Phthalocyanines as High-Temperature Lubricants

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THE TERM "high-temperature lubrication" as used here refers to the temperature range 800° to 1300° F. Metal-free phthalocyanine, a solid organic compound, has been used successfully in this range to lubricate rolling and sliding contact bearings. It possesses remarkable thermal stability for an organic compound because of its highly resonating structure. This property, combined with the fact that the molecule has a planar structure, prompted experiments with phthalocyanine as a solid lubricant.

Studies using a modified 4-ball and a rolling disk apparatus have shown that metal-free phthalocyanine will reduce friction to a low level and will greatly decrease wear in the temperature range 800° to 1300° F. However, in order to achieve the best results, a pretreatment of the metal surface has been found advisable. The pretreatment consists of forming a film of the metal phthalocyanine on the bearing before use. These films were evaluated in a specially designed stick-slip apparatus.

STRUCTURE OF PHTHALOCYANINES

Phthalocyanines constitute a class of compounds characterized by the presence of a 16-membered ring, somewhat related to the fundamental structure found in chlorophyll and hemin. Figure 1 shows how four molecules of phthalonitrile (1, 2-benzenedicarbonitrile) can be considered to combine to form phthalocyanine. This particular reaction gives a very low yield of metal-free phthalocyanine, although this approach can be used to prepare many metal derivatives of phthalocyanine.

The two hydrogen atoms which are attached to the central nitrogen atoms of the phthalocyanine molecule are replaceable by a metal, which may form either ionic or covalent bonds with the organic molecule. The alkali and alkaline earth metals form ionic phthalocyanines, and most other metals have covalent bonds with two of the central nitrogen atoms and coordinate bonds with the remaining two nitrogen atoms. Figure 2 illustrates the structure of the copper phthalocyanine molecule. This compound is a well-known pigment, sold under the name of phthalocyanine blue. Corresponding compounds are known for practically every metal in the periodic table.

Thermal stability is one of the outstanding properties of phthalocyanines. The metal-free compound is slightly less stable than some of the metal derivatives, such as copper and iron phthalocyanines. In air, the metal-free phthalocyanine shows only a slight darkening after 4 hours at 850° F. In a vacuum it can be sublimed without decomposition at 950° F. Samples held at 1000° F. for several hours turn black, evolving ammonia and nitrogen.

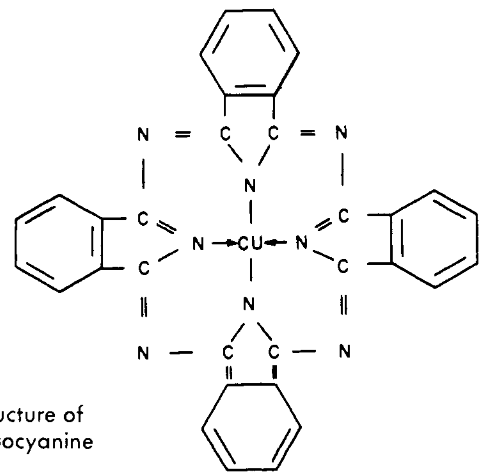

Figure 2. Structure of copper phthalocyanine

Metal-free phthalocyanine can exist in two crystalline modifications. The metastable alpha form is tetragonal, while the stable beta form is monoclinic. These forms can be distinguished readily by differences in their infrared spectra (2). The molecule is planar, and the x-ray data indicate that the planes are separated about the same distance as those in graphite. Figure 3 is an enlargement of an electron micrograph of copper phthalocyanine, made recently at Battelle Memorial Institute, showing the copper atoms in the 201 planes to be separated 12.5 A. The magnification is almost 2,000,000 times.

METAL COATING WITH PHTHALOCYANINE

Two approaches have been used to form a metal phthalocyanine on the surface of a metal: immersion in molten phthalonitrile, and high-temperature treatment with metal-free phthalocyanine in a controlled atmosphere. Immersion in a bath of molten phthalonitrile at 530° F. is an effective treatment for metals which form the most stable phthalocyanines, such as copper and iron. Four to 6 hours is generally required to obtain a suitable coating.

High-temperature treatment with metal-free phthalocyanine has proved to be the most effective, because it can be used with any metal. In this method, the metal sample is packed in metal-free phthalocyanine and heated for several hours in a nitrogen atmosphere. Three variables have been shown to be important to this process: temperature, gaseous environment, and time of treatment.

A temperature of 900° to 950° F. has been best for forming

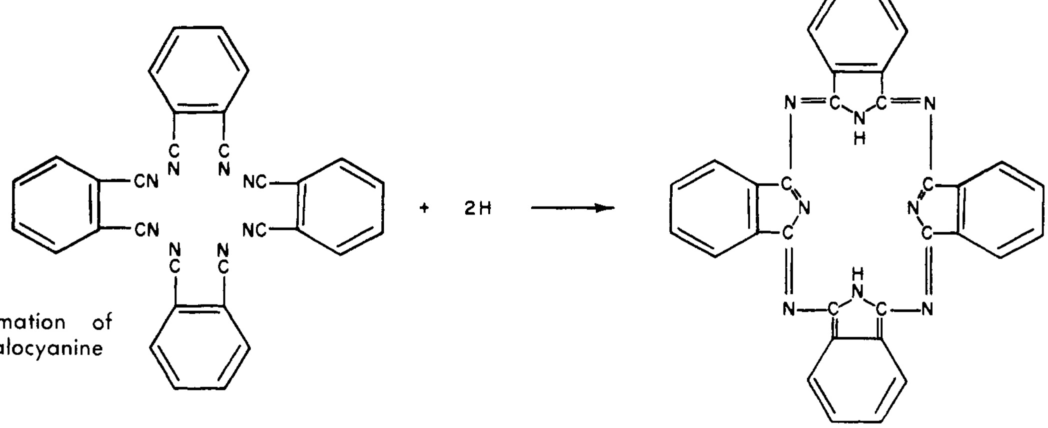

Figure 1. Formation of metal-free phthalocyanine

an adherent coating of the phthalocyanine derivative on the surface of the metal. Lower temperatures result in spotty coatings, or no coating at all, while higher temperatures promote decomposition of the phthalocyanine.

Phthalocyanine treatment has been attempted in hydrogen, ammonia, and nitrogen atmospheres, as well as in a vacuum. The best coatings have been obtained in nitrogen, and none were obtained with treatment in a vacuum. Table I gives the results of a series of experiments with stellite and with a TiC-Ni-Mo cermet in which temperature and atmosphere were varied. Although there was some evidence of a phthalocyanine coating in the ammonia environment, by far the best results were obtained in nitrogen.

Table I. Effect of Gaseous Atmosphere and Temperature on Coating of Stellite and Kentanium Bearing Alloys with Phthalocyanine

		Results for Stellite and Kentanium	
Atmosphere	Temp., °F.	Machined surface	Polished surface
Nitrogen	800	No coating	No coating
	900	Coated	No coating
	950	Coated	Coated
	1000	Blackened	Blackened
Ammonia	900	Slight coating	No coating
	1000	Blue-black	Blue-black
Hydrogen	900	No coating	No coating

A treatment time of 3 hours has been required to get the best coatings. Longer periods of treatment do not improve the coating.

Preparation of the metallic surface for treatment has consisted of degreasing with hexane, followed by boiling for 5 minutes in an alkaline cleaner commonly used to prepare metals for electroplating.

The "hole" in the center of the phthalocyanine molecule has been found by x-ray diffraction to have a radius of 1.35 A. The most stable metal phthalocyanines are those in which the effective radius of the metal atom approximates that size, as is the case with copper. The ease of formation of the phthalocyanine coating on the metal surface is in the order: copper, Armco iron, tool steel, stellite, and stainless steel. TiC-Ni-Mo cermet has also been successfully coated by the "hot pack" method. Presumably the coating forms and adheres by a reaction of the metal-free phthalocyanine with the metallic surface to give the metal phthalocyanine.

EXPERIMENTAL FRICTION AND WEAR EVALUATIONS OF PHTHALOCYANINE COMPOUNDS AS LUBRICANTS

A wide variety of experiments involving lubrication with phthalocyanine compounds have been made in this investigation (*1,3,4*). These include lubrication of rolling and sliding contact bearings and lubrication in metal-forming and cutting operations. The studies reported in the following sections are strictly applications research and as such were not directed at discovering the mechanisms of lubrication by solids or solid lubrication films. Naturally, many questions arise as to the underlying reasons for the lubrication behavior of phthalocyanine compounds. The authors hope to present information on certain of the fundamental aspects of phthalocyanine lubrication in the near future.

Plain Bearing Lubrication from −90° to 1500° F. Using Metal-Free Phthalocyanine. The first experiments at Battelle in which metal-free phthalocyanine was used as a lubricant were made 3 years ago, using plain journal bearings operating under conditions simulating airframe-bearing service (*1*).

Pendulum Plain-Bearing Experiments. Preliminary lubricant screening evaluations were performed on a pendulum apparatus in which the test bearing and lubricant were contained in a housing attached to a 900-pound pendulum. The journal bearing was 1 inch in diameter and consisted of two narrow bands. The unit stress on the bearing was about 10,000 p.s.i. Solid lubricant materials were applied as a paste of polyisobutylene and dry powder lubricant. Prior to the experiments, the bearing surfaces were "buttered up" with the paste. The pendulum was cocked to an angle of 45° and when the desired bearing temperature was reached, the pendulum was allowed to fall freely. The average coefficient of friction was determined from the average of the total number of pendulum oscillations for each of six free falls. The bearing material used was age-hardened silicon-Inconel and the shaft was a nitrided iron base superalloy (16–25–6).

Table II compares results of several pendulum experiments using metal-free phthalocyanine with those using well-known lubricant materials in the same apparatus.

It can be seen that the level of friction using metal-free phthalocyanine was lowest at temperatures of about 800° F. At this temperature, a deep purple film was present on the surfaces of the bearing and shaft. The film was adherent and even resisted knife scraping. At temperatures above 1000° F., there was no observable evidence of a phthalocyanine film.

Copper phthalocyanine did not lubricate nearly as well as metal-free phthalocyanine. From this, one might conclude that the chelating ability of metal-free phthalocyanine has a profound influence on lubricating behavior.

Oscillating Plain Bearing Lubrication at 25,000 P.S.I. and 1200° F. Silicon-Inconel bearings, 1 inch in diameter and 1 inch in length, were fitted into a link and assembled in a hydraulically actuated airframe-bearing apparatus. Shafts of nitrided iron base alloy (16-25-6 alloy) were pretreated with phthalonitrile to form an adherent phthalocyanine film. The buttered-up bearing-shaft unit was assembled in the machine. The shaft motion was oscillatory at a frequency of 12 cycles per minute; the surface speed was about 10 feet per minute. Bearing stresses up to 25,000 p.s.i., based on projected area, were imposed on the bearing-shaft-lubricant system. The load direction was reversed each half cycle of shaft oscillation.

Table II. Coefficient of Friction at Temperatures of −90° to 1500° F. Using Metal-Free Phthalocyanine Lubricant in a Pendulum Bearing Machine

Bearing material: age hardened S-Inconel
Shaft material: nitrided iron-base superalloy
Atmosphere: air

Lubricant	Bearing Ambient Temp., °F.	Av. Coefficient of Friction	Surface Appearance
None	Room	0.45	Some scoring
None	1000	0.44	Burnished
None	1200	0.40	Burnished
Metal-free	800	0.038	Burnished
phthalocyanine	1000	0.065	Burnished
plus polyisobutylene	1200	0.29	Burnished, slight galling
	1500	0.40	Burnished, spalled
	−90	0.21	No damage
Copper phthalocyanine	800	0.30	Slightly galled
Lead monoxide	1000	0.27	Slightly galled
	1500	0.26	Burnished
Graphite plus chlorofluorocarbon $Cl(CF_2CFCl)_4Cl$	600	0.14	Slightly galling
Molybdenum disulfide plus chlorofluorocarbon $Cl(CF_2CFCl)_4Cl$	600	0.15	Slight scoring

The results of simulated airframe-bearing experiments at various constant temperatures are summarized in Table III. Starting with an initial load of 5000 p.s.i., the lubricated bearing was permitted to oscillate at constant load until the friction coefficient appeared to be rising steadily. At this point the experiment was interrupted, the bearing was relubricated, and the coefficient at 5000 p.s.i. was checked before the load was increased by an increment of 5000 p.s.i. Figure 4 presents the friction-load-life behavior for an ambient temperature of 1000° F. The conditions indicated on each section of the graph prevailed until an interruption in the plot occurs. As can be seen, the coefficient of friction was reproducible after each relubrication at 5000 p.s.i. and 1000° F. As before, the coefficient of friction was relatively high at room temperature and dropped steadily, reaching a minimum in the vicinity of 750° to 800° F. This behavior was consistently reproducible and reversible.

At the conclusion of the experiment depicted in Figure 4, the cumulative number of cycles of shaft oscillation was about 16,000. The contacting surface had a black, burnished appearance, and no measurable wear could be detected. Some microscopic pitting was in evidence, but no scoring or galling was observed. The distinctive purple color of the pretreated shaft was not present. Electron diffraction patterns of the surface were not interpretable, apparently because of the complexity of the surface film composition. No evidence of a phthalocyanine compound was discernible.

These early experiments indicated that metal-free phthalocyanine possessed some interesting high-temperature lubricant potentialities.

Evaluation of Phthalocyanine-Pretreated Films in Stick-Slip Friction Apparatus in Air and Pure Argon. A special, very sensitive friction measuring apparatus was used to establish the behavior of solid lubricant films formed by pretreatment of iron base metal surfaces with phthalonitrile. A sketch of the apparatus is shown in Figure 5. Sliding contact specimens consist of a ½-inch diameter ball sliding on a flat block. The apparatus in capable of operation at ambient pressures as low as 10^{-5} mm. of Hg and temperatures up to 1350° F. The facility, therefore, provides a means of carefully and accurately controlling the gaseous environment. The instrument was used to determine the frictional behavior of the treated surface both in air and in very pure argon.

Experiments were performed using a tool steel ball and an Armco iron flat. The specimens were pretreated in phthalonitrile and an adherent purple film was formed. No additional lubricant was used in these experiments.

Friction data were obtained in air and in argon over the temperature range of 80° to 1000° F. These data are presented in Figures 6 and 7. Each represents the average friction coefficient for 2 to 6 passes over the same contact area at the temperature indicated. A fresh track on the flat was used for each point on the curves. However, the same area of the ball was used throughout the temperature range. The linear sliding speed was 0.17 mm. per second and sliding occurred in both directions in a reciprocating fashion. The coefficient of friction in air of pretreated solid lubricant films of phthalocyanine generally decreased with increasing temperature. On cooling, the friction increased. No stick-slip frictional behavior was observed as long as the solid lubricant film was not worn through.

The level of friction at the higher temperatures in very dry, high purity argon did not fall as low as when the environment was air. In contrast, friction was lower at low temperatures and remained almost constant over the temperature range of 80° to 1000° F. Again, no stick-slip frictional behavior was observed.

The life of the reacted solid lubricant films varied with temperature. At lower temperatures, wear life, both in air and argon, before the onset of large friction variations, was about 5 to 6 passes over the same track. At temperatures above 800° F., 2 or 3 passes appeared to be sufficient to wear through the film. Of course, it is expected that significant volatilization and decomposition of the lubricant film occurred at temperatures above 900° F. In all cases, it appears that the wear life of the preformed films is relatively low.

The coefficient of friction of these films might be lower for continuous sliding in one direction over the same surface, in that the phthalocyanine molecules would have an opportunity to assume a preferred orientation. In the experiments just described, reciprocating motion would tend to disorient the film with each reversal.

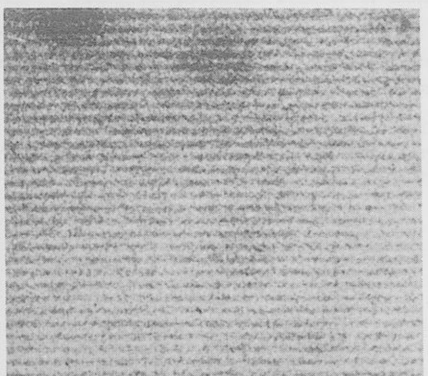

Figure 3. Electron micrograph of a copper phthalocyanine crystal at a magnification of almost 2,000,000 times showing the layer-lattice spacing of 12.5A. between layers

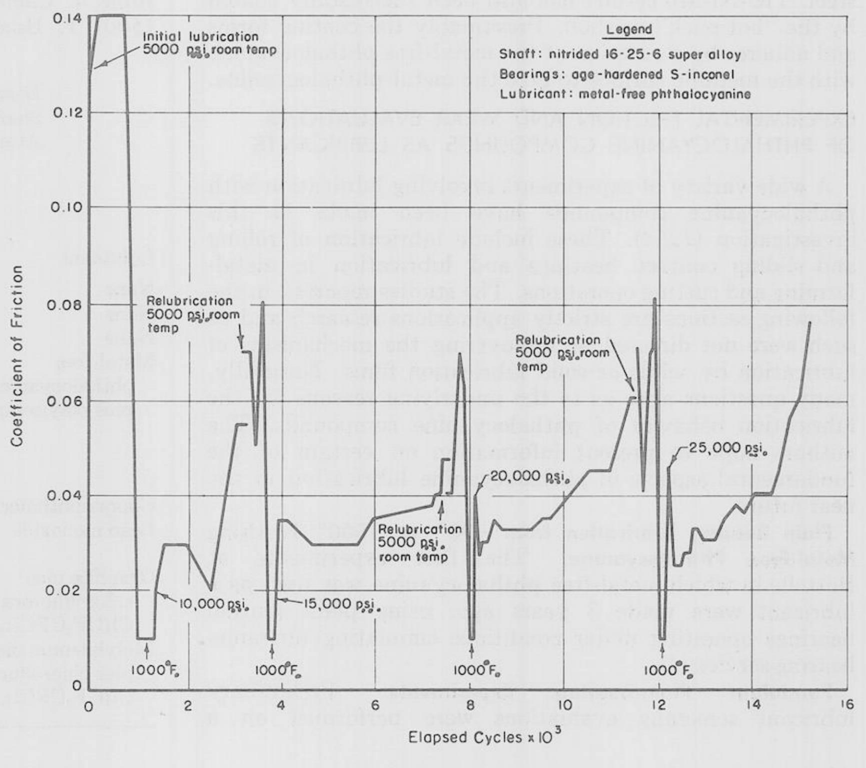

Figure 4. Friction-load-life behavior of oscillating-type plain journal bearing ⟶

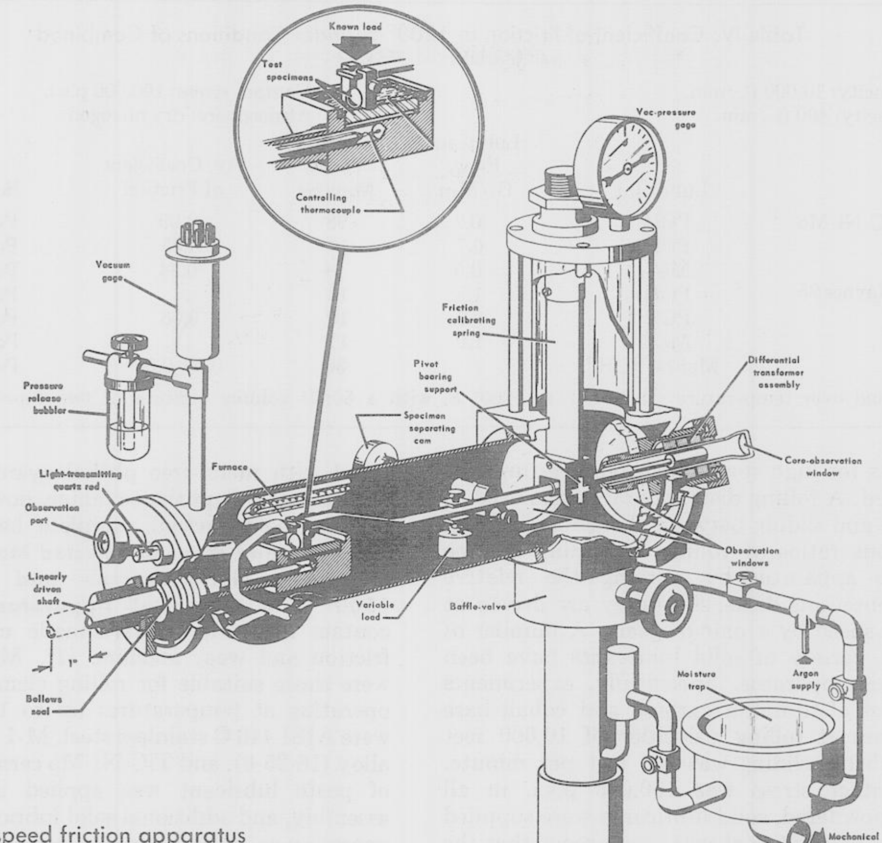

Figure 5. Stick-slip slow-speed friction apparatus

Table III. Coefficient of Friction Using Metal-Free Phthalocyanine to Lubricate Oscillating Plain Bearing at Unit Stresses up to 25,000 P.S.I. and Temperatures to 1200° F.

Bearing material: age-hardened S-Inconel
Shaft material: nitrided iron-base superalloy
Atmosphere: air

Lubricant	Bearing Ambient Temp., ° F.	Bearing Stress, P.S.I.	Av. Coefficient of Friction[a]
Metal-free phthalocyanine plus polyisobutylene	Room	5,000	0.075
	1000	5,000	0.01
	1000	10,000	0.035
	1000	15,000	0.035
	1000	20,000	0.05
	1000	25,000[b]	0.055
	Room	5,000	0.06
	1200	5,000	0.03
	1200	10,000	0.11
	1200	15,000	0.08
	1200	20,000	0.11
	1200	25,000[c]	0.08
	750	5,000	0.08
	750	10,000[d]	0.25
	–75	5,000[e]	0.23
Molybdenum disulfide	Room	5,000	0.01
	750	10,000[f]	0.12
Graphite	Room	5,000	0.01
	750	5,000	0.07
	750	10,000[g]	0.23
	600	5,000	0.05
	600	10,000	0.09
	600	20,000[h]	0.08

[a] Bearing assembly was disassembled after each 5000-p.s.i. load increment and relubricated. Generally from 1500 to 3000 cycles of shaft motion occurred between relubrication intervals.
[b] Specimen in good condition. [c] Bearing exhibited slight galling at edges. [d] Slight galling. [e] No damage after 20 cycles. [f] Bearing in good condition. [g] Galled. [h] Support bearing failed.

The frictional behavior of preformed phthalocyanine films is unlike graphite in that good lubrication is provided by the phthalocyanines in the absence of oxygen and water vapor. Also, good lubrication is provided over a wider temperature range than can normally be provided by graphite.

Lubrication with Phthalocyanine under Conditions of Combined Rolling and Sliding at Temperatures Up to

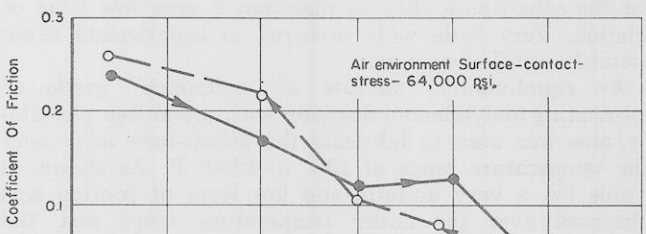

Figure 6. Friction-temperature plot for iron-base material pretreated with phthalonitrile

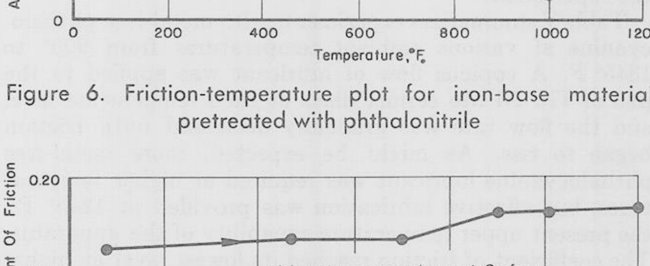

Figure 7. Coefficient of friction as a function of temperature for phthalonitrile-pretreated tool steel specimens

Table IV. Coefficient of Friction at 1200° F. under Conditions of Combined

Rolling velocity: 10,000 ft./min.
Sliding velocity: 400 ft./min.
Contact stress: 100,000 p.s.i.
Atmosphere: dry nitrogen

Disk Materials	Lubricant	Lubricant Flow, G./Min.	Running Time, Minutes	Av. Coefficient of Friction	Surface Appearance
TiC-Ni-Mo *vs.* TiC-Ni-Mo	PCH_2	0.2	98	0.09	Polished, black film
	PCH_2	0.7	16	0.05	Polished, black film
	MoS_2	0.3	8	0.34	Polished, black film
Stellite Star *J* *vs.* Haynes 25	PCH_2	1.5	13	...	Polished, black film
	PCH_2	0.9	19	0.03	Polished, black film
	MoS_2	1.0	17	...	Polished, slight pits
	$MoS_2 + PCH_2$[a]	...	36	0.03–0.09	Polished and smooth

[a] Experiment conducted over temperature range 130° to 1200° F. with a 50:50 volume mixture of two lubricants.

1345° F. Lubricants for high-speed, high-temperature ball bearings were studied. A rolling disk apparatus was used to simulate the rolling and sliding between elements of rolling bearings (*4*). Various ratios of rolling to sliding can be achieved with this apparatus by varying the relative diameters of two contacting disks, since they are driven at the same rotational speed by a pair of gears. A number of experiments with a variety of solid lubricants have been performed using this apparatus. Specifically, experiments using disk specimens of titanium carbide and cobalt-base alloys have been run at rolling velocities of 10,000 feet per minute in which the sliding was 400 feet per minute. The maximum contact stress was 100,000 p.s.i. in all experiments. Dry, powdered, solid lubricants were supplied continuously and no pretreatment was used except that the lubricant passed over the specimens during a brief run-in period. A dry nitrogen carrier gas was used so that molybdenum disulfide could also be used at high temperatures.

Table IV shows that the coefficient of friction of phthalocyanine-lubricated titanium carbide-nickel-molybdenum cermet is low in comparison with molybdenum disulfide. The level of friction appears to become lower as the quantity of phthalocyanine is increased.

Although good lubrication was provided for both TiC-Ni-Mo and cobalt-base alloys, more lubricant was needed for the cobalt-base alloy to maintain a very low level of friction. Very little wear occurred in experiments using metal-free phthalocyanine.

An equal-volume mixture of "microfine" grade of lubricating molybdenum disulfide with metal-free phthalocyanine was used to lubricate the cobalt-base alloy over the temperature range of 130° to 1200° F. As shown in Table IV, a very uniform and low level of friction was observed over the entire temperature range and the contacting surfaces were in excellent condition after the experiment.

Table V summarizes experiments with metal-free phthalocyanine at various ambient temperatures from 900° to 1345° F. A copious flow of lubricant was applied to the pair of TiC-Ni-Mo cermet disks at each temperature level and the flow rate was gradually decreased until friction began to rise. As might be expected, more metal-free phthalocyanine lubricant was required at higher temperatures, but effective lubrication was provided at 1345° F., the present upper temperature capability of the apparatus. The coefficient of friction reached its lowest level at higher temperatures. It is possible that lubricant reactions are more rapid at higher temperatures and thus provide a better lubricating film.

In all experiments where metal-free phthalocyanine was used very little powdery lubricant debris remained in the test chamber of the machine. Such residues did remain after experiments with molybdenum disulfide. Therefore, it would be expected that rolling element bearings lubricated with metal-free phthalocyanine would not clog up with metal-free phthalocyanine powder. No clogging was experienced in actual complete bearing experiments (*4*).

Friction and Wear of Selected Materials Lubricated with Metal-Free Phthalocyanine and Other Lubricants at 1000° F. in a Four-Ball Apparatus. A number of sliding contact experiments were made using a modified 4-ball friction and wear machine (*1*). Materials and lubricants were those suitable for rolling element bearings and gears operating at temperatures up to 1000° F. Ball materials were AISI 440 C stainless steel, M-1 tool steel, and iron-base alloy (16-25-6), and TiC-Ni-Mo cermet. A copious quantity of paste lubricant was applied initially on the 4-ball assembly, and additional solid lubricant was injected during operation as "puffs" in a nitrogen carrier gas.

Results of these experiments are presented in Table VI. The most striking result is the remarkably low wear and coefficient of friction of TiC-Ni-Mo cermet, when lubricated with metal-free phthalocyanine. With the exception of experiments with the M-1 tool steel, metal-free phthalocyanine provided lower friction and wear than either molybdenum disulfide or lead oxide.

After experimentation, the TiC-Ni-Mo balls had a deep purple film indicative of phthalocyanine, while the 440-C steel had only a slight straw colored film. Apparently, an adherent phthalocyanine film did not form (at least not a thick one) on the 440-C material. The post-test appearance of M-1 tool steel was similar to the blue-black oxide film that might appear on steel when subjected to elevated temperature. The iron-base alloy had a bright gold appearence after use with phthalocyanine lubricant.

The appearance of the TiC-Ni-Mo cermet and 440-C stainless steel is of special interest in that pretreatment with metal-free phthalocyanine did not produce any visible

Table V. Coefficient of Friction at Temperatures up to 1345° F. Under Conditions of Combined Rolling and Sliding Contact Using Metal-Free Phthalocyanine Lubricant

Rolling velocity: 10,000 ft./min.
Sliding velocity: 400 ft./min.
Specimens: TiC-Ni-Mo
Contact stress: 100,000 p.s.i.
Atmosphere: dry nitrogen blanket and carrier

Temp., °F.	Minimum PCH_2 Supply to Disks to Maintain Minimum Coefficient of Friction, G./Min.	Av. Coefficient of Friction
900	0.20 or less	0.28
1000	0.20 or less	0.20
1100	0.20	0.12
1200	0.24	0.08
1345	0.29	0.10

Table VI. Friction and Wear of Selected Materials Lubricated with Metal-Free Phthalocyanine and Other Lubricants at 1000° F. in a 4-Ball Apparatus

Sliding velocity: 700 ft./min.
Initial Hertz contact stress: 250,000 p.s.i.
Atmosphere: dry nitrogen

Wear Material	Lubricant[a]	Av. Equilibrium Coefficient of Friction	Av. Wear, Cu. In. per Min. 10^6
TiC-Ni-Mo Cermet	PCH_2	0.04	0.016
	MoS_2	0.25	1.8
	PbO	0.10	2.3
M-1 tool steel	PCH_2	0.14	2.4
	MoS_2	0.21	0.66
	PbO	0.15	1.4
AISI 440C stainless steel	PCH_2	0.25	2.3
	MoS_2	0.25	30.6
	PbO	0.21	20.0
Iron-base superalloy	PCH_2	0.2	4.8
	MoS_2	0.25	8.6
	PbO	0.3	14.3

[a] PCH_2, metal-free phthalocyanine; MoS_2, molybdenum disulfide; PbO, yellow lead monoxide.

adherent films on the 440-C steel, while extremely thick and adherent films formed very readily on the cermet. Apparently, chelation or other surface reactions of the lubricant with the various substrates are different.

Low Speed Complete Rolling Bearing Experiments. Laboratory and in-service evaluations of phthalocyanine lubricants on full rolling element bearings were made.

Laboratory Evaluation of Phthalocyanine. The laboratory bearings were of 440-C stainless steel and were of the tapered roller design. A 20-mm. bore bearing was run at a thrust load of 1000 pounds at 10 r.p.m. The solid lubricants were suspended in a commercial polyalkylene glycol lubricant to the extent of 10% by weight. The dispersion was made merely by mixing and agitation. The quantity of lubricant added to the bearing was sufficient to coat the surfaces. The results are shown in Table VII. The coefficient of friction was about the same with all three lubricants, but no wear was detected with metal-free phthalocyanine.

Service Evaluation of Phthalocyanine. Laboratory tests prompted a field trial in cylindrical roller bearings in a kiln car. Bearings of 25-mm. bore were normally lubricated with a 10% graphite–polyalkylene glycol mixture after each pass through the kiln. Roughly, 5 ml. of the lubricant mixture was squirted onto the bearing. Each pass consisted of about 36 hours, during which the bearings were exposed to temperatures of 500° to 550° F. The dead weight load was of the order of 700 to 800 pounds per bearing. The average force to move the car when relubricated with graphite after each pass was about 61 pounds. When a 10% metal-free phthalocyanine–polyalkylene glycol lubricant was used to relubricate the bearings only after each six passes, the average force was 54 pounds. It was noted that the phthalocyanine film on the rollers was beginning to rupture on the fifth pass after relubrication.

Table VII. Performance of Low Speed Tapered Roller Bearing at 600° F. Using Phthalocyanine Lubricants

Bearing material: 440 C. stainless steel
Lubricant: 10% by weight of solid in a polyalkylene glycol fluid
Atmosphere: air

Solid Lubricant Component	Friction Coefficient	Surface Appearance
Metal-free phthalocyanine	0.056	No wear detected
Chlorinated metal-free phthalocyanine	0.067	Roller worn and scored
Graphite	0.054	Slight wear

Low Speed Sliding Experiments at 600° F. The low speed sliding contact friction of cupped flat washers was evaluated using various solid lubricants dispersed (10% by weight) in a commercial polyalkylene glycol. A few drops of the dispersion were applied initially and no more was added during the course of the experiment. The contact stress on the M-2 tool steel washers was 3000 p.s.i. and the velocity was 30 feet per minute. The experimental results in Table VIII show that the phthalocyanine compounds performed outstandingly well.

Hot Forging, Cold Drawing, and Machining with Phthalocyanine Lubricants. Metal-free phthalocyanine performed very well as a hot forging lubricant for ferritic stainless steel. Forged specimens could be easily removed from the dies; excellent surface finish and die penetration were obtained. On the other hand, phthalocyanine lubricants performed poorly as compared with graphite, when forging an aluminum alloy.

Type 17-4PH stainless steel was cold drawn using a petroleum oil–lead soap as a standard. This lubricant provided low initial and steady draw forces, but the surface finish was poor. A 5% addition of metal-free phthalocyanine did not provide any reduction in draw force or improvement in surface finish.

Water-soluble, metal-free phthalocyanine sodium sulfonate (2% aqueous solution) provided lathe cutting efficiency superior to that of pure water or when dry. Results with water-soluble oil emulsions were comparable to aqueous solutions of metal-free phthalocyanine sodium sulfonate.

PREPARATION AND PROPERTIES OF PHTHALOCYANINES

The metal phthalocyanines are best prepared by the reaction of a salt of the metal with phthalonitrile in a high-boiling solvent such as trichlorobenzene. The copper derivative is prepared commercially by combination of a copper salt, phthalic anhydride, and urea with ammonium molybdate as catalyst.

In order to prepare metal-free phthalocyanine, it is necessary to form the lithium or sodium phthalocyanine derivative by reacting phthalonitrile with the metal salt of isoamyl alcohol. Demetallizing is then accomplished by exchange with a mineral acid or acid salt. In order to obtain a high purity product, the crude phthalocyanine is slurried in concentrated sulfuric acid and then poured onto crushed ice. This treatment destroys organic contami-

Table VIII. Low-Speed Sliding Contact Performance at 600° F. Using Metal-Free Phthalocyanine and Phthalocyanine Derivatives

Bearing material: M-2 tool steel
Contact stress: 3000 p.s.i.
Lubricant: 10% by weight of solid in a polyalkylene glycol fluid
Atmosphere: air

Solid Lubricant Additive	Minutes of Operation	Av. Coef. of Friction	Surface Appearance
No additive	5	. . .	Severe galling
Metal-free phthalocyanine	80	0.19	Good condition
Chlorinated metal-free phthalocyanine	400	0.17	Fair condition
Phthalonitrile	440	0.20[a]	Good condition
Graphite	1 to 10	. . .	Severe galling
C_{12}-amine sulfonate of metal-free phthalocyanine	120	0.10	Surface satisfactory

[a] Experiment performed at 825° F.

nants and consumes about 25% of the yield of phthalocyanine. Thorough washing after sulfuric acid treatment will give a product with only 0.05% ash. This low-ash, metal-free phthalocyanine has proved to be the most suitable material for lubrication purposes.

Ordinary solvents do not dissolve phthalocyanine, but it has slight solubility in chlorinated aromatic compounds, such as trichlorobenzene. Metal-free phthalocyanine can be purified by recrystallizing it from concentrated sulfuric acid. Strong chemical oxidizing agents will decompose it, but it is not affected by nonoxidizing acids, alkalies, or mild oxidants.

The stability of the compound to radiation is good. Data on neutron irradiation showed only 0.05% decomposition in 100 hours at 2×10^{13} neutrons per sq. cm. per second. Gaseous products were methane, hydrogen, and nitrogen. Phthalocyanine also proved to be stable to gamma radiation.

Semiconductor properties have been observed for phthalocyanine, and this activity can be ascribed to mobile pi electrons in the structure. Conductivity has been shown to be a linear function of the applied field.

CONCLUSIONS

Experimental data have been presented which demonstrate that metal-free phthalocyanine is a potential lubricant for extreme conditions of load and temperature. For the conditions under which the experiments were performed, metal-free phthalocyanine is most efficient as a lubricant in the temperature range of 800° to 1350° F. The phthalocyanine may be capable of lubrication at temperature in excess of 1350° F.

Although precise mechanisms of lubrication with phthalocyanines are not known at this time, it is believed that lubrication processes are similar to those which occur with other planar structure, solid lubricants, and that strongly adherent and protective lubricating films are formed by chelation of metal-free phthalocyanine with metal substrates. The apparent lack of lubrication provided by metallated phthalocyanines—for example, copper phthalocyanine—appears to support this concept of a lubricant film attached by chemical reaction to the substrate.

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Synthesis and Investigation of Polynuclear Alkyl-Polyphenyl Hydrocarbons as Potential High Temperature and Radiation-Resistant Fluids

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THE OBJECTIVE of the research program conducted at the University of Denver's Research Institute (*15*) was to investigate the feasibility of polynuclear aromatic compounds as potential high-temperature and radiation-resistant materials and to alter the molecular structure of the most promising representatives of this class of compounds in such a way as to improve their liquid range and lubricity with the least loss in thermal, oxidative, and radiation stability.

Promising compounds of this class were biphenyls, and low molecular weight polyphenyls such as terphenyls and quaterphenyls. The parent compounds of these classes have in themselves remarkable thermal stability, and it was therefore expected that a careful investigation of this group would lead to derivatives meeting the requirements of the Air Force.

A rather comprehensive literature survey of polyphenyl compounds and their derivatives revealed a series of biphenyl, terphenyl, and quaterphenyl compounds with high boiling points and sufficiently low melting points to suggest their use as starting materials for the synthesis of derivatives with more desirable properties.

DISCUSSION

A survey of the literature showed that the influence of the chemical structure of the parent compounds, as well as that of the substituents, on physical properties, particularly melting or pour points, can be summarized as follows:

The melting point (or pour point) of the polyphenyl compounds or their derivatives is in general higher if the over-all symmetry of the compound is high and is lower whenever this symmetry is reduced by change in structure of the parent compounds or the introduction of substituents.