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POLYSILOXANE STATIONARY PHASES

J. K. HAKEN

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

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CONTENTS

1. INTRODUCTION

Since JAMES AND MARTIN[1] employed a commercially available silicone as the stationary phase in their pioneering gas chromatographic works a considerable number of related materials frequently of unknown properties and composition have been reported. Developments frequently occurred independently and while some early attempts were made to characterise stationary phases using separation factors increasingly successful procedures for general application have since been reported by BROWN[2], ROHRSCHNEIDER[3–5] and most recently by MCREYNOLDS[6].

The vast majority of stationary phases were not developed for use in gas chromatography but were materials of commercial quality provided for some other purpose. It has become apparent that many of the materials are produced to specifications completely suitable for their prime purpose but with composition variations unacceptable for a pure compound or for gas chromatography where the column process is directly related to the chemical nature of the stationary phase used[7]. Similarly the presence of organic additives may lead to thermal instability, while fillers may contribute to the column process and low-molecular-weight homologs will produce excessive column bleed.

Polysiloxanes of stated composition are now offered specifically as stationary phases by the Ohio Valley Specialty Company and as ROHRSCHNEIDER[4] and MCREYNOLDS constants[6] are available for the materials it is possible to consider the polar character of the phases in terms of their composition.

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PRESTON[7] has recently drawn attention to the excessively large number of materials that have been used as stationary phases in gas chromatography and has indicated certain redundancies concerning polysiloxanes while other repetitions have since become apparent[8].

PRESTON has shown the position of polysiloxanes as the major group of stationary phases by the partial tabulation of stationary phases[7] used in papers abstracted by The Preston Abstracting Service during 1968 and 1969. Approximately 300 different phases were reported and siloxanes cited in 20 or more reports are shown in Table 1, together with several other leading phases. Later data extracted from the same source material are also shown in Table 1.

TABLE 1

SILOXANE STATIONARY PHASES REPORTED DURING 1968 TO 1972

Stationary phase	*1968*	*1969*	*1970*	*1971*	*1972*[b]
SE-30	569	371	300	238	227
Apiezon L	[a]	147	[a]	[a]	[a]
PEG-20M	359	140	[a]	[a]	[a]
QF-1	215	131	120	98	57
DEGS	274	118	[a]	[a]	[a]
DC-200	161	68	63	48	25
XE-60	118	67	53	54	35
OV-1	40	60	67	74	48
OV-17	51	60	92	111	103
SF-96	61	38	29	9	21
Silicone JXR	[a]	25	24	9	10
SE-52	100	23	37	23	23
DC-11	[a]	22	17	13	3
EGSS-X	[a]	21	23	10	14
DC-550	41	20	18	14	11
OV-225	[a]	[a]	13	15	17
OV-210	[a]	[a]	6	13	14
OV-101	[a]	[a]	10	22	15
W-98	[a]	[a]	13	24	17
E-301	[a]	[a]	2	27	10
Other silicones	[a]	760	90	144	112
Other phases	[a]		1255	1244	836
Total citations	2744	2322	2186	2202	1598

[a] Not reported.
[b] January–September.

Siloxanes as stationary phases have been previously included in brief Eastern European reviews on silicones by WURST[9], SLADKOV[96], ROTZSCHE[97], and DE BRUYN[125] and also in part in a work describing the development of chemically bonded chromatographic supports[10]. The reviews describe the physical properties of the principal polysiloxane structures and provide information concerning Eastern European products not otherwise available but data from the Western World suffer from many minor errors.

The present work seeks to show some of the early applications of silicone materials as stationary phases and their development during the past two decades together with the procedures that have become available for indicating the relative polar character of the phases. Many of the phases that have been reported in the literature are tabulated with regard to their structure or chemical composition and polar character.

2. EARLY STUDIES

The work of JAMES AND MARTIN[1] in 1952 demonstrated the development of gas–liquid partition chromatography with the separation of low-molecular-weight isomeric fatty acids, *i.e.* acetic to dodecanoic acids. Acid-washed Celite 545 was coated with DC-550 silicone containing both 10% of stearic and phosphoric acids and packed to form a 4-ft. column operated at 100° and 137° by immersion in a boiling vapour jacket. Both integral and differential chromatograms were produced and the improvements in resolution with the addition of stearic acid and stearic and phosphoric acids were clearly evident. The stearic acid present in large excess was suggested to compete with the volatile fatty acids in the formation of association complexes and reduce the partial pressure of the acids thus rendering the distribution between the two phases almost independent of concentration.

With the silicone–stearic acid column a regular increase of retention volume with chain length was found to occur with the straight-chain acids, the retention volume at 100° increasing by a factor of approximately 2.2 for each increase in chain length of a methylene group, formic acid showing the maximum deviation. At 137° the increase for a methylene group was shown to be 1.9.

Silicone High Vacuum Grease, *i.e.* DC-11, appears to have been first used as a stationary phase by CROPPER AND HEYWOOD[11] in extending the work of JAMES AND MARTIN[1] to allow separation of the C_{12}–C_{22} fatty acids as their methyl esters. With the grease a higher column temperature, *i.e.* 230°, was possible and with a 3-ft. column elution of methyl C_{22} was achieved in 50 min; the resolution of the esters was, however, poor.

The fatty ester separations were soon found[12] to be greatly influenced by the silicone grease used. Treatment of the grease with ethyl acetate followed by the addition of ethanol and decantation of solvent removed an oily fraction leaving a residual grease possessing satisfactory separatory properties.

The variability of performance of Silicone High Vacuum Grease was also observed by CASON AND MILLER[13], who recommended "curing" or conditioning before use by heating for at least 50 h at temperatures of 325–335° in a slow stream of nitrogen to remove volatile constituents. The conditioned grease was reported to be stable indefinitely when used at temperatures below 275°. At temperatures near 300° a slow decrease in retention time was observed but 2000 h of operation were claimed before resolution was impaired.

KEPLER *et al.*[14] evaluated stationary phases including silicone oils DC-550 and DC-703, High Vacuum Grease DC-11 and a silicone rubber for use at 200°. Of the silicone materials it was observed that both oils showed significant bleed while the grease and rubber were shown to be more suitable. A subsequent paper by the same workers[15] included Silicone Elastomers DC-123 and DC-152 and Silastic DC-132 and DC-156 compounds all being recommended for use at 215°.

HUNTER *et al.*[16] reported the first application of gas chromatography to amino acids in 1956. Isoleucine and leucine were oxidised with ninhydrin and the volatile aldehydes formed were resolved on a column of Celite coated with silicone oil. Soon after BAYER *et al.*[17] separated the methyl esters of glutamic acid, leucine, methionine, norleucine, norvaline, phenylalanine, sarcosine and valine on a silicone oil sodium caproate column. BAYER[18] later extended this work and described the effectiveness of several metal caproates in reducing the peak tailing that was experienced.

Considering the low volatility of sterols a high column temperature, *i.e.* 287°, was used by BEERTHUIS AND RECOURT to achieve separation[19]. The stationary phase was the residue from a molecular distillation of MS-550 silicone carried out at 200° and 2 μ pressure coated onto Celite 545 which had been acid washed and treated with dichlorodimethyl silane.

3. PHASE CHARACTERISATION

While much of the early endeavour was directed towards obtaining materials of suitable thermal stability it was appreciated that the separations achieved were dependent on solute–solvent interactions. Polarity, chemical interaction, hydrogen bonding and other cohesive forces all affecting the selectivity of the stationary phase.

The earliest attempts of indicating selectivity employed separation factors, the ratio of retention measurements of two members of a homologous series[1] or of two isomers[20,21] being determined on the various phases, the stationary material showing the greatest separation factors for a particular situation being preferred.

KEULEMANS and his co-workers[22] observed differences in the separating characteristics of a hydrocarbon oil which is non-polar with the attractive interaction energy solely of the London type and of non-paraffins which contain polar or polarisable functional groups. The interaction of these groups present in the sample and stationary phase was named the "polarity of the liquid phase".

ROHRSCHNEIDER[3,23] presented a classification of stationary phases that considered the concept of "polarity". This "polarity" (P) considers the difference between a polar and a non-polar phase and is the difference between the logarithms of the ratio of retention measurements of butadiene and n-butane on a polar and a non-polar stationary phase as shown in eqn. 1.

$$P_a = a\left(\log \frac{V_a(\text{butadiene})}{V_a(n\text{-butane})} - \log \frac{V_b(\text{butadiene})}{V_b(n\text{-butane})}\right) \tag{1}$$

To allow the assignment of values to the polarity of the phases, the non-polar material squalane is assigned polarity $P = 0$ while oxydipropionitrile is assigned as $P = 100$. a is a constant, *i.e.* 144, calculated to provide a value of $P = 100$ for oxydipropionitrile.

A similar scheme has been proposed by BAYER[24], who used the ratio of retentions of two members of a homologous series corrected to identical boiling point as a selectivity coefficient. While of some value, the characterisation of stationary phases using a single factor, *i.e.* such as P, can only be a partial solution as the intermolecular interactions differ in a variety of ways.

BROWN[8] described the classification of stationary phases as electron donors or acceptors by the measurement of retention volumes of three selected compounds, *i.e.* one non-polar, one an acceptor and one a donor, on each phase. Using compounds of these types it is possible to determine the relative polarity of the phase as well as its donor or acceptor properties. If $V_{R(1)}$, $V_{R(2)}$ and $V_{R(3)}$ are the retention values on three stationary phases under standard conditions, a retention fraction (R) may be calculated for each phase as shown in eqn. 2.

$$F_{R(1)} = \frac{V_{R(1)}}{V_{R(1)} + V_{R(2)} + V_{R(3)}} \tag{2}$$

ROHRSCHNEIDER[4] proposed a scheme for the characterisation of stationary phases based on the additivity of intermolecular forces, it being essentially the representation of the retention data as Kovats indices related to retention on a non-polar standard phase.

The retention of a substance A on a non-polar phase may be shown as I_{NP}(A) and on a polar phase by a greater value I_P(A). The index difference ΔI(A) is shown by eqn. 3.

$$I_P(\mathrm{A}) = I_{NP}(\mathrm{A}) + \Delta I(\mathrm{A}) \tag{3}$$

As we assume dispersion or London forces to be non-polar and induction, orientation, charge transfer and hydrogen bonding forces to be polar then it appears that the non-polar forces can be substantially eliminated by comparison of retention indices with those obtained on a non-polar phase such as squalane.

ROHRSCHNEIDER attempted to describe index differences in terms of three products of three polarity terms but found it necessary to consider five terms, as shown in eqn. 4.

$$\Delta I = ax + by + cz + du + es \tag{4}$$

To determine data characteristic of the substances and the stationary phases 660 index differences of thirty substances on twenty-two phases were used. For five substances on one column there are five equations with twenty-five unknown substances and five unknown column polarities each corresponding to eqn. 4.

For the five standard substances arbitrary values as shown below were used as substance polarities.

	a	b	c	d	e
Benzene	100	0	0	0	0
Ethanol	0	100	0	0	0
2-Butanone	0	0	100	0	0
Nitromethane	0	0	0	100	0
Pyridine	0	0	0	0	100

and for every phase $x = \frac{\Delta I}{100}$ (benzene)

$y = \frac{\Delta I}{100}$ (ethanol)

$z = \frac{\Delta I}{100}$ (2-butanone)

$u = \frac{\Delta I}{100}$ (nitromethane)

$s = \frac{\Delta I}{100}$ (pyridine)

TABLE 2

CHARACTERISTICS OF POLYSILOXANE STATIONARY PHASES

Suppliers: A = Ohio Valley Specialty Chemical Co., Ohio, U.S.A.; B = Dow Corning Corp., Mich., U.S.A.; C = Supelco Inc., Pa., U.S.A.; D = General Electric Co., N.Y., U.S.A.; E = Midlands Silicones Ltd., Wales, Great Britain; F = Bayer Farbenfabriken AG, G.F.R.; G = I.C.I. Ltd., Great Britain; H = May and Baker Ltd., Dagenham, Great Britain; I = VEB Chemiewerk, Nunchritz, D.D.R.; J = Russian manufacture; K = East Bohemian Chemical Co., "Synthesia", Kolin, Czechoslovakia; L = Perkin-Elmer Corporation, Conn., U.S.A. obsolete materials; M = Pierce Chemical Company, Ill., U.S.A. manufacturer D; N = Union Carbide Corp., N.Y., U.S.A.; O = Applied Science Laboratories, Pa., U.S.A.; P = S. V. Lebedev VNIISK Institute, Leningrad, U.S.S.R.; Q = Rhone-

Name	*Substituent*	*Nominal viscosity*	*Physical properties*	*Polarity*
Methyl fluids				
OV-101	methyl	1200 cS	M.W. 30,000	13.0(a)
DC-200/MS-200	methyl	50.0–100,000 cS	sp. gr. 0.97 (25°)	13.0(a)
Perkin-Elmer Column C	(DC-200)	packed column		13.0(a)
SF-96	methyl	50.0–100,000 cS		13.0(a)
L-45	methyl	50.0–100,000 cS		13.0(a)
Bayer M	methyl	50.0–300,000 cS		13.0(a)
F-111	methyl	50.0–100,000 cS		13.0(a)
L-46	methyl	50.0–100,000 cS		13.0(a)
SP-2100	methyl	600 cS		13.0(a)
Embaphase Oil	methyl	300–400 cS	sp. gr. 0.970-3 (20°)	13.0(a)
Silicone Oil 81705	methyl			
DC-220	methyl	44 cS		
DC-330	methyl	50 cS		
NM1-50	methyl	50 cS		
NM1-200	methyl	200 cS		
PMS-100	methyl	100 cS	M.W. 5,000 sp. gr. 0.97 (20°)	9.0(a)(b)
PMS-200	methyl	200 cS	sp. gr. 0.97 (20°)	
PMS-400	methyl	400 cS	M.W. 780 sp. gr. 0.98 (20°)	9.0(a)(b)
PMS-1000	methyl			
PMS-30,000	methyl	30,000 cS		
Lukooil M-50	methyl	50 cS		
Lukooil M-100	methyl	100 cS		
Lukooil M-200	methyl	200 cS		
Lukooil M-500	methyl	500 cS		
Methyl gums				
OV-1	methyl	gum	M.W. 3.0–4.0 × 10^6	13.0(a)
SE-30	methyl	gum	M.W. 1.0–2.5 × 10^6	13.0(a)
SE-30 G.C	methyl	gum	M.W. 1.0–2.5 × 10^6	13.0(a)
SE-30 Ultraphase	methyl	gum	M.W. 1.0–2.5 × 10^6	13.0(a)
Perkin-Elmer column Z	methyl	packed column	M.W. 1.0–2.5 × 10^6	13.0(a)
E-301	methyl	gum	M.W. 1.0–2.5 × 10^6	13.0(a)
DC-410	methyl	gum		
Silastic 401	methyl	gum		
DC-401	methyl	gum		
Silastic 132	methyl	gum		
Silastic 152	methyl	gum		
W-95	methyl	gum		
W-950	methyl	gum	sp. gr. 0.96	
MS-2211	methyl	gum (10^{12}–10^{14} cS)		

Poulenc, France; R = Wacker Chemie GmbH, G.F.R.; S = Bevaloid Aust. Pty. Ltd., Sydney, Australia; T = Institute for Silicone & Fluorocarbon Chemistry, Radebeul, D.D.R.; U = Lachat Chem. Inc. Ill., U.S.A; V = Analbs Inc., Conn., U.S.A.; W = Olin Corporation, Conn., U.S.A.; X = Japanese manufacture; Y = obsolete material; Z = Analabs Inc. Conn., U.S.A., manufacturer Hewlett-Packard, Pa., U.S.A.; AA = Analabs Inc., Conn., U.S.A., manufacturer N. Polarity: (a) = Rohrschneider polarity. butadiene/*n*-butane (ref. 3); (b) = Rohrschneider polarity. benzene/cyclohexane (ref. 97); (c) = Bayer selectivity (ref. 43).

Rohrschneider constant (ref. 4)					*McReynolds constant (ref. 6)*						*Supplier*	*Ref.*
X	*Y*	*Z*	*U*	*S*	*X'*	*Y'*	*Z'*	*U'*	*S'*	*H*		
0.16	0.20	0.50	0.85	0.48	17	57	45	67	43	33	A	
					16	57	45	66	43	33	B, E	
					16	57	45	66	43	33	L	
					12	53	42	61	37	31	D	
					16	56	65	41	33	33	N	
											F	
											G	
					16	56	44	65	41	33	N	
					17	57	45	67	43	33	C	88
					14	57	46	67	43	33	H	
											D	89
											B	
					13	51	42	61	36	31	B	
											I	9
											I	9
					16	56	44	65	43	33	J	96
											J	99
											J	100
											J	9
											J	101
											K	9
											K	
											K	
											K	
0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32	A	
0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32	D	
0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32	D	
0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32	M	
0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32	L	
0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32	G	
					18	57	47	68	44	34	B	
					17	58	47	66	46	34	B	
					17	58	47	66	46	34	B	
											B	
											B	15
											N	
											N	
					15	56	44	66	40	32	E, Y	

(Continued on p. 426)

TABLE 2 *(continued)*

Name	*Substituent*	*Nominal viscosity*	*Physical properties*	*Polarity*
E-300	methyl	gum (10^{12}–10^{14} cS)		
DC-400	methyl	gum (10^{12}–10^{14} cS)		
SP-70	methyl	gum		
OD-1	methyl	gum		
Silicone M-430	methyl	gum		
Silicone JXR	methyl	gum		13.0(a)
G-7100	methyl	gum		
NG-100	methyl	gum		
Gi 7000 FF	methyl	gum		
MO 2000,000	methyl	gum		
KS 1014	methyl	gum		
LC-1	methyl	gum		
Lukopren M50	methyl	gum		
SKT	methyl	gum	M.W. 4.0–6.5 × 10^5	6.8(a)
SKSV(T)	methyl	gum		8.0(a)
SE-31	methyl vinyl (1%)	gum		
Silastic 430	methyl vinyl (1%)	gum		
DC-430	methyl vinyl (1%)	gum		
E-302	methyl vinyl (1%)	gum		
SE-33	methyl vinyl (1%)	gum		
E-303	methyl vinyl (1%)	gum		
W-96	methyl vinyl (1%)	gum	sp. gr. 0.96	
W-98	methyl vinyl (1%)	gum	sp. gr. 0.98	
W-960	methyl vinyl (1%)	gum	sp. gr. 0.96	
W-982	methyl vinyl (0.15%)	gum		
SKTV	methyl vinyl (0.04%)	gum	M.W. 4.0–6.5 × 10^5 sp. gr. 0.975	6–8(a)
SKTV-1	methyl vinyl (0.18%)	gum	M.W. 4.0–6.5 × 10^5 sp. gr. 0.975	6–8(a)
Rhodorsil Comme 785	methyl vinyl	gum		
Silicone Rubber Polymer	methyl vinyl	gum		
Lukopren G 1000	methyl vinyl	gum		
Gi 7300 F	methyl vinyl	gum		
NG 300	methyl vinyl	gum		
DC-11	methyl (10% silica)	grease		
Hi Vac Grease	methyl (10% silica)	grease		
Perkin-Elmer Column O	methyl (10% silica)	grease		
Hi Vac Grease Extract	methyl (10% silica)	fluid	12,500 cS	
DC-730	ethyl	fluid		
VKZh-94	ethyl	16–33 cS (50°)	M.W. 780 sp. gr. 0.949 (20°)	9(b)
SKT(e)	ethyl vinyl (0.05%)			5.0(a)
S-2116	30% stearoyl	m.p. 62°	M.W. 4.0–6.5 × 10^5	
F-157	stearyl ester	10.0 cS at 50° m.p. 25°		
DC-230	stearyl	1200–1600 cS		
Phenyl substitution				
OV-3	10% phenyl			
OV-7	20% phenyl			
XE-61	33% phenyl			
OV-61	33% phenyl			
OV-11	35% phenyl			

Rohrschneider constant (ref. 4)					*McReynolds constant (ref. 6)*						*Supplier*	*Ref.*
X	*Y*	*Z*	*U*	*S*	*X'*	*Y'*	*Z'*	*U'*	*S'*	*H*		
					15	56	44	66	40	32	G	
					15	56	44	66	40	32	B	
											C,Y	
											V	
											G	90
0.16	0.20	0.50	0.85	0.48	16	55	44	65	42	32	O	
											I	9
											I	9
											T	97
											T	97
											N	97
											U	104
											K	
											P	
											P	
					16	54	45	65	43	32	D	
					16	54	45	65	43	32	B	
					16	54	45	65	43	32	B	
					16	54	45	65	43	32	G	
					17	54	45	67	42	33	D	
					17	54	45	67	42	33	B	
											N	
											N	
											N	
					16	55	45	66	42	33	N	
											P	30
											P	30
											Q	9
											R	9
											K	9
											T	97
											I	97
					17	86	48	69	56	36	B	119
1.05	1.50	1.61	2.51	1.90							B	
					17	86	48	69	56	36	L	
0.16	0.20	0.50	0.85	0.48							B	12
											B	
											P	96
											P	30
0.23	0.50	0.48	0.75	0.56							S	
											B	
											B	
0.42	0.81	0.85	1.52	0.89	44	86	81	124	88	55	A	
0.70	1.12	1.19	1.98	1.34	69	113	111	171	128	77	A	
0.98	1.30	1.57	2.38	1.85							D	37, 38
											A	
1.13	1.57	1.69	2.66	1.95	102	142	145	219	178	100	A	

(Continued on p. 428)

TABLE 2 *(continued)*

Name	*Substituent*	*Nominal viscosity*	*Physical properties*	*Polarity*
OV-17	50% phenyl	1500 cS	M.W. 30,000	
OV-22	60% phenyl			
OV-25	75% phenyl	almost gum	M.W. 30,000	
85% Phenyl	85% phenyl	M.P. 135–165°		
SP-2250	50% phenyl			
DC-510	5% phenyl	50–1000 cS	sp. gr. 1.00 (25°)	
DC-550	25% phenyl	100–150 cS	sp. gr. 1.04 (25°)	
DC-555	low phenyl (cyclics)	(see text)		
		10–30 cS	sp. gr. 1.06 (25°)	
DC-556	10% phenyl	15–30 cS		
DC-701	phenyl	10–15 cS	sp. gr. 1.03 (25°)	
DC-702	25% phenyl	(see text) 45 cS		
DC-703	25% phenyl	(see text) 55 cS		
DC-704	50% phenyl	(see text) 39 cS		
OE-4008	50% phenyl	(see text)	sp. gr. 1.066 (20°)	2.3(c)
DC-705	62.5% phenyl	(see text) 175 cS		
OE-4007	62.5% phenyl	(see text)	sp. gr. 1.095 (20°)	2.7(c)
DC-710	50% phenyl	475-525 cS	(M.W. 570)	
			sp. gr. 1.11 (25°)	3.1(c)
OE-4006	75% phenyl	(see text)		
OE-4011				
Silastic 123	phenyl	gum		
NM3-200	3.3% phenyl			
NH4-500	25.0% phenyl			
NM5-500	35.0% phenyl			
FM-6	low phenyl			
PN-200	medium phenyl			
AR-200	25% phenyl	200 cS	sp. gr. 1.04 (25°)	
SE-52	5% phenyl	gum		12.0(a)
E-350	5% phenyl	gum		
SP-392	55% phenyl			
PHSi 191-43	40% phenyl		b.p. 245–275°	
			(5 × 10^{-5} mm Hg)	
287-149-243	20% phenyl			
287-149-244	35% phenyl			
Lukooil MF	50% diphenyl	(see text)		
Supolimer 2	high phenyl			
SKTF-100	phenyl		sp. gr. 1.13 (20°)	36.0(a)
SKTA-1	phenyl		sp. gr. 1.09 (20°)	21.0(a)
PFMS-2	low phenyl			
PFMS-4	50% phenyl	500–1000 cS	M.W. 1500	24.0(a)(b)
PFMS-6	high phenyl	45.0 cS (150°)	M.W. 2000	33.0(a)(b)
SE-54	5% phenyl 1% vinyl	gum		
E-351	5% phenyl 1% vinyl	gum		
SKTFV-803	methyl, phenyl	gum	M.W. 5.0–7.5 × 10^5	
	vinyl (0.15%)		sp. gr. 0.975 (20°)	10.0(a)
SKTNFT-50	unknown			15.0(a)
Gi 7500F	methyl phenyl	gum		
	vinyl			
X 525	unknown 0.1			
L 525	unknown 0.1			
SR-119	unknown resin			
Chlorophenyl substitution				
F-61	11% *p*-chlorophenyl	500 cS		

Rohrschneider constant (ref. 4)					*McReynolds constant (ref. 6)*						*Supplier*	*Ref.*
X	*Y*	*Z*	*U*	*S*	*X'*	*Y'*	*Z'*	*U'*	*S'*	*H*		
1.30	1.66	1.79	2.83	2.47	119	158	162	243	202	112	A	
1.58	1.80	2.04	3.27	2.59	160	188	191	283	253	133	A	102
1.76	2.00	2.15	3.34	2.81	178	204	208	305	280	144	A	
1.88	2.33	2.15	4.73	3.04							A	33–35
					119	158	162	243	203	112	C	
					25	65	60	89	57	42	B,E	
					74	116	117	178	135	81	B,E,Y	
											B,E	
					37	77	80	118	79	53	B,Y	
					77	124	126	189	142	90	B	
					76	123	126	189	140	89	B	
											B	
											T	
											B	
											T	
1.05	1.50	1.61	2.51	1.90	107	149	153	228	190	170	B,E,Y	
											T	103
											T	103
											B	15
											I	9
											I	9
											I	9
											J	9
											F	9
											R	9
					32	72	65	98	67	44	D	
					32	72	65	98	67	44	I	
1.37	1.73	1.87	2.85	2.23	133	169	176	258	219	123	C	
											D	91, 92
											D	93
											D	93
											K	9
											J	9
											P	
											P	
											J	105
											J	96
											J	96
					33	72	66	99	67	46	D	
					33	72	66	99	67	46	I	
											P	30
											P	30
											T	97
											Z	
											AA	
					166	238	221	314	299	175	D	
0.31	0.49	0.82	1.08	0.83							B	

(Continued on p. 430)

TABLE 2 *(continued)*

Name	*Substituent*	*Nominal viscosity*	*Physical properties*	*Polarity*
F-60	11% *p*-chlorophenyl	63 cS		
DC-560	11% *p*-chlorophenyl	75 cS		
SP-400	11% *p*-chlorophenyl			
F-4050	3,5-dichlorophenyl	(see text)		
Lukooil X-100	4.1% 3,4,5-trichlorophenyl, 4.1% trisilyl ether		sp. gr. 1.074 (20°)	
Lukooil X-200	5.5% 3,4,5-trichlorophenyl, 5.5% trisilyl ether		sp. gr. 1.121 (20°)	
Lukooil X-600	8.3% 3,4,5-trichlorophenyl, 8.3% trisilyl ether		sp. gr. 1.155 (20°)	
Versilube F-50	see text	50 cS		
Wacker CR	chlorophenyl	20–100 cS		
Chlorosilicone CHS-1				
(kk) S-2-1	chlorophenyl			
(kk) S-2-1-VV	chlorophenyl			
Cyanoalkyl substitution				
XE-60	25% cyanoethyl			52.0(a)
XF-1125	25% cyanoethyl			52.0(a)
AN-600	25% cyanoethyl	gum		
OE-4910	cyanoethyl			
OV-225	25% cyanopropyl 25% phenyl			
Silar 5CP	cyanoalkyl phenyl			
XF-1105	5% cyanoethyl			
XF-1112	12% cyanoethyl			
XF-1150	50% cyanoethyl			
238-149-99	50% cyanoethyl			
238-149-239	50% cyanoethyl			
287-149-251	8% cyanoethyl			
287-149-203	20% cyanoethyl			
287-149-300	65% cyanoethyl			
XF-1165	65% cyanoethyl			
NPS-50	25% cyanoethyl	350 cS	M.W. 1200	37.0(b)
NPS-100	50% cyanoethyl	1340 cS	M.W. 1290	62.0(b)
OE-4178	37.5% cyanopropyl			
NSKT-25	12.5% cyanopropyl			38 (a)
NSKT-33	16.5% cyanopropyl			43.0(a)
NSKT-X	16.5% cyanopropyl			43.0(a)
NSKT-50	25% cyanopropyl	350 cS	M.W. 1200	53 (a)
NSKT-100	50.0% cyanopropyl	1340 cS	M.W. 1300	71.2(a)
Fluoroalkyl substitution				
QF-1	50% trifluoropropyl		300, 1,000, 10,000 cS	
FS-1265	50% trifluoropropyl		300, 1,000, 10,000 cS	
QF-1-0065	50% trifluoropropyl		300, 1,000, 10,000 cS	
OV-210	50% trifluoropropyl			
SP-2401	50% trifluoropropyl	700 cS		
LSX-3-0295	50% trifluoropropyl 1% vinyl	gum		
Silastic LS420	50% trifluoropropyl 1% vinyl	gum		

Rohrschneider constant (ref. 4)					*McReynolds constant (ref. 6)*						*Supplier*	*Ref.*
X	*Y*	*Z*	*U*	*S*	*X'*	*Y'*	*Z'*	*U'*	*S'*	*H*		
0.33	0.49	0.82	1.08	0.83							B	
0.33	0.49	0.82	1.08	0.83	32	72	70	100	68	49	B	
0.33	0.49	0.82	1.08	0.83	32	72	70	100	68	49	C	103
											B	
											K	
											K	
											K	
					19	57	48	69	47	36	D	
											R	9
											J	107
											P	
											P	
2.08	3.85	3.62	5.33	3.45	204	381	340	493	367	289	D	
2.08	3.85	3.62	5.33	3.45	204	381	340	493	367	289	D	96
											V	
											T	97
2.17	3.20	3.33	5.16	3.69	228	369	338	492	386	282	A	
					319	495	446	637	531	379	O	124
											D	
											D	27
3.18	5.33	3.81	7.02	5.04	308	520	470	669	528	401	D	
											D	46
											D	
											D	
											D	
											D	
											D	
											J	96
											J	96
											T	9
											P	
											P	30
											P	30
											P	
											P	30
1.41	2.13	3.55	4.73	3.01	144	233	355	463	305	203	B	
1.41	2.13	3.55	4.73	3.01	144	233	355	463	305	203	B	
1.41	2.13	3.55	4.73	3.04	144	233	355	463	305	203	B	
1.41	2.13	3.55	4.73	3.04	146	238	355	468	310	206	A	
1.41	2.13	3.55	4.73	3.04	145	238	355	468	310	206	C	
					152	241	366	479	319	208	B	
					152	241	366	479	319	208	B	

(Continued on p. 432)

TABLE 2 *(continued)*

Name	*Substituent*	*Nominal viscosity*	*Physical properties*	*Polarity*
FS-5	trifluoropropyl			
FS-16	trifluoropropyl	35 cS	M.W. 980 sp. gr. 1.21 (20°)	26.0(a)
FS-56	trifluoropropyl			
FS-169	trifluoropropyl	55 cS	M.W. 1610 sp. gr. 1.11 (20°)	17.0(a)
FS-303	trifluoropropyl	1000 cS	M.W. 2420 sp. gr. 1.33 (20°)	42.0(a)
SKTFT-25	12.5% trifluoropropyl		sp. gr. 1.07 (20°)	15.0(a)
SKTFT-50	25% trifluoropropyl		M.W. 100,000 sp. gr. 1.15 (20°)	21.0(a)
SKTFT-50 X	25% trifluoropropyl		M.W. 100,000 sp. gr. 1.17 (20°)	21.0(a)
SKTFT-75	37.5% trifluoropropyl		sp. gr. 1.24 (20°)	35.0(a)
SKTFT-100	50% trifluoropropyl	gum	M.W. 100,000 sp. gr. 1.33 (20°)	35.0(a)
NFS-100	50% trifluoropropyl	gum	M.W. 100,000 sp. gr. 1.33 (20°)	35.0(a)
Fluorosilicone 88				
Lukooil-X				
Lukooil-H				
Organosilicone polymers				
EGSS-X	low methyl			
EGSS-Y	medium methyl			
EGSP-A	low phenyl			
EGSP-Z	medium phenyl			
ECNSS-S	low cyanoethyl			
ECNSS-M	medium cyanoethyl			
Copolymer 3	(see text)		M.W. 2,500	
Carborane–siloxane polymer				
Dexsil 300 GC	carborane–siloxane	m.p. 30–38°	M.W. 16,000–20,000	
Miscellaneous				
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/Cl Silicone				
Silicone FM-1322		300 cS		
Silicone MS-4				
Silicone KF-54				
Silicone Oil 2/300				
Silicone 5				
Silicone Oil 580				
Silicone M 500				

Rohrschneider constant (ref. 4)					*McReynolds constant (ref. 6)*						*Supplier*	*Ref.*
X	*Y*	*Z*	*U*	*S*	*X'*	*Y'*	*Z'*	*U'*	*S'*	*H*		
											J	9
											J	9
											J	9
											J	9
											J	
											P	
											P	
											P	30
											P	
											P	30
											P	30
												125
											K	
											K	
					484	710	585	831	778	566	O	58
					391	597	493	693	661	469	O	58
											O	58
					308	474	399	548	549	373	O	58
											O	58
3.96	6.01	5.39	—	6.50	421	690	581	803	732	548	O	58
											J	98
0.43	0.64	1.11	1.51	1.01							W	87
												1
												17
												17
												94
												95
											J	110
											J	111
											J	112
											X	113
											J	117
											J	114
												115
												118

The five substance polarities can be defined as measures of: orientation forces (factor *c*), charge transfer forces, *i.e.* donor (factor *a*) and acceptor (factor *d*), and hydrogen bonding, *i.e.* hydrogen donor (factor *b*) and hydrogen acceptor (factor *e*).

McReynolds[6] has recommended variation of some of the standard substances suggested by Rohrschneider, *viz.* *n*-butanol, 2-pentanone and nitropropane replacing ethanol, 2-butanone and nitroethane, respectively. These particular changes are of considerable practical value as on polar phases the retention times of the lower homologs are very small. The addition of 2-methyl-2-pentanol improved the prediction of retention of branched-chain compounds, particularly of alcohols. For each phase $X' = \Delta I$ (benzene), $Y' = \Delta I$ (*n*-butanol), $Z' = \Delta I$ (2-pentanone), $U' = \Delta I$ (nitropropane), $S' = \Delta I$ (pyridine), and $H = \Delta I$ (2-methyl-2-pentanol).

The stationary phase constants proposed by Rohrschneider[4] and by McReynolds[6] have appeared extensively in the literature of the American organisation Supelco Incorporated. The schemes, although far from ideal, provide a semi-quantitative basis for characterising stationary phases and data for the polysiloxanes, as shown in Table 2.

A third scheme for the classification of stationary phases has been proposed by Rohrschneider[5] and is offered as an alternative to his earlier scheme[4]. The stationary phases are characterised by the logarithm of six retention ratios of selected solutes *i.e.* decane, benzene, nitromethane, ethanol, 2-butanone and pyridine, compared with *n*-octane. There is probably little value in the continued introduction of such schemes which are all essentially similar until a more vigorous evaluation of their general applicability becomes available.

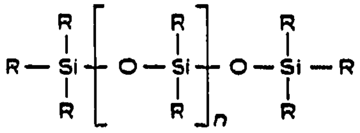
Weiner and his co-workers have proposed the use of factor analysis[120] for the selection of preferred stationary phases by the analysis of the retention indices for a large number of compounds on a variety of stationary phases. The minimum number of terms in the summation shown in eqn. 4 is chosen explicitly rather than by the arbitrary selection of 4, or 5, or 6 .. 8 terms. The number of factors are dependent on the systems considered as paraffinic solutes with stationary phases of similar composition can obviously be described by an equation with fewer terms than a set of data of mixed functional classes on polar and non-polar phases. The procedure has currently been examined with alcohols[121] and some homologous esters[122] but like the schemes of Rohrschneider the developments are embryonic.

4. DIMETHYL POLYSILOXANES

From Table 1 it is evident that these low polarity simple polysiloxanes, where separation is largely dependent on boiling point have continued to occupy a major position as stationary phases. The same data also indicate the international acceptance of materials of American or British manufacture although comparable materials of local manufacture are available in the European countries. A large number of proprietary products have been used as stationary phases and are shown in Table 2.

The properties of siloxane polymers result from their partly inorganic and partly organic structure. Stability and other properties characteristic of their completely inorganic homologs are substantially retained while the organic groups in the molecule may be varied to provide compounds with a wide range of properties.

The polymethyl siloxanes have the general formula



$$R-\underset{R}{\overset{R}{Si}}-\left[O-\underset{R}{\overset{R}{Si}}\right]_n-O-\underset{R}{\overset{R}{Si}}-R$$

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 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 the relationship shown in eqn. 5 is applicable to fluids of average molecular weight greater than 2500 (ref. 25).

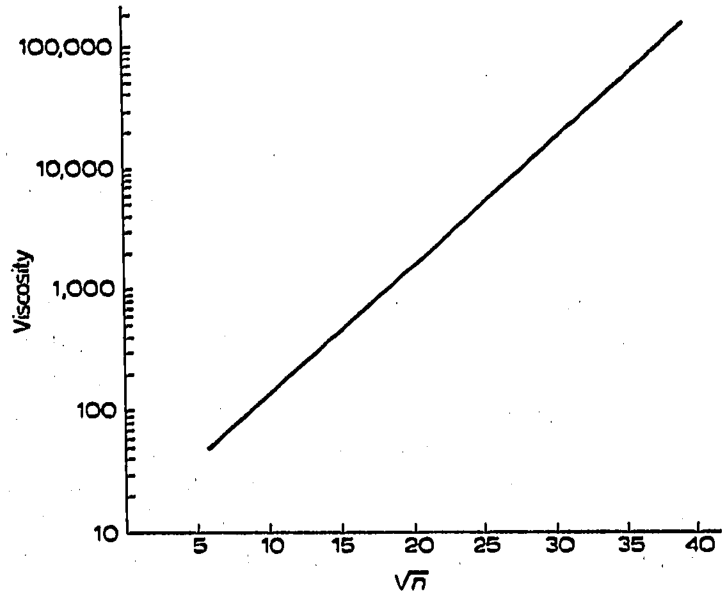


Fig. 1. Relationship between viscosity in centistokes at 25° and molecular weight of dimethyl polysiloxanes, where n is the number of dimethyl polysiloxane units.

$$\log(\text{visc. in cS}) = 1 + 0.0123\ (\text{M.W.})^{\frac{1}{2}} \tag{5}$$

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

Fluids of very low viscosity are unsuitable for use in gas chromatography 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.

The bond energy of the Si–O bond 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 half-lives of substituent groups in air at 250° calculated[26] from weight loss and silicon content values determined before and after exposure for 100 h are shown in Table 3.

TABLE 3

THERMAL LIFE OF VARIOUS SUBSTITUENTS ON SILICON

Group covalently bonded to Si	*Approximate half-life*[a] *at 250° (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

[a] Time at which one-half of the groups are replaced by $\mathrm{O}_{1/2}$.

Baumann *et al.*[27] considered gas chromatographic 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 cS oil, at −60°.

More recently **Merritt** *et al.*[28] 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 publication 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° (ref. 29). It is apparent that a silicone fluid rather than a gum may have proved more suitable[9].

TABLE 4

LOW TEMPERATURE OPERATING LIMITS[27]

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

Dimethyl polysiloxanes containing small amounts of vinyl groups and capable of undergoing crosslinking with peroxide catalysts find industrial acceptance and have been used as stationary phases. The low concentration of polar vinyl groups which are not thermally stable is such that the phase constants are not affected (*cf.* OV-101 with SE-31 and SE-33).

High vacuum greases, elastomers and compounds frequently contain silica, often surface treated, in concentrations up to 10%. The effect of this addition is apparent in the Y and Y' phase constants (*cf.* OV-1 and DC-11). Elastomers which are substantially dimethyl polysiloxane *i.e.* Silastic 132 and 152, usually contain fillers, peroxides and other additives and are less satisfactory than a pure gum such as OV-1.

During recent years limited information has become available concerning some Russian produced polysiloxanes supplied by the S. V. Lebedev VNIISK Institute, Leningrad[30–32]. These materials have been evaluated by RUDENKO and his co-workers against SE-30, SE-52 and XE-60 and satisfactory performance, comparable bleed and ROHRSCHNEIDER relative polarity values indicate the materials to be as acceptable as the imported materials for use in gas chromatography. The data concerning the phases are shown in Table 2. It is apparent that several of the materials SKTE(K) (ethyl substitution), SKT and SKSV(K) have lower relative polarity values than imported dimethyl polysiloxane, *i.e.* SE-30 and are comparable to phases of the Apiezon type in performance while possessing greater thermal stability. The use of phases with other alkyl substitutents 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[33,34] and glycol ether derivatives[35].

5. PHENYL-SUBSTITUTED POLYSILOXANES

Since the use of DC-550 (25% phenyl substitution) by JAMES AND MARTIN[1] 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. Higher-molecular-weight gums or elastomers 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 percent level while the chain consists of a sequence of dimethyl siloxane and methylphenyl siloxane units although Lukooil MF consists of equal numbers of dimethyl and diphenyl siloxane units.

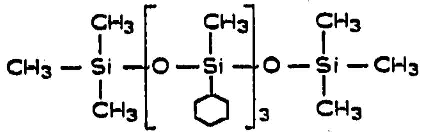
Several low-molecular-weight phenyl siloxanes of known structure are shown on p. 438.

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 Ohio Valley Company in the United States have in recent years[116] introduced a range of phenyl substituted polysiloxanes of stated composition specifically for use as stationary phases. With higher molecular weights the considerable thermal

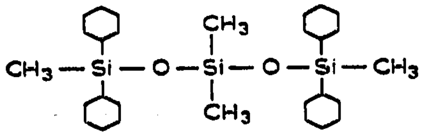
Nonamethyl - triphenylpentasiloxane

DC - 703



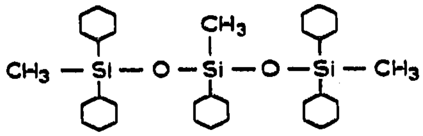
1,3,3,5 - Tetramethyl - 1,1,5,5 - tetraphenyltrisiloxane

DC - 704
OE - 4008



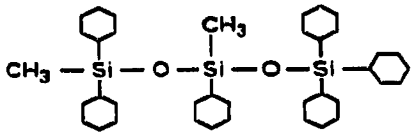
1,3,5 - Trimethyl - 1,1,3,5,5 - pentaphenyltrisiloxane

DC - 705
OE - 4007



1,3 - Dimethyl - hexaphenyltrisiloxane

OE - 4006



stability of the phenyl siloxanes may be utilised and OV-17 (50% phenyl) is recommended for use at temperatures to 375°. The Supelco organisation have introduced SP-2250[36] which is chemically identical to OV-17 but for which higher column efficiency, lower bleed and extended-life at elevated temperature are claimed.

A material of the same composition as an experimental phenyl phase XE-61 (33% phenyl), which was described by Ikekawa *et al.*[37] for the separation of sterols with comparative studies using SE-30, SE-52, QF-1, XE-60 and NGS and by Withers[38] in the analysis of glycol ethers as their trimethyl silyl ethers, is now available as OV-61 from the Ohio Valley Company.

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 reported[33–35] and a 100% substituted material has been prepared in this laboratory[39]. The effect of increased phenyl substitution and increasing polar character on the Rohrschneider constants is shown in Fig. 2.

6. CHLOROPHENYL-SUBSTITUTED POLYSILOXANES

Siloxanes containing *p*-chlorphenyl and phenyl groups have been offered as stationary phases, the materials DC-560, F-60, F-61 and SP-400 all being of similar composition with approximately 11% chlorophenyl substitution.

While the phases have been used in this laboratory[33,35], it is now apparent that any specific contribution due to the halogen is trivial. The McReynolds constants equated to the basis of x' are shown below, from which it is apparent that the above

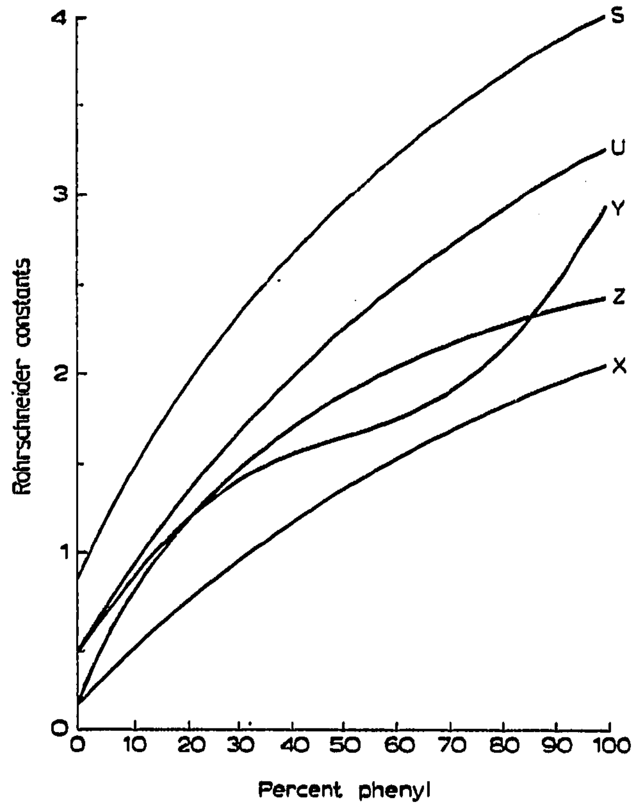


Fig. 2. Relationships between ROHRSCHNEIDER constants and phenyl substitution.

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 co-workers[40].

	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 groups[41], methyl (10%) trichlorophenyl groups[42] and methyl, trichlorophenyl and trisilyl ether groups[9]. The MCREYNOLDS values of the material[6] 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 phase[43] and consists of a relatively short-chain dimethyl polysiloxane end terminated with a 3,5-dichlorphenyl group.

7. CYANOALKYL-SUBSTITUTED POLYSILOXANES

Silicone oils containing cyanopropyl groups were offered as a new class of polar stationary phases by Rotzsche in 1962[44,123]. By varying the number of cyanopropyl groups, phases of varying polarity and selectivity were produced. Retention volumes for homologous hydrocarbons and oxygen containing compounds were produced at 100° and selectivity constants as described by Bayer[43] are shown in Table 5.

TABLE 5

SEPARATION 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/n-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 5 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.*[46]. 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.

Scholfield and Dutton[47], 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 siloxane[35] are substantially lower than those reported for DEGS. An early report by Supina[48] indicated XF-1150 to be almost as polar as ethylene glycol adipate, the Rohrschneider constants for the two materials being similar[49].

Bayer *et al.*[50] 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.*[46] on the basis of studies of stable π-complexes[51–53] and the similarity of elution behaviour in silver ion chromatography with Ag^+/olefin π-complexes of the same fatty esters[54–56].

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 below by equating the contents to the basis of x'.

	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.

8. FLUOROALKYL-SUBSTITUTED POLYSILOXANES

The siloxane polymer QF-1 or FS-1265 Fluid and first described as QF-1-0065 was introduced as a stable polar phase for gas chromatography by VANDENHEUVEL *et al.*[57], for the analysis of steroids in 1961. The phase corresponds to dimethyl polysiloxane with 50 mole percent replacement of methyl groups with trifluoropropyl groups and it thus possesses what is recognised as a marked acceptor character.

VANDENHEUVEL *et al.*[57] indicated the significant polar character of QF-1 by determining separation factors for the $-CH_2-CH_2-$ 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'.

	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'.

	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.

	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

Two 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 losses[58].

	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

9. ORGANOSILICONE POLYMERS

A range of organosilicone polymers produced by the reaction of a polyester adduct of ethylene glycol succinate and an organosilane are commercially available[59]. These 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.

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[8].

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[60].

It has been observed that significant variations in the polarity of the column occur with variation of the stationary phase loading. The effect has been demonstrated with EGSS-X[60] and by ACKMAN[61] with fatty esters using representatives of each type of the polymers. The separations that have been reported include fatty esters[62]. Glyceryl ethers[63] and trimethylsilyl derivatives of carbohydrates[64] on EGSS-X, catecholamines[65] and sterol sulphonates[66] on EGSP-Z and fatty esters[67], fatty amines[68] and monosaccharides[69] on ECNSS-M.

McREYNOLDS constants for certain of these phases are shown in Table 2, data for both of the dimethyl polysiloxane copolymers are available and as expected a decrease in the polarity character of the phase 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 hexamethyldisiloxane[98].

10. 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 the 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.

11. SILICA–SILOXANE BONDED SUPPORTS

The ability to bond polysiloxanes onto silaceous materials was demonstrated by MARTIN and HOWARD[70,71] in 1949. Reactive surface sites were deactivated by treatment with haloalkyl silanes to provide supports for partition chromatography studies. The reactive hydroxyl groups were largely converted but the added organic groups were not in sufficient amounts to undergo specific interactions or to function as partitioning media.

Since this time a variety of materials have been developed suitable for both gas–liquid and liquid–liquid chromatographic operation. The present work is restricted to the development of siloxane additions although other types of materials are commercially available. The Durapak products* earlier described as "brushes" by HALASZ AND SEBASTIAN[72] are produced by the esterification of an alcohol with a porous silica surface and their performance has been studied by LITTLE and his co-

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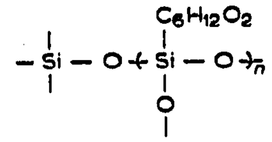
* Waters Associates Inc., Framingham, Mass. U.S.A.

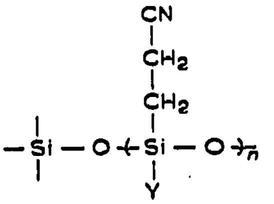
workers[73]. The thermal stability of the Durapaks is between 135° and 160° and is related to the stability of the Si–O–C bond.

KIRKLAND AND STEFANO[74] have produced bonded phases using "Zipax", a controlled-surface porosity glass bead[75] support, as the substrate. The polymer loadings are low, *i.e.* near 1%, the principal interest being in liquid–liquid chromatographic applications. The bonding is via a Si–O–Si bond and the use of "ether" and "nitrile" bonded phases has been described for use in both liquid–liquid and gas–liquid chromatography. The general structures of the surfaces of the two types of material are shown below.



$-Si-O\!-\!\left(Si(C_6H_{12}O_2)(O-)-O\right)_n$

"ether" bonded



$-Si-O\!-\!\left(Si(CH_2CH_2CN)(Y)-O\right)_n$

where Y = -CH_3 or -O-

nitrile bonded

ODS-"Permaphase", octadecylsilane bonded to the surface of "Zipax", is commercially available. The support contains approximately 1% of bonded organic material and its recommended temperature limit of 75° restricts its use in gas chromatography.

The chemical bonding of substantial amounts of siloxane stationary phases to solid supports was reported by ABEL *et al.*[76], who polymerised hexadecyltrichlorosilane onto Celite to the extent of 14%. Gas chromatographic performance compared to Silicone E-301 showed enhanced resolution and peak symmetry. The E-301 was considered suitable for use at 250° while the bonded material was stable to about 320°, where rupture of the C–Si bond might be anticipated. The same procedure was used by STEWART AND PERRY[77] to prepare a packing for liquid partition chromatography containing 20% octadecyl groups. BOSSARD[78,79] treated Chromosorb D and W with a series of ten alkyl silanes and reported characteristics of the materials.

HASTINGS *et al.*[80], using a fluidised bed process, produced siloxanes polymerised as well as chemically bonded onto the silaceous support, the procedure being more satisfactory than the first report of these workers[81]. Eight alkyl chlorosilanes, *i.e.* methyl to butyl, were used and six parameters including bleed rates, thermal stability, resistance to solvent extraction and chromatographic efficiency were studied to characterise the materials. Scanning electron microscopy[82] was used to examine support-bonded siloxanes based on octadecyltrichlorosilane and dimethyldichlorosilane in comparison with conventional supports coated with SE-30 and E-301. The micrographs indicated the bonded polymer to be present on the exterior of the particles while with conventional supports the polymer was evident both within the particle and on its exterior. Further refinements in procedure have recently been reported[83] and using dimethyldichlorosilane, octadecyltrichlorosilane and phenylmethyldichlorosilane supports containing up to 10% polymer have been produced.

12. CARBORANE–SILOXANE POLYMERS

The Olin Corporation has developed a series of linear polymers incorporating both carborane and siloxane units within the chain[84–86] and has offered a material as a high-temperature stationary phase. The carborane group is dicarbaclosododecaborane ($B_{10}H_{10}O_2$), 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 shown is considered quasiaromatic and capable of assuming many resonance states and stabilising adjoining groups against thermal degradation. The boron content of the material is quite high, the carborane group consisting of 70.58% boron and the total molecule containing 33.3% boron.

Thermal gravimetric analyses showed XE-60 to lose weight at about 228°, SE-30 at about 350° and the carborane Dexsil 300 GC at about 625° (ref. 87). Although the recommended maximum temperature limits are 450° for extended periods and 500° for limited periods, the material offers a major advance in stationary phases for high-temperature operation.

The ROHRSCHNEIDER constants of the material indicate a modest polar character, somewhat similar to that of OV-3, *i.e.* 10% phenyl substitution, and separations have been reported for a variety of high-temperature applications, including methyl esters, aromatic amines, halogenated alcohols, polyphenyl ethers, low-molecular-weight dimethyl siloxane, and butter triglycerides.

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