Polyphenyl Ethers as High-Temperature Radiation-Resistant Lubricants

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THE EVER-INCREASING speed of jet aircraft, coupled with the possible use of nuclear-powered vehicles, has prompted the development of lubricants capable of withstanding high temperatures in an oxidizing atmosphere and in the presence of large amounts of radiation. Such lubricants must possess good oxidation, radiation, and thermal stability and at the same time be capable of lubricating high-speed bearings and moderately-loaded gear trains. Furthermore, physical properties must permit operation over a wide temperature range.

Preliminary experiments established that the antioxidant activity of conventional inhibited lubricants is very sensitive to radiation damage. For example, lubricants containing as much as 5 weight % of inhibitor lost all antioxidant activity after irradiation with gamma rays (cobalt-60 in a nitrogen atmosphere) to 10^{10} ergs per gram. At the same radiation level, physical property changes were small. The combined effect of radiation and high-temperature oxidation destroyed antioxidant activity before 5×10^9 ergs per gram was absorbed. In the absence of oxygen, the antioxidant apparently functions as a scavenger for the alkyl radicals and is selectively deactivated. In the presence of oxygen, however, the reaction rate between the radicals and oxygen (to form peroxy radicals) is so fast that the inhibitors cannot successfully compete with oxygen for the radicals. Hence, radiation accelerates the oxidation rate by initiating alkyl radicals that subsequently form peroxy radicals so extensively that moderate concentrations of inhibitors are of little value. It was soon obvious that a highly oxidation-stable radiation-resistant lubricant would have to be developed from synthetic chemicals rather than from existing base stocks and additives.

Because aromatic compounds are much more resistant to radiation than aliphatic compounds (*2, 4, 5*), it was logical to attempt to design aromatic molecules with optimum physical properties and lubrication characteristics; the polyphenyl ethers offered the greatest potentialities. Consequently, many of their properties such as viscosity-temperature coefficients and oxidation, thermal, and radiation stabilities, as well as lubrication characteristics, were investigated in detail.

PHYSICAL PROPERTIES

Melting Point. The desired maximum liquid operating temperature range is of course provided by low melting point and high boiling point. Whereas the boiling point of the polyphenyl ethers is highly dependent upon their molecular weight, the melting point is predominantly a function of molecular symmetry. Thus, para- and ortho-linked unsubstituted polyphenyl ethers have a much higher melting point than do the corresponding meta-linked ethers (*10*) (Table I).

Mixtures of isomeric polyphenyl ethers also possess lower melting points than do the paraisomers. For example, 1-(*p*-α-cumylphenoxy)-4-phenoxybenzene has a melting point of 131° to 135° F. whereas the isomeric mixture, designated in Table I as 1-(*p*-α-cumylphenoxy)-mixed 2-, 3-, and 4-phenoxybenzene, is a liquid with a pour point of 30° F. Similarly, attachment of alkyl substituents to the polyphenyl ether nucleus in an asymmetrical pattern lowers the melting point much more than does a symmetrical arrangement. Thus, the melting point of bis[*p*-(*p*-*tert*-butylphenoxy)phenyl] ether is 175-8° F. while the isomeric *tert*-butylated bis(*p*-phenoxyphenyl) ether is a viscous liquid having a pour point of 85° F.

Viscosity-Temperature Coefficient. In contrast to most aromatic compounds, the viscosity-temperature characteristics of polyphenyl ethers are very good. Chain flexibility imparted by the ether linkages is undoubtedly responsible because the corresponding polyphenyls have poor viscosity-temperature properties—i.e., high ASTM slopes; compare bis(*o*-phenoxyphenyl) ether and *o*,*o*′-quaterphenyl (Table II). Some differences in viscosity and viscosity-temperature coefficients can be noted for isomeric unsubstituted polyphenyl ethers (Figure 1). The para-linked isomers have the highest viscosities and the lowest viscosity-temperature slopes. Meta-linked isomers have lower slopes than do the

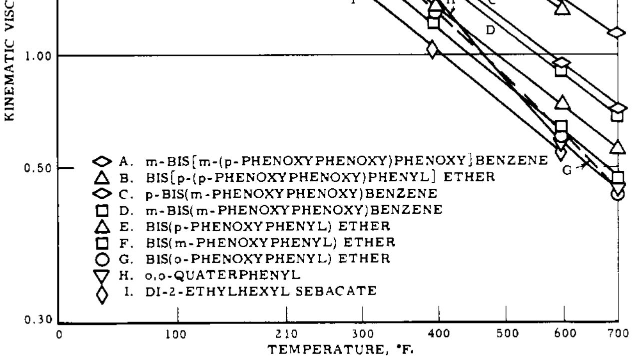


Figure 1. Viscosities of unsubstituted polyphenyl ethers

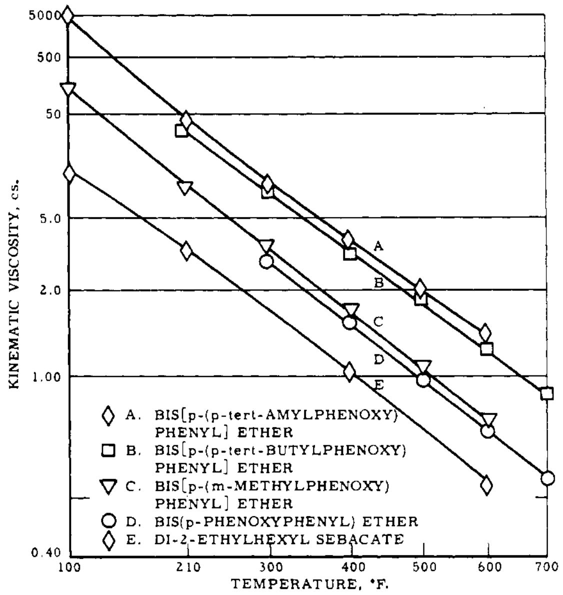


Figure 2. Viscosities of alkyl-substituted polyphenyl ethers

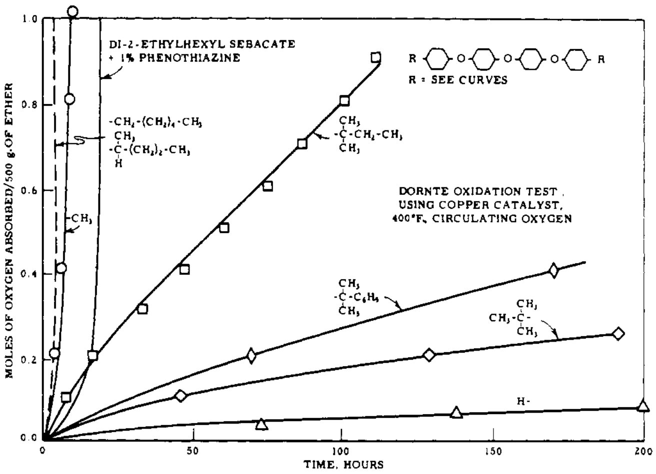


Figure 4. Effect of alkyl groups on the oxidation stability of polyphenyl ethers

ortho-linked ethers but still higher than those of para-linked ethers. Compounds containing both para- and meta-links are intermediate in slope between the all-meta and all-para isomers. Incorporation of alkyl groups on the terminal benzene rings increases the viscosity (Figure 2) but has little effect on the ASTM slope (Table II).

Effect of Radiation on Viscosity. Polyphenyl ethers are less sensitive to radiation-induced viscosity changes than are aliphatic hydrocarbons or esters. For example, 1-(*p*-α-cumylphenoxy)-4-phenoxybenzene showed only a moderate increase in viscosity at radiation levels of nearly 10^{11} ergs per gram. After absorption of 5×10^{11} ergs per gram, the viscosity was high but gelation had not occured. In contrast, a methyl phenyl silicone became very viscous above 5×10^{10} ergs per gram and gelled at 10^{11} ergs per gram. Di-2-ethylhexyl sebacate was very viscous at 10^{11} ergs per gram and had gelled at 2.5×10^{11} ergs per gram. An aliphatic hydrocarbon was slightly more resistant to radiation but still a gelled at 2.5×10^{11} ergs per gram (Figure 3). Other alkyl substituted polyphenyl ethers were affected similarly while the unsubstituted ethers were somewhat more resistant to radiation, approaching the stability of polyphenyls, aryl silanes, and condensed aromatic hydrocarbons such as phenanthrene (Table III).

Volatility and Flash Points. Volatility, like viscosity, is dictated primarily by molecular weight but is also influenced to some extent by molecular configuration. As shown in Table III, the ortho-linked unsubstituted polyphenyl ethers are appreciably more volatile than the meta compounds which are in turn more volatile than the para-linked isomers. Mixed para-meta ethers have volatilities intermediate between the corresponding all-meta and all-para ethers.

The flash points of the ethers vary inversely with their volatilities. Consequently, the influence of molecular configuration on flash point is in proportion to its influence on volatility (Table IV).

OXIDATION STABILITY

Because radiation is known to accelerate oxidation, it is essential for some applications that the potential lubricant be superior in oxidation stability (7) both in the presence and absence of radiation. As illustrated in Figure 4, unsubstituted polyphenyl ethers, as exemplified by bis(*p*-phenoxyphenyl) ether, exhibit excellent oxidation stability. Incorporation of alky groups to lower melting point has a deleterious effect, the magnitude of which is a function of the structure of the alkyl group (Figure 4). In general, the most stable substituents are free of benzyl, methylene, and

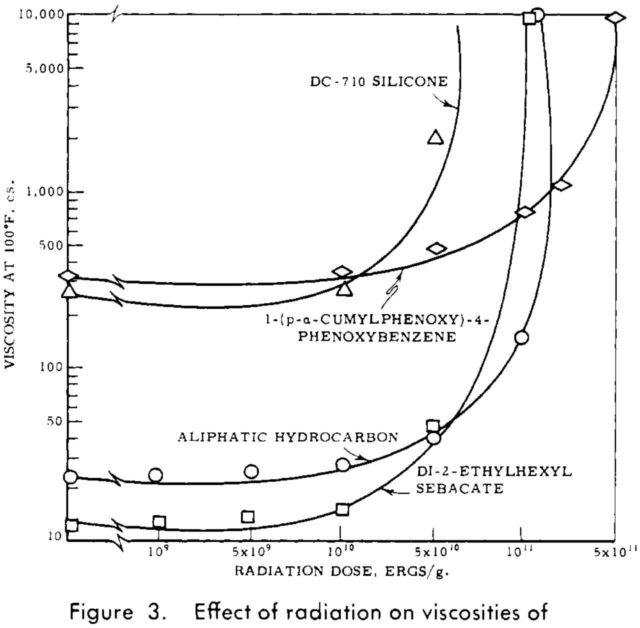


Figure 3. Effect of radiation on viscosities of various types of lubricants

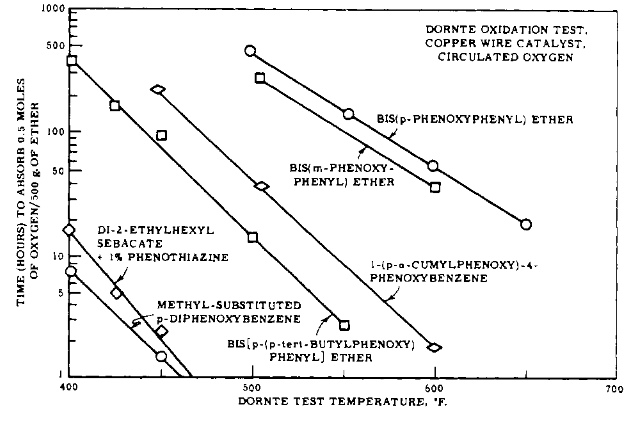


Figure 5. Effect of temperature on the oxidation stability of polyphenyl ethers

Table I. Physical Properties of Polyphenyl Ethers

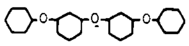
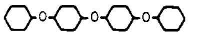
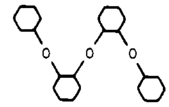
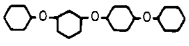
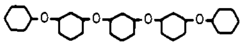
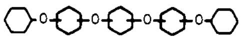
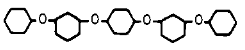
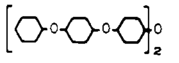
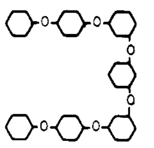
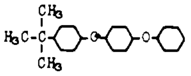
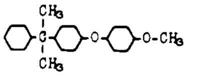
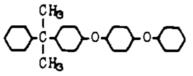
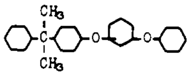
Ether	Structure	Molecular Weight	Boiling Point, ° F./Mm.	Melting Point, ° F.	Pour Point,[a] ° F.	Viscosity, Cs., ° F. 100	210	400	600	700
Unsubstituted Ethers										
Bis(*m*-phenoxy phenyl) ether		354	518-23/1.0	106	5	60.9	5.98	1.34	0.62	0.47
Bis(*p*-phenoxyphenyl) ether		354	473/2	230	. . .	. . .	2.83[b]	1.51	0.71	0.53
Bis(*o*-phenoxyphenyl) ether		354	365-419/0.4	249	. . .	. . .	2.84[b]	1.39	0.60	0.44
m-Phenoxyphenyl *p*-phenoxyphenyl ether		354	. . .	118	10[c]	71.8	6.56	1.43	0.66	0.49
m-Bis(*m*-phenoxyphenoxy)-benzene		447	500-10/0.3	. . .	40	332	12.7	2.04	0.86	0.63
mix-Bis(mix-phenoxyphenoxy)benzene[d]		447	500-535/0.5	. . .	40	349	13.0	2.08	0.86	. . .
p-Bis(*m*-phenoxyphenoxy)-benzene		447	554-585/1	171-4	40[c]	439	14.0	2.24	0.92	0.69
Bis[*p*-phenoxyphenoxy)-phenyl[ether		539	. . .	342-5	. . .	. . .	. . .	4.20	1.55	. . .
m-Bis[*m*-(*p*-phenoxy-phenoxy)-phenoxy]benzene		631	705/0.4	189-91	85[c]	21,200	52.4	4.38	1.54	1.10
Substituted Ethers										
1-(*p*-*tert*-Butylphenoxy)-4-phenoxybenzene		318	360-369/0.2	127-31	. . .	. . .	5.1	1.25	0.59	. . .
1-(*p*-α-Cumylphenoxy)-4-methoxybenzene		318	372-405/0.15	. . .	10	95.9	6.61	1.33	0.59	. . .
1-(*p*-α-Cumylphenoxy)-4-phenoxybenzene		381	464-491/2.5	131-5	35[c]	. . .	11.33	1.95	0.82	0.60
1-(*p*-α-Cumylphenoxy)-mixed 2-,3- and 4-phenoxybenzene		381	505-9/2	. . .	30	284	10.9	1.72	0.76	0.57

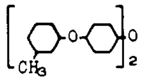
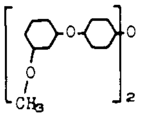
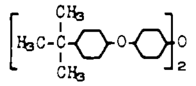
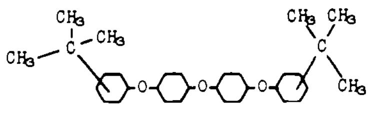
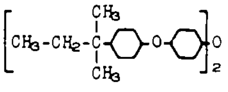
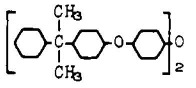
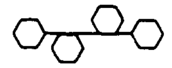
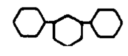
Table II. ASTM Slopes of Polyphenyl Ethers

Ether	Slope Over Indicated Temperature Range, ° F. 100-210	210-400	400-600	600-700
Bis(*p*-phenoxyphenyl) ether	. . .	0.79	0.83	0.98
Bis(*m*-phenoxyphenyl) ether	0.84	0.83	0.87	1.03
Bis(*o*-phenoxyphenyl) ether	. . .	0.95	0.98	1.22
m-Phenoxyphenyl *p*-phenoxyphenyl ether	0.86	0.81	0.86	1.06
Bis[*p*-(*p*-*tert*-amylphenoxy) phenyl] ether	0.94	0.75	0.79	. . .
Bis[*p*-(*p*-*tert*-butylphenoxy)-phenyl] ether	. . .	0.76	0.78	0.91
Bis[*p*-(*m*-methylphenoxy)-phenyl[ether	0.93	0.79	0.85	. . .
o,*o*′-Quaterphenyl	. . .	. . .	1.13	1.28
Di-2-ethylhexyl sebacate	0.70	0.79	0.83	decomposes

methenyl hydrogens. Thus, of the substituents compared in Figure 4, the *tert*-butyl and α-cumyl groups are the most stable, *tert*-amyl next in order, while methyl and longer alkyl groups are the least stable. The relative stabilities of various ethers at 500° F. are indicated in Table IV.

The effect of temperature on the oxidation stability of polyphenyl ethers is illustrated in Figure 5. Whereas unsubstituted bis(*p*-phenoxyphenyl) ether is considerably more resistant to oxidation over a wide temperature range than either bis[*p*-(*p*-*tert*-butylphenoxy)phenyl] ether or 1-(*p*-α-cumylphenoxy)-4-phenoxybenzene, the latter two ethers are manyfold more stable than conventional antioxidant-containing lubricants. The difference in temperature sensitivity between the unsubstituted and alkyl-substituted ethers can be expressed in terms of their apparent activation energies. For example, the activation energy for the copper-catalyzed reaction of bis(*p*-phenoxyphenyl) ether is 16.5 kcal. over the temperature interval, 550° to 600° F., while it is in the order of 31 kcal. for bis[*p*-(*p*-*tert*-butylphenoxy)-phenyl] ether from 525° to 550°

Table I. Continued

Ether	Structure	Molecular Weight	Boiling Point, ° F./Mm.	Melting Point, ° F.	Pour Point,[a] ° F.	Viscosity, Cs., ° F. 100	210	400	600	700
Bis[*p*-(*m*-methylphenoxy)-phenyl] ether		382	482/1	131-6	...	138	8.58	1.69	0.75	...
Bis[*p*-(*m*-methoxyphenoxy)-phenyl] ether		441	420-510/0.3	...	30	236	14.0	2.07	...	...
Bis[*p*-(*p*-*tert*-butylphenoxy)-phenyl] ether		467	509/0.1	175-128	75[c]	...	31.4	3.17	1.19	0.84
tert-Butylated bis(*p*-phenoxy-phenyl) ether		460	545-55/0.6	...	85	...	42.7	3.33	1.18	0.83
Bis[*p*-(*p*-*tert*-amylphenoxy)-phenyl] ether		495	545-63/0.3	...	70	6270	41.1	3.72	1.32	...
Bis[*p*-(*p*-α-cumylphenoxy)-phenyl] ether		591	680/.001	...	90	...	116	6.40	1.99	...
Reference Materials										
MIL-L-7808 lubricant (diester base)		...	...	...	−75	14.1	3.57	...	...	...
Methyl phenyl silicone (DC 710)		...	...	...	...	437	46.9	...	...	...
o,o'-Quaterphenyl		306	...	245	...	...	4.63[b]	1.64	0.60	0.46
m-Terphenyl		230	690/760	187	...	...	3.85	0.91	0.43	0.34

[a] Small-scale test that can be compared directly with results of large-scale test.
[b] At 300° F. instead of 210° F.
[c] Pour point of super-cooled liquid.
[d] A mixture of isomeric ethers. The term mix and the lines inside the benzene rings denote a mixture of ortho-, meta- and para-ether linkages but they are predominately (about 85%) meta linkages.

phenyl] ether from 525° to 550° F.; the value for mineral oil is 26 kcal. from 482° to 500° F. and would undoubtedly be higher at higher temperatures (*6*).

As a convenient approximation, the simple Arrhenius equation can be applied—i.e., log t is taken as linear in $1/T$—over small temperature intervals. Activation energies calculated in this way are by no means constant over the whole temperature range. It is fortuitous that the deviation from linearity of log t in $1/T$ is such that log t appears to be linear in T.

Effect of Additives on Oxidation Stability. Although alkyl groups can effect considerably lowering of the melting point of para-linked polyphenyl ethers, they concomitantly decrease the oxidation stability. Some consideration was therefore given to the possibility or restoring at least a portion of this stability through the use of oxidation inhibitors. With bis[*p*-(*p*-*tert*-butylphenoxy)phenyl] ether as the base stock, it was found that none of the conventional oxidation inhibitors such as phenyl-α-naphthylamine, phenothiazine, morpholine tetrasulfide, or morpholine diselenide increased stability by a factor of more than 1.25 at 500° F. for either copper-catalyzed or uncatalyzed oxidation. Such marginal improvement does not, of course, begin to compensate for the large difference in stability between the unsubstituted ether and the *tert*-butyl derivative, the former being about 25 times as stable as the latter under these conditions. From these exploratory results, it appears that any substantial upgrading of oxidation stability of the alky-substituted ethers cannot be expected through use of known types of inhibitors.

Effect of Radiation on Oxidation-Stability. The oxidation resistance of polyphenyl ethers is affected more by radiation than are physical properties such as viscosity. For example, unirradiated bis(*p*-phenoxyphenyl) ether absorbed 0.5 moles of oxygen per 500 grams [500° F., copper catalyst, Dornte (*7*) apparatus] in 470 hours. After irradiation to 2.5 × 10^{10} ergs per gram the same amount of oxygen was absorbed in 325 hours; 5 × 10^{10} ergs per gram, 170 hours; 1 × 10^{11} ergs per gram, 65 hours; 2.5 × 10^{11} ergs per gram, 18 hours; 5 × 10^{11} ergs per gram, 4.4 hours (Figure 6). The *tert*-butyl and

Table III. Effect of Radiation on Viscosity of Polyphenyl Ethers

Ether	Temp. of Measurements, ° F.	Radiation Dose, Ergs/G.[a]												
		None	1.0×10^{10}		2.5×10^{10}		5.0×10^{10}		1.0×10^{11}		2.5×10^{11}		5.0×10^{11}	
		Viscosity,												
		Cs.	Cs.	Increase, %	Cs.	Increase, %	Cs.	Increase, %	Cs.	Increase, %	Cs.	Increase, %	Cs.	Increase, %
Unsubstituted Ethers														
Bis(*m*-phenoxyphenyl) ether	100	61.1	66.2	8	...	...	88.1	44	...	...	...	...	...	...
	210	6.15	6.29	2	...	...	7.11	16	...	...	...	...	...	...
	400	1.34	1.35	1	...	...	1.45	8	...	...	...	...	...	...
	600	0.62	.61	0	...	...	0.66	6	...	...	...	...	...	...
	700	0.47	...	...	...	...	0.49	5	...	...	...	...	...	...
m-Phenoxyphenyl-*p*-phenoxyphenyl ether	100	71.8	77.8	8	...	...	102.5	43	...	...	...	...	...	...
	210	6.59	6.82	3.5	...	...	7.63	16	...	...	...	...	...	...
	400	1.43	1.47	2.8	...	...	1.55	8	...	...	...	...	...	...
	600	0.66	0.66	0	...	...	0.68	3	...	...	...	...	...	...
Bis(*p*-phenoxyphenyl) ether	300	2.86	2.94	3	3.04	7	3.20	12	3.53	23	4.48	57	6.16	116
	400	1.51	1.55	2.5	1.63	8	1.70	12	1.80	19	2.17	40	2.71	79
	600	0.71	...	...	...	...	0.74	4	...	...	0.90	27	1.07	51
m-Bis(*m*-phenoxyphenoxy)benzene	100	332	356	7	...	...	503	51	...	...	...	...	...	...
	210	12.7	13.1	3	...	...	15.3	20	...	...	...	...	...	...
	400	2.05	2.06	1	...	...	2.22	8	...	...	...	...	...	...
	600	0.86	0.86	0	...	...	0.90	4	...	...	...	...	...	...
	700	0.63	0.63	0	...	...	0.66	4	...	...	...	...	...	...
Substituted Ethers														
Bis[*p*-(*tert*-butylphenoxy)phenyl] ether	210	31.4	33.18	6	35.0	11	41.0	31	48.0	53	95.5	202	339	980
	400	3.17	3.26	3	3.33	5	3.57	13	3.76	18	4.90	55	8.00	150
	600	1.19	...	...	1.23	3	1.25	5	1.30	9	1.55	30	2.09	76
1-(*p*-α-(Cumylphenoxy)-4-phenoxybenzene	100	324	352	9	375	16	472	46	697	115	1,970	510	10,450	320
	210	11.5	12.3	7	12.8	10	13.7	20	16.1	40	25.5	118	47.9	3100
	400	1.94	1.96	1	2.02	4	2.13	10	2.30	18	2.78	43	3.78	95
	600	0.84	0.82	1	0.85	3	0.86	5	0.89	9	1.00	22	1.24	51
1-(*p*-*tert*-Butylphenoxy)-4-phenoxybenzene	100	...	...	...	...	...	...	...	...	...	...	...	...	...
	210	5.1	...	...	...	...	...	...	...	...	...	...	21.8	328
	400	1.25	...	...	...	...	...	...	...	...	...	...	2.50	100
	600	0.59	...	...	...	...	...	...	...	...	...	...	0.94	59
1-(*p*-α-(Cumylphenoxy)-4-methoxybenzene	100	95.9	...	...	...	...	131	37	...	...	...	...	...	...
	210	6.61	...	...	...	...	7.57	15	...	...	...	...	...	...
Reference Materials														
Di-2-ethylhexyl sebacate	100	12.6	15.5	23	...	...	63.1	400	780	6100	Gelled		...	...
	210	3.55	3.84	8	...	...	10.4	190	64	1700	Gelled		...	...
Aliphatic hydrocarbon (C_{33})	100	24.0	27.8	16	...	...	63.4	160	117	390	Gelled		...	...
	210	4.98	5.42	9	...	...	10.4	110	22.9	360	Gelled		...	...
Methyl phenyl silicone (DC 710)	100	437	...	27	...	...	1,970	350	Gelled		...	...	...	...
	210	46.9	...	2	...	...	167	250	Gelled		...	...	...	...
Triphenyl-*p*-biphenylyl silane	400	3.55	...	...	...	...	3.83	8	3.97	12	4.44	25	5.83	63
	600	1.05	...	...	...	...	1.07	2	1.09	4	1.20	14	1.41	34
m-Terphenyl	210	3.84	3.92	2	3.96	3	4.04	5	4.19	9	4.71	22	5.84	52
	400	0.89	0.90	1	0.91	2	0.92	3	0.94	5	1.00	12	1.12	25
Phenanthrene	300	1.05	...	...	...	...	...	...	1.12	7	...	...	123	17
	400	0.64	...	...	...	...	...	...	0.68	6	...	...	0.75	17

[a] Sample irradiated with electrons from 3 m.e.v. Van de Graaff generator in nitrogen atmosphere for 0.25 to 1 hr. at 300° to 370° F.

Table IV. Performance Properties of Polyphenyl Ethers

Ether	Flash Point,[a] ° F.	Fire Point,[a] ° F.	Evaporation Loss,[a] Wt. % 400° F.	Evaporation Loss,[a] Wt. % 500° F.	Panel Coke,[b] Mg. at 800° F.	Initial Thermal Decompn. Temp., ° F.	0.5 Mole Dornte (7) Oxidation Time[c] at 500° F., Hr.
Unsubstituted Ethers							
Bis(*m*-phenoxyphenyl) ether	465	555	2.9	33.3	0.5	835	280
Bis(*p*-phenoxyphenyl) ether	500	560	2.2	21.7	2.3	835	400+
Bis(*o*-phenoxyphenyl) ether	445	505	...	55.1	...	825	...
m-Phenoxyphenyl *p*-phenoxyphenyl ether	465	530	1.8	27.9	1.6	805	265
m-Bis(*m*-phenoxyphenoxy)benzene	540	610	...	3.6	0.2	870	330
mix-Bis(mix-phenoxyphenoxy)benzene	540	604	...	5.1	...	860	400
p-Bis(*m*-phenoxyphenoxy)benzene	545	645	...	3.4	0.2	875	400+
Bis[*p*-(*p*-phenoxyphenoxy)phenyl] ether	635	710	...	0.1	...	...	...
m-Bis[*p*-phenoxyphenoxy)phenoxy]benzene	660	775	...	0.1	0.2	860	...
Substituted Ethers							
1-(*p*-*tert*-Butylphenoxy)-4-phenoxybenzene	435	489	10.9	98	6.5	...	21
1-(*p*-α-Cumylphenoxy)-4-methoxybenzene	430	500	7.4	61	29.3	...	11
1-(*p*-α-Cumylphenoxy)-4-phenoxybenzene	509	567	...	12.6	1.1	ca 700	37
1-(*p*-α-Cumylphenoxy)-mixed 2-,3- and 4-phenoxybenzene	490	565	...	19.6	0.2	...	40
Bis[*p*-(*m*-methylphenoxy)phenyl] ether	538	599	...	14.6	6.4	720	6 (at 400° F.)
Bis[*p*-(*m*-methoxyphenoxy)phenyl] ether	530	625	...	10.6	...	670	20 (at 450° F.)
Bis[*p*-(*p*-*tert*-butylphenoxy)phenyl] ether	572	657	0.3	2.9	1.2	770	17
tert-Butylated bis(*p*-phenoxyphenyl) ether	525	640	...	3.8	1.9	...	20
Bis[*p*-*tert*-amylphenoxy)phenyl] ether	586	667	...	2.7	...	625	60 (at 400° F.)
Bis[*p*-(*p*-α-cumylphenoxy)phenyl] ether	668	...	0.4	1.2	...	...	175 (at 400° F.)
Reference Materials							
MIL-L-7808 Lubricant (diester base)	460	...	9	90	37	575	0.3[d]
Methyl phenyl silicone (DC 710)	...	...	...	...	2.2	590	400+
o,*o*'-Quaterphenyl	...	...	...	...	...	...	...
m-Terphenyl	...	...	...	...	...	...	400+

[a] Small-scale tests directly comparable to results of large-scale tests (*1*).

[b] Small-scale test. Coke level is approximately 1/50 of that found in the full-scale Model C coker.

[c] Time in hours to absorb 0.5 mole of oxygen for each 500 g. of ether using copper catalyst and circulating oxygen.

[d] Extrapolated value.

Table V. Effect of Radiation[a] on Oxidation Stability

Radiation dose, ergs/G.	Unirradiated	1×10^{10}		2.5×10^{10}		5×10^{10}		1×10^{11}		2.5×10^{11}		5×10^{11}	
Time required for absorption of 0.5 moles of oxygen per 500 g. of compound[b]. Compound	Time, hr.	Time, hr.	% of Unirradiated time	Time, hr.	% of Unirradiated time	Time, hr.	% of Unirradiated time	Time, hr.	% of Unirradiated time	Time, hr.	% of Unirradiated time	Time, hr.	% of Unirradiated time
Bis(*p*-phenoxyphenyl) ether	470[c]	...	...	325[c]	69	170	36	65	14	18	4	4.4[c]	0.9
Bis[*p*-(*p*-*tert*-butylphenoxy)-phenyl] ether	19	6.4	34	5.7	30	2.8	15	2.6	14	...	...	...	...
1-(*p*-α-Cumylphenoxy)-4-phenoxybenzene	35	18	51	9	26	4.5	13	2.5	7	...	...	...	...
m-Terphenyl	800[c]	350[c]	44	340[c]	42	230[c]	29	63	8	22	3	3.1	0.4
Phenanthrene	210[c]	...	...	...	...	...	...	80	38	...	...	6.6	3.1
Methyl phenyl silicone (DC 710)	600[c]	...	...	...	...	30	5	3.0[c]	0.5	...	...	...	...
MIL-L-7808C lubricant	0.3[c]	...	...	...	...	...	...	...	...	...	...	...	...

[a] Samples irradiated with electrons from 3 m.e.v. Van de Graaff generator. All irradiations were under nitrogen at 320°–375° C. for times from 1/2 to 2 hours.

[b] Dornte oxidation test, 5-g. sample, copper wire catalyst surface 1 sq. cm./g. of compound, circulated oxygen, 500° F.

[c] Extrapolated value.

Table VI. Effect of Radiation During Oxidation[a] of Polyphenyl Ethers

Ether	Bis(*p*-phenoxyphenyl) Ether		Bis[*p*-(*p*-*tert*-butylphenoxy)phenyl] Ether		*m*-Terphenyl		Methyl Phenyl Silicone (DC-710)	
Test temperature, ° F.	475		475		450		450	
Test duration, hr.	51		51		48		48	
Total radiation[b] absorbed, ergs/g.	None	1 × 10^9	None	1 × 10^9	None	1 × 10^9	None	1 × 10^9
	Viscosities before Oxidation Test, Cs.							
Temp., ° F.								
100	...	...	...	...	...	...	234	234
210	...	...	31.3	31.3	3.85	3.85	31.8	31.8
300	2.83	2.83	...	...	1.63	1.63	...	...
400	1.51	1.51	3.04	3.04	...	...	...	...
	Viscosities after Oxidation Test, Cs.[a]							
100	...	...	...	...	...	...	317	358
210	...	...	48.2	48.1	4.08	3.98	38.2	41.1
300	2.88	2.96	...	...	1.64	...	...	...
400	1.60	1.55	3.85	3.73	...	...	...	...
	Viscosity Increase, %							
100	...	...	...	...	...	...	36	54
210	...	...	22	37	5	3	20	29
300	2	4	...	...	4	...	...	...
400	6	3	27	23	...	...	...	...
Acid neut. no., mg. KOH/g.	0	0.94	1.1	3.6	0.6	0	0.4	0.98
Metal weight loss, mg./cm^2,								
Cu.	+0.06	0	0.85	1.79	0.02	−0.31	+0.06	+0.38
Mg.	+0.05	+0.09	0.06	0.14	+0.20	+ 0.05	+0.02	0.06
Fe.	0	0.06	0.06	0.05	+0.28	+ 0.20	+0.15	+0.15
Ag.	+0.09	+0.08	0.11	0.02	+0.42	0.72	+0.20	0.08
Al.	0	0.08	0	0.08	0.06	0	0.12	0
Ti.	0	0.17	0	0.15	0.14	0.03	0.09	0.09
Deposits	None	None	None	None	None	None	None	None

[a] Small-scale oxidation-corrosion test using a 5-g. sample of ether, 200 ml. air/hr. and in presence of the indicated 6 metals.
[b] Gamma radiation from 4000 curie cobalt-60 source.

α-cumyl derivatives show a greater decrease in oxidation stability after absorbing a comparable amount of radiation. Polyphenyls—e.g., *m*-terphenyl, have approximately the same sensitivity to radiation as does bis(*p*-phenoxyphenyl) ether while phenanthrene is somewhat more resistant. Methyl phenyl silicone (DC 710) is considerably more susceptible, losing essentially all its oxidation stability after the absorption of 5 × 10^{10} ergs per gram (Table V). Although loss in oxidation stability due to radiation is great, even the most highly irradiated samples of polyphenyl ethers are still more resistant to oxidation than are typical unirradiated inhibitor-containing diester lubricants—i.e., MIL-L-7808C oils.

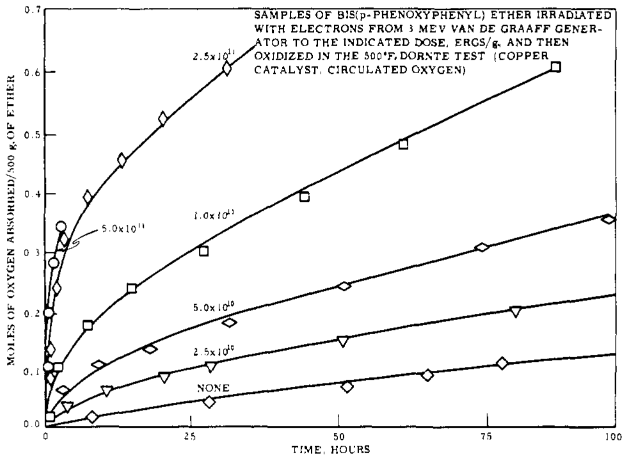


Figure 6. Effect of radiation on the oxidation stability of bis(*p*-phenoxyphenyl) ether

Several of the polyphenyl ethers, when subjected to simultaneous irradiation (total accumulated dosage about 10^9 ergs per gram) and oxidation showed only slightly greater deterioration than that due to oxidation alone (Table VI). Of these, the unsubstituted ones—e.g., bis(*p*-phenoxy-phenyl) ether—were more stable than the alkyl-substituted ethers—e.g., bis[*p*-(*p*-*tert*-butylphenoxy)phenyl] ether. In no case was the degradation severe enough to seriously affect viscosity, acid number, or the corresion of metals. Similarly, *m*-terphenyl and a silicone (DC 710) showed only slight deterioration at this level of radiation. In contrast, a di-2-ethylhexyl sebacate base oil, inhibited with 1% phenothiazine, was oxidized to a solid at 450° F. even in the absence of radiation. Although the oxidation stability of polyphenyl ethers still needs to be examined in the presence of high dosages of radiation before an upper limit of stability can be established, the data show clearly that the ethers are far more resistant to oxidation in the presence of moderately high levels of gamma radiation than are conventional lubricants in absence of radiation.

THERMAL STABILITY

Thermal stability was assessed by measuring vapor pressure at various temperatures (with an isoteniscope) and plotting as an inverse function of temperature. The point at which volatile fragments are formed is indicated by a change in slope of the line and is defined as the initial decomposition temperature (Figure 7). Data on several polyphenyl ethers are compared with other classes of synthetic lubricants in Table IV. As in the case of oxidation

Table VII. Coking Tendencies of Polyphenyl Ethers

Ether	Coke[a] Formed at Indicated Panel Temp., Mg.		
	700° F.	800° F.	900° F.
Unsubstituted Ethers			
Bis(*p*-phenoxyphenyl) ether	0.2	0.2	2.0
Bis(*m*-phenoxyphenyl) ether	0.4	0.5	0.9
m-Phenoxyphenyl *p*-phenoxyphenyl ether	. . .	1.6	. . .
m-Bis(*m*-phenoxyphenoxy)benzene	. . .	0.2	0.6
p-Bis(*m*-phenoxyphenoxy)benzene	. . .	0.2	. . .
m-Bis[*m*-(*p*-phenoxyphenoxy)-phenoxy]benzene	. . .	0.2	0.7
Alkyl-substituted Ethers			
Bis[*p*-(*p*-*tert*-butylphenoxy)-phenyl] ether	0.6	1.2	9.0
tert-Butylated bis(*p*-phenoxyphenyl) ether	. . .	1.9	. . .
1-(*p*-α-Cumylphenoxy)-4-phenoxybenzene	0.6	1.1	6.2
1-(*p*-α-Cumylphenoxy)-mixed 2-, 3-, and 4-phenoxybenzene	. . .	0.2	. . .
Mixed methyl-substituted *p*-diphenoxybenzene	14.4	36.7	23.0
Reference Fluids			
MIL-L-7808 Lubricant (diester base)	35	37	17
Chlorophenyl silicone (GE 81406)	14	373	267
Methyl phenyl silicone (DC 710)	0	2.2	159

[a] Determined in small-scale test using 5 g. of oil, air rate through vapor space, 2 l./hr., test duration 1 hr. Sump temperature, 300° F. lower than indicated panel temperature—e.g., 700° F. panel or 400° F. sump. Coke level in this test is approximately 1/50 of that found in the full-scale test using the Model C coker.

stability, the unsubstituted polyphenyl ethers display better thermal stability than do the alkyl-substituted ethers; both are far superior to currently used base stocks. Hence, the unsubstituted polyphenyl ethers offer a potential operating temperature advantage of about 200° F. over present-day mineral oil and ester-base lubricants. This criterion alone is inadequate for evaluating thermal stability under service conditions but is probably a safe screening index, because gross fragmentation of the molecules may not occur in practice until much higher temperatures are encountered.

COKING TENDENCIES

The tendency of polyphenyl ethers to form coke deposits in an oxidizing atmosphere at high temperatures was assessed by using a modified panel coke apparatus. The results, summarized in Table VII, show that bis(*p*-phenoxyphenyl) ether gives essentially no coke deposits at 800° F. and only a small amount of coke at 900° F. The α-cumyl and *tert*-butyl derivatives give low coke levels at 700° and 800° F. The methyl-substituted ethers, like the di-2-ethylhexyl sebacate base lubricants, give heavy deposits at 600° F., whereas a methyl phenyl silicone does not show heavy deposits until 900° F. Thus, the unsubstituted polyphenyl ethers and many of the alkyl-substituted ethers display better stability under these conditions than any of the present-day lubricants examined.

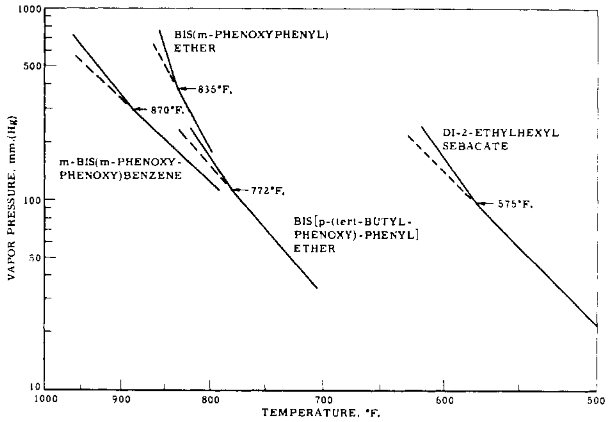


Figure 7. Initial thermal decomposition temperatures of polyphenyl ethers

The deposit-forming tendencies of polyphenyl ethers are not greatly affected by irradiation. As shown in Table VIII, the coke values for either bis(*p*-phenoxyphenyl) ether or bis[*p*-(*p*-*tert*-butylphenoxy)phenyl] ether at 800° F. are increased by a factor of two or three after irradiation to 10^{11} ergs per gram. The coke level of the irradiated samples is still far below that of present-day lubricants that have not been irradiated (Table VII).

Samples were irradiated with electrons from a 3 m.e.v. Van de Graaff generator. Equivalent damage occured when the same amount of gamma radiation was substituted for electrons.

LUBRICATION CHARACTERISTICS

In addition to their excellent oxidation, thermal, and radiation stability, the polyphenyl ethers also display good lubrication characteristics. For example, the wear properties of the unsubstituted polyphenyl ethers, as measured in the four-ball test (*8*), are comparable to di-2-ethylhexyl sebacate and far superior to those of silicones or unsubstituted aromatic hydrocarbons such as *m*-terphenyl or *o,o′*-quaterphenyl (Figure 8). The alkyl-substituted ethers show even lower wear than do the unsubstituted ethers. Thus, the polyphenyl ethers are not only superior to their polyphenyl analogues in physical properties but are also much better lubricants.

Frictional characteristics of the polyphenyl ethers, measured under the same conditions in the four-ball machine, also resemble those of di-2-ethylhexyl sebacate and again are far better than polyphenyls or silicones (Figure 9). The frictional characteristics of alkyl-substituted ethers are also somewhat better than those of the unsubstituted aryl ethers.

The polyphenyl ethers display satisfactory lubrication qualities in high-speed bearings; a 25-mm. bearing (*9*)

Table VIII. Effect of Radiation on Coking Tendencies of Polyphenyl Ethers

Ether	Radiation Level,[a] Ergs/G.	Coke Formed[b] at 800° F., Mg.
Bis(*p*-phenoxyphenyl) ether	None	0.2
	2.5×10^{10}	2.0
	5×10^{10}	3.2
	1×10^{11}	3.5
Bis[*p*-(*tert*-butylphenoxy)phenyl] ether	None	1.2
	2.5×10^{10}	1.5
	5×10^{10}	3.2
	1×10^{11}	4.4
Reference Compound		
MIL-L-7808 diester lubricant	None	0.3[c]
	1×10^{10}	41.4[c]

[a] Samples irradiated with electrons from 3 m.e.v. Van de Graaff generator. All irradiations were under nitrogen at 300 to 370° F. for 0.5 to 2 hr.

[b] See footnotes of Table VII for description of test conditions.

[c] 600° F. test temperature instead of 800° F.

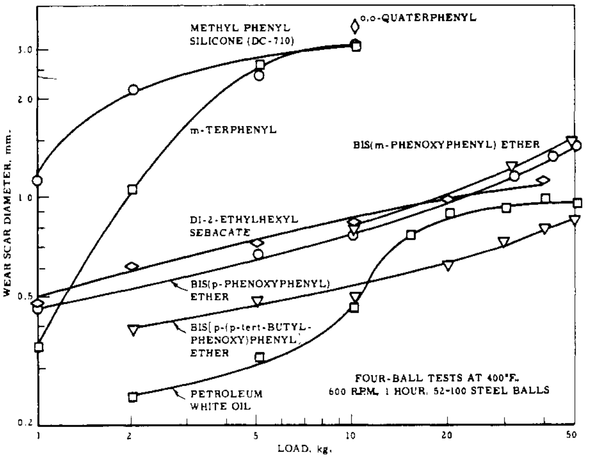


Figure 8. Four-ball wear test results with polyphenyl ethers

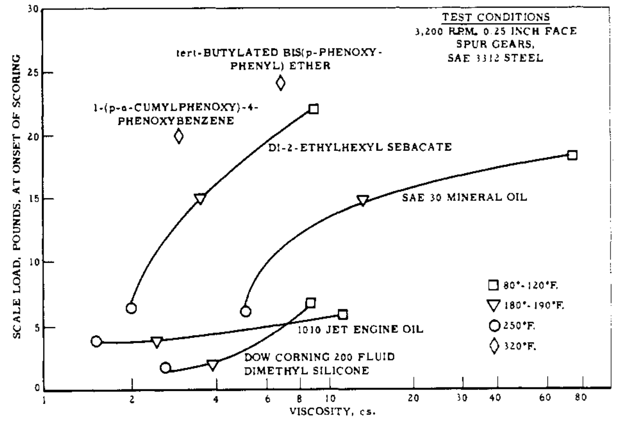


Figure 10. Performance of alkyl-substituted polyphenyl ethers in solw-speed gear tests

operated satisfactorily at 40,000 r.p.m., 200 pounds axial load and temperatures as high as 700° F. with either bis(*p*-phenoxyphenyl) ether or *tert*-butylated bis(*p*-phenoxyphenyl) ether. Under the same conditions a silicone fluid would not permit operation above 350° F. because of high friction.

Limited spur-gear performance data on the polyphenyl ethers are also promising. With 17- and 19-tooth gears of 6 diametral pitch (*3*), 20° pressure angle, and 0.25-inch face, operating at 3200 r.p.m. and a bulk oil temperature of 320° F., the two alkyl-substituted polyphenyl ethers exhibited better load-carrying capacities than would be predicted from their absolute viscosities alone. As illustrated in Figure 10, 1-(*p*-α-cumylphenoxy)-4-phenoxybenzene and *tert*-butylated bis(*p*-phenoxyphenyl) ether both display better load-carrying capacity than mineral oils or silicones of the same absolute viscosity. Although examined at only one temperature (320° F.), these ethers also carried somewhat higher loads than di-2-ethylhexyl sebacate was capable of supporting at lower temperatures where the absolute viscosities of the ethers and the ester are the same. Thus, the limiting score load of *tert*-butylated bis(*p*-phenoxyphenyl) ether at 320° F. is slightly higher than that of di-2-ethylhexyl sebacate at 130° F. where the viscosity of each fluid is 7 centipoises. Similarly, the score load of 1-(*p*-α-cumylphenoxy)-4-phenoxybenzene at 320° F. is higher than that of di-2-ethylhexyl sebacate at 195° F. where the viscosity of each is 3 centipoises.

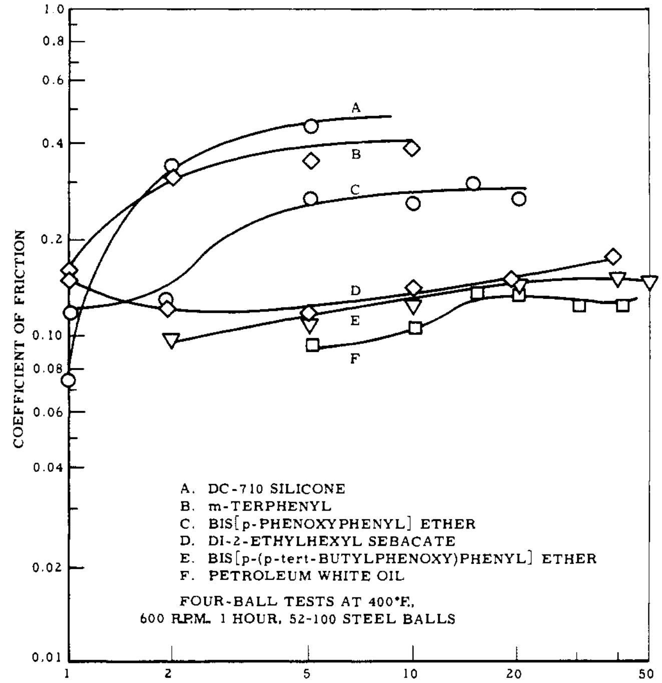


Figure 9. Coefficient of friction of some polyphenyl ethers

Further investigation of lubrication characteristics of the polyphenyl ethers is underway.

REMARKS

Although the polphenyl ethers were developed for the general requirements of future turbo-jet engines, their properties indicate that they may also find application in other fields where extreme conditions are encountered—e.g., high-temperature hydraulic fluids, base stocks for high-temperature and/or radiation resistant greases, heat-transfer media, reactor coolants and moderator fluids.

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LITERATURE CITED

(1) Am. Soc. Testing Materials, Philadelphia, Pa., Federal Test Method Standard No. **791**, Method **5106.2**, ASTM **D 664-54**, Method **1103.5**, ASTM **D 92-52** and Method **351.1**, ASTM **D 972-51T**.
(2) Bolt, R. O., Carroll, J. G., *Ind. Eng. Chem.* **50**, 221 (1958).
(3) Borsoff, V. N., *Trans. Am. Soc. Mech. Engrs., J. of Basic Eng.*, **81D**, 79 (1959).
(4) Burton, M. J., *J. Phys. & Colloid Chem.* **51**, 786 (1947).
(5) Colichman, E. L., Gercke, R. H. J., *Nucleonics* **14** (7), 50 (1956).
(6) Diamond, H., Kennedy, H. C., Larsen, R. G., *Ind. Eng. Chem.* **44**, 1834 (1952).
(7) Dornte, R. W., *Ibid.*, **28**, 26 (1936).
(8) Larsen, R. G., Perry, G. L., *Trans. Am. Soc. Mech. Engrs.* **67**, No. 1, 45 (1945).
(9) Reichenbach, G. S., Accinelli, J. B., Beaubien, S. J., *Am. Soc. Lubrication Engrs. Trans.* 1, 259 (1958).
(10) Sax, K. J., Saari, W. S., Mahoney, C. L., Gordon, J. M., *J. Org. Chem.*, to be published.

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