

# The Wettability and Detection of Fluorescent Barrier Films

VINCENT G. FITZSIMMONS

*Surface Chemistry Branch  
Chemistry Division*

and

ELAINE G. SHAFRIN

*Laboratory for Chemical Physics*

March 31, 1972



**NAVAL RESEARCH LABORATORY**  
**Washington, D.C.**

Approved for public release: distribution unlimited.

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)		2a. REPORT SECURITY CLASSIFICATION	
Naval Research Laboratory Washington, D.C. 20390		Unclassified	
		2b. GROUP	
3. REPORT TITLE			
THE WETTABILITY AND DETECTION OF FLUORESCENT BARRIER FILMS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)			
Interim report on one phase of the problem.			
5. AUTHOR(S) (First name, middle initial, last name)			
Vincent G. FitzSimmons and Elaine G. Shafrin			
6. REPORT DATE		7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
March 31, 1972		18	9
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S)	
NRL Problems C02-04.301 and C02-10		NRL Report 7391	
b. PROJECT NO.			
RR 001-01-43-4751			
c. AirTask A32-520/652/70F51-543-203			
OrdTask 934-023/173-1/UF 17-546-401			
d. Strategic Systems Proj. Off. P01-0064		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
10. DISTRIBUTION STATEMENT			
Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY	
		ONR, NAVAIR, NAVORD, NAVMAT Department of the Navy (Office of Naval Research, Naval Air Systems Command, Naval Ordnance Systems Command, Strategic Systems Project Office)	
13. ABSTRACT			
<p>The storage and operational life of instrument ball bearings are greatly improved by NRL-developed "barrier films," i.e., thin films of fluorinated organic polymers applied to the metal surface to prevent the spread or migration of lubricant liquid away from critical bearing areas. Because major operational and economic advantages are derived from the use of extremely thin films (0.1 to 1.0 micron), the optimum coatings are difficult to detect visually. This poor visibility hampers inspection of the films for location and continuity, two factors which are critical to effective barrier performance.</p> <p>Current difficulties in determining barrier-film location could be alleviated by incorporating a suitable fluorescent indicator in the dilute solutions used to prepare the barrier films. Air-dried and heat-dried coatings solvent-deposited from an experimental formulation containing such an indicator are shown to exhibit a useful level of fluorescence under uv radiation (<math>\lambda = 3660 \text{ \AA}</math>) after solidification <i>in situ</i>. Continuing observations over a 44-month period confirm that the fluorescence of the solidified fluoropolymer is long lived. Parallel studies over a 34-month period indicate a small loss of fluorescence for films stored in a dry atmosphere (RH &lt; 50%), and a greater loss was experienced by those stored in a water-saturated atmosphere. The rate of loss for films subjected to such condensed water is much slower than that for films exposed to bulk water, however. The moisture sensitivity of the indicator roughly equals the corrosion sensitivity of the instrument ball bearings themselves and thus does not represent any additional limitation to the use of the coated bearings.</p> <p>Silicone oil-retention experiments and extensive contact angle measurements for a variety of organic liquids reveal no significant difference in wettability between the commercial and the experimental films under three conditions. The conditions of the films were as initially prepared, after prolonged storage, or after a 34-month simultaneous contact with a humid environment and a difficulty retained, chemically deleterious, but widely used lubricant (a chlorinated silicone oil). It is therefore recommended that the Revised Military Specifications for Barrier Coating Solutions and Processes contain a requirement for a long-lived fluorescent indicator.</p>			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Oil-barrier films						
Fluorescence						
Lubrication						
Lubricants						
Ball bearings						
Miniature electrical equipment						
Life expectancy						
Servo motors						
Synchros						
Gyroscopes						
Specifications						
Surface properties						
Fluorine compounds						
Silicon compounds						
Coatings						
Films						

## CONTENTS

Abstract .....	ii
Problem Status .....	ii
Authorization .....	ii
INTRODUCTION .....	1
EXPERIMENTAL APPROACH .....	2
Materials and Film Preparation .....	3
Equipment and Methods .....	5
BARRIER FILM FLUORESCENCE .....	5
RETENTION OF CHLORINATED-SILICONE LUBRICANT .....	7
FILM WETTABILITY .....	8
Comparison of Freshly Prepared Films .....	8
Effect of Moisture and Storage Conditions .....	10
SUMMARY AND CONCLUSIONS .....	11
ACKNOWLEDGMENTS .....	12
REFERENCES .....	12

## ABSTRACT

The storage and operational life of instrument ball bearings are greatly improved by NRL-developed "barrier films," i.e., thin films of fluorinated organic polymers applied to the metal surface to prevent the spread or migration of lubricant liquid away from critical bearing areas. Because major operational and economic advantages are derived from the use of extremely thin films (0.1 to 1.0 micron), the optimum coatings are difficult to detect visually. This poor visibility hampers inspection of the films for location and continuity, two factors which are critical to effective barrier performance.

Current difficulties in determining barrier-film location could be alleviated by incorporating a suitable fluorescent indicator in the dilute solutions used to prepare the barrier films. Air-dried and heat-dried coatings solvent-deposited from an experimental formulation containing such an indicator are shown to exhibit a useful level of fluorescence under uv radiation ( $\lambda = 3660 \text{ \AA}$ ) after solidification *in situ*. Continuing observations over a 44-month period confirm that the fluorescence of the solidified fluoropolymer is long lived. Parallel studies over a 34-month period indicate a small loss of fluorescence for films stored in a dry atmosphere ( $\text{RH} < 50\%$ ), and a greater loss was experienced by those stored in a water-saturated atmosphere. The rate of loss for films subjected to such condensed water is much slower than that for films exposed to bulk water, however. The moisture sensitivity of the indicator roughly equals the corrosion sensitivity of the instrument ball bearings themselves and thus does not represent any additional limitation to the use of the coated bearings.

Silicone oil-retention experiments and extensive contact angle measurements for a variety of organic liquids reveal no significant difference in wettability between the commercial and the experimental films under three conditions. The conditions of the films were as initially prepared, after prolonged storage, or after a 34-month simultaneous contact with a humid environment and a difficultly retained, chemically deleterious, but widely used lubricant (a chlorinated silicone oil). It is therefore recommended that the Revised Military Specifications for Barrier Coating Solutions and Processes contain a requirement for a long-lived fluorescent indicator.

## PROBLEM STATUS

This is an interim report; work on this problem is continuing.

## AUTHORIZATION

- AirTask A32-520/652/70F51-543-203
- OrdTask 934-023/173-1/UF 17-546-401
- Strategic Systems Project Office, Project Order P01-0064
- NRL Problem C02-10, Project RR 001-01-43-4751
- NRL Problem C02-04.301

Manuscript submitted January 19, 1972.

## THE WETTABILITY AND DETECTION OF FLUORESCENT BARRIER FILMS

### INTRODUCTION

Navy synchros and servo motors have been investigated to determine the cause of their early failure during service and storage (1). The principal cause of their unsatisfactory service and storage life has been identified as the creeping away of the limited supply of silicone lubricant from the load-carrying areas. Under the resulting boundary-lubrication conditions, failure occurs in the instrument ball bearings within these devices.

Recommendations were made (1) to use a novel technique developed at NRL (2,3). This technique involved applying a thin film of low-energy fluorochemical polymer to the metal surface to prevent the spread or migration of the lubricant liquid away from the active bearing areas. These barrier-coated instrument ball bearings increased the life expectancy of the assembled motors five- to tenfold. As a result of the success of barrier coatings, coated components now enjoy wide usage in a variety of Navy equipment having rotating components and ball bearings as well as in much civilian apparatus.

The barrier coating is formed by applying a thin film of dilute solution (2.0%) of a highly fluorinated polymer directly on the metal bearing just beyond those areas which require lubrication, as described in MIL-STD-1334(AS) (4). The solvent-deposited material quickly solidifies *in situ* to form a continuous, adherent coating so tenuous that its added weight and thickness do not alter the operational characteristics of the bearing. The effectiveness of the barrier is independent of film thickness, but is dependent on the film's location, continuity, adherence to the metal substrate, and continuing ability to restrict the spreading of the lubricating oil over prolonged periods under varied conditions of temperature and humidity.

Since major economic and operational advantages are derived from the use of the thinnest possible barrier layers, current commercial practice often results in transparent films of such thinness (0.1 to 1.0 micron) that they are difficult to detect visually. This limitation seriously hampers inspection of the barrier coatings for location and continuity, two factors which are critical to effective barrier performance.

The original specification (4) for the preparation of barrier coatings recommended that the coating operation be observed at low magnification (3X) under fluorescent light. Such observations verify the completeness and continuity of the film as evidenced by the rainbow colors of interference patterns on the treated surface. These color patterns are visible at oblique angles with fluorescent light after the coating has dried. The method has not proved completely successful as a production inspection procedure, however, since individuals vary in their visual response even to films which are completely acceptable. An additional limitation is the restricted applicability of the technique to detecting slight traces of fluoropolymer which might inadvertently have been permitted to contact areas of the bearings which require lubrication. Misapplication of the coating to the balls,

race grooves, or the land of land-riding metallic ball separators will prevent the lubricant from functioning and catastrophic ball bearing failure is certain.

Alternate ways to expedite inspection of coated bearings have been suggested, including the use of radiographic analysis. Preliminary studies by Autonetics Inc.\* indicated the possible utility of the method, but the complications attendant to the handling of radioactive systems made it economically inadvisable.

The method now under study for facilitating coating inspection was originally proposed by one of the authors (Mr. FitzSimmons). He suggested that if a fluorescent indicator were incorporated in the dilute fluoropolymer solution used to prepare the barrier films, the resulting solidified coating might fluoresce sufficiently under ultraviolet radiation to be readily detectable. In 1967 the supplier of the barrier film formulation, the Minnesota Mining and Manufacturing Company, complied with Mr. FitzSimmons' request. The supplier made available a solution combining a small amount (0.0039 wt-%) of the fluorescent dye "Tinopal SSG" (Geigy Chemical Company) with the basic commercial formulation for the barrier coatings.

Preliminary observations of coatings prepared at NRL from this experimental formulation indicated a usefully high degree of fluorescence even from extremely thin coatings which had been allowed to solidify on metal surfaces. This confirmed the potential of the method for the inspection of barrier films and for the detection of undesirable traces of fluoropolymer in forbidden areas.

The present investigation has the following objectives:

1. To establish that the introduction of a fluorescent indicator results in sufficient improved detectability of the barrier coatings to expedite their inspection immediately after preparation for film continuity or misapplication;
2. To determine whether the fluorescent indicator is sufficiently long lived within the solidified polymer coating to be useful for identifying aged coated specimens after storage or use (a frequent problem in stock inventory and routine maintenance and overhaul); and
3. To determine the extent to which the introduction of the fluorescent indicator alters properties of the film critical for effective barrier performance, such as adherence to the substrate or ability to retain oil either immediately after preparation of the barrier film or after prolonged storage or use.

Particular attention is paid to the effects of moisture on these properties, since many fluorescent materials have appreciable solubility in water.

## EXPERIMENTAL APPROACH

Several properties of the polymerized fluorescent formulation and the same formulation without the fluorescent indicator were compared for films: (a) as initially prepared,

\*J. L. Bray, Engineering Assurance, North American Aviation, Inc., Autonetics Division, Anaheim, California, presented "A Radiographic Method of Barrier Film Detection and Measurement" at the meeting of the Instrument Precision Ball Bearing Section, American Ordnance Association, Indianapolis, Indiana, on June 13, 1967.

(b) after brief exposure to bulk water (including both condensate and quiescent or running water), (c) after 44 months of storage in a dry atmosphere, and (d) after 34 months of storage in a humid environment in direct contact with a difficult and chemically deleterious lubricant (a chlorinated silicone). These conditions were chosen to provide information on the effects of storage; no attempt was made to simulate conditions of coated-bearing usage.

Experimental observations were made on (a) fluorescent behavior, as estimated by the unaided, dark-adapted eye; (b) oil-retaining ability of the films as measured by contact angles exhibited by a series of selected pure organic liquids; (c) the ability of the films to retain a notoriously "creeping" and chemically damaging lubricant (a widely used chlorinated silicone-type oil) for long periods of time; and (d) the adherence of the films to the metal substrates.

### Materials and Film Preparation

The barrier film formulations studied in this investigation were (a) FX706A, the standard nonfluorescent formulation distributed commercially by the Minnesota Mining and Manufacturing Company, and (b) FX 706-23866-43A, an experimental fluorescent formulation from the same source. Basically, both formulations comprise a 2% solution by weight in xylene hexafluoride of a perfluoroalkyl-substituted methacrylate polymer. This polymer is capable of air-drying at room temperature to form a solid characterized by an outermost surface rich in perfluoroalkyl groups and, as a consequence, similar in wetting properties to the surfaces of polymers A and S studied earlier by Bernett and Zisman (5). To this basic solution the manufacturer has added the fluorescent dye Tinopal SSG (from the Geigy Chemical Corporation) in a concentration of 0.2% based on the weight of the fluoropolymer (i.e., equivalent concentration of 0.0039% of the total solution). As used, therefore, the added cost of the fluorescent indicator is minimal, despite the \$32/lb price of the dye. The finished solution was filtered to remove an insoluble haze.

To facilitate subsequent measurements of contact angles and oil-retaining ability, the barrier films were applied to flat metal specimens, rather than to actual ball-bearing assemblies. The specimens were square (1-3/4 by 1-3/4 by 1/64 in.) stainless-steel (type 304) plates similar in composition to the type 440C steel used in manufacturing miniature ball bearings. These plates were abraded with a random motion against #600 waterproof carborundum paper under running water with a slurry of nonionic detergent, flushed with warm water followed by distilled water, and observed to be completely water-wetted. They were then dried by flushing with reagent-grade acetone to simulate the conditions specified in the preparation of commercial coatings.

The barrier films were prepared by lightly wiping the clean, dry metal surface with a dilute polymer solution and allowing the solvent to evaporate. Most specimens were allowed to air-dry at room temperature, thus simulating commercial instrument bearing coating practice at the time this research was initiated. With the subsequent requirement for heat curing of barrier coatings (6), a coating of the fluorescent experimental formulation was prepared by heating the solvent-deposited film to 100°C for 15 minutes, to determine whether heat treatment would destroy the fluorescent response of the indicator. Because this heat-treated specimen was prepared relatively late in the research program, no data

were obtained on the storage life of heat-cured coatings which, however, were found to be relatively unaffected by this recent requirement on a short-term basis.

Two types of specimens were prepared. Those designed for extensive contact angle measurements were fully coated over their whole upper surfaces and are identified in Table 1 by a code number preceded by the letter F. The second type of specimens, bearing the code letter R, were prepared with their barrier coatings in the form of an annular ring approximately 1/8 in. broad surrounding an area of bare metal about 1/2 in. in diameter. Each specimen had a minimum of three such rings well spaced on its upper surface. This ring form of the coating permitted observations to be made on the ability of the coating to retain a drop of chlorinated silicone lubricant in direct contact with the metal. The ring configuration also provided a physical situation giving maximum opportunity for the silicone to penetrate the metal/coating interface.

Table 1  
The Effect of Exposure to Moisture on the Fluorescence of Barrier Films of  
FX706-23866-43A (Fluorescent MMM Formulation) on Stainless-Steel Substrates

Specimen History			Fluorescent Behavior		
Identification	Exposure to Liquid Water	Exposure to Water Vapor at $T = 22^{\circ} \pm 3^{\circ}C$	Specimen Age at Time of UV Exposure	$\lambda = 2537 \text{ \AA}$ (short uv)	$\lambda = 3660 \text{ \AA}$ (long uv)
R-5 R-5	None None	None 10 Months dry	1 Day 10 Months	Bright all over Moderate	Bright all over Moderate
F-3 F-3	None None	None 34 Months dry	1 Day 34 Months	— Moderate — but over large central area only	Bright all over Moderate — but over large central area only
F-3 R-2	None None	44 Months dry 34 Months in $H_2O$ -sat'd air	44 Months 34 Months	As above None	As above Faint
F-2 F-2	None Immersed 140 min in dist. $H_2O$ at $38^{\circ}C$	None None	1 Day 1 Day	— —	Bright all over Whole surface is less fluorescent than before, but much more fluorescent than flushed specimen F-1
F-2	Same	34 Months dry	34 Months	Only one faint streak fluoresces	Only one faint streak fluoresces
F-1 F-1	None Flushed 140 min in running distilled $H_2O$ at $30^{\circ}$ - $45^{\circ}C$	None None	1 Day 1 Day	— —	Bright all over Whole surface fluoresces, less than before and much less than immersed specimen F-2
F-1	Same	34 Months dry	34 Months	Only one tiny spot fluoresces	Only one tiny spot fluoresces
R-3	Same	34 Months in $H_2O$ -sat'd air	34 Months	None	Faint

The silicone used for these observations was an additive-free, methyl chlorophenyl silicone (Versilube F50, General Electric Company) with a viscosity of 70 cs at  $25^{\circ}C$  ( $77^{\circ}F$ ), a specific gravity of 1.05 at  $25^{\circ}C/25^{\circ}C$ , and a low surface tension of 21.0 dynes/cm at  $25^{\circ}C$  (7). It was chosen for the long-term oil-retention studies because it is the most difficult to retain of all of the silicone oils currently used to lubricate precision instrument bearings. It is extensively used because of its wide temperature range viscometric capability and thermal stability, despite its poor behavior in lubricating steel-on-steel contacts under boundary conditions. However, its potential degradation products, including those from hydrolysis, could be chemically injurious to the metal/barrier

coating system, particularly at temperatures in excess of 175°C, the realistic operating temperature for instrument bearings.

### Equipment and Methods

The extent of fluorescent response of the indicator-tagged barrier coatings was estimated visually for coatings illuminated with ultraviolet radiation from Mineralight Model SL 2537 lamp (short uv,  $\lambda = 2537 \text{ \AA}$ ) or from Mineralight Model SL 3660 lamp (long uv,  $\lambda = 3660 \text{ \AA}$ ) in an otherwise unilluminated darkroom.

The wettability of the barrier coating was determined by measurements at 20°C of the angles of contact ( $\theta$ ) exhibited by sessile drops of a series of purified organic liquids of the surface tension ( $\gamma_{LV}$ ) indicated. Measurements with a direct-reading goniometer telescope (8) were made by viewing the profile of a slowly advanced drop obtained by adding successive small increments of liquid to the original drop. This drop-buildup method (8) generally results in a maximum, reproducible value of  $\theta$  which is slightly higher than that exhibited by the sessile drop originally contacting the surface.

The storage experiments were all conducted in a temperature-controlled and humidity-limited room. During the 44-month observation period, the temperature was maintained at  $22^\circ \pm 3^\circ \text{C}$ . The relative humidity never exceeded 50% and for better than half of each year it was below 20%.

For the so-called "dry" storage, each specimen was placed in an acid-cleaned, dry weighing bottle capped with a close-fitting unlubricated ground-glass stopper. The closed container was not further protected from contact with the room atmosphere. For the "humid" storage, each specimen was mounted on an acid-cleaned, dry, open-ended glass cylinder resting on a perforated shelf suspended inside a conventional laboratory desiccator (Fig. 1), closed with an unlubricated, close-fitting ground-glass lid. In place of the conventional desiccant, however, the lower chamber of the desiccator contained about 200 cc of distilled water. To ensure equilibrium between this water reservoir and the enclosed vapor space above it, disks of filter paper were placed along the desiccator walls so that their lower portions were immersed in the water. Capillary action then continuously wicked moisture up into the air space for evaporation while keeping the filter paper securely anchored to the desiccator walls. The glass cylinders supporting the specimens were staggered in length so there would be minimal mechanical contribution to stratification of the moisture-saturated atmosphere (Fig. 1).

### BARRIER FILM FLUORESCENCE

Extensive, bright fluorescence was observed for both air-dried and heat-cured coatings prepared from the experimental formulation. The fluorescent response to long wave uv ( $\lambda = 3660 \text{ \AA}$ ) was stronger than to short uv ( $\lambda = 2537 \text{ \AA}$ ). Under either radiation, however, the intensity of fluorescence varied widely across a coated area, reflecting the uneven distribution of the polymer solution during its application by wiping.

The effect of various treatment and storage conditions on the fluorescence of air-dried coatings is summarized in Table 1. Indoor storage (temperature =  $22^\circ \pm 3^\circ \text{C}$ ) in a dry atmosphere (relative humidity < 50%) in a closed container for periods of 10, 34, and

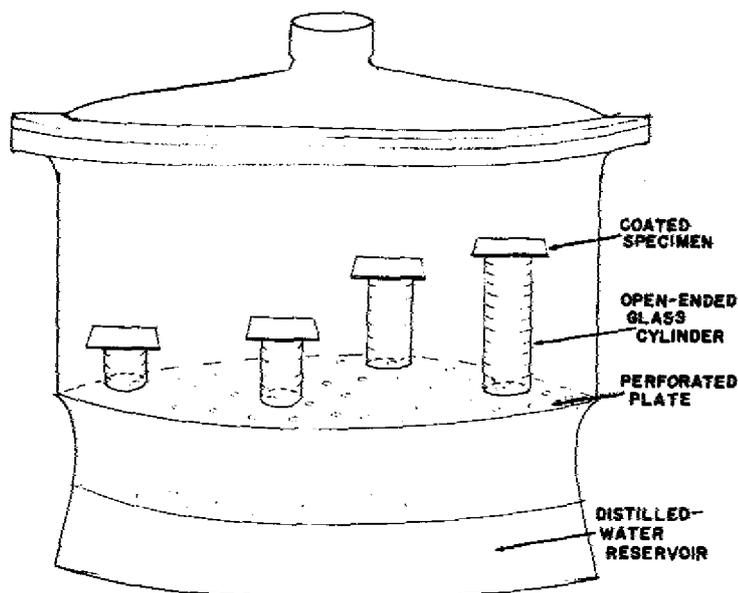


Fig. 1 — Chamber for storage of barrier-coated specimens in water-saturated atmosphere

44 months resulted in a progressive, small decrease in both the intensity and area of fluorescence. Comparison of the 34-month-old film with a film freshly prepared from the same stock solution of experimental formulation showed the freshly prepared film to be more fluorescent than the aged film. Either there was a loss of fluorescent material from the solidified film during prolonged standing or the rate of deterioration of the fluorescing dye was greater in the solidified coating than in the dilute polymer solution. Even after 44 months of dry storage there was still sufficient fluorescence to permit the ready detection of the solidified coating, but an accurate definition of the precise area covered by the coating (i.e., film continuity) would no longer be possible.

Indoor storage for 34 months in a water-saturated atmosphere resulted in a complete loss of fluorescent response to short uv and a pronounced, but not total, loss to long uv. Thus, although the coating was still detectable under long uv, it is apparent that the fluorescent component is strongly susceptible to water vapor.

Two experiments were performed to determine the sensitivity of the fluorescent component to liquid water. In the first, the film-coated metal was immersed 2 hours in a limited volume ( $\approx 10$  cc per square centimeter of barrier coating) of distilled water at  $38^\circ\text{C}$  ( $100^\circ\text{F}$ ); the resultant loss of fluorescent response indicated considerable extraction of the dye. In the parallel experiment, an identically prepared specimen was continuously flushed with freshly distilled water at temperatures close to  $38^\circ\text{C}$  for the same 2-hour period. This specimen showed a much greater loss of fluorescence than that contacted with a limited supply of water, indicating that the loss of fluorescence was the result of dissolving out the fluorescent indicator into the surrounding bulk water.

When both of these specimens were stored in closed, dry containers for 34 months, there was a considerable further decrease in their fluorescent behavior. The loss of fluorescence was even greater when storing a flushed specimen in a water-saturated atmosphere,

with only a faint residual fluorescence detectable under long uv and none at all under short uv.

These results suggest that the fluorescent indicator would be useful for barrier films stored or used at length in dry environments only. Nevertheless, the persistence of fluorescent behavior under long-uv radiation over periods as long as 44 months indicates considerable promise for the use of the fluorescent formulation.

It might be noted that at no time was there any evidence that the fluorescent indicator migrated or transferred to areas of the surface other than those to which the indicator-tagged barrier coating had been applied.

## RETENTION OF CHLORINATED-SILICONE LUBRICANT

Qualitative observations were made on the spreading behavior of Versilube F50 chlorinated silicone placed on bare metal surfaces surrounded by barrier rings prepared from the original and the experimental formulations. A drop of silicone was placed within each of the three (or more) widely separated rings on each metal specimen. Regardless of which formulation was employed, the silicone spread rapidly over the bare metal ( $\theta \approx 0$ ) until it reached the inner edge of the ring, at which point it abruptly ceased spreading and remained in the form of a lens of liquid ( $\theta \neq 0$ ). No difference in oil retentiveness could be detected between the plain and the fluorescent barrier films.

Parallel observations were made on a second set of plain and fluorescent film specimens which had been exposed to running, warm distilled water for 2 hours and then allowed to dry for several more hours. Again, there was no discernible difference between the two formulations. Moreover, the behavior of the Versilube on these water-washed specimens was indistinguishable from that on specimens which had not been exposed to bulk water.

On each of the above specimens, the drops of Versilube were allowed to remain in simultaneous contact with the bare metal and the enclosing barrier ring for the duration of the 34-month high-humidity storage test. After removal from the water-saturated atmosphere of the test chamber, the specimens were allowed to air-dry at room temperature for several hours before observations were made on the 34-month-old drops of silicone oil. Although the Versilube was still visible within the ringed areas of all four specimens, there were qualitative differences in the appearance of the liquid lenses. For the fluorescent coatings, both the water-extracted and the unwashed specimens were found to retain the Versilube as a relatively thick lens of liquid. This was also the case for the nonfluorescent coating which had not been exposed to bulk water. The water-extracted nonfluorescent specimen (R-4), however, showed considerable variability in its retention abilities. Thus, the silicone retained by two of the rings appeared as a very flat lens, while that remaining within the third ring was essentially just a damp patch. Additionally, in the case of the third ring, minute droplets of the silicone were visible resting on the barrier coating itself, but there was no evidence that any of this oil had been able to strike through the coating or to spread on the bare metal beyond the barrier ring.

In the first two rings of the nonfluorescent, water-extracted specimen R-4, the contact angles of the retained liquid lenses were estimated at between  $5^\circ$  and  $15^\circ$  with some variation around the perimeter of each lens. If some of that aged Versilube liquid was

then "teased" away from the original lens of retained liquid with a clean platinum wire and moved onto the adjacent barrier coating, there was an immediate and marked increase in the contact angle exhibited by the oil. Thus, on the first ring, the "teased" drop of old oil exhibited a contact angle of  $58^\circ$ ; this compares very favorably with the contact angle of  $64^\circ$  exhibited by a built-up drop of Versilube freshly transferred from the stock bottle onto the 34-month-old barrier ring.

In the case of the third ring of the nonfluorescent, water-extracted specimen R-4, there was not sufficient aged Versilube liquid present within the barrier ring to permit "teasing" a portion onto the barrier itself. It was possible, however, to measure the contact angles exhibited by the minute droplets of Versilube which had migrated onto the barrier ring during prolonged storage. Because of their small size and their closeness, the drops did not lend themselves to precise measurements of  $\theta$ . Nevertheless, measurements made on five different optically accessible limbs of the droplets all fell within the range of  $39^\circ$  to  $45^\circ$ , which still represents an effective range for preventing the spreading of the silicone oil. Further confirmation of the effectiveness of the ring was provided by the  $63^\circ$  contact angle observed for a built-up drop of freshly applied Versilube.

Final confirmation of the oil-retaining effectiveness of all of the barrier films, fluorescent or not, came when fresh drops of Versilube F50 were placed on the area between the 34-month-old rings (i.e., on bare metal surface which had never previously been in contact with liquid silicone). In each case the silicone spread rapidly until it approached the outer perimeter of the rings, at which point spreading in the direction of the rings ceased abruptly, although continuing in all other directions.

The above results prove that the barrier coatings, whether fluorescent or plain, remain tightly adherent to the metal surface and retain a high degree of oil retentiveness even after prolonged exposure to a hostile environment, including high humidity and the possible presence of potentially damaging hydrolytic degradation products of the chlorophenyl silicone. These results are of special interest because they represent the first known observations on the long-term adherence and oil retentiveness of the commercial formulations under such controlled, adverse conditions.

## FILM WETTABILITY

To quantify the oil-retaining ability of the barriers after various conditions of storage, measurements were made of the contact angle ( $\theta$ ) exhibited by a series of liquids of different surface tensions whose sessile drops rested on the barrier films. The liquids were chosen to represent various classes of compounds so the results would permit a generalized view of the ability of the barrier coatings to retain various types of liquids.

### Comparison of Freshly Prepared Films

Table 2 lists the values of  $\theta$  observed on several related polymer surfaces. The data are grouped according to the wetting liquids. The upper portion of the table contains the data observed for a variety of miscellaneous liquids with surface tensions ( $\gamma_{LV}$ ) at  $20^\circ\text{C}$  ranging from 72.8 dynes/cm for water to 21 dynes/cm for the chlorinated silicone studied in the previous section. In a separate tabulation below are the data for the homologous

Table 2  
Comparison of Wetting Properties of Freshly  
Prepared Barrier Film Materials

Liquid	Surface Tension at 20°C (dyne/cm)	Contact Angles (degrees) on				
		Commercial Barrier Film (Nonfluorescent) FX 706A	Fluorescent Barrier Film FX 706-23866-43A		Polymer A*	Polymer S*
			Film F-0	Film F-2		
Miscellaneous Liquids						
Water	72.8	117	117	117	120	118
Formamide	58.2	—	109	107	110	109
Methylene iodide	50.8	—	94	96	98	97
Ethylene glycol	47.7	—	99	101	103	102
Hexachloropropylene	38.1	—	80	78	78	77
Dicyclohexyl Chlorinated silicone (Versilube F50)	32.8	—	74	73	77	76
	21	—	—	—	—	—
n-Alkanes						
Hexadecane	27.6	71	71	71	74	73
Tetradecane	26.7	69	67	68	71	71
Tridecane	25.9	67	64	66	70	69
Dodecane	25.4	63	63	66	68	67
Decane	23.9	64	61	62	64	64
Critical surface tension for n-alkanes, $\gamma_c$ (dyne/cm)	—	—	11		10.6	11.1

\*Data from Ref. 5.

series of n-alkanes which are conventionally used to determine the critical surface tension ( $\gamma_c$ ) for spreading on low-energy surfaces.

Columns 4 and 5 of Table 2 list the values of  $\theta$  observed on independently prepared films of the fluorescent barrier formulation, freshly prepared. For comparison, the third column presents data for many of the same liquids on a freshly prepared barrier film of the same formulation without the fluorescent indicator. Comparison of these data proves that the introduction of the fluorescent component does not alter the wettability of the barrier. Moreover, both barrier formulations closely resemble in their wetting behavior their polymer precursors, polymer A and polymer S, whose data have been reproduced in the sixth and seventh columns of the table. These data were originally published as  $\cos \theta$ -vs- $\gamma_{LV}$  plots by Bennett and Zisman (5), and the values given in Table 2 were determined from the plots. The close similarity in wetting of all of the polymer surfaces facilitates subsequent comparisons (see below) of the effect of humid storage on the present barrier films with the fog-chamber tests reported earlier (9) for the barrier-film prototypes.

When the cosines of the contact angles exhibited by the series of n-alkanes are plotted as a function of the liquid surface tension, the data points are found to describe a good straight line (Fig. 2). The extrapolation of this line to the  $\cos \theta = 1$  axis indicates a value of the critical surface tension for spreading ( $\gamma_c$ ) of the n-alkanes as 11 dynes/cm for both types of barrier films. The limited number of specimens measured makes it unrealistic to assign a more precise value to the intercept.

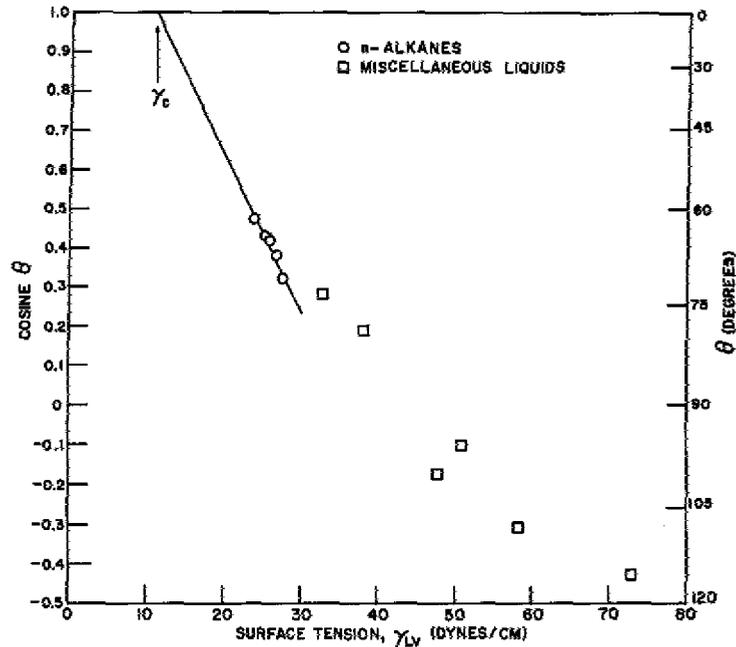


Fig. 2 — The wettability of freshly prepared fluorescent barrier films

#### Effect of Moisture and Storage Conditions

No significant changes occur in the wettability of the fluorescent films during prolonged storage in dry atmospheres (RH < 50%). The variations in contact angles shown in Table 3 are minor and nonsystematic; they are readily explained by the limited number of specimens examined and the experimentally imposed restrictions against cleaning the surfaces during the continuing storage studies.

Table 3  
Effect of Storage Conditions on Barrier Film Wettability

Storage Conditions		Contact Angles (degrees)							
Relative Humidity (%)	Length of Storage	Experimental (Fluorescent) Film				Commercial (Nonfluorescent) Film			
		Water	Methylene Iodide	Hexa-decane	Chlorinated Silicone	Water	Methylene Iodide	Hexa-decane	Chlorinated Silicone
<50	1 Day	117	95	71	—	117	—	71	—
<50	1 Month	118	98	71	56	—	—	—	—
	34 Months	115	102	72	65	—	—	—	—
100	34 Months	113	98	74	64	118	103	71	68

4. Military Standard Process for Barrier Coating of Anti-Friction Bearings MIL-STD-1334(AS), Dec. 23, 1969.
5. M. K. Bennett and W. A. Zisman, J. Phys. Chem. 66, 1207 (1962).
6. V. G. FitzSimmons, NRL Letter Report 6170-417a:VGF:blr, Aug. 12, 1971, Subject: "Barrier Film Contamination, Report to Chairman, NavAirSysCom Bearing Action Team concerning," serial 6362.
7. General Electric Technical Data Book S-96, "Silicone Fluids."
8. H. W. Fox and W. A. Zisman, J. Colloid Sci. 5, 514 (1950).
9. M. K. Bennett and W. A. Zisman, "Hydrophobic and Oleophobic Fluoropolymer Coatings of Extremely Low Surface Energy — Properties and Applications," NRL Report 6039, Feb. 1964.