The same synthesis was conducted[280] using SILAR 10C, polycyanopropylmethyl siloxane and with the new stationary phase, baseline separations of D,L-proline were achieved. Lower thermal stability was observed with the maximum operating temperature being 160°C, this behaviour confirming earlier reports that the chiral centres required to be separated by seven units[267].

The polysiloxane OV-225 has also been used as a backbone for chiral phases by König and Benecki[281]. The reaction scheme as shown in Fig. 7 employs reduction of the nitrile groups to amino groups with $LiAlH_4$ and then coupling to benzoloxycarbonyl-L-valine and -L-leucine. Both phases gave poor separation of amino acid enantiomers. However, the separation factors for amino alcohols and amines are high. The
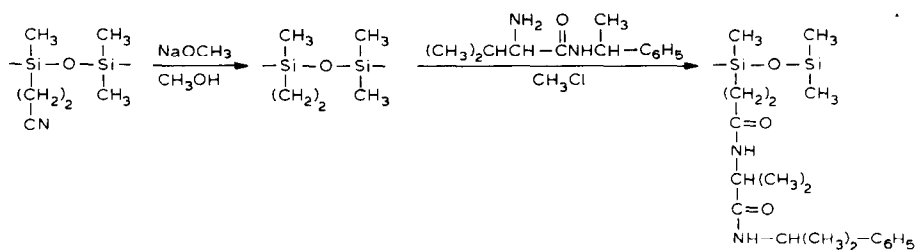
Fig. 8. Conversion of XE-60 to a chiral siloxane via reaction with sodium methoxide in methanol.

elution behaviour is not consistent with the other chiral polysiloxanes. On the L-valine phase the derivatives of D-valine, D-isoleucine and D-*allo*-isoleucine have longer retention times than the D-enantiomers, while the L-leucine phase, the derivative of L-alanine and D-valine are retarded. With the amino alcohols the D-enantiomers consistently have longer retention times than the L-enantiomers on both phases, while the S-enantiomers have longer retention times with 2-aminopentane and phenylethylamine[282].

Similar phases have been prepared[283,284] based on XE-60, the nitrile group of the stationary phase being converted to the acid by reaction with sodium methoxide in methanol and a condensation then being affected with L-valine-(S or R)-α-phenylethylamide in dicyclohexylcarbodiimide and chloroform as shown in Fig. 8. Using the L-valine-S-phase a separation of enantiomers of carbohydrates was achieved on a 40-m Pyrex capillary column. Either O-trifluoroacetylated -D- or -L-aldoses or their methylglycosides were prepared. Separation of the enantiomers of α- and β-methylglucopyranosides were also achieved. The order of elution was not consistent for different stereoisomers. The L-valine-R- phase with a reversed configuration of the α-phenylethylamine moiety also exhibited enantioselectivity for carbohydrate enantiomers. The separation factors for this phase are not as large as for the other one but the elution order of the enantiomers is the same, the elution order depending apparently only on the configuration of the valine moiety. The L-valine-S-phase was used successfully up to 140°C.

With the L-valine-S-α-phenylethylamide derivatives of some pentoses and fucose (6-deoxygalactose) were only partly separated. To investigate the influence of the configuration of two asymmetric centres in the phases the diastereoisomers of XE-60- and OV-225-L-valine-R-α-phenylethylamide were prepared[285] from the appropriate acids as indicated previously[283,284] except that R-α-phenylethylamine was used. The following conclusions were indicated: (1) Better separation is observed for the fully trifluoroacetylated pentoses than for the trifluoroacetylated methylglycosides. (2) The enantiomer elution order depended only on the configuration of the valine moiety as previously reported[285]. (3) The elution order of D- and L-enantiomers is not consistent. (4) Separation factors for derivatives of pyranose are greater than those of furanose, the indication being that the enantioselectivity of the stationary phase is dependent on the ring size. (5) The phases based on XE-60 and OV-225 are thermally stable at least up to 200°C.

Subsequent work[286] has shown that enantiomer separation is not only affected by the enantioselectivity of the stationary phase but is also influenced by the type of derivative used. Urea derivatives of chiral amines[286] and urethane derivatives of chiral α-hydroxy acids[286] and alcohols[287] have been prepared by reaction with isopropyl isocyanate and the enantiomers separated on the XE-60-L-valine-S-α-phenylethylamide stationary phase. The derivatives have much larger separation factors than the corresponding trifluoroacetyl derivatives. The increase in enantioselectivity is ascribed to the additional NH–group in the urea and urethane derivatives as a site for hydrogen bonding of dipolar interaction with phase. With β-hydroxytetradecanoic acid the S-enantiomer is eluted before the R-enantiomer.

Little success has been reported in the separation of chiral ketones. A recent separation of ketones[289] with an asymmetric centre next to the carbonyl group has been achieved using an oxime derivative. The ketone in pyridine solution is heated with hydroxylamine hydrochloride at 100°C and the separation is conducted using XE-60-L-valine-S-α-phenylethylamine.

Phases similar to those of König and co-workers[283,284] derived from the acid hydrolysis of XE-60 were prepared by reaction of the acid chloride with L-valine-*tert.*-butylamide, *i.e.*, N-propionyl-L-valine-*tert.*-butylamide methyldimethyl polysiloxane[290]. This compound was reacted with both octamethyl cyclotetrasiloxane and decamethyl cyclopentasiloxane where a base-catalyzed chain opening polymerization[291] occurred, tetramethylammonium hydroxide being used as catalyst. The reaction is shown in eqns. 12–14.

$$
\begin{array}{ccc}
CH_3 & CH_3 & \\
| & | & \\
-(Si & -O-Si & -O)_n \xrightarrow{(CH_3)_4NOH}
\end{array}
$$

$$
\begin{array}{cc}
CH_3 & CH_3 \\
| & | \\
-Si\ {}^+OH^- + (CH_3)_4N^+\ {}^-O-Si & -
\end{array}
$$

$$
\begin{array}{l}
CH_3 \quad\quad\quad CH_3 \\
| \quad\quad\quad\quad\quad | \\
R \quad\quad\quad\quad\quad CH_3
\end{array}
$$

I   (12)

$$
\begin{array}{c}
CH_3 \\
| \\
(Si\ -O)_n \xrightarrow{(CH_3)_4NOH}
\end{array}
$$

$$
,HO^-\ Si\ {}^{+}-O-(Si\ -O)_{n-2}-Si\ -O^-{}^+N(CH_3)_4
$$

with CH_3 groups as substituents

II   (13)

$$
I + II \rightarrow -Si\ -O-(Si\ -O)_{\overline{n+1}}
$$

with CH_3 and R substituents   (14)
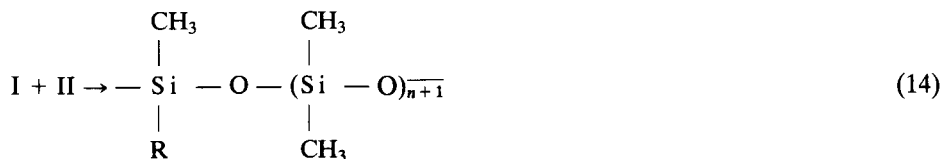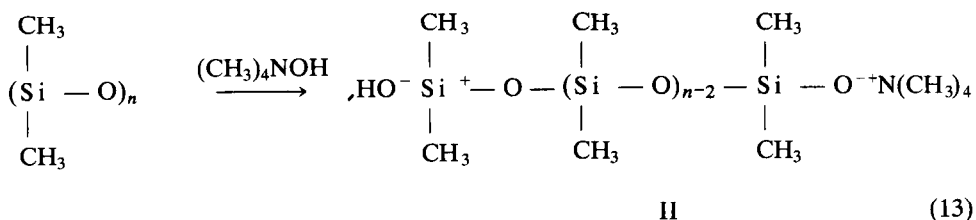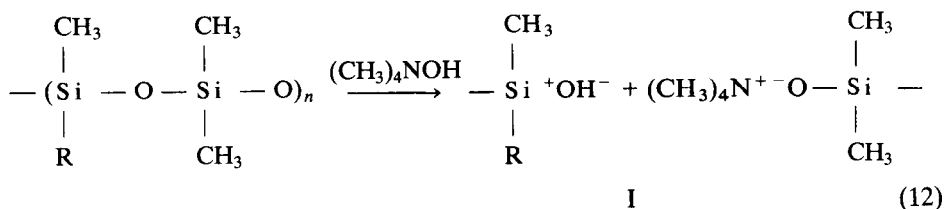
In eqn. 12 attack of the L-valyl-*tert.*-butylamide derivative occurs with formation of an active intermediate. The reaction shown in eqn. 13 is chain opening of the cyclic siloxane while eqn. 14 is reaction of the reactive species to form a polysiloxane where separation of the active centres is five or six polysiloxane units. These resulting polymers are thus extremely similar to Chirasil-Val.

The three phases prepared were evaluated as 20 m × 0.25 mm I.D. capillary columns with amino acids derivatized into N(O)-TFA isopropylesters. Considerable overlap of volatile amino acids occurred with the phase with active centres separated by one SiO unit. The second column prepared by reaction with octamethyl cyclotetrasiloxane and with the active centres separated by five siloxane units showed that almost all amino acids were well resolved. The phase with separation of active centres by six polysiloxane units showed reduced separation factors.

The Dutch suppliers of chromatographic specialties Chrompack are offering fused-silica capillary columns coated with either XE-60-L-valine-(S or R)-α-phenylethylamide[292].

It should be noted that the chiral phases bearing in their titles XE-60, OV-225 or SILAR 10C have no relationship to the original materials whose particular character was dependent on the substituent groups. In the present application these groups have been

TABLE 29

EFFICIENCY OF MESOGENIC POLYSILOXANE STATIONARY PHASE USING TRIPHENYLENE

Stationary phase	Plates/m
PMMS	2200
SE-52	3000
20% BBT/80% SE-52	1710
50% BBT/50% SE-52	858
BBT	880

removed. The phases used simply provide a convenient methyl or methylphenyl polysiloxane backbone for attachment of the active groups.

17. MESOGENIC POLYSILOXANE STATIONARY PHASES

Mesogenic liquid-crystalline stationary phases are capable of achieving separations on the basis of molecular geometry and the nematic type has been shown to be highly selective for polycyclic aromatic hydrocarbons and polycyclic sulphur compounds which co-elute on other phases[293-296].

Liquid-crystal phases have exhibited high volatility and poor column efficiency although Laub and co-workers[297-299] have employed a blend of N,n'-bis(p-butoxybenzylidene)-α,α'-bi–p-toluidine (BBT) with SE-52 with some success. A difficulty of the mixed phase is that the solid nematic transition temperature of 168°C of the liquid crystal is not reduced.

Poly(mesogenic-methyl) siloxane (PMMS) offers a solution and the first phase with a transition temperature of 97°C exhibited high column efficiency but with a low nematic range[300]. The synthesis of mesogenic polymers with considerably higher nematic/isotropic transition temperatures has recently been reported by Apfel et al.[301].

A gum-like material with a nematic temperature range 70–300°C as indicated by differential scanning calorimetry has capabilities much greater than those of other liquid-crystal stationary phases.

The utility of the phase has been demonstrated[302-304] using 19 m × 0.32 mm I.D. fused-silica capillary columns coated statically with comparison against a similar SE-52 column for a wide variety of polycyclic aromatic and sulphur compounds. Temperature programming from 120°C to 270°C at 4°C/min was used.

High column efficiency was indicated for the new phase using triphenylene as solute at 220°C as shown in Table 29. The PMMS exhibits slightly superior thermal stability to that of SE-52 liquid-crystal mixtures.

18. METALLOORGANIC SILOXANE STATIONARY PHASES

While a few isolated polysiloxanes have been described[305] where other organic groups are present in the siloxane backbone other elements have not been used with the exception of carboranes which are quite different in that a caged co-ordination structure is present.

The polymetalloorganosiloxanes have been extensively studied by Andrionov[198] with the difference that the major difference between the two groups is that a divalent or trivalent metal forms part of the polysiloxane chain. Polymers of linear or cyclic structure[306] are formed (M = metal):

$$\underset{\underset{OH}{|}}{-O-\underset{\underset{|}{|}}{\overset{\overset{C_6H_5}{|}}{Si}}O-M-O-\underset{\underset{OH}{|}}{\overset{\overset{C_6H_5}{|}}{Si}}-O-\underset{\underset{OH}{|}}{\overset{\overset{C_6H_5}{|}}{Si}}-O- \qquad (15)$$

$$-O-\underset{\underset{OH}{|}}{\overset{\overset{C_6H_5}{|}}{Si}}O-\underset{\underset{OH}{|}}{\overset{\overset{O}{|}}{M}}-\underset{\underset{|}{|}}{\overset{\overset{C_6H_5}{|}}{Si}}-O-\underset{\underset{OH}{|}}{\overset{\overset{C_6H_5}{|}}{Si}}- \qquad (16)$$
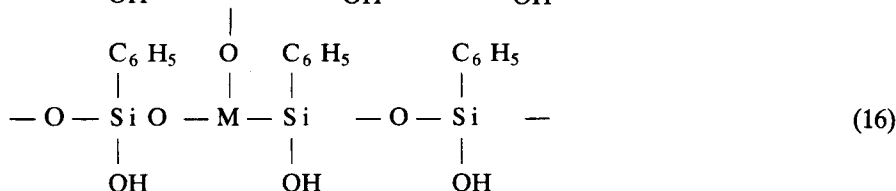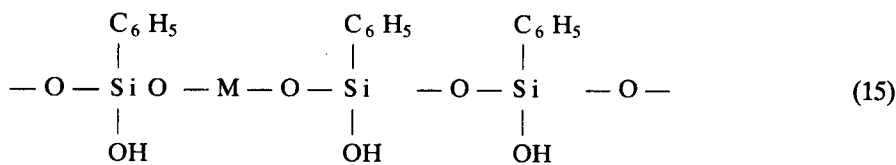
The molecular weight of the polymers depends on the conditions of synthesis and the amount and type of metal ion introduced. The introduction of a new metal into the siloxane chain influences the various properties. The thermal stability may be altered by altering the electronic nature of the bond. As the ionic nature of the bond is increased or with a covalent bond its polarizability so is its thermal stability. Substitution of part of the $-Si-O$ structure with $-M-O$ a metal more electropositive than silicon leads to increased $-Si-O-$ polarity and increased thermal stability. Weak bonding in siloxanes is similarly enhanced by the introduction of a metal which is capable of co-ordinating with again increased thermal stability[307,308]. Interaction occurs with unsaturated compounds or those heteroatoms with lone pair electrons.

The conditions of synthesis are far from clear, however, phenyltrichlorosilane is hydrolyzed to form the trisilanol, simultaneous condensation tends to occur and the conditions must be such as to minimize this reaction. The monosodium salt is formed[309] by reaction with stoichiometric reaction of the appropriate metallic compounds.

Polylanthanophenyl siloxane was prepared by an exchange reaction of the sodium salt with lanthanyl nitrate. The nitrate in ethanol was added slowly to the sodium salt in benzene. At the conclusion of the addition the mixture was refluxed for 16 h and the solvent removed under reduced pressure. The polymer was then extracted with benzene in a Soxhlet apparatus for 16 h. The polymetalloorganic siloxanes of copper, chromium, lanthanum, neodymium and magnesium were prepared using this procedure. Analyses of the polymers, their molecular weight determined by osmometry and the degradation tem-

TABLE 30

MOLECULAR WEIGHT, DEGRADATION TEMPERATURE AND ANALYSES OF POLYMETALLOPHENYL SILOXANES OR MOLAR RATIO

Phase	Molecular weight	Degradation temperature (C)	Si/M	C/Si
Polychromium phenyl siloxane	3064	220	9.48	5.98
Polycopper phenyl siloxane	4280	419	5.16	6.10
Polymagnesium phenyl siloxane	1806	220	2.58	5.49
Polylanthanium phenyl siloxane	7032	505	10.92	6.03
Polyneodymium phenyl siloxane	5661	419	9.92	6.03
Polyphenyl siloxane	3721	220	—	5.90

peratures are shown in Table 30. It should be noted that the polymers as shown in eqns. 15 and 16 are hydroxyl-terminated and it has been shown that the thermal stability is markedly reduced[52] in these circumstances. Thus, if the polymers had been end-capped with trimethylsilyl or trimethylphenyl groups higher values would have been expected. The value of polyphenyl siloxane of 220°C is unrealistically low. It is evident, however, that in the final application as a bonded phase, where some of the hydroxyl groups are bonded to silica and the bulk of the remainder capped with trimethyl chlorosilane, superior performance would be expected.

The bonding procedure involved the reaction of dried silica gel, i.e., 6 h at 180°C, with 30% thionyl chloride in anhydrous benzene for 12 h. The silica was then washed with benzene and then refluxed and reacted with the polymers in benzene for 16 h. Residual hydroxyl groups were reacted with trimethyl chlorosilane.

The reactions are shown in eqns. 17 and 18.

$$\equiv Si{-}OH \;+\; SOCl_2 \;\longrightarrow\; \equiv Si{-}Cl \;+\; HCl \;+\; SO_2 \tag{17}$$

$$(18)$$
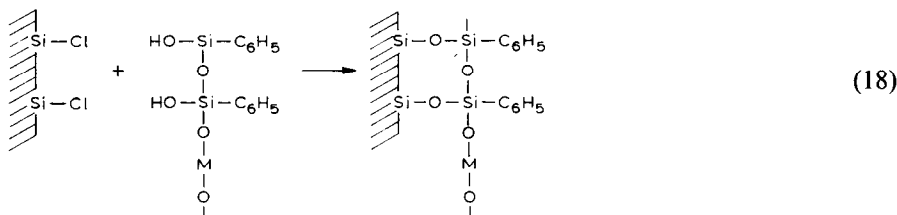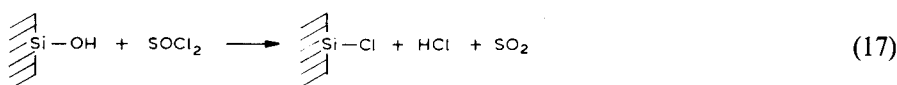
The dried packings (6 h at 150°C) were packed into 1-m columns and conditioned at 180°C for 12 h. Using benzene and hexane the efficiency of the columns was determined with 950 and 650 plates and corresponding HETP values of 1.05 and 1.46 mm.

The columns were ranked according to a decreasing affinity to olefins: Cu > Cr > Ph > Mg > La.

Copper- and chromium-containing phases showed a strong affinity to unsaturated compounds due to the effect of π-electron interactions. The other phases according to the authors do not show π-type interactions because of the absence of complex forming agents or to the presence of a metal with very poor complex forming properties, i.e., La.

It is clear from the work that this type of phase may be worthy of further study, separations shown by the authors being of various saturated, unsaturated and chlorinated hydrocarbons and of ketones.

Similar organosiloxane polymers of the type $CH_3CO_2(Si(Ph)_2M_3)COCH_3$ where the metal element M is either chromium or beryllium have been described as stationary phases[310].

19. POLYSILSESQUIOXANES

Al-Taiar et al.[311] prepared a wide variety of cross-linked polysiloxanes by aqueous hydrolysis of organotrichlorosilanes and a small amount of silicon tetrachloride to yield solid polymers suitable as GC absorbents. Octadecyl trichlorosilane proved to be most suitable while methyl trichlorosilane and phenyl trichlorosilane were unsatisfactory.

Polyphenyl siloxane ladder polymers were prepared by Guillot *et al.*[312] and showed good chromatographic properties and were stable to 420°C. At high temperatures, *i.e.*, 150–230°C, the behaviour was similar to other granulated polymers with water being rapidly eluted without tailing. The retention times decreased more rapidly with temperature increase than available commercial phases. Peak symmetry was only satisfactory if the temperature was high enough, *i.e.*, about 50°C above the boiling points of the compounds involved, this effect having been previously observed with low-molecular-weight polyphenyl siloxane oligomers[72] which exhibited broader peaks than with a 75 mole% phenyl product. Aromatic compounds were preferentially retained, styrene (b.p. 146°C) being eluted after dimethyl formamide (b.p. 156°C).

Vlismas[313–315] has described the preparation of particulate cross-linked organosilicon materials for use as packing materials for GC by reacting an organopolysiloxane containing silicon-bonded olefinically unsaturated groups with a hydrogen-substituted organopolysiloxane. The resulting cross-linked polymer may contain any of the functional groups that are currently used in stationary phases. The separation of simple hydrocarbons, aromatics, alcohols and water was shown at 100°C. With representative phases a column efficiency of about 120 theoretical plates was obtained with 2,2,4-trimethyl pentane.

Mixtures of methyl and phenyl trichlorosilanes have been hydrolyzed by Sosa and co-workers[316,317] to produce cross-linked polysiloxanes often referred to as polysilsesquioxanes. The procedure was similar to that used by Unger[241] to prepare porous silica involves hydrolysis in aqueous ammonium chloride. The polymers are useful as adsorbents in gas–solid chromatography and behave similarly to their linear counter-parts in gas–liquid chromatography. The properties were compared with OV-17 and it was shown that small polar compounds were eluted early in a manner similar to macroporous polymers such as Porapaks.

The polymers in general are comparable with gas–solid chromatographic materials and as a class the polysilsesquioxanes have found negligible acceptance.

20. SOVIET POLYSILOXANES

While Soviet chromatographic works would probably continue to show a marked preference for polysiloxanes of Western manufacturers, a considerable variety of products of Soviet manufacturers are available and reported in various papers. Earlier reviews by the author[1] have included the brief available data of Soviet products, however, in recent years more detailed information has become available and a separate review of these products is envisaged[318].

The most detailed work available would appear to be that of Itsikson and co-workers[25,26] who have provided McReynolds constants of the Soviet products for the first time. Use of McReynolds constants in Russia has lagged behind Western reports, the polarity having previously been reported as Rohrschneider polarity[319] the values being determined using benzene and cyclohexane at 70°C and interpolated between values using squalane and oxydipropionitrile as 0 and 100 respectively as proposed by Rohrschneider[319]. A work by Yudina and Ananieva[111] has shown Rohrschneider constants using the usual five solutes for fluoralkyl polysiloxanes.

It is evident that there are more chemical types of polysiloxane materials developed for use as stationary phases than in the Western world, however, the majority of reports

show that products of substantially identical composition are used in both areas. Certain of the dimethyl, phenylmethyl and cyanoalkyl siloxanes are offered with both hydroxyl and methyl terminal groups, the hydroxyl termination having been shown[52] to be of lower thermal stability than with trimethylsilyl end-groups.

21. JAPANESE POLYSILOXANES

Although an extensive range of siloxane products for industrial purposes comparable with those available in the Western world are produced in Japan by three major manufacturers, i.e., Shin-Etsu Chemical Co. Ltd., Toray Silicones Ltd., Toshiba Silicone Co. Ltd., the vast majority of Japanese chromatographers employ the products of the American suppliers of chromatographic specialties.

During recent years a few workers have used indigenous products all produced by the Shin-Etsu Co. The physical properties of the various products are shown in Table 31, together with the approximate chemical composition, and while details of their chromatographic properties, i.e., bleed, thermal limits, etc., are not reported these would be similar to other industrial products of comparable properties and composition.

One product SS-4 with 50% cyanoethyl functional groups is offered by The Chromato Packing Center[320] in capillary columns both in the simple coated form and also in the barium carbonate layer form where the column has the surface consisting of the phase on a surface covered with a crystalline layer of barium carbonate as developed by Grob et al.[321].

The Shimadzu Co.[322] also offers SS-4 columns in both cases for fatty ester analyses where the polarity is indicated to be slightly lower than diethylene glycol succinate and the applicable temperature ranges from 30°C to 190°C.

An application has been reported by Kobayashi[323] where the separation of the eight geometric isomers of the methyl esters of linolenic acid using a 60-m glass capillary column coated with SS-4 is shown for the first time.

TABLE 31

PROPERTIES OF JAPANESE SILOXANES

Silicone	Substituent	Viscosity (cSt) at 25°C	Sp.gr.	Refractive index at 25°C
KF-96L*	Methyl	0.65–2.0	0.760–0.762	1.375
			0.870–0.875	1.39–1.40
KF-96**	Methyl	10.0–3000.0	0.930–0.940	1.398–1.400
			0.965–0.975	1.403–1.404
KF-96H**	Methyl	6000.0–1,000,000	0.970–0.980	1.403–1.404
			0.970–0.980	1.403–1.404
H.V.G.	High vac grease			
KF-50	5% Phenyl	100	0.98—1.000	1.420–1.430
		1000	0.98–1.000	1.420–1.430
		3000	0.98–1.00	1.420–1.430
KF-53	20% Phenyl			
KF-54	25% Phenyl	400	1.06–1.08	1.500–1.510
KF-56	18% Phenyl	10–20	0.99–1.00	1.490–1.500
FL-500	50% Trifluoro phenyl			

  * Two other intermediate viscosity products available.
 ** Eight other intermediate viscosity products available.

A mixed stationary phase consisting of Silicone KF-54 and 3% sodium hydroxide has been used by Ono to separate effectively all six dichloraniline isomers[324] and to show a partial separation of the xylidene isomers[325].

Ono[326] has also shown the separation of the six nitroxylene isomers using the same mixture while in the same work the use of other methyl-, phenyl- and trifluoropropyl-substituted polysiloxanes was discussed.

22. DUTCH POLYSILOXANES

A limited range of specialty polysiloxanes have recently been offered by the Dutch supplier of chromatographic specialities Chrompack[292]. Little data are available about the products except the composition. These suppliers have further complexed the polarity/selection problem by the introduction of yet another arbitrary polarity scheme, it being based on a summation of the five most commonly used McReynolds constants with the value proportioned between squalane as zero and OV-275 as 100. The products are shown below, however, in the absence of definite performance data there would seem little reason to consider their use in preference to the established American products. Four siloxane phases are available, C.P. Sil 5 (dimethylpolysiloxane), C.P. Sil 8 (5% phenyl substitution, 95% methyl), C.P. Sil 19 (cyanopropyl-methylpolysiloxane) and C.P. Sil 88 (100% cyanopropylpolysiloxane).

23. ACKNOWLEDGEMENTS

A compilation of this type cannot be considered to be exhaustive and the author would be grateful for details of any errors or omissions.

A very large number of people and corporations has provided details of polysiloxane materials during the last decade and their assistance has largely made this work possible.

24. SUMMARY

Although the requirements of stationary phases have continued to become more stringent with the development of instrumental techniques the polysiloxanes have remained as the major group of stationary phases.

While the early industrial polysiloxane products have long been replaced by refined specialty products, development has continued with the preparation of polysiloxanes specifically for gas chromatography and particularly capillary gas chromatography. The efficiency of polar capillary columns has been low but recent advances with immobilized phases have been most promising.

The acknowledged thermal stability of the polysiloxane backbone has been employed in several ways. Such as with chiral pendant groups to facilitate the separation of optically active materials and with mesogenic groups to provide phases with superior properties to the low-molecular-weight liquid-crystal materials. Further modification of the polysiloxanes has been achieved by the inclusion of other metallic atoms.

The most important development in recent years is the introduction of bonded or immobilized phases. Extensive studies have allowed the production of efficient polar capillary columns which are now commercially available.

REFERENCES

1 J. K. Haken, *J. Chromatogr.*, 141 (1977) 247.
2 A. T. James and A. J. P. Martin, *Biochem. J.*, 50 (1952) 679.
3 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
4 H. Rotzsche, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworth, London, 1962, p. 111.
5 H. Rotzsche and Institute for Silicon and Fluorocarbon Chemistry, *Brit. Pat.* 1,018,800; *F.R.G. Pat.* 1, 137,897; *G.D.R. Pat.* 25,747; *Fr. Pat.* 1,343,831.
6 Anonymous, *Gas Chromatogr. Newslett. (Applied Science Labs.)*, 13, No. 4 (1972) 1.
7 Anonymous, *OV Product Catalogue*, Ohio Valley Specialty Chem. Co., Marietta, OH, 1974.
8 W. R. Supina, *U.S. Pat.* 3,263,401 (Aug. 2, 1962).
9 J. K. Haken, *J. Chromatogr. Sci.*, 13 (1975) 430; and references therein.
10 S. T. Preston, *J. Chromatogr. Sci.*, 8 (No. 5) (1970) 18A.
11 J. K. Haken, *J. Chromatogr.*, 73 (1972) 419.
12 L. Blomberg, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 520.
13 M. Wurst, *Chem. Listy*, 65 (1971) 268.
14 A. Z. Sladkov, *Zavod. Lab.*, 36 (1970) 1017.
15 H. Rotzsche, *Plaste Kautsch.*, 15 (1968) 477.
16 H. Rotzsche and M. Hoffman, in E. Leibnitz and H.G. Struppe (Editors), *Handbook of Gas Chromatography*, Verlag Chemie, Berlin, 1967, pp. 338–408.
17 A. De Bruyn, *Ind. Chim. Belg.*, 33 (1968) 155.
18 A. De Bruyn, *Inf. Chim.*, 65 (1968) 83.
19 B. M. Luskina and G. N. Turkeltaub, *Zavod. Lab.*, 35 (1969).
20 M. Reidmann, *Z. Anal. Chem.*, 260 (1972) 341.
21 G. E. Bailescu and V.A. Ilie, *Stationary Phases in Gas Chromatography*, Pergamon Press, Oxford, 1975
22 B. I. Anvaer, *Itogi Nauki Tekl. Khromatogr.*, 1 (1974) 107.
23 J. Cermak, *Apl. Nov. Druhov Mater Baze*, PH5 (1973) 101.
24 N. Kotsev, *Handbook on Chromatography*, World Publishing Agency, Moscow, 1976.
25 L. B. Itsikson, V.F. Snegirev and L.N. Yudkina, *J. Anal. Chem. U.S.S.R.*, 33 (1978) 569.
26 L. B. Itsikson, *J. Anal. Chem. U.S.S.R.*, 34 (1978) 917.
27 F. W. Karasek, *Res. Develop.*, 22, (1971) 34.
28 H. Frank, G. J. Nicholson and E. Bayer, *Angew. Chem., Int. Ed. Engl.*, 17 (1978) 363.
29 H. Finkelmann and R. J. Laub, *Report DOE/ER/10554-25*, Department of Energy, Washington, DC, (1982).
30 W. Wasiak and W. Szczepaniak, *J. Chromatogr.*, 157 (1983) 13.
31 C. R. Trash, *J. Chromatogr. Sci.*, 11 (1973) 196.
32 L. H. Brown, in R. R. Myers and J. S. Long (Editors), *Treatise on Coatings*, Vol. I, Part III, Marcel Dekker, New York, 1972, p. 513.
33 M. B. Evans, *Chromatographia*, 15 (1982) 355.
34 G. G. Freeman, *Silicones: An Introduction to their Chemistry and Applications*, The Plastics Institute, London, 1962.
35 A. J. Barry, *J. Appl. Phys.*, 17 (1946) 1020.
36 E. L. Warrick, W. A. Piccola and F. O. Stark, *J. Amer. Chem. Soc.*, 77 (1955) 5017.
37 G. Garzo and G. Alexander, *Chromatographia*, 4 (1971) 554.
38 M. G. Voronkov, V. P. Mileshkevich and Ya. Y. Yuzhelevskii, *The Siloxane Bond*, Consultants Bureau, New York, 1978.
39 K. E. Polmanteer, *Rubber Chem. Technol.*, 54 (1981) 1081.
40 F. Baumann, R. F. Claver and J. F. Hanson, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworth, London, 1962, p. 152.
41 C. Merritt, Jr., J. T. Walsh, D. A. Forss, P. Angelina and S. M. Swift, *Anal. Chem.*, 36 (1965) 1502.
42 A. G. Altenau, R. E. Kramer, D. J. McAdoo and C. Merritt, Jr., *J. Gas Chromatogr.*, 4 (1966) 96.
43 W. Noll, *Chemistry and Technology of Silicones*, Academic Press, New York, 1968.
44 *Product Literature*, Dow Corning Corp., Midland, MI, 1949–1982.
45 F. Riedo, D. Fritz, G. Tarján and E. sz. Kováts, *J. Chromatogr.*, 126 (1976) 63.
46 L. Butler and S. J. Hawkes, *J. Chromatogr. Sci.*, 10 (1972) 518.
47 J. M. Kong and S. J. Hawkes, *J. Chromatogr. Sci.*, 14 (1976) 279.
48 J. M. Kong and S. J. Hawkes, *Macromolecules*, 8 (1975) 685.

49 W. Mullen and S. J. Hawkes, *J. Chromatogr. Sci.*, 15 (1977) 148.
50 V. B. Kapoor and K. L. Mallik, *Res. Ind.*, 16 (1971) 62.
51 V. B. Kapoor, S. K. Chopra and K. L. Mallik, *Res. Ind.*, 18 (1973) 139.
52 R. M. Aseeva, A. A. Berlin and S. M. Mezhikovsky, *Chem. Zvesti*, 26 (1972) 397.
53 B. Lengyel, T. Szekely and G. Garzo, *Acta. Chim. Acad. Sci. Hung.*, 74 (1972) 253.
54 C. Earborn, *Organosilicon Compounds*, Butterworth, London, 1960.
55 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 221. •
56 A. Venema, L. G. J. v.d. Ven and H. v.d. Steege, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 69.
57 A. Venema, L. G. J. v.d. Ven and H. v.d. Steege, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 405.
58 F. Vernon and C. O. E. Ogundipe, *J. Chromatogr.*, 132 (1977) 181.
59 F. Riedo, D. Fritz, G. Tarjan and E. sz. Kováts, *Helv. Chim. Acta*, 62 (1979) 2495.
60 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 60 (1971) 33.
61 J. R. Ashes and J. K. Haken, *J. Chromatogr.*, 62 (1971) 39.
62 J. K. Haken and V. Khemangkorn, *J. Chromatogr. Sci.*, 10 (1972) 41.
63 Petrarch Systems Inc., Levittown, PA, personal communication.
64 A. E. Coleman, *J. Chromatogr. Sci.*, 11 (1973) 198.
65 J. Vauvrin Vychodeceske, Chemicke Zavody, Kolin, Czechoslovakia, personal communication, 1977.
66 *Product Literature*, Lachema, Brno, Czechoslovakia.
67 F. J. van Lenten, J. E. Conaway and L. B. Rogers, *Separ. Sci.*, 10 (1975) 517.
68 F. J. van Lenten, J. E. Conaway and L. B. Rogers, *Separ. Sci.*, 12 (1977) 1.
69 F. J. van Lenten, J. E. Conaway and L. B. Rogers, *Contract Report SRO-854-6*, U.S. Government Washington, DC, 1975, p. 42.
70 W. R. Supina, *Chromatogram (Barber Coleman)*, 7, No. 3 (1967) 3.
71 W. R. Supina, N. Pelick, L. P. Rose and G. C. Waler, *Lipids*, 3 (1968) 374.
71a E. F. Barry, P. Ferioli and J. A. Huball, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 172.
72 J. R. Ashes and J. K. Haken, unpublished data, 1977.
73 N. Ikekawa, R. Watanuki, K. Tsuda and K. Sakai, *Anal. Chem.*, 40 (1968) 1139.
74 M. K. Withers, *J. Gas Chromatogr.*, 6 (1968) 242.
75 Anonymous, *Gas Chromatogr. Newslett. (Applied Science Labs.)*, 20 (No. 2)(1979) 3.
76 A. A. Spark and M. Ziervogel, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 206.
77 Anonymous, *Chromatogr. Lipids (Supelco Inc.)*, 6, No. 1 (1972) 1.
78 D. H. McCloskey and S. J. Hawkes, *J. Chromatogr. Sci.*, 13 (1975) 1.
79 D. J. Gordon, *U.S. Pat.* 3,464,183 (Sept. 2, 1969); *Brit. Pat.* 1,166,173.
80 I. P. Yudina, Y. A. Yuzhelevskii, K. A. Sakodynskii and G. I. Nikolayev, *U.S.S.R. Pat.* 304,493 (Oct. 17, 1971).
81 E. V. Sivtsova, *J. Appl. Chem. U.S.S.R.*, 45 (1972) 193.
82 I. P. Yudina, K. I. Sakodynskii, V. P. Mileshkerich, G. A. Nikolsev, Yu. A. Semina and V. E. Prilepsheva, *U.S.S.R. Pat.* 842,572 (June 30, 1981).
83 M. V. Sobelevskii, L. A. Chistyakova, V. V. Stegalkina, D. V. Nazarova and L. V. Konovalova, *Plast. Massy*, 9 (1972) 9.
84 W. H. Daudt and J. F. Hyde, *J. Amer. Chem. Soc.*, 74 (1952) 386.
85 B. M. Luskina, M. A. Kleinovska, N. N. Troitakaya and O. A. Safranova, *Zh. Anal. Khim.*, 37 (1982) 2260.
86 B. W. Wright, P. A. Peaden and M. L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 413.
87 H. W. Fox, P. W. Taylor and W. A. Zisman, *Ind. Eng. Chem.*, 39 (1947) 1401.
88 P. A. Peaden, B. W. Wright and M. L. Lee, *Chromatographia*, 15 (1982) 584.
89 R. Komers and M. Černý, *J. Chromatogr.*, 207 (1981) 345.
90 J. R. Mann and S. T. Preston, *J. Chromatogr. Sci.*, 11 (1973) 216.
91 D. F. Lynch, F. A. Palocsay and J. J. Leary, *J. Chromatogr. Sci.*, 13 (1975) 533.
92 *Chromatography Catalogue*, Alltech Associates, Arlington Heights, IL, 1977.
93 P. H. Weiner and J. F. Parcher, *J. Chromatogr. Sci.*, 10 (1974) 612.
94 C. Giles and S. N. Nahkiva, *J. Appl. Chem.*, 11 (1961) 197.
95 E. C. Horning, W. J. A. VandenHeuvel and B. G. Greech, *Methods Biochem. Anal.*, 11 (1963) 69.

96 T. R. Lynn, C. L. Hoffman and M. M. Austin (Editors), *Guide to Stationary Phases*, Analabs, North Haven, CT, various editions.
97 *Catalogue No. 14*, Applied Science Labs., State College, PA, 1971.
98 *Silicone Materials as Substrates for Gas–Liquid Chromatography, Bulletin U-1-100*, Dow Corning Corp., Midland, MI, 1961.
99 E. Wurstova and M. Wurst, *Czech. Pat.* 124,727 (Oct. 15, 1967).
100 E. Wurstova and M. Wurst, *Czech. Pat.* 124,014 (Aug. 15, 1967).
101 O. R. Pierce and Y. P. Kim, *J. Elastoplast.*, 3 (1971) 82.
102 E. L. Warrick, O. R. Pierce, K. E. Polmanteer and J. C. Saam, *Rubber Chem. Tech.*, 52 (1971) 437.
103 S. N. Novikov, Ye. G. Kaganand and A. N. Pravednikov, *Polymer Sci. U.S.S.R.*, 8 (1966) 1114.
104 W. J. A. VandenHeuvel, E. O. A. Haachte and E. C. Horning, *J. Amer. Chem. Soc.*, 83 (1961) 1513.
105 Supelco Inc., personal communication, 1971.
106 Anonymous, *Chromatogr. Lipids (Supelco Inc.)* 5, No. 6 (1971), 1.
107 L. F. Hanneman and H. M. Klimisch, *J. Chromatogr.*, 70 (1972) 81.
108 J. A. Bourke and W. J. Holswade, *J. Ass. Offic. Anal. Chem.*, 49 (1966) 374.
109 R. S. Henly, R. F. Kruppa and W. R. Supina, *J. Agr. Food Chem.*, 14 (1966) 667.
110 M. F. Prokopeva, K. Sh. Maryanovskaya and V. K. Bukina, *Deposited Publication Vinita*, (1972) 5849.
111 I. P. Yudina and L. I. Ananieva, *Sb. Nauchn. Tr. Gazov. Khromatogr.*, No. 24 (1974) 49.
112 D. E. Schaal and S. L. McKinley, *J. Anal. Tox.*, 3 (1979) 66.
113 Anonymous, *Gas Chromatogr. Newslett. (Applied Science Labs.)*, 13 (No. 4) 1972, 1.
114 R. F. Kruppa and A. E. Coleman, *U.S. Pat.* 3,960,521 (June 1, 1976).
115 E. Bayer, *Gas Chromatographie*, Springer, Berlin, 1959, p. 103.
116 C. R. Litchfield, R. Reiser, A. F. Isbell and G. L. Feldman, *J. Amer. Oil Chem. Soc.*, 41 (1964) 52.
117 C. R. Litchfield and C. R. Dutton, *J. Amer. Oil Chem. Soc.*, 47 (1970) 1.
118 W. R. Supina, in H. A. Szymanski (Editor), *Lectures on Chromatography*, Plenum Press, New York, 1963.
119 Anonymous, Ohio Valley Specialty Chem. Co., Marietta, OH 1975.
120 E. Bayer, K. P. Hope and H. Mack, in A. Zlatkis (Editor), *Proc. Int. Symp. Advan. Gas Chromatogr., Houston, 1963*, Preston Technical Abstracts, Niles, IL, 1963.
121 R. H. Bauer, *Anal. Chem.*, 35 (1963) 107.
122 S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, 60 (1938) 836.
123 R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, 80 (1958) 2278.
124 H. J. Dutton, C. R. Scholfield and E. P. Jones, *Chem. Ind. (London)*, (1961) 1874.
125 B. De Vries, *Chem. Ind. (London)*, (1962) 1049.
126 B. De Vries, *J. Amer. Oil Chem. Soc.*, 40 (1963) 184.
127 H. Schweer, *J. Chromatogr.*, 243 (1982) 149.
128 W. C. Hamman and C. F. Hobbs, *J. Org. Chem.*, 33 (1968) 1277.
129 J. J. Myher, L. Maria and A. Kuksis, *Anal. Biochem.*, 62 (1974) 188.
130 R. G. Ackman and S. N. Hooper, *J. Chromatogr. Sci.*, 12 (1974) 131.
131 P. R. Scholly and L. S. Ettre, *Chromatogr. Newslett. (Perkin-Elmer Corp.)*, 2, No. 1 (1973) 12.
132 Anonymous, *Gas Chromatogr. Newslett. (Applied Science Labs.)*, 14, No. 5 (1973) 1.
133 Anonymous, *Gas Chromatogr. Newslett. (Applied Science Labs.)*, 15, No. 2 (1974) 1.
134 Anonymous, *Gas Chromatogr. Newslett. (Applied Science Labs.)*, 15, No. 6 (1974) 2.
135 Anonymous, *Chromatogr. Lipids (Supelco Inc.)*, 8, No. 2 (1974) 3.
136 Anonymous, *Chromatogr. Lipids (Supelco Inc.)*, 8, No. 5 (1974) 1.
137 Anonymous, *Chromatogr. Lipids (Supelco Inc.)*, 8, No. 6 (1974) 1.
138 Anonymous, *Gas Chromatogr. Newslett. (Applied Science Labs.)*, 16, No. 1 (1975) 8.
139 O. W. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
140 R. Y. Golovnya, V. P. Uralets and T. E. Kumenko, *Zh. Anal. Khim.*, 32 (1977) 340.
141 D. M. Ottenstein, D. A. Bartley and W. R. Supina, *J. Chromatogr.*, 119 (1976) 401.
142 H. Heckers, K. Dittmar, F. W. Melcher and H. O. Kalinowski, *J. Chromatogr.*, 135 (1977) 93.
143 E. S. Van Vleet and J. G. Quinn, *J. Chromatogr.*, 151 (1978) 396.
144 G. R. Jamieson, A. L. McMinn and E. H. Reid, *J. Chromatogr.*, 178 (1979) 555.
145 H. B. S. Canacher and J. R. Iyengar, *J. Ass. Offic. Anal. Chem.*, 61 (1978) 70.
146 E. Lanza and H. T. Slaver, *Lipids*, 16 (1981) 260.
147 J. Sampugna, L. A. Pallansch, M.G. Mark and M. Keeney, *J. Chromatogr.*, 249 (1982) 245.
148 B. L. Walker, *Lipids*, 16 (1981) 468.

149 I. M. Yousef, M. M. Fisher, J. J. Myher and A. Kuksis, *Anal. Biochem.*, 75 (1976) 538.
150 D. F. Zinkel and C. C. Engler, *J. Chromatogr.*, 136 (1977) 245.
151 T. Takagi, Y. Itabashi, T. Ota and K. Hayashi, *Lipids*, 11 (1976) 354.
152 T. Takagi and Y. Itabashi, *J. Chromatogr. Sci.*, 15 (1977) 121.
153 J. R. Ashes and J. K. Haken, *Anal. Chem.*, 45 (1973) 1131.
154 J. K. Haken and D. K. M. Ho, *J. Chromatogr.*, 112 (1975) 135.
155 J. D. Fisk, *Ph. D. Dissertation*, Duke University, Durham, NC, 1981.
156 J. V. Hinshaw, *Ph. D. Dissertation*, Duke University, Durham, NC, 1979.
157 C. H. Lochmüller and J. V. Hinshaw, Jr., *J. Chromatogr.*, 202 (1980) 363.
158 J. K. Haken, *J. Chromatogr. Sci.*, 9, No. 5 (1970) 13A.
159 D. H. Shaw and G. W. Moss, *J. Chromatogr.*, 41 (1969) 350.
160 R. G. Ackman, *Lipids*, 2 (1967) 502.
161 O. V. Privett, J. D. Nadenicek, F. J. Pusch and E. C. Nickell, *J. Amer. Oil Chem. Soc.*, 46 (1969) 13.
162 E. N. Lambremont and E. Woods, *Lipids*, 3 (1968) 503.
163 W. R. Sherman and S. L. Goodwin, *J. Chromatogr. Sci.*, 7 (1969) 167.
164 C. J. Brooks and E. C. Horning, *Anal. Chem.*, 36 (1964) 1540.
165 W. J. A. VandenHeuvel, *J. Chromatogr.*, 26 (1967) 396.
166 G. L. Feldman and C.K. Grantham, *J. Gas Chromatogr.*, 2 (1964) 12.
167 R. A. Morrisette and W.E. Link, *J. Gas Chromatogr.*, 3 (1965) 67.
168 J. S. Sawardeker, J.H. Sloneker and A. Jeanes, *Anal. Chem.*, 37 (1965) 1602.
169 A. B. Terentiev, N.S. Ikonnikov and R. Kh. Freidinia, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1 (1971) 73.
170 S. Papetti, B.B. Schaeffer, A.P. Gray and T.L. Heying, *J. Polym. Sci.*, A1 (1966) 1263.
171 H. Schroeder, O. Schaffling, T. Larcher, F. Frullee and T. Heying, *Rubber Chem. Technol.*, 39 (1966) 1184.
172 H. Schroeder, *Amer. Chem. Soc., Div. Rubber Chem., Cleveland, April 1968*, Paper No. 24.
173 R. W. Finch and W. A. Nichols, *U.S. Pat.* 3,660,966 (May 9, 1972).
174 D. T. Haworth, *Endeavour*, 31 (1972) 16.
175 R. W. Finch, *Analabs Res. Notes*, 10 No. 3 (1970) 1.
176 J. A. Yancey and T. R. Lynn, *Analabs Res. Notes*, 41, No. 1 (1974) 1.
177 J. A. Yancey and T. R. Lynn, *Analabs Res. Notes*, Suppl. (1975).
178 K. A. Kvenvolden, E. Petersen and C. E. Pollock, *Advances in Organic Geochemistry*, Pergamon Press, Oxford, 1971, p. 387.
179 G. E. Pollock, *Anal. Chem.*, 44 (1972) 634.
180 M. Novotny, R. Segura and A. Zlatkis, *Anal. Chem.*, 44 (1972) 9.
181 Chemical Systems, Irvine, CA, personal communication, 1976.
182 I. Yudina, *Sb. Nauchn. Tr. Gazov. Khromatogr., N-1, Fiz.-Khim*, No. 23 (1974) 20.
183 V. G. Berezkin, E. Yu. Sorokina, A. S. Shapatin, G. Ya. Ryzhov and T.I. Shulyatleva, *Vysokoeffekt., Gazov. Khromatografiya*, M (1982) 106.
184 G. Wright and C. S. Oliver, *U.S. Pat.*, 2,448, 565 (1948).
185 C. J. Bossart, *ISA Trans.*, 7 (1968) 283.
186 C. J. Bossart, *U.S. Pat.*, 3,514,925 (1970).
187 K. Grob, *Helv. Chim. Acta*, 51 (1968) 729.
188 K. Grob, G. Grob and K. Grob, Jr., *Chromatographia*, 10 (1977) 185.
189 M. Rigard, P. Chebroux, J. Maclouf and C. Madani, *Tetrahedron Lett.*, (1976) 3935.
190 C. Madani, E. M. Chambaz, M. Rigaud, J. Durand and P. Chebroux, *J. Chromatogr.*, 126 (1976) 161.
191 W. Patnode and D. F. Willock, *J. Amer. Chem. Soc.*, 68 (1946) 358.
192 C. Madani, E. M. Chambaz, M. Rigaud, P. Chebroux, J. C. Breton and F. Berthou, *Chromatographia*, 10 (1977) 466.
193 C. Madani and E. M. Chambaz, *Chromatographia*, 11 (1978) 725.
194 C. Madani and E. M. Chambaz, *J. Amer. Oil Chem. Soc.*, 58 (1981) 63.
195 L. Blomberg, J. Buijten, J. Gawdzik and T. Wännman, *Chromatographia*, 11 (1978) 521.
196 L. Blomberg and T. Wännman, *J. Chromatogr.*, 168 (1979) 81.
197 K. Grob, *Chromatographia*, 10 (1977) 625.
198 K. A. Andrianov, *Metalloorganic Polymers*, Interscience, New York, 1965.
199 J. C. Diez-Masa, M. I. Nieto, J. L. Otego and M. V. Dabrio, *Anal. Quim.*, 78C (1982) 79.
200 F. Fairbrother and A. E. Stubbs, *J. Chem. Soc. (London)*, (1935) 277.
201 L. Blomberg and T. Wännman, *J. Chromatogr.*, 186 (1979) 159.

202 L. Blomberg, K. Markides and T. Wännman, *J. Chromatogr.*, 203 (1981) 217.
203 G. D. Cooper and M. Prober, *J. Org. Chem.*, 25 (1960) 240.
204 L. Blomberg, J. Buijten, K. Markides and T. Wännman, *J. Chromatogr.*, 208 (1981) 231.
205 K. Grob, G. Grob and K. Grob, Jr., *J. Chromatogr.*, 211 (1981) 243.
206 K. Grob and G. Grob, *J. Chromatogr.*, 213 (1981) 211.
207 K. E. Polmanteer, *J. Electroplast*, 2 (1970) 165.
208 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 491.
209 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 13.
210 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 153.
211 P. Sandra, G. Redant, E. Schacht and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 411.
212 K. Grob, G. Grob and K. Grob, Jr., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 31.
213 M. Godefroot, M. van Roelenbosch, M. Verstaffe, P. Sandra and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 337.
214 L. Blomberg, J. Buijten, K. Markides and T. Wännman, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 579.
215 K. Grob, G. Grob and K. Grob, Jr., *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1977) 677.
216 L. Blomberg, K. Markides and T. Wännman, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 527.
217 L. Blomberg, K. Markides and T. Wännman, in R.E. Kaiser (Editor), *Proc. 4th Int. Symp. on Capillary Chromatography, Hindelang,* Hüthig, Heidelberg, 1981, p. 73.
218 P. Tarrant, G. W. Dyckes, R. Dunmire and G. B. Butler, *J. Amer. Chem. Soc.*, 79 (1957) 6536.
219 L. Blomberg, J. Buijten, K. Markides and T. Wännman, *J. Chromatogr.*, 239 (1982) 51.
220 S. R. Lipsky and W.J. McMurray, *J. Chromatogr.*, 239 (1982) 61.
221 R. Lewis and E. Martin, *U.S. Pat.* 4,066,680 (1978).
222 G. Schomburg, R. Dielmann, H. Borwitzki and H. Husmann, *J. Chromatogr.*, 167 (1978) 337.
223 W. Lynch, *Handbook of Silicone Rubber Technology,* Van Nostrand-Reinhold, New York, 1978.
224 P. A. Peaden, B.W. Wright and M.L. Lee, *Chromatographia,* 15 (1982) 335.
225 A. R. Gilbert and S. W. Cantor, *J. Polym. Sci.*, 40 (1959) 35.
226 L. C. Scala and W. M. Hickman, *Ind. Eng. Chem.*, 50 (1958) 1583.
227 B. A. Wright, P. A. Peaden, M. L. Lee and T. J. Stark, *J. Chromatogr.*, 248 (1982) 17.
228 T. J. Stark, R. D. Dandeneau and L. Mering, *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, 1980,* p. 002.
229 L. S. Ettre, *J. Gas Chromatogr.*, 3 (1965) 100.
230 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 349.
231 N. Grassie and I. G. MacFarlane, *Eur. Polym. J.*, 14 (1978) 875.
232 B. W. Wright, P. A. Peaden and M. L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 413.
233 J. Buijten, L. Blomberg, K. Markides and T. Wännman, *J. Chromatogr.*, 237 (1982) 465.
234 P. Sandra, M. van Roelenbosch, I. Temmerman and M. Verzele, *Chromatographia,* 16 (1982) 63.
235 P. Sandra, M. Schelfaut and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 49.
236 J. Buijten, L. Blomberg, K. Markides and T. Wännman, *Chromatographia,* 16 (1982) 183.
237 O. K. Johannson, *Can. Pat.* 570,580 (1959).
238 A. Mosely and E. D. Pellizzara, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 472.
239 K. Markides, L. Blomberg, J. Buijten and T. Wännman, *J. Chromatogr.*, 254 (1983) 53.
240 K. Markides, L. Blomberg, J. Buijten and T. Wännman, *J. Chromatogr.*, 267 (1983) 29.
241 K. Unger, *Porous Silica,* Elsevier, Amsterdam, 1978.
242 K. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 493.
243 W. Bertsch, V. Pretorius, M. Pearce, J. C. Thompson and N. G. Schnautz, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 432.
244 G. Schomburg, H. Husmann, S. Ruthe and M. Herraiz, *Chromatographia,* 15 (1982) 599.
245 Y. Masada, K. Hashimoto, T. Inoue, Y. Sumida, T. Kishi and Y. Suwa, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 400.
246 L. F. Thompson and G. Smolinsky, *J. Appl. Polym. Sci.*, 16 (1972) 1179.
247 *Catalogue,* J. & W. Scientific Inc., California, 1981.
248 *Product Literature, GC9,* S.G.E. Pty. Ltd., Melbourne, Aug. 1982.

249 A. B. Blakeney, P. J. Harris, R. J. Henry, B. A. Stone and T. Norris, *J. Chromatogr.*, 249 (1982) 180
250 A. B. Blakeney, P. J. Harris, R. J. Henry, B. A. Stone and T. Norris, *Carbohyd. Res.*, (1982) in press.
251 J. Klok, E. H. Nieberg-van Velzen, J. W. de Leeuw and P. A. Schenk, *J. Chromatogr.*, 207 (1981) 273.
252 N. Shibuya, *J. Chromatogr.*, 208 (1981) 96.
253 W. F. Lindner, in R. W. Frei and J. F. Lawrence (Editors), *Chemical Derivatization in Analytical Chemistry*, Vol. 2, Plenum Press, New York, 1982, pp. 145–190.
254 W. A. König, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 588.
255 R. Charles, G. Fisher and E. Gil-Av, *Israel J. Chem.*, 1 (1963) 234.
256 G. Pollack, V. Oyama and R. Johnson, *J. Gas Chromatogr.*, 3 (1965) 174.
257 E. Gil-Av, R. Charles and G. Fischer, *J. Chromatogr.*, 17 (1965) 408.
258 B. Halpern and J. Westley, *Biochem. Biophys. Res. Commun.*, 19 (1965) 361.
259 E. Gil-Av, B. Feibush and R. Charles, *Tetrahedron Lett.* (1966) 1009.
260 B. Feibush and E. Gil-Av. *Tetrehedron Lett.*, (1967) 3345.
261 S. Nakaparksin, P. Birrell, E. Gil-Av and J. Oro, *J. Chromatogr. Sci.*, 8 (1970) 177.
262 W. A. König, K. Stoelting and K. Kruse, *Chromatographia*, 10 (1977) 444.
263 R. Charles, U. Beitler, B. Feibush and E. Gil-Av, *J. Chromatogr.*, 112 (1975) 121.
264 *U.S. Catalogue No. 21*, Applied Science Lab. Inc., State College, PA, 1978, p. 190.
265 H. Frank, G. J. Nicholson and E. Bayer, *J. Chromatogr. Sci.*, 15 (1977) 174.
266 G. J. Nicholson, H. Frank and E. Bayer, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 411.
267 H. Frank, G. J. Nicholson, and E. Bayer, *J. Chromatogr.*, 146 (1978) 197.
268 B. Feibush and E. Gil-Av, *Tetrahedron*, 26 (1970) 1361.
269 H. Frank, G. J. Nicholson and E. Bayer, *J. Chromatogr.*, 167 (1978) 187.
270 W. Woiwode, H. Frank, G. J. Nicholson and E. Bayer, *Chem. Ber.*, 111 (1978) 3711.
271 H. Frank, W. Woiwode, G.J. Nicholson and E. Bayer, *Justus Liebigs Ann. Chem.*, (1981) 354.
272 I. Abe, K. Izumi, S. Kuramoto and S. Musha, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 549.
273 E. Bailey, P. B. Farmer and J. H. Lamb, *J. Chromatogr.*, 200 (1980) 145.
274 R. Liardon, S. Ledermann and U. Ott, *J. Chromatogr.*, 203 (1981) 395.
275 W. R. Shermann and A. L. Leavitt, *Abstracts 29th Annual Meeting on Mass Spectrometry and Allied Topics*, Minneapolis, 1981, p. 49.
276 A. L. Leavitt and W. R. Sherman, *Carbohyd. Res.*, 103 (1982) 203.
277 W. R. Sherman, A. L. Leavitt, M. P. Honchar, L. M. Hallcher and B. L. Phillips, *J. Neurochem.*, 36 (1981) 1947.
278 D. W. Ulff, *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City*, 1982, p. 791.
279 T. Saeed, P. Sandra and M. Verzele, *J. Chromatogr.*, 186 (1980) 611.
280 T. Saeed, P. Sandra and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 35.
281 W. A. König and I. Benecke, *J. Chromatogr.*, 209 (1981) 91.
282 W. A. König, S. Sievers and I. Benecke, in R. E. Kaiser (Editor), *Proc. 4th Int. Symp. on Capillary Chromatography*, Hindelang, Hüthig, Heidelberg, 1981, p. 703.
283 W. A. König, I. Benecke and H. Bretting, *Angew. Chem., Int. Ed. Eng.*, 20 (1981) 693.
284 W. A. König, I. Benecke and S. Sievers, *J. Chromatogr.*, 217 (1981) 71.
285 I. Benecke, E. Schmidt and W. A. König, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 553.
286 W. A. König, I. Benecke and S. Sievers, *J. Chromatogr.*, 238 (1982) 427.
287 W. A. König, W. Francke and I. Benecke, *J. Chromatogr.*, 239 (1982) 227.
288 I. Benecke and W. A. König, *Angew. Chem., Int. Ed. Eng.*, 21 (1982) 709.
289 W. A. König, I. Benecke and K. Ernst, *J. Chromatogr.*, 253 (1983) 267.
290 S. E. Kantor, W. T. Grubb and R. S. Osthoff, *J. Amer. Chem. Soc.*, 76 (1954) 5190.
291 I. Abe, S. Kuramoto and S. Musha, *J. Chromatogr.*, 258 (1983) 35.
292 *General Catalogue*, Chrompack, Middelburg, The Netherlands, 1982.
293 G. M. Janini, K. Johnson and W. L. Zielinski, Jr., *Anal. Chem.*, 47 (1975) 670.
294 G. M. Janini, G. M. Muschik and W. L. Zielinski, Jr., *Anal. Chem.*, 48 (1976) 809.
295 W. L. Zielinski, R. A. Scanlan and M. M. Miller, *J. Chromatogr.*, 209 (1981) 87.
296 J. E. Haky, G. M. Muschik, *J. Chromatogr.*, 214 (1981) 161.

297 R. J. Laub and W. L. Roberts, in A. Bjorseth and A. J. Dennis (Editors), *Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Proc. 4th Int. Symp. on Polynuclear Aromatic Hydrocarbons*, Battelle Press, Columbus, OH, 1980, pp. 25–58.

298 R. J. Laub, W. L. Roberts and C. A. Smith, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 355.

299 R. J. Laub, W. L. Roberts and C. A. Smith, in M. W. Cooke and A. J. Dennis (Editors), *Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Proc. 5th Int. Symp.*, 1981, pp. 287–295.

300 H. Finkelmann, R. J. Laub, W. L. Roberts and C. A. Smith, in M. W. Cooke and A. J. Dennis (Editors), *Polynuclear Aromatic Hydrocarbons: Chemistry and Biological Effects, Proc. 6th Int. Symp. on Polynuclear Aromatic Hydrocarbons*, in press.

301 M. Apfel, H. Finkelmann, R. J. Laub, B. H. Luhmann, A. Price, W. L. Roberts and C. A. Smith, *Makromol. Chem. Rapid Comm.*, in press.

302 M. L. Lee, R.C. Kong, Y. Tominaga, M. Iwaio, R. M. Castle and S. A. Wise, presented at *17th Int. Symp. Advan. in Chromatogr., Las Vegas, April, 1982*.

303 R. C. Kong, M. L. Lee, Y. Tominaga, R. Pratap, M. Iwao and R. N. Castle, *Anal. Chem.*, 54 (1982) 1802.

304 H. Finkelmann and R. J. Laub, *Report DOE/ER/10554-25*, Department of Energy, Washington, DC, 1982.

305 W. Wasiak and W. Szczepaniak, *J. Chromatogr.*, 257 (1983) 13.

306 A. A. Zhdanov, K. A. Andrianov and M. M. Levitskii, *Vysokomol. Soedin, Ser. A*, 18 (1976) 224.

307 M. F. Laffert and G. J. Leigh, *Developments in Inorganic Polymer Chemistry*, Elsevier, Amsterdam, 1962.

308 F. G. A. Stone and W. A. G. Graham, *Inorganic Polymer Chemistry*, Academic, New York, 1962.

309 K. A. Andrianov and A. A. Zhdanov, *Dokl., Akad. Nauk SSSR*, 114 (1957) 1005.

310 E. O. Kirichenko, A. D. Damseva, B. A. Markov, I. Kostylev, T. I. Rybkina and V.A. Kochetov, *Russian Pat.* 930,115 (May 23, 1982).

311 A. H. Al-Taiar, J. R. Smith and D. J. Waddington, *Anal. Chem.*, 42 (1970) 935.

312 J. Guillot, C. Janin and A. Guyot, *J. Chromatogr. Sci.*, 11 (1973) 375.

313 T. Vlismas, *F.R.G. Pat.*, 1,908,104; *Brit. Pat.* 1,237,393; *Fr. Pat.*, 2,002,418.

314 T. Vlismas, *Fr. Pat.*, 1,573,349; *Brit. Pat.* 1,228,376; *F.R.G. Pat.*, 1,773,665; *U.S. Pat.* 3,639,498.

315 T. Vlismas, *Brit. Pat.* 1,228,377; *Fr. Pat.* 1,573,349.

316 J. M. Sosa, R. Hernandez and G. McBrayer, *J. Chromatogr.*, 189 (1980) 169.

317 J. M. Sosa, *Macromolecules*, 13 (1980) 1260.

318 V. G. Berezkin and J. K. Haken, in preparation.

319 L. Rohrschneider, *Z. Anal. Chem.*, 170 (1959) 256.

320 *Capillary Columns Application Data*, Chromato Packing Center, Shinwakako Co. Ltd., Kyoto, Japan, 1982.

321 K. Grob, Jr., G. Grob and K. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 149.

322 *Company Bulletin*, Vol. 20, Shimadzu, Tokyo, Japan, 1979, p. 5.

323 T. Kobayashi, *J. Chromatogr.*, 194 (1980) 404.

324 A. Ono, *Analyst (London)*, 107 (1982) 600.

325 A. Ono, *Chromatographia*, 14 (1981) 692.

326 A. Ono, *Niigata Daigaku Kyoikugakubu, Kiyo, Shizen Kagaku Hen*, (1981) 23.

327 Anonymous, OV GC Supplies, *Catalog 32*, Ohio Valley Specialty Chemical Inc., Marietta, OH, 1982.

328 Anonymous, *Supelco Reporter*, 2, No. 4 (1983) 8.

329 B. E. Richter, J. C. Kuel, J. I. Shelton, L. W. Castle, J. S. Bradshaw and M. L. Lee, *J. Chromatogr.*, 279 (1983) 21.

330 B. E. Richter, J. C. Kuel, H. J. Park, S. J. Crowley, J. S. Bradshaw and M. L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 371.

331 S. R. Lipsky and W. J. McMurray, *19th International Symposium Advances in Chromatography*, Amsterdam, October 3–6, 1983, Abstract 22.

332 A. J. Barry and H. N. Beck, in F. G. A. Stone and W. A. G. Graham (Editors), *Inorganic Polymers*, Academic Press, New York, 1962, p. 189.

333 J. Buijten, L. Blomberg, S. Hoffman, K. Markides and T. Wännman, *J. Chromatogr.*, 283 (1984) 341.

334 J. Buijten, L. Blomberg, K. Markides and T. Wännman, *19th International Symposium Advances in Chromatography*, Amsterdam, October 3–6, 1983, Abstract 23.

335 J. A. Hubball, P. DiMauro, E. F. Barry and G. E. Chabot, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 241.

336 K. K. Curry, J. W. Evans and G. Schwab, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983)
    510.
337 I. Abe, S. Kuramoto and S. Muska, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 366.
338 R. H. Liu and W. W. Ku, *J. Chromatogr.*, 271 (1983) 309.