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POLYSILOXANE STATIONARY PHASES IN GAS CHROMATOGRAPHY

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1. INTRODUCTION

Polysiloxanes tend to occupy a somewhat unique position in gas chromatography (GC), as materials described in the earliest work¹ that have continued as the major group of stationary phases and are currently probably finding greater application despite the introduction of a seemingly endless number of interesting new products.

The vast majority of stationary phases were not developed for use in GC but were materials of commercial quality provided for some industrial purpose. Many of these materials are produced to specifications completely suitable for their prime purpose but with compositional variations unacceptable for GC where the column process is directly related to the chemical composition of the solvent and where for reproducibility an essentially identical product is required.

The presence of organic additives tends to negate the stability of the siloxane and lead to thermal deterioration while fillers may contribute to the column process and low molecular weight homologs will produce excessive column bleed. With the increasing sensitivity of available detectors and the analysis of trace concentrations,

the acceptable limits of column bleed have been greatly reduced. Similarly the stringent requirements of phases for use in association with mass spectrometry (MS) have been described². A primary list of preferred stationary phases for GC-MS reported by Leibrand³ consists of refined grades of polydimethylsiloxane gum, polyphenylmethylsiloxane, poly-3-cyanopropyl phenylsiloxane and polydi-3-cyanopropylsiloxane. However it is extremely unlikely that such a limited selection would prove to be generally suitable.

The introduction of several polysiloxanes of stated composition offered specifically as stationary phases was reported during 1967 (refs. 4, 5) by the Ohio Valley Specialty Chemical Company. Since this time an increasing number of siloxane phases have become available, including refined grades of the majority of the earlier industrial products, several former experimental products which had become unavailable and recently the most polar polysiloxane as yet described. During this decade the two principal suppliers of chromatographic specialties, Applied Science Labs. and Supelco have also both introduced specialty polysiloxanes while Silar Labs. introduced a range of cyanoalkyl substituted products. Petrarch Systems have recently introduced a range of specialty polysiloxanes but their use in GC has not been reported⁶. Semi-quantitative schemes for characterizing stationary phases have made it possible to consider the polar character of solvents in terms of their composition and constants proposed by Rohrschneider⁷ and by McReynolds⁸ have found considerable acceptance due largely to their early adoption by the Supelco organization.

Preston⁹ made editorial comment in the *Journal of Chromatographic Science* about the excessively large number of materials that have been used as stationary phases and indicated certain redundancies concerning polysiloxanes while other repetitions have since become apparent¹⁰. Much attention has been directed to the selection of standard or preferred stationary phases¹¹ but the acceptance of the proposals has been negligible¹².

The position of the polysiloxanes as the major group of stationary phases was first demonstrated by Preston⁹ who prepared a partial tabulation of stationary phases using data extracted from the papers abstracted by *Gas Chromatography Literature, Abstracts and Index* for the years 1968 and 1969. Approximately 300 phases were reported and polysiloxanes cited in 20 or more reports are shown in Table I together with several other important phases. Data extracted from the same source has been reported for 1970-1972¹³ and this and later data are also included in Table I.

The wide applicability of polysiloxanes is further indicated by the work of Hawkes¹⁴ who reported that almost all separations in GC may be achieved using six preferred phases five of which are polysiloxanes. The limitations of this proposal have been discussed elsewhere¹⁵.

Siloxanes as stationary phases have previously been included in Brief Eastern European reviews on silicones by Wurst¹⁶, Sladkov¹⁷, Rotzsche¹⁸, Rotzsche and Hoffman^{19,20}, De Bruyn²¹, Luskina and Turkeltaub²², Reidmann²³, Bailescu and Ilie²⁴, Anvzer²⁵, Cermak²⁶ and Kotsev²⁷ and also in part in a work describing the development of chemically bonded chromatographic supports²⁸. This review describes the physical properties of the principal polysiloxane structures and provides information concerning Eastern European products which is believed to be accurate together with details of Western products which in the foreign reports do not reflect current use and suffer from many minor errors.

TABLE I
POLYSILOXANE STATIONARY PHASES REPORTED DURING 1968-1977

Phase	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977*
SE-30, E-301	569	371	302	265	302	308	260	404	295	120
DC-200	161	68	63	48	43	35	50	70	54	25
SF-96	61	38	29	9	25	13	16	17	16	6
JXR		25	24	9	15	4	11	11	12	3
DC-11		22	17	13	6	9	6	16	5	2
W98			13	24	23			23	15	4
OV-1	40	60	92	111	64	91	64	163	186	73
OV-101			10	22	21	38	36	93	98	42
SE-52	100	23	37	23	28	29	20	39	21	9
OV-7						5	8	12	12	3
OV-17	51	60	92	111	126	150	115	307	302	104
OV-25							3	10	16	3
DC-550	41	20	18	14	13	10	11	12	5	3
QF-1	215	131	120	98	82	109	93	156	118	45
OV-210			6	13	17	14	19	47	34	15
OV-225			13	15	20	13	22	56	40	36
XE-60	118	67	53	54	46	38	39	38	35	34
Silars								20	18	9
SP2300 series									2	1
EGSS-X		21	23	10	22	16	15	13	12	18
Dexsils					1	1	14	46	36	9
Russian					10	54	67	31	29	16
Other siloxanes } Other phases }	1388	1416	1255	1244	1067	1160	1070	1381	1381	420
Total	2744	2322	2186	2202	2053	2221	2026	3107	2518	1010

* January-August.

The present work does not repeat the previously detailed¹³ historical development of silicone materials as stationary phases but includes tabulations of many phases reported in the literature with regard to structure and/or chemical composition and polar character. The two areas where siloxanes are currently finding acceptance are described in detail and concern the highly polar cyanoalkyl products for use with fatty esters and the relatively low polarity carborane-polysiloxane copolymers for high temperature operation.

In the earlier report bonded siloxane phases were included but these materials have now largely displaced the pellicular packings that revolutionised liquid chromatography (LC) a decade ago. These phases bonded to a silica base have become of prime importance and since the earlier report have been the subject of a recent book²⁹ and a large number of reviews³⁰⁻⁴⁰ and therefore are not repeated in this work.

2. DIMETHYL POLYSILOXANES

The low polarity dimethyl polysiloxanes continue to be the most widely reported of the polysiloxanes, the General Electric Gum Rubber SE-30 finding greatest use. The product as offered to chromatographers has been improved since the early reports and utilizes a different catalyst to that of the industrial product to allow it to compete more favourably with the specialty product of the Ohio Valley

Company. Thermal degradation is in part promoted by the presence of catalyst residues required during the polymer preparation and catalyst selection and residual removal are of importance.

The chemistry, manufacture, purification and use of dimethyl polysiloxanes as stationary phases in GC has been reported by Trash⁴¹.

The properties of polysiloxanes result from their partly inorganic and partly organic structures. Thermal and chemical stability characteristics of their completely inorganic homologs are substantially retained while the organic pendant groups may be varied to provide compounds with greatly varying properties.

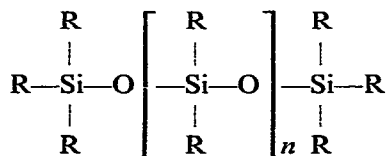
The bond energy of the Si-O is considerably greater than that of the C-C linkage while the Si-C bond is also strong and thermal stability and low vapour pressure have always been a feature of polysiloxane phases. The effective strength of the various bonds is however greatly influence by the neighbouring atoms and the half-lives of substituent groups in air at 250° calculated from weight loss and silicon content values determined before and after exposure for 100 h are shown in Table II⁴².

TABLE II
THERMAL LIFE OF VARIOUS SUBSTITUENTS ON SILICON

<i>Group covalently bonded to Si</i>	<i>Approximate half-life* at 250° (h)</i>
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[±].

The poly.methyl siloxanes have the general formula



where R is a methyl group. Materials are available for industrial purposes as fluids with nominal viscosities in the range of 0.65–1,000,000 cS at 25° and with chain lengths from 2 to over 2,000 dimethyl polysiloxane units. The relationship between average molecular weight and viscosity at room temperature is shown in Fig. 1, while

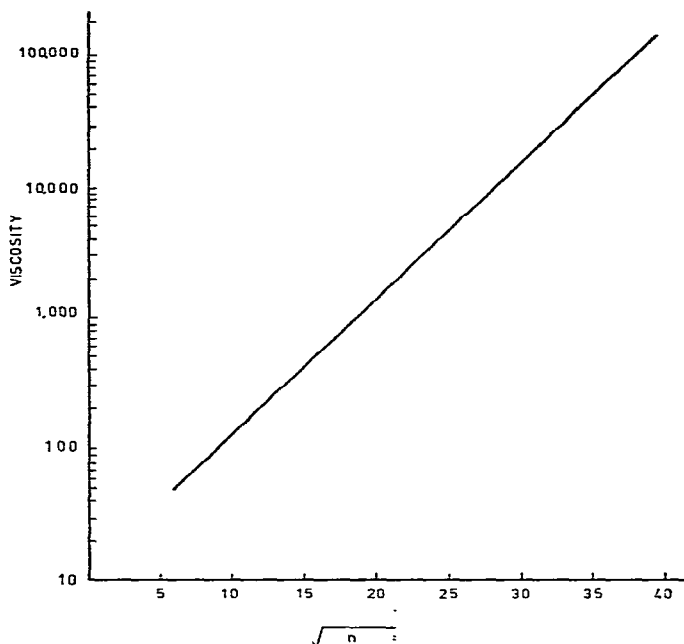


Fig. 1. Relationship between viscosity in centistokes at 25° and molecular weight of dimethyl polysiloxanes, where n is the number of dimethyl polysiloxane units.

the relationship shown in eqn. 1 is applicable to fluids of average molecular weight greater than 2500 (ref. 43).

$$\log(\text{viscosity in cS}) = 1 + 0.0123 (\text{M.W.})^{\frac{1}{2}} \quad (1)$$

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

Fluids of very low viscosity are unsuitable for use in GC at the higher operating temperatures possible with polydimethylsiloxanes, *i.e.* 300°, due to excessive column bleed. Fluids of 12,500 cS have been extensively used although much lower viscosities can be tolerated in many applications, *i.e.*, 50–500 cS. The viscosity of silicone oils is much less affected by variations in temperature than hydrocarbons and this property is of value for operation at both elevated and reduced temperatures.

Baumann *et al.*⁴⁴ considered GC operation at sub-ambient temperatures and found siloxane polymers to be suitable as stationary phases. The materials considered are shown in Table III and no loss in resolution was observed with SF-96, *i.e.* a 1000 cS oil, at –60°. Merritt *et al.*⁴⁵ have studied stationary phase performance at cryogenic temperatures. Initial reports showed that a 5% tris(cyanoethoxypropane) column was superior to a 5% SE-30 one when programmed from –170° at 3°/min. A subsequent publication⁴⁶ 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° while squalane gradually freezes over the range –60° to –100° and Carbowax 20M melts at 52°. It is apparent that a silicone fluid rather than a gum may have proved more suitable¹⁶.

TABLE III
LOW TEMPERATURE OPERATING LIMITS⁴⁴

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

The refractive index and specific gravity of dimethyl polysiloxanes both increase with molecular weight and these measurements make it possible to differentiate between methyl and phenyl substituted fluids. The characteristics for various types of polysiloxanes are shown in Table IV⁴⁷.

The molecular weight distributions of OV-101 and three viscosity grades of DC-200 have been determined by Trash⁴¹ 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 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 various coworkers. Diffusion⁴⁸ of *n*-alkanes was much faster with dimethylpolysiloxane gum (SE-30) than with a lower molecular weight oil (SF-96-200). The energy of diffusion was lower with dimethylpolysiloxanes than with polyethylene glycols making them more suitable for programmed temperature use. A subsequent study⁴⁹ 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 normal alkanes were shown to diffuse faster in SE-30

TABLE IV
PHYSICAL PROPERTIES OF SOME TECHNICAL METHYLSILICONE OILS AND METHYLPHENYLSILICONE OILS

η (20°)	d_4^{20}	n_D^{20}	η (20°)	d_4^{20}	n_D^{20}
<i>Methylsilicone oils</i>			<i>Methylphenylsilicone oils (low phenyl content)</i>		
60	0.96	1.4041	200	1.03	1.465
140	0.97	1.4045	1000	1.04	1.475
440	0.97	1.4053	<i>Methylphenylsilicone oils (high phenyl content)</i>		
680	0.97	1.4053	300	1.06	1.505
1,440	0.97	1.4053	1000	1.09	1.515
10,000	0.97	1.4058			
50,000	0.97	1.4058			
100,000	0.97	1.4058			
300,000	0.97	1.4058			

than in 2000-cS methyl fluid (SF-96-2000) the opposite effect was later shown for longer chain *n*-paraffins^{185,186}. 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 polydimethylsiloxanes 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. A compilation of retention data using dimethyl polysiloxane has been undertaken by the ASTM but as yet has not appeared⁵⁰.

An interesting recent application of dimethyl polysiloxane gum, *i.e.* SE-30, has concerned the analysis of basic drugs^{51,52}. Eight columns of varying polarity were evaluated with 62 drugs⁵¹, and it was evident that the less polar columns eluted all of the drugs while the more polar columns failed to elute certain drugs due largely to the lower operating temperatures possible. A subsequent work⁵² detailed the retention behaviour of 480 drugs.

During recent years 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 appeared⁵³⁻⁵⁵ and are described in a subsequent section of this work. Several evaluations of dimethylpolysiloxanes with viscosities 500-100,000 cS and produced in India^{56,57} have appeared. Performance equivalent to SE-30 is indicated but the equipment used is probably not sufficiently sensitive to allow vigorous testing.

It is widely recognized that the stability is enhanced when the polymer is endcapped with methyl groups and while most phases are designed in this way, a recent study has used dimethyl vinyl gum SKTV which contains hydroxy end groups. Aseeva and coworkers⁵⁸ 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 dimethylpolysiloxanes with various terminal groups and with metallic atoms was also studied by Lengyel *et al.* using thermogravimetry and pyrolysis GC⁵⁹.

Vlismas⁶⁰⁻⁶² has described the preparation of particulate crosslinked organo-silicon 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 crosslinked 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°. With representative phases a column efficiency of about 120 theoretical plates was obtained with 2,2,4-trimethylpentane.

The properties of dimethylpolysiloxanes, offered as chromatographic specialties are shown in Table V while other commercial products that have been reported as stationary phases are listed in Table VI.

3. POLYALKYL SILOXANES

With the Russian-produced polysiloxanes shown in Table VII it is apparent that several of the materials SKTE(K) (ethyl substitution), SKT and SKSV(K) have lower relative polarity values than imported dimethyl polysiloxanes, *i.e.* SE-30, and are comparable to phases of the Apiezon type in performance while possessing greater

TABLE V

SPECIALTY POLYSILOXANES FOR GAS CHROMATOGRAPHY

Suppliers: A = Ohio Valley Specialty Chem. Co., Marietta, Ohio, U.S.A.; B = Supelco, Bellefonte, Pa., U.S.A.; C = Applied Science Labs., State College, Pa., U.S.A.; D = General Electric Co., New York, N.Y., U.S.A.; E = Analabs, Conn., U.S.A.; F = Silar Lab. (distrib. Applied Science Labs.); G = Olin Corp. (distrib. Analabs.).

Phase	Substituent	Supplier	Nominal viscosity (cS) at 25°	M.W.	Density	Ref index	Rohr-schneider constants							McReynolds constants						
							X	Y	Z	U	S	X'	Y'	Z'	U'	S'	h			
OV-1	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			
ASI-100	100% Methyl	C	12,500									17	55	44	67	43	32			
Methyl																				
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	65	42	32			
SE-30 GC	100% Methyl	D	9.47×10^6	$1.0-2.5 \times 10^6$	0.996 (30°)		0.16	0.20	0.50	0.85	0.48	16	53	44	65	42	32			
OD-1	100% Methyl	E	Gum				0.16	0.20	0.50	0.85	0.48	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-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	7,000	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	4,000	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	50% Phenyl	C					1.30	1.60	1.79	2.83	2.47	119	158	162	243	202	112			
Methyl*																				
OV-22	60% Phenyl	A	>50,000	8,000	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	>10,000	10,000	1.150 (25°)	1.5825	1.76	2.00	2.15	3.34	2.81	178	204	208	305	280	144			
SP-400	11% Chlorophenyl	B					0.33	0.49	0.82	1.08	0.83	32	72	70	100	68	49			
OV-210	50% Trifluoropropyl	A	10,000	18,600	1.284 (25°)	1.3816	1.41	2.13	3.55	4.73	3.04	146	238	358	468	310	206			
SP-2401	50% Trifluoropropyl	B	700	2,600	1.30 (25°)	1.41	2.13	3.55	4.73	3.04	146	238	358	468	310	206				

ASI-50 Methyl**	50% Trifluoropropyl					146	238	358	468	310	206
OV-105	5% Cyanoethyl	A				36	108	93	139	86	74
AN-600	25% Cyanoethyl	D, E	Gum			202	369	332	482	408	—
OV-225	25% Cyanopropyl, 25% phenyl	A	9,000		1.5016	2.17	3.20	3.33	5.16	3.69	
					1.096						
					(25°)						
ASI-50	25% Cyanopropyl,	C				228	369	338	492	386	282
Methyl***	25% phenyl										
Silar 5CP	50% Cyanopropyl,	F				319	495	446	637	530	379
SP-2300	50% phenyl	B				319	495	446	637	530	379
ASI-50	50% Cyanopropyl	C									
Phenyl†											
Silar 7CP	75% Cyanopropyl,	F				440	638	605	844	673	492
SP-2310	25% phenyl	B				440	638	605	844	673	492
Silar 9CP	90% Cyanopropyl,	F				489	725	631	913	778	566
SP-2330	10% phenyl	B				490	725	630	913	778	566
Silar 10C	100% Cyanopropyl	F				523	755	659	942	801	584
SP-2340		B				520	757	659	942	800	584
OV-275	100% Cyanoethyl	A				781	1006	885	1177	1089	—
<i>Organosilicone polymers</i>											
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			3.96	6.01	5.39	—	6.50		
<i>Carborane siloxane polymers</i>											
Dexsil	Methyl	G	30-38°		0.43	0.64	1.11	1.51	1.01		
300 GC						37	78	113	154	117	—
Dexsil	Phenyl†	G	Viscous			72	107	118	168	123	—
400 GC											
Dexsil	2-Cyanoethyl	G	Viscous			71	286	174	249	171	—
410 GC											

* ASI-50 Methyl 50 Phenyl.

** ASI-50-Methyl 25 Cyanopropyl 25 Phenyl.

*** ASI-50 Phenyl 50 Cyanopropyl.

† ASI-50 Phenyl 50 Cyanopropyl.

TABLE VI

INDUSTRIAL, MISCELLANEOUS AND OBSOLETE POLYSILOXANE STATIONARY PHASES

Suppliers: A = Dow Corning, Midlands, Mich., U.S.A.; B = Midlands Silicone, Barry, Great Britain; C = Perkin-Elmer, Norwalk, Conn., U.S.A.; D = Union Carbide, New York, N.Y., U.S.A.; E = General Electric Co., New York, U.S.A.; F = Bayer Farbenfabriken AG, G.F.R.; G = Imperial Chem. Industries, Great Britain; H = May & Baker, Dagenham, Great Britain; I = VEB Chemiewerk, Nunchritz, G.D.R.; J = East Bohemian Chem. Co. Synthesia, Kolin, Czechoslovakia; K = Metroark Private, Calcutta, India; L = Institute for Silicone & Fluorocarbon Chem., Radebeul, G.D.R.; M = Lachat Chemical, Ill., U.S.A.; N = Rhone-Poulenc, France; O = Wacker Chemie, G.F.R.; P = Bevaloid Pty., Sydney, Australia; Q = Analabs., obsolete; R = Supelco, Bellefonte, Pa., U.S.A., obsolete; S = Japanese unknown; T = French unknown; U = Czechoslovakian unknown; V = Russian unknown.

<i>Phase</i>	<i>Substituent</i>	<i>Supplier</i>	<i>Viscosity (cS) at 20°</i>	<i>M.W.</i>
DC-200/MS200	Methyl	A, B	50-100,000	
Perkin-Elmer Column C	DC-200	C	Packed column	
SF-96	Methyl	D	50-100,000	
SF-96-200	Methyl	D	200	11,000
SF-96-2000	Methyl	D	2000	34,975
Viscasil	Methyl	E	100,000	103,000
L-45	Methyl	D	50-100,000	
Bayer M	Methyl	F	50-300,000	
F-111	Methyl	G	50-100,000	
L-46	Methyl	D	50-100,000	
Embaphase Oil	Methyl	H	300-400	
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	
MO-50	Methyl	I	50	
MO-200	Methyl	I	200	
Lukooil M-50	Methyl	J	50	
Lukooil M-100	Methyl	J	100	
Lukooil M-200	Methyl	J	200	
Lukooil M-500	Methyl	J	500	
Silicone B		I	100	
DMF-05	Methyl	I	500 (25)	
DMF-1	Methyl	K	1000 (25)	
DMF-12	Methyl	K	12,500 (25)	
DMF-30	Methyl	K	30,000 (25)	
DMF-100	Methyl	K	100,000 (25)	
Silicone Vaseline	Methyl	U		3,500
Methyl Gums				
SE-30	Methyl	E	9.47×10^6	$1.0-2.5 \times 10^6$
SE-30 Ultraphase	Methyl	E	9.47×10^6	$1.0-2.5 \times 10^6$
Perkin-Elmer Column Z (SE-30)	Methyl	C	9.47×10^6	$1.0-2.5 \times 10^6$
E-301	Methyl	G	Gum	$1.0-2.5 \times 10^6$
DC-410	Methyl	A	Gum	
Silastic 401	Methyl	A	Gum	
DC-401	Methyl	A	Gum	
Silastic 132	Methyl	A	Gum	
Silastic 152	Methyl	A	Gum	

Density	Refractive index	Rohrschneider constants					McReynolds constants						Ref.
		X	Y	Z	U	S	x'	y'	z'	u'	s'	h	
0.97 (25°)		0.16	0.20	0.50	0.85	0.48	16	57	45	66	43	33	
		0.16	0.20	0.50	0.85	0.48	16	57	45	66	43	33	
		0.15	0.20	0.48	0.82	0.47	14	53	42	61	37	31	
0.972 (25°)		0.15	0.20	0.48	0.82	0.47	14	53	42	61	37	31	
0.974 (25°)		0.15	0.20	0.48	0.82	0.47	14	53	42	61	37	31	
0.978 (25°)							16	57	45	66	43	33	
							16	57	45	65	43	33	
							16	57	45	66	43	33	
							16	57	45	66	43	33	
							16	56	44	65	41	33	
0.970-3 (20°)							14	57	45	66	43	33	
													159
													160
							13	51	42	61	36	31	
0.96-0.98 (20°)													16
0.96-0.98 (20°)													16
0.96-0.98 (20°)													16
0.973-0.977	1.403-1.407												157,
													158
1.03 (20°)													16
0.972 (25°)	1.4033												56, 57
0.972 (25°)	1.4035												56, 57
0.973 (25°)	1.4035												56, 57
0.973 (25°)	1.4035												56, 57
0.973 (25°)	1.4035												56, 57
0.966 (25°)		0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32	
0.966 (25°)		0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32	
0.966 (25°)		0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32	
		0.16	0.20	0.50	0.85	0.48	16	55	44	65	44	32	
							18	57	47	68	44	34	
							17	58	47	68	46	34	
							17	58	47	68	46	34	

(Continued on p. 258)

TABLE VI (continued)

Phase	Substituent	Supplier	Viscosity (cS) at 20°	M.W.
W95	Methyl	D	Gum	
W950	Methyl	D	Gum	
MS-2211	Methyl	B	10 ¹² -10 ¹⁴	
DC-123	Methyl	A	10 ¹² -10 ¹⁴	
E-300	Methyl	G	10 ¹² -10 ¹⁴	
DC-400	Methyl	A	10 ¹² -10 ¹⁴	
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	
GL1100F	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	
Silastic 430	Methylvinyl (1%)	A	Gum	
DC-430	Methylvinyl (1%)	A	Gum	
E-302	Methylvinyl (1%)	G	Gum.	
SE-33	Methylvinyl (1%)	E	Gum	
E-303	Methylvinyl (1%)	G	Gum	
W-96	Methylvinyl (1%)	D	Gum	
W-98	Methylvinyl (1%)	D	Gum	
W-960	Methylvinyl (1%)	D	Gum	
W-982	Methylvinyl (0.15%)	D	Gum	
Rhodorsil Comme 785	Methylvinyl	N	Gum	
Silicone Rubber Polymer	Methylvinyl	O	Gum	
Lukopren G1000	Methylvinyl	J	Gum	3.5-6.0 × 10 ⁵
Gi 7300 F	Methylvinyl	L	Gum	
NG 300	Methylvinyl	I	Gum	
DC-11	Methyl (10% silica)	A	Paste	
Hi Vac Grease	Methyl (10% silica)	A	Paste	
Perkin-Elmer Column O	Methyl (10% silica)	C	Paste	
Hi Vac Grease extract	Fluid	A	12,500	
DC-730	Ethyl	A		
S-2116	30% Stearoyl	P	M.p. 62°	
DC-230	Stearyl	A	1200-1600	
F-157	Stearyl ester	A	M.p. 25°, 10 cS (50°)	
<i>Phenyl siloxanes</i>				
DC-510	5% Phenyl	A	50-1000	
DC-556	10% Phenyl	A	15-30	
DC-550	25% Phenyl	A	100-150	
DC-555	Low Phenyl (cyclic)	A	"	
DC-701	Low Phenyl	A	10-15	
DC-702	25% Phenyl*	A	45	
DC-703	25% Phenyl*	A	55	
DC-704	50% Phenyl*	A	39	

Density	Refractive index	Rohrschneider constants					McReynolds constants						Ref.	
		X	Y	Z	U	S	x'	y'	z'	u'	s'	h		
0.96														
0.96							15	56	44	66	40	32		
							15	56	44	66	40	32		
							15	56	44	66	40	32		160
														16
														161
														16
							16	55	45	66	42	33		
														157
							17	86	48	69	56	33	163	
		1.05	1.50	1.61	2.51	1.90	17	86	48	69	56	33		
		0.16	0.20	0.50	0.85	0.48	16	57	45	66	43	33	164	
		0.23	0.50	0.48	0.75	0.56								
1.00 (25°)							25	65	60	89	57	42		
							37	77	80	118	79	53		
1.068 (25°)							74	116	117	178	135	81		
1.03 (25°)							77	124	126	189	142	90		
							76	123	126	189	140	89		

(Continued on p. 260)

TABLE VI (continued)

Phase	Substituent	Supplier	Viscosity (cS) at 20°	M.W.
OE-4008	50% Phenyl*	L		
DC-705	62.5 Phenyl*	A	175	
OE-4007	62.5 Phenyl*	L		
DC-710	50% Phenyl	A	475-525	2,660
OE-4006	75% Phenyl*	L		
OE-4011	35% Phenyl	L		
OE-4130	33% Phenyl	L		
NM3-200	33% Phenyl	I		
NM4-500	25.0% Phenyl	I		
NM5-500	35.0% Phenyl	I		
PN-200	Med Phenyl	F		
AR-20	25% Phenyl	O	200	
SE-52	5% Phenyl	E	Gum	
E-350	5% Phenyl	G	Gum	
SP-392	55% Phenyl	X		
PHSi 191-43	40% Phenyl	E	b.p. 245-275° (5 × 10 ⁵ mm Hg)	
287-149-243	20% Phenyl	E		
187-149-244	35% Phenyl	E		
Lukooil MF	Diphenyl*	J	100-200	
Lukooil DF	50% Phenyl	J	500 min	
Supolimer 2	High phenyl	V		
SE-54	5% Phenyl 1% vinyl	E		
E-351	5% Phenyl, 1% vinyl	G		
Gi 7500F	5% Phenyl, 1% vinyl	L		
X525	Unknown oil	Q		
L-525	Unknown oil	Q		
SR-119	Unknown resin	E		
<i>Chlorophenyl</i>				
F-61	11% <i>p</i> -Chlorphenyl	A	500	
F-60	11% <i>p</i> -Chlorphenyl	A	63	
DC-560	11% <i>p</i> -Chlorphenyl	A	75	
F-4050	3,5-Dichlorphenyl	A		
Lukooil X-100	41% 3,4,5-Trichlorphenyl	J		4.1% trimethylsilyl
Lukooil X-200	5.5% 3,4,5-Trichlorphenyl	J		5.5% trimethylsilyl
Lukooil X-600	8.3% 3,4,5-Trichlorphenyl	J		8.3% trimethylsilyl
Versilube F-50	"	E	70 (25°)	
Wacker CR	Chlorphenyl	O	20-1000	
Chlorsilicone CHS-1	Chlorphenyl	U		
<i>Cyanoalkyl substitution</i>				
XF-1105	5% Cyanoethyl	E		
XE-60	25% Cyanoethyl	E		
XF-1125	25% Cyanoethyl	E		
OE-4910	"	L		
XF-1112	12% Cyanoethyl	E		
XF-1150	50% Cyanoethyl	E		
238-149-99	50% Cyanoethyl	E		
238-149-239'	50% Cyanoethyl	E		
287-149-251	8% Cyanoethyl	E		

Density	Refractive index	Rohrschneider constants					McReynolds constants						Ref.	
		X	Y	Z	U	S	x'	y'	z'	u'	s'	h		
1.066 (20°)														
1.095 (20°)														
1.10 (25°)		1.05	1.50	1.61	2.51	1.90	107	149	153	228	190	170		165
1.04-1.11 (20°)														
0.99-1.04 (20°)														27
0.99-1.04 (20°)														27
1.04-1.07 (20°)														27
1.04-1.11 (20°)														27
1.04 (25°)														
							32	72	65	98	67	44		
							32	72	65	98	67	44		
		1.37	1.73	1.87	2.85	2.23	133	169	176	258	219	123		
														166
														167
														168
1.0322-1.042	1.472-1.479													157, 158
1.08-1.10	1.52-1.55													157, 158
														27
0.98							33	72	66	98	67	46		
							33	72	66	98	67	46		
							166	238	221	314	299	175		
		0.31	0.49	0.82	1.08	0.83	32	72	70	100	68	49		
		0.33	0.49	0.82	1.08	0.83	32	72	70	100	68	49		
		0.33	0.49	0.82	1.08	0.83	32	72	70	100	68	49		
1.045 (25°)	1.4280 (25°)						19	57	48	69	47	36		27
														169
		2.08	3.85	3.62	5.33	3.45	204	381	340	493	367	289		
		2.08	3.85	3.62	5.33	3.45	204	381	340	493	367	289		17
														18
														44
		3.18	5.33	3.81	7.02	5.04	308	520	470	669	528	401		
														96

(Continued on p. 262)

TABLE VI (continued)

Phase	Substituent	Supplier	Viscosity (cS) at 20°	M.W.
287-149-203	20% Cyanoethyl	E		
287-149-300	65% Cyanoethyl	E		
XF-1165	65% Cyanoethyl	E		
QE-4178	37.5% Cyanopropyl	L		
<i>Fluoralkyl substitution</i>				
QF-1	50% Trifluoropropyl	A	300-1000, 10,000	24,600
FS-1265				
QF-1-10065				
LSX-3-0295	50% Trifluoropropyl, 1% vinyl	A	Gum	
Silastic LS420				
Fluorosilicone 88		U		
Lukooil-X		J		
Lukooil-H		J		
<i>Organosilicone polymer</i>				
Copolymer 3		V		2,500
<i>Miscellaneous</i>				
DC-550/stearic acid				
Silicone Grease C/lithium capronate				
Silicone Grease C/sodium capronate				
Hi Vac Grease/Craig Polyester	45% Methyl			
Carbowax 20M/SE-30	42.8% Methyl			
SPMN/CI silicone		V		
Silicone FM-1322		V	300	
Silicone MS-4		V		
Silicone KF-54		S		
Silicone 5		V		
Silicone M500		V		
Silicone KF-96		S		
Silicone Oil 2/300		V		
Silicone Siss		V		
Silicone Liquid 139-15		V		
E Silicone				
Silicone MBL				
Silicone A				
Silicone B			100	
DOW-X2405	Low phenyl resin	A		

* See text.

thermal stability. 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^{63,64} and glycol ether derivatives⁶⁵. The recently available range of products of Petrarch Systems⁶ include a variety of higher alkyl polysiloxanes.

Density	Refractive index	Rohrschneider constants					McReynolds constants						Ref.	
		X	Y	Z	U	S	x'	y'	z'	u'	s'	h		
														27
		1.41	2.13	3.55	4.73	3.01	144	233	355	463	305	203		
							152	241	366	479	319	208		21
														135
														1
														176
														176
														177
														179
														179
														181
														182
														170
														171
														24-27
														173
														174
														175
														27
0.97 (20°)														27
1.03 (20°)														27
														172

4. METHYL VINYL 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 crosslinking with peroxide catalysts. The low concentration of polar groups which are not thermally stable do not influence the phase constants (*cf.* OV-101 with

TABLE VII

RETENTION BEHAVIOUR OF METHYL ESTERS OF UNSATURATED FATTY ESTERS ON CYANOALKYLPOLYSILOXANES

Phase	methyl esters (relative retention)				
	18:0	18:1	18:2	18:3	20:0
<i>10% Phase at 200^o116</i>					
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
<i>10% Phase at 180^o113</i>					
Silar-5CPI	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
<i>Separation at 175^o113</i>					
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

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.

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 cS, 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

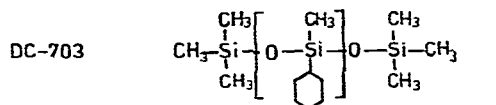
Since the use of DC-550 (25% phenyl substitution) by James and Martin¹ a wide variety of commercially available phenyl fluids, some of straight-chain-structure, others cyclic and largely produced by Dow Corning in the U.S.A. or Midlands Silicones in the United Kingdom, have found use as stationary phases. 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.

The presence of phenyl groups with some electron-donating properties in a polysiloxane stationary phase tends to increase the general polarity and introduce an

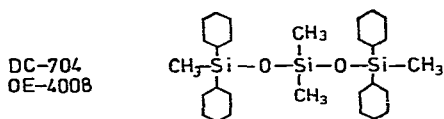
increasing measure of selectivity not apparent with dimethyl polysiloxane. The products are normally methyl terminated with substitution from the 5-mole % level. Wurst¹⁶ has reported that Lukooil MF consists of equal numbers of dimethyl and diphenyl units and Coleman⁶⁶ that SE-52 has 5% substitution as diphenyl groups. The manufacturers of Lukooil MF^{156,157} however report 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.

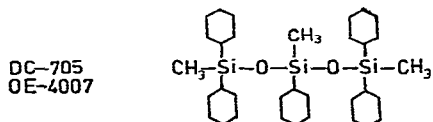
Several low molecular weight phenyl siloxanes of known structure are shown below.



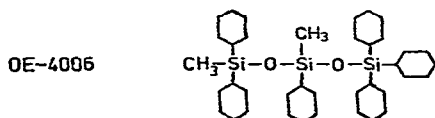
Nonamethyl-triphenylpentasiloxane



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



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



1,3-Dimethyl-hexaphenyltrisiloxane

The Ohio Valley Company in the United States have in recent years^{4,5} introduced 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°.

A material of the same composition as an experimental phenyl phase XE-61 (33% phenyl), which was described by Ikekawa *et al.*⁶⁷ for the separation of sterols with comparative studies using SE-30, SE-52, QF-1, XE-60 and NGS and by Withers⁶⁸ in the analysis of glycol ethers as their trimethyl silyl ethers, is available as OV-61 from the Ohio Valley Company.

The Supelco organization have introduced SP-2250 (ref. 69) which is chemically identical to OV-17 but for which higher column efficiency, lower bleed and extended life at elevated temperature are claimed.

The available phenyl siloxanes of increasing polar character range between 10 and 75% phenyl substitution while the use of an 85% experimental material has been reported⁶³⁻⁶⁵ and a 100% substituted material has been prepared in this laboratory⁷⁰ and a 100% substituted material has been prepared in this laboratory⁷⁰ and by Guillot *et al.*⁷¹ for use as a granulated polymer. At high temperatures, *i.e.* 150-230°, 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° above the boiling points of the compounds involved, this effect having been previously observed with low molecular weight polyphenyl siloxane oligomers⁷⁰ which exhibited broader peaks than with a 75-mole % phenyl product. Aromatic compounds were preferentially retained, styrene (b.p. 146°) being eluted after dimethylformamide (b.p. 156°). McCloskey and Hawkes⁷² in a study of the selection of standard phases reduced McReynolds' data⁸ 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% phenylmethylpolysiloxane may be more satisfactory, a conclusion supported by studies with diphenylpolysiloxane⁷⁰. Related polymers reported as stationary phases include methylphenyl and diphenylsilylmethylenes⁷³ with a backbone structure of repeating silicon and methylene units, methylphenylsiloxanes with diphenyloxy groups in the main chain⁷⁴ and poly(4-dimethylsilyl-4'-dimethylsiloxy) phenyleneoxide⁷⁵.

The effect of increased phenyl substitution and increasing polar character on the Rohrschneider constants is shown in Fig. 2. 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 substitution. Mann and Preston⁷⁶ showed that a 1:1 mixture of dimethyl polysiloxane and a 50% phenyl substituted polymer were equivalent to a product of 25% phenyl substitution while Lynch *et al.*⁷⁷ 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%.

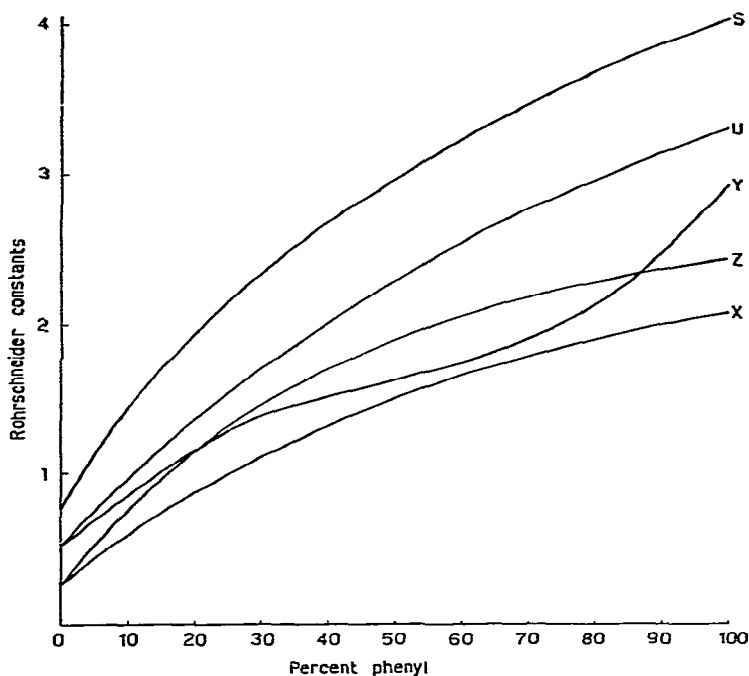


Fig. 2. Relationships between Rohrschneider constants and phenyl substitution.

7. PHENYL VINYL SILOXANE GUMS

Analogous to the methyl vinyl 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 groups⁶⁶ but with products of this type the level of substitution is not sufficiently high to provide any worthwhile selectivity.

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 has reported spectral bands due to dichlorophenyl groups⁶⁶. The Supelco product is the only material specifically offered as a stationary phase.

While the phases have been used in this laboratory^{65,73}, 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 Parcher⁷⁸. Giles and Nakhwa⁷⁹ 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 in Table VIII, 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 and his coworkers⁸⁰.

TABLE VIII

McREYNOLDS CONSTANTS FOR CHLOROPHENYL-SUBSTITUTED SILOXANES EQUATED TO x'

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

The composition of Versilube F-50 remains in doubt, it having been variously described as containing methyl *p*-chlorophenyl groups⁸¹, methyl, (10%) trichlorophenyl groups⁸², methyl, trichlorophenyl and trisilyl ether groups⁶ and tetrachlorophenyl groups⁶⁶. The McReynolds values of the material however are in agreement with values for dimethyl polysiloxane.

A further type of chlorophenyl substitution is illustrated by Dow Corning Fluid F-4050. The material has been suggested as a stationary phase⁸³ and consists of a relatively short-chain dimethyl polysiloxane end terminated with a 3,5-dichlorophenyl group. A similar type of material has been described by Wurst⁶ and its preparation described by the chlorination of phenyl trichlorosilane⁸⁴ to form a mixture of trichlorophenyl (73.5%) and tetrachlorophenyl trichlorosilane (22.8%), the trichlorophenyl trichlorosilane being reacted with dimethyldichlorosilane⁸⁵.

9. FLUOROALKYL SUBSTITUTED POLYSILOXANES

The currently available fluoroalkyl siloxanes are all homopolymers of 3,3,3-trifluoromethyl siloxane produced by base catalysed polymerisation of the cyclic trimer. 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 Vandenneuvel *et al.*⁸⁶, for the analysis of steroids in 1961. The phase corresponds to dimethyl polysiloxane with 50 mole % replacement of methyl groups with trifluoropropyl groups and it thus possesses what is recognised as a marked acceptor character.

Vandenneuvel *et al.*⁸⁶ indicated the significant polar character of QF-1 by determining separation factors for the $-\text{CH}_2-\text{CH}_2-$ group in a series of homologous aliphatic esters with about twenty to thirty carbon atoms. The following values were obtained using 1% of the phases at 190–210°: SE-30, 1.87; neopentyl glycol succinate (NGS), 1.74; QF-1, 1.66.

Selective functional group retention effects were examined using a series of steroids. The 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, 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 IX).

TABLE IX

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

Simplification is possible by equating the phases to x' (Table X).

TABLE X

McREYNOLDS CONSTANTS EQUATED TO x'

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

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 XI).

TABLE XI

McREYNOLDS CONSTANTS EQUATED TO z'

Phase	x'	y'	z'	u'	s'	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

The other materials of the same composition as QF-1, *i.e.* OV-210 and SP-2401, are available and offer greater thermal stability. Thermogravimetric analyses run from 200° to 300° at a heating rate of 2°/min in a helium atmosphere show the following percentage weight losses⁸⁷ presented in Table XII.

TABLE XII
WEIGHT LOSSES ON THERMOGRAVIMETRY OF POLYSILOXANES

Phase	200°	225°	250°	275°	300°
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

The column efficiencies of QF-1 and OV-210 are not high, *i.e.* less 500 theoretical plates per foot for a packed column, and greater efficiency is reported for SP-2400. The manufacturers report that a 6-ft. column gives efficiencies of 800 and 1040 theoretical plates per foot for cholesterol and mannitol, respectively⁸⁸.

The variation in performance of fluoroalkylsiloxane columns has been reported by Hanneman and Klimisch⁸⁹ 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 much inferior to SP-2401. The molecular weights indicated were QF-1 (24,600), OV-210 (18,600) and SP-2401 (2,600).

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 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 Holswade⁹⁰. Henly *et al.*⁹¹ 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 on various phases⁹² and dialkyl phthalates, dialkyl adipates and fluorinated silicones were recommended as the most suitable stationary phases.

10. CYANOALKYL SUBSTITUTED POLYSILOXANES

Silicone oils containing cyanopropyl groups were offered as a new class of polar stationary phases by Rotzsche in 1962^{93,94} but a decade passed before specialty grades were available to chromatographers and in the past few years the newer and more highly polar grades have found some acceptance for lipid separations. Rotzsche 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° and selectivity constants as described by Bayer⁹⁵ are shown in Table XIII.

TABLE XIII
SEPARATION FACTORS ON CYANOPROPYL-SUBSTITUTED STATIONARY PHASES

Stationary phase	(%Methyl:%phenyl:%cyanopropyl)					
	100:0:0	75:25:0	75:0:25	50:15:35	62.5:0:37.5	50:0:50
Alkylbenzene/ <i>n</i> -paraffin	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

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

Cyanoethyl siloxanes produced by the General Electric Co. appear to have been first described in detail by Litchfield *et al.*⁹⁶. 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 C₁₈ fatty esters was achieved. Another experimental material, XF-1105 with 5% cyanoethyl substitution, was offered for sale by Applied Science Labs. until supplies were exhausted. Subsequently⁹⁷ OV-105 has become available as a chromatographic specialty product of the same composition.

Scholfield and Dutton⁹⁸, using 238-149-99, have reported separations of unsaturated fatty esters. Retention data of octadecenoates and of octadecynoates were very similar to values obtained on diethylene glycol succinate although the Rohrschneider constants for the siloxane⁹⁶ are substantially lower than those reported for DEGS. An early report by Supina⁹⁹ indicated XF-1150 to be almost as polar as ethylene glycol adipate, the Rohrschneider constants for the two materials being similar⁹³.

Bayer *et al.*¹⁰¹ 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.*⁹⁶ on the basis of studies of stable π -complexes¹⁰²⁻¹⁰⁴ and the similarity of elution behaviour in silver ion chromatography with Ag⁺/olefin π -complexes of the same fatty esters¹⁰⁵⁻¹⁰⁷.

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 polar character of the phase is increased and the selectivity somewhat altered. The effect is shown in Table XIV by equating the contents to the basis of *x'*.

TABLE XIV

McREYNOLDS CONSTANTS OF OV-225 AND XE-60 EQUATED TO x'

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

The values of u' and s' both associated with acceptor characteristics are higher with XE-60.

The β -cyanoethyl and γ -cyanopropyl groups possess similar thermal and oxidative stability while the γ -cyanoethyl group is much inferior, the position weakening the silicon-carbon bond. A phenyl group on the same silicon atom as the γ -cyanopropyl group increases the thermal stability⁶⁶.

β -Cyanoethylmethyl siloxane XF-1150 remained the most polar siloxane phase available for almost a decade, but possesses poor thermal stability. With the introduction of Silar 5CP during 1972 (ref. 108) a slightly more polar material (γ -cyanopropylphenyl 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 esters¹⁰⁹⁻¹¹¹. Phases of intermediate polarity were introduced and two equivalent series (Silars¹¹²⁻¹¹⁴ and the SP-2300 series¹¹⁵⁻¹¹⁷) are shown in Table V. During a trademark difficulty Silar 10C appeared as Apolar 10C¹¹⁸, an absurd and confusing alternative name considering the long established European use of the term apolar to imply non-polar properties.

Scholly and Ettore¹¹¹ in an early study separated some simple fatty acid methyl esters with an open tubular column operated at 190° while Ackman and Hooper¹⁰⁹ separated the *cis*- and *trans*- Δ 9,- Δ 12,- Δ 15 isomers of six monoenoic, twelve dienoic and 8 trienoic methyl esters on an open tubular column. *Trans* unsaturation alone or with *cis* compounds reduced retention sufficiently on Silar 5CP relative to butanediol succinate to permit identification by small peak shifts.

During 1974 a further more polar cyanoalkyl siloxane (OV-275) appeared and is reported to be stable at 275°. This material is variously suggested to be di- α -cyanoethyl polysiloxane or a copolymer with γ -cyanopropyl groups. Use with fatty esters has been limited but the several varying reports of the McReynolds constants^{97,118} show some potential. A separation is shown in Fig. 3a and the increased polarity is evident from the overlap of 18:2 ω 6 and 20:0 (ref. 117).

The high thermal stability of Silar 5CP has been demonstrated by Myher, Maria and Kuksis¹¹⁰ 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°.

The use of reproducible tabulations of retention data has been proposed as a method for providing reliable identification of fatty acid methyl esters and Golovnya *et al.*¹¹⁹ have proposed the use of Silar 5CP and Silar 10C as more thermally stable standard phases than polyester phases. Bede¹²⁰ with Silar 10C reported polarity similar to diethyleneglycol adipate or diethyleneglycol succinate with the separation of the methyl esters of Krebs cycle, pyruvic, lactic and oxalic acids. The polysiloxane being substantially more thermally stable than the polyesters.

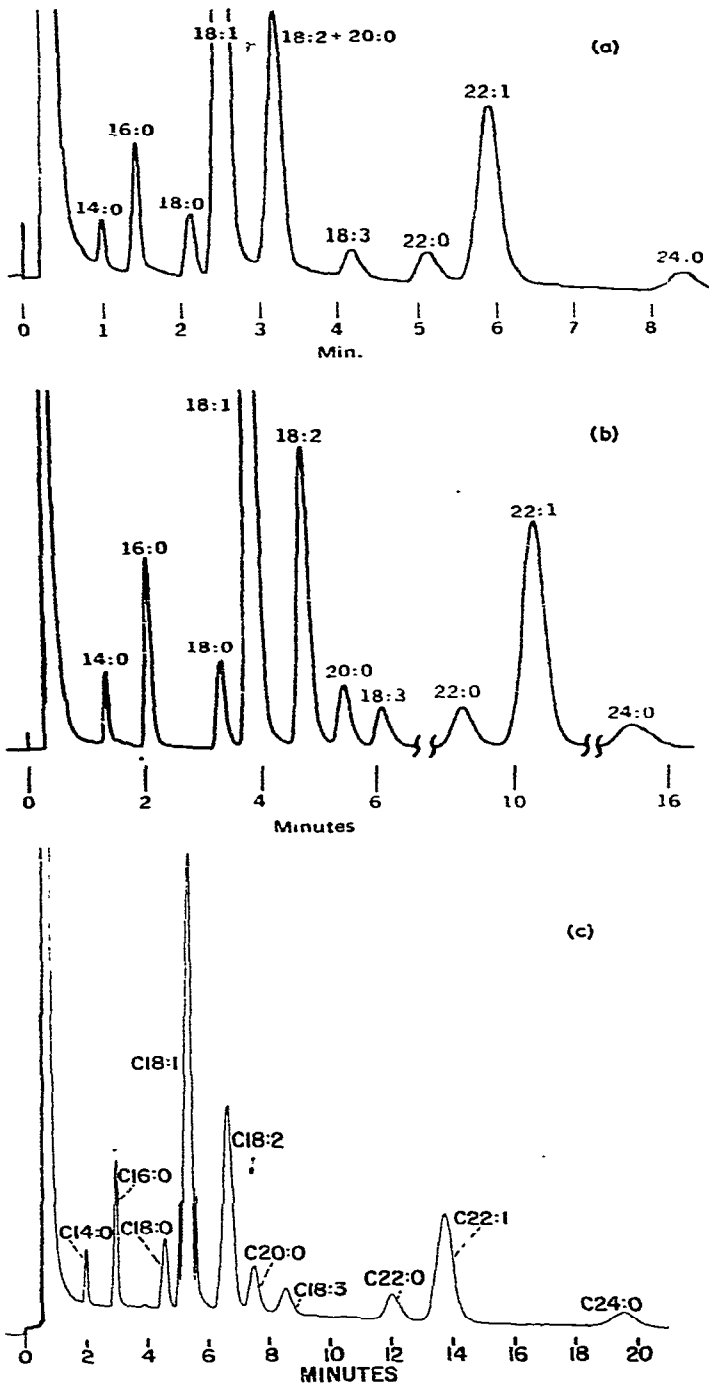


Fig. 3. (a) High-speed separation of fatty acid methyl esters on the extremely polar cyano-based OV-275. Note coincidence of 18.2 ω 6 and 20:0. For operating and other details see ref. 118. (b) Separation of some C₁₈-C₂₀ and other fatty acids of biological and commercial interest on the cyanosilicone phase SP-2340. Note that polarity is similar to that of high-polarity polyesters. For operating and other details see ref. 116. (c) Demonstration of chain-length overlap (18:3 ω 3 after 20:0) for fatty acid methyl esters on the high polarity polyester DEGS-PS. For further details see ref. 156.

TABLE XV

McREYNOLDS x' CONSTANT AND GENERAL POLARITY OF SUPELCO CYANOPROPYL SILOXANES

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

Use of the intermediate polarity cyanopropyl polysiloxanes appears to be restricted to a series of reports by the individual suppliers. The x' values and "general polarity" of the SP-2300 series are listed in Table XV.

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, 18:3 ω 3 is eluted before 20:0. With SP-2330 and SP-2340 (Fig. 3b) 18:3 ω 3 eluted after 20:0, the value X of 490 being similar to DEGS (Fig. 3c) while with SP-2340 the X value of 520 is higher. Retention data for the series is shown in Table VII 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 also shown in Table VII. The *cis* and *trans* isomers, methyl oleate and methyl elaidate have been separated using 15% of SP-2340 or OV-275 at 220° (ref. 121). To optimise the column parameters to facilitate the separation the amount of stationary phase, type of support and the nature of the support surface must be considered. Increasing the loading of 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 support¹¹⁶ offers greater column efficiencies with highly polar phases.

A comparison of the phases Silar 10C, Silar 9CP, SP-2340 and OV-275 for the separation of methyl esters of fatty acids on packed columns has recently been reported by Heckers and his co-workers¹²². Seven pairs of *cis-trans* isomeric methyl esters were separated on 12% Silar 10C and SP-2340, minimum overlap was observed with the C₁₅ acids and the maximum with the C₁₈ 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 4 phases for various separations being similar. Molecular weight determinations estimated from 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 trimethyl silyl groups.

The same workers^{122a} have reported the use of SP 2340 as a replacement of FFAP for the separation of fatty acid methyl esters using a 30 m \times 0.3 mm glass

capillary column, the fatty acid systems studied being concerned with the red cell phospholipids in humans of varying age groups.

Recent work by Zinkel and Engler^{122b} 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 *et al.*^{183,184} 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 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 aminoalkyl substituted polysiloxanes as stationary phases in GC has been reported¹²³. Polymers containing an ethylene diamine moiety with both primary and secondary amino groups have been used and on-column chemical reaction occurs 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° and 130° 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 reaction a series of support bonded aminoalkylsilanes were prepared from silanes of similar molecular weight and containing individually each type of amino group¹²⁴. 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 on molecular shape, with branched-chain compounds shielding the carbonyl and exhibiting reduced reactivity. The primary amino groups are more reactive than the secondary amino groups but the compound containing both groups was most reactive due simply to a concentration effect. While reaction with tertiary amino groups might be expected on theoretical grounds, this did not occur. The composition and McReynolds constants of the compounds used are shown in Table XVI.

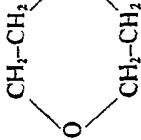
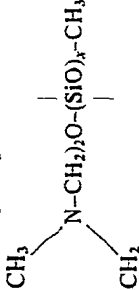
12. ORGANOSILICONE POLYMERS

Supina¹²⁵ developed a range of organosilicone polymers which are commercially available from Applied Science Labs. by the reaction of a polyester adduct of ethylene glycol succinate and an organosilane. The products are largely offered as substitutes for polyester phases but improved thermal stability is claimed. 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.

TABLE XVI

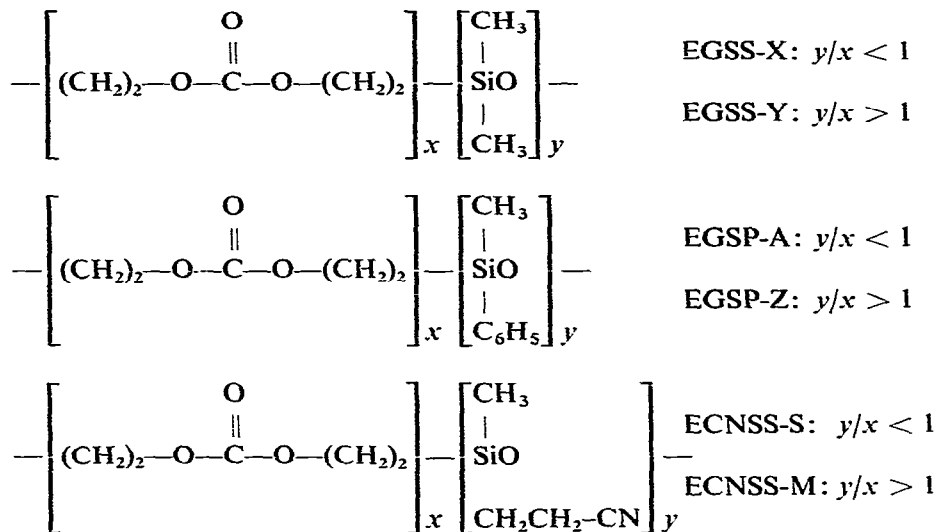
COMPOSITION AND McREYNOLDS CONSTANTS OF AMINOALKYLSILANE AND SILOXANE COMPOUNDS

Manufacturers: 1 = Dow Corning Corp., Midlands, Mich., U.S.A.; 2 = Union Carbide Corp., New York, N.Y., U.S.A.; 3 = Shin-Etsu Chemical Industries, Tokyo, Japan; 4 = Imperial Chemical Industries, Organics Division, Stevenston, Ayrshire, Great Britain; 5 = Midlands Silicones Ltd., Barry, Great Britain.

Trade Designation	Manufacturer	Chemical composition	Formula	Viscosity at 25° (cS)	Specific gravity at 25°	Boiling point (°C)	Refractive index at 25°	McReynolds constants				
								x'	y'	z'	u'	s'
Z6020	1	N-β-Aminoethyl-γ-aminopropyltrimethoxysilane	$\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	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-Aminopropyltriethoxysilane	$\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{O}_2\text{CH}_3)_3$	1.6	0.942	217	1.420	145	426	226	313	297
X12-563	3	N-Allyl-γ-aminopropyltrimethoxysilane	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	3.0	0.975	107 (7.5 mm Hg)	1.434	323	653	441	593	555
X12-570	3	γ-Morphinylpropyltrimethoxysilane		4.1	1.05	122 (5 mm Hg)	1.444	72	539	129	511	469
S4150/41	4	N,N-Dimethyl-γ-aminoethoxymethylpoly-siloxane		106.0		—	1.462	—8	143	76	69	82
DC-530	1	Copolymer Z6020 and dimethylpolysiloxane 50% solution DC-530 in 2-propanol and aliphatic solvents		80.0	1.00	—	1.420	63	269	129	204	116
DC-531	1			150.0	0.86	—	1.410	30	155	119	84	62
DC-535	1	Low molecular weight dimethyl polysiloxane (DP = 100) approx. 2% ethylenediamine moiety		3000.0	0.98	—	1.4147	24	159	70	93	70
MS-2560	5			As DC-535 but approx. 2½% amine moiety								
X-22-857	4			80.0-100.0				31	166	67	95	78

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 examined¹⁰.

The compositions as recently described²⁴ are shown below:



The variability of composition is probably not unexpected as possibly the only work that has considered multiple samples of these materials shows variable retention performance¹²⁶. 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-X¹²⁶ and by Ackman¹⁰⁰ with fatty esters using representatives of each type of the polymers.

The separations that have been reported include fatty esters¹²⁷, Glyceryl ethers¹²⁸ and trimethylsilyl derivatives of carbohydrates¹²⁹ on EGSS-X catecholamines¹³⁰ and sterol sulphonates¹³¹ on EGSP-Z and fatty esters¹³², fatty amines¹³³ and mono-saccharides¹³⁴ on ECNSS-M.

McReynolds constants for the phases are shown in Table V 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 recent Russian works is Copolymer 3, the copolymerisation product of liquid polymethylphenyldisiloxane and hexamethyl disiloxane¹³⁵.

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 trimethyl silyl 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 chain¹³⁶⁻¹³⁹ and various applications have been reviewed¹⁴⁰. Three materials have been marketed by Analabs as high temperature stationary phases and while Olin Corp. have discontinued manufacture it is anticipated that an alternate supplier will be obtained. The carborane group is dicarba-*closo*-dodecaborane ($B_{10}H_{10}C_2$), which has silicore 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 stabilising 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 dimethylsiloxane 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 polysiloxane units the central silicone atom having one phenyl and one 2-cyancethyl group, respectively.

Thermal gravimetric analyses showed XE-60 to lose weight at about 228°, SE-30 at about 350° and the Dexsil 300 GC at about 625° (ref. 141). Although the recommended maximum temperature limits are 450° for extended periods and 500° 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 V 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 bibliography¹⁴² and later supplement¹⁴³ 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^{144,145}, with the butyl esters of some trifluoroacetyl amino acids. A 150-ft. capillary column was temperature programmed to 300° and Dexsil 400 GC was used as commercially offered, *i.e.*, end capped with trimethylsilyl groups; an experimental product with hydroxyl end groups was also used. 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 reported¹⁴⁶ for the capillary column separation at 360° of cholesterol esters, tri-

glycerides and high boiling hydrocarbons. The materials experimental carborane polymers 7001-8-73 and 7001-8-95C are available from Chemical Systems¹⁴⁷ as 5-SiB-1 and 5-SiB-1.5 with 2.0 and 2.5 dimethyl polysiloxane groups per carborane nucleus, respectively. Both are reported¹⁴⁷ to perform indefinitely at 270° and for short periods at 400°. For GC-MS the first product is preferred as hydrogen is reported to be the sole decomposition product.

15. RUSSIAN POLYSILOXANES

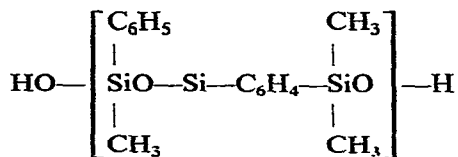
While the vast majority of Russian works that use siloxane phases employ Western products there is a continuing minor increase in the use of indigenous products. Manufacturers' literature is not readily available but a compilation of available data is shown in Table XVII where it is apparent that industrial products equivalent to the usual Western products are generally available. As described in Section 3 several products are of lower polarity than dimethylpolysiloxane but no other functional types are included that offer any additional selectivity over the Western products. From Table XVII it is evident that certain of the dimethyl, phenylmethyl and cyanoalkyl siloxanes are offered with both hydroxyl and methyl terminal groups, the hydroxyl termination having been shown⁵⁸ to be of lower thermal stability than with trimethyl silyl end groups. The minor vinyl contents of methyl, ethyl and phenyl gums as determined by Krasikova and Kaganova¹⁴⁹ are also shown in Table XVII.

Luskina and Turkeltaub²² have reported maximum operating temperatures for almost half of the phases shown in Table XVII together with separation efficiencies using a mixture of C₂₆-C₃₄ hydrocarbons, separation coefficients for the *n*-C₂₉-C₃₀ hydrocarbons and the number of theoretical plates. Some early studies of phase stability were reported by Rudenko *et al.* for four Russian and three Western siloxanes¹⁵⁰.

The coefficients of linear expansion for use in the study of the contact area contribution of the gas-liquid-solid interface to the retention time have been determined for DC-550 and several Russian polysiloxanes¹⁵¹, other work previously reported having concerned DC-702 (ref. 151) and representative Ohio Valley phases⁴⁹.

While the Russian phases are reported as Rohrschneider polarity¹⁷ the values as shown in Table XVII were determined using benzene and cyclohexane at 70° and interpolated between values of squalane and oxydipropionitrile as 0 and 100, respectively, as proposed by Rohrschneider¹⁵³.

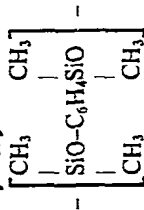
Yudina *et al.*¹⁵⁴ have investigated the fluorosiloxanes (SKTFT-25, -50, -75, -100) and an arylenesiloxane (SKTA) with the structure



as high-temperature phases in preparative GC. The thermal properties of the siloxanes were determined by thermal gravimetry and by GC and all of the products were of greater stability than SE-30 which was used as a control. The fluorosiloxanes were

TABLE 17
PHYSICAL CHARACTERISTICS OF RUSSIAN POLYSILOXANES

Name	Substituent	M.W.	d_4^{20}	Viscosity (cS) at 20°	n_D^{20}	Rohrschneider Polarity ¹⁵³	Max. Oper. Temp. (°C)
<i>Dimethyl polysiloxane</i>							
SKT	Hydroxyl terminated	400,000-6,000,000	0.975	Gum		6-8	350
PMS-100	Methyl terminated	5,000	0.968	95-105	1.400	9	300
PMS-400	Methyl terminated	20,000	0.980	400	1.402	9	300
PMS-200	Methyl terminated		0.973	200		9	300
PMS-1000	Methyl terminated		0.976	1000		9	300
PMS-5000	Methyl terminated		0.976	5000	1.4069	9	300
PMS-30,000	Methyl terminated		0.976	30,000		9	300
PMS-50 v/v	Methyl terminated	5,888	0.968	83.0	1.4102	9	300
FM-6 v/v	Methyl terminated	3,110	0.986	61.7	1.4280	9	300
VK Zh-94	Diethyl	780	0.949	16-33 (50°)	1.4461	9	150
SKT(e) Type A	Dimethyl diethyl (vinyl 0.06%)	400,000-650,000	0.975	Gum		5	280
SKTV	Methyl vinyl (0.04%) (OH terminated)	400,000-650,000	0.975	Gum		6-8	350
SKTV-1	Methyl vinyl (0.20%) (OH terminated)	400,000-650,000	0.975	Gum		6-8	350
<i>Methyl phenyl polysiloxane</i>							
PFMS-2	Low phenyl	1,500	1.104	450-1000	1.540	24	350
PFMS-4		1,400	1.079 (100°)	90 (100°)	1.557	30	350
PFMS-5		2,000	1.15	Not less	1.585	33	400
PFMS-6	High phenyl			150 (100°)			
PFMS-10	High phenyl		1.13			36	250
SKTF-100	Methyl phenyl vinyl (0.15%)		0.975	Gum		10	330
SKTV-803	Hydroxyl terminated		1.09			21	450



<i>Trifluoropropyl methyl</i>							
SKTFT-25	12.5% Trifluoropropyl		1.07	Gum		15	350
SKTFT-50X	25% Trifluoropropyl	1,000,000	1.15	Gum		21	450
SKTFT-50	25% Trifluoropropyl	1,000,000	1.15	Gum		21	450
SKTFT-75	37.5% Trifluoropropyl		1.24	Gum		26.5	350
SKTFT-100X	50% Trifluoropropyl	1,000,000	1.33	Gum		32	350
SKTFT-100	50% Trifluoropropyl	1,000,000	1.33	Gum		32	350
FS-5			1.080				
FS-16	37.5% Trifluoropropyl	980	1.2087	35	1.3857	26	150
FS-56	20% Trifluoropropyl	5790	1.1500	597	1.3913	19	300
FS-169	15% Trifluoropropyl	1610	1.1074	55	1.3911	17	300
FS-303		2420	1.3262	1000	1.3818	42	250
FS-328	25% Trifluoropropyl	2280	1.1168	65	1.3785	20	300
<i>Cyanoalkyl</i>							
NSKT-25	25% Cyanopropyl OH terminated			Gum		37-38	300
NSKT-33	33% Cyanopropyl OH terminated			Gum		42	300
NSKT-X	33% Cyanopropyl OH terminated			Gum		42	300
NSKT-50	50% Cyanopropyl OH terminated			350		53	300
NSKT-100	100.0% Cyanopropyl OH terminated			1340		71	300
NPS-25	12.5% Cyanoethyl methyl terminated	1500	0.9980	80	1.4230	22	
NPS-50	25% Cyanoethyl methyl terminated	1200	1.0493	350	1.4390	37	250
NPS-100	50% Cyanoethyl methyl terminated	1290	1.09	1340	1.4664	62	220
KhS-2-i	Chlorphenyl		1.031	40-47		9	300
KhS-2-1-VV	Chlorphenyl	2770	1.04	68	1.4420	9	300

TABLE 18
 PHYSICAL PROPERTIES OF RUSSIAN SILOXANE-CARBORANE STATIONARY PHASES

Formula	M.W.	d_4^{20}	Viscosity at 20° (cS)	n_D^{20}	Polarity ^{1,3}	Max. Oper. Temp.
$(CF_3CH_2CH_2)_7-SiO-\left[\begin{array}{c} [CH_3] \\ \\ -SiO- \\ \\ [CH_3]_{12} \end{array} \right]_6$ $\left[\begin{array}{c} CH_3 \\ \\ -SiCB_{10}H_{10}CSiO \\ \\ CH_3 \end{array} \right]_6$ $-Si(F_2CH_2CH_2C)_3$	1930	1.0569	535.8	1.4750	17.5	500°
$(CH_3)_3SiO-\left[\begin{array}{c} [CH_3] \\ \\ -SiO- \\ \\ [CH_3]_9 \end{array} \right]_3$ $\left[\begin{array}{c} CH_3 \\ \\ -SiCB_{10}H_{10}CSiO \\ \\ CH_3 \end{array} \right]_3$ $-Si(CH_3)_3$	1325	0.9922	134	1.4672	12	450-500°
$(C_6H_5)_2SiO-\left[\begin{array}{c} [CH_3] \\ \\ -SiO- \\ \\ [CH_3]_{12} \end{array} \right]_6$ $\left[\begin{array}{c} CH_3 \\ \\ -SiCB_{10}H_{10}CSiO \\ \\ CH_3 \end{array} \right]_6$ $-Si(CH_3)_2(C_6H_5)_2$	2942	1.0211	404	1.4946	12	450-500°

used for the separation of siloxanes from reaction mixtures and the arylene polymer exhibited better selectivity for aromatic substances.

The properties and physical characteristics of siloxane-carborane polymers for the separation of high boiling compounds have been described by Luskina *et al.*¹⁴⁸. The compounds containing trifluoropropyl, methyl and phenyl groups are shown in Table XVIII.

A work on the selection of stationary phases¹⁵⁵ has reported retention volumes relative to hexane at 80° of 2,4-dimethylpentane, cyclohexane, cyclohexene, benzene, methyl ethyl ketone, isopropanol, *tert.*-butanol and ethanol on a large number of stationary phases including several Russian polysiloxanes, *i.e.* PMS-100, PMS-500, NPS-50, NPS-100, PFMS-4 and KhS-2-1.

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17. SUMMARY

Polysiloxanes since the development of gas chromatography have continued to find use as the major group of stationary phases despite more stringent requirements associated with improved detectors, combination with mass spectrometry and the introduction of a seemingly endless number of alternative materials.

While siloxane stationary phases were formerly industrial products a wide range of specialty products have become available. These are described with regard to structure and or chemical composition and polar character together with the two areas of increasing acceptance which concern the highly polar cyanoalkyl derivatives for use with fatty acids and other naturally occurring products and the relatively low polarity carborane-polysiloxane copolymers for high temperature operation.

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NOTE ADDED IN PROOF

Since the preparation of this work, the three Dexsil phases have become available from the R.F.R. Corporation, Rhode Island, U.S.A.¹⁸⁷, while three alternative materials have been offered by Alltech Association, Arlington Heights, Ill., U.S.A. as Alltech PS-300, PS-400 and PS-410¹⁸⁸. These are described as phenyl siloxanes and have lower temperature limits. The McReynolds constants show that the materials have the same general polarity as the appropriate Dexsil and the phenyl substitutions would appear to be about 15%, 25% and 45%, respectively.