TABLE I

RESULTS OF WEAR MEASUREMENTS USING THE SHELL FOUR BALL WEAR TESTER

	Steel on					
	Steel			Brass		
Oil Load	5 kg.	10 kg.	20 kg.	5 kg.	10 kg.	20 kg.
Room temperature, 1 hour at 600 r.p.m.						
Methylsilicone	0.35 mm.[a]	0.49 mm.	. .	0.59 mm.	2.33 mm.	. .
Methyl-*p*-chlorophenylsilicone	.21	.33	. .	.42	0.60	. .
Methyl-*m*-chlorophenylsilicone	. .	.35	0.53	. .	.39	0.60
Room Temperature, 1 hour at 1200 r.p.m.						
Methyl-*m*-chlorophenylsilicone	. .	0.41	0.49	. .	0.42	0.59

[a] Average diameter of wear scar, in mm., on the three stationary balls in the Shell Four Ball Wear Tester.

cyclotrisiloxane was isolated from the hydrolysis product of methyl-*p*-chlorophenyldichlorosilane.

The chlorophenyl-containing organopolysiloxanes were prepared by the reaction of hexamethyldisiloxane and methylchlorophenylpolysiloxanes in the presence of sulfuric acid.[1] It was of interest to note that only negligible cleavage of the chlorophenyl-to-silicon bond occurred during the equilibration reaction whereas extensive cleavage of the phenyl-to-silicon bond occurs under similar conditions in phenylsiloxanes.[2]

It has been found that when these chlorophenyl-containing organopolysiloxane oils are used as lubricants they reduce the wear of steel and brass bearings over that obtained by use of the conventional methylsilicone oils. The oils were evaluated on the Shell Four Ball Wear Tester and the results of these tests are given in Table I.

Experimental

Methyl-*p*-chlorophenyldichlorosilane.—Three moles (574.5 g.) of *p*-chlorobromobenzene and 72 g. (3 moles) of magnesium turnings were allowed to react in 1.5 l. of anhydrous ether. After the reaction had proceeded to completion the ether solution of *p*-chlorophenylmagnesium bromide was added slowly with stirring to 470 g. of methyltrichlorosilane in 1 l. of anhydrous ether. After complete reaction had been effected the ether was stripped from the reaction flask and chlorosilanes were recovered by a very rapid vacuum distillation. By use of an efficient rectification column 197.2 g. of methyl-*p*-chlorophenyldichlorosilane, b.p. 161–164° (99–100 mm.), was recovered (34% yield).

Anal. Calcd. for $C_7H_7SiCl_3$: Cl (hydrolyzable), 31.44. Found: Cl (hydrolyzable), 30.9.

Methylbis-*p*-chlorophenylchlorosilane.—The low yield of methyl-*p*-chlorophenyldichlorosilane is due in part to the formation of methylbis-*p*-chlorophenylchlorosilane. In a second preparation of methyl-*p*-chlorophenyldichlorosilane 9 moles of *p*-chlorobromobenzene was used. From this run it was possible to separate cleanly methylbis-*p*-chlorophenylchlorosilane from the high boiling residue, b.p. 187° (5 mm.).

Anal. Calcd. for $C_{13}H_{11}SiCl_3$: Cl (hydrolyzable), 11.20; Cl (total), 33.59. Found: Cl (hydrolyzable), 11.5, 11.5; Cl (total), 34.5, 34.0, 33.6, 33.3, 33.1.

Methyl-*m*-chlorophenyldichlorosilane.—To a mixture of 144 g. of magnesium turnings in 3 l. of anhydrous ether was added dropwise 1000 g. of *m*-bromochlorobenzene. When the reaction had run to completion the solution of the Grignard reagent was added dropwise with stirring, to a solution of 1000 g. of methyltrichlorosilane in 500 ml. of anhydrous ether. Distillation of the reaction product gave 490.6 g. (yield 41.6%) of methyl-*m*-chlorophenyldichlorosilane, b.p. 150° (61 mm.).

Anal. Calcd. for $C_7H_7SiCl_3$: Cl (hydrolyzable), 31.44; Cl (total), 47.16. Found: Cl (hydrolyzable), 31.2; Cl (total), 47.0.

Equilibrated Methyl-*p*-chlorophenylsilicone Oil.—A solution of 160 g. of methyl-*p*-chlorophenyldichlorosilane in 150 ml. of ether was added to a vigorously stirred mixture of water and ether. After the hydrolysis was complete the ether layer was washed free of acid and then evaporated on a steam-bath until all the ether had been removed. A 98.7-g. portion of the siloxane so obtained was mixed with 98.7 g. of hexamethyldisiloxane and 4 ml. of concentrated sulfuric acid. This mixture was placed in a glass-stoppered bottle and shaken vigorously at room temperature for 24 hours. Then the oil was washed to free it of acid and distilled to remove the excess hexamethyldisiloxane (about 80 cc. recovered). This oil had a viscosity of 55.0 ctks. at 100°F. and 8.61 ctks. at 210°F.

Anal. Found: Cl, 16.9, 16.7, 16.9.

Equilibrated Methyl-*m*-chlorophenylsilicone Oil.—A sample (353.5 g.) of polymethyl-*m*-chlorophenylsiloxane was prepared by hydrolysis of methyl-*m*-chlorophenyldichlorosilane in an ice–water–ether system.

Anal. Calcd. for $[C_7H_7SiClO]_x$: Cl, 20.8. Found: Cl, 20.4.

An equilibrated oil was prepared by the reaction of 353 g. of polymethyl-*m*-chlorophenylsiloxane with 353 g. of hexamethyldisiloxane in the presence of 9 ml. of concentrated sulfuric acid. The method of carrying out the reaction and recovery of the desired oil is essentially the same as that described for methyl-*p*-chlorophenylsilicone oil. The viscosity of the final oil was 37.1 ctks. at 100°F. and 8.21 ctks. at 210°F.

Anal. Found: Cl, 18.1, 18.2.

1,3,5-Tris-*p*-chlorophenyl-1,3,5-trimethylcyclotrisiloxane.—In the preparation of polymethyl-*p*-chlorophenylsiloxane by the hydrolysis of methyl-*p*-chlorophenyldichlorosilane it was noted that a white crystalline solid was formed. This crystalline product was recrystallized from glacial acetic acid and shown to be 1,3,5-tris-*p*-chlorophenyl-1,3,5-trimethylcyclotrisiloxane, m.p. 125–126°.

Anal. Calcd. for $C_{21}H_{21}Si_3Cl_3O_3$: C, 49.3; H, 4.14; Cl, 20.8; mol. wt., 512. Found: C, 49.5; H, 5.0; Cl, 20.2; mol. wt., 512, 510.

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Preparation of Deuteroporphyrin IX Dimethyl Ester[1]

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As described in the literature, deuteroporphyrin IX dimethyl ester is generally prepared from hemin

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by the procedure of Fischer and Hummel,[2] and of Schumm.[3] The procedure involves three steps: fusion of hemin with resorcinol, demetalation of deuterohemin by a reducing mixture, and esterification of deuteroporphyrin. Recently Walter[4] reported a yield of 26.3% after the method of Fischer, *et al.*[2,5] A yield as high as 46.2% was obtained by us, when we increased the proportion of hemin and resorcinol to 1:5 and used iron powder in acetic acid and hydrochloric acid for demetalation as described by Corwin and Krieble.[6]

A much simpler method was worked out for preparation of the porphyrin directly from red blood cells. Demetalation takes place during the resorcinol fusion and a lengthy procedure of preparing hemin[7,8] from red blood cells is omitted.

In place of resorcinol, two of its derivatives, orcinol and 4-chlororesorcinol, were also tried. The former was found to give a comparable yield with resorcinol, while the latter gave a lower yield.

Paper chromatography[9] has been used as a guide to the purity of the product in these preparations.

Experimental

Preparation from Hemin and Resorcinol.—A sample of 100 mg. of hemin was thoroughly mixed with 500 mg. of resorcinol in an erlenmeyer flask and fused in an oil-bath at 190–200° for 15 minutes. The reaction mixture was then dissolved in 50 ml. of glacial acetic acid and 0.5 ml. of concd. HCl, treated with 50 mg. of iron powder and boiled for 10 minutes. It was then diluted with an equal volume of water, mixed with 80 ml. of saturated solution of sodium acetate and extracted with 50 ml. of ethyl acetate. The extraction was repeated twice with 25-ml. portions of ethyl acetate. The porphyrin in ethyl acetate solution was transferred into 5% HCl and returned to ethyl acetate. After removal of the solvent, the residue was esterified with 20 ml. of $CH_3OH–H_2SO_4$ (20:1) overnight. The ester was successively extracted with ethyl acetate, 5% HCl, and immediately transferred into chloroform. The chloroform extract was washed with 10 ml. of water four times. Crystals of the porphyrin ester separated out on standing. The yield after recrystallization from chloroform and methanol was 46.2 mg.

Preparation from Red Blood Cells (RBC) and Resorcinol.—A sample of 20 ml. of RBC about 2 months old was treated with 400 ml. of a solution of 1% oxalic acid in acetone according to a procedure[10] previously described. The residue weighing about 2 g. was fused with 5 times its weight of resorcinol as before. The fusion mass without any other treatment was extracted with ethyl acetate. After the porphyrin was transferred back from 5% HCl to ethyl acetate, it was esterified and extracted. The yield of porphyrin ester was 40.4 mg.

The yield and purity of the product depend upon the age of the blood used. When a sample of 7 g. of hemoglobin (Eastman Kodak Co.) was used instead of RBC, the yield of porphyrin ester was 7.2 mg.

When orcinol was used in the place of resorcinol in the fusion mixture, 20 ml. of RBC yielded 39.8 mg. of porphyrin ester. When 4-chlororesorcinol was used, the yield from 20 ml. of RBC was 30.0 mg.

Further Purification of Deuteroporphyrin IX Dimethyl Ester.—As shown in the papergram (Fig. 1), the crystalline porphyrin ester was contaminated with traces of several unknown porphyrin products which will be described in a later publication. Therefore it was chromatographed on a column of $CaCO_3$. Chloroform–benzene mixture (1:3) was used as the developing agent. The deuteroporphyrin ester constituted the lowest compact zone of the chromatogram, which was then cut out, repacked in a sintered glass funnel, and eluted with chloroform. After recrystallization from chloroform and methanol fine and microscopically uniform needles of deuteroporphyrin IX dimethyl ester were obtained, m.p. 223°. The absorptions of the product in ethyl acetate at 621, 568, 527 and 498 mμ, and in 5% HCl at 590 and 547 mμ were read. Its copper complex was also prepared in very fine and shining red needles, m.p. 234°. Its absorptions in ethyl acetate at 558 and 523 mμ, in acetic acid at 559 and 523 mμ were observed. Fischer and Lindner[11] reported a m.p. of 230° for the copper complex.

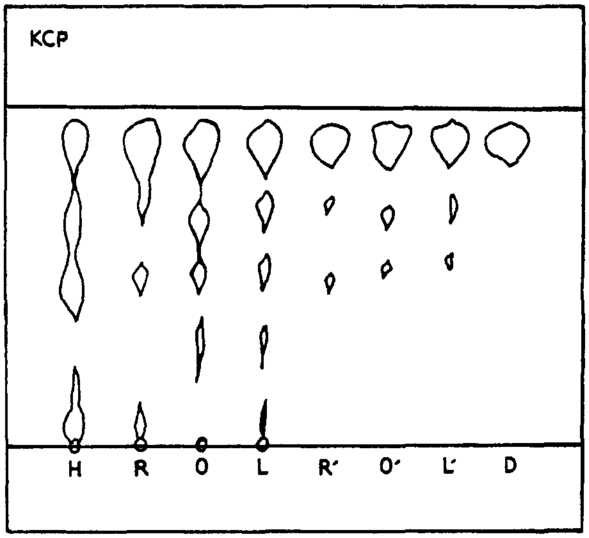

Fig. 1.—Papergrams of crude and purified deuteroporphyrin IX dimethyl ester from different sources. The developing solvent system, KCP, composed of 3.5 ml. of kerosene, 3 ml. of chloroform and 0.2 ml. of 1-propanol under chloroform atmosphere. H stands for the crude porphyrin ester prepared from hemoglobin and resorcinol, R that from RBC and resorcinol (hemin products followed the same pattern as R), O from RBC and orcinol, L from RBC and 4-chlororesorcinol, R′, O′ and L′ the corresponding recrystallized products, and D the chromatographically purified deuteroporphyrin IX dimethyl ester.

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Iodine Inhibition in the Flash Photolysis of Methyl Iodide

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The photolysis of methyl iodide vapor with mercury arc light sources has been studied in some detail.[1–3] The quantum yield is small, due to reac-

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