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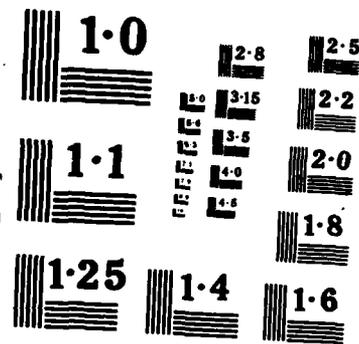
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<p>The subject of this investigation was the use of polymeric films to prevent fretting corrosion and wear. The friction and wear of the films was measured in an apparatus in which a ball was reciprocated on a flat. In some tests, the films were on the balls, but in most tests the films were on the flats. The measure of wear was the time required for the film to be worn through to the substrate. All of the polymers tested were thermoplastics or non-crosslinked elastomers. The following factors were investigated: normal load, frequency and amplitude of motion, film thickness, humidity, and atmosphere composition. The major conclusions from the study were as follows.</p> <p>There was a wide variety in the lives of polymeric films in a fretting interface. Polyvinyl chloride consistently exhibited the longest film lives. Some of the films caused damage to the steel ball, e.g., polyvinyl chloride, while others, such as polystyrene, did not.</p>			
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**The Effects of Thin Polymeric Surface Films
in Reducing Fretting Corrosion and Wear**

Final Report

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1. Problem Statement

This proposed research consists of a systematic investigation of the effects of thin polymeric surface films on fretting corrosion, metallic contact, and wear under both oscillatory and unidirectional sliding contact; emphasis will be on fretting phenomena in steel-on-steel systems. The primary goal is to attempt to understand the mechanism(s) by which such films are capable of protecting the surfaces from damage. Variables to be studied using pre-formed polymeric films will include polymer type and structure, adhesion, rheological behavior, and film thickness. In addition, the "in situ" mechanism of formation of protective polymeric films on rubbing surfaces, proposed by one of the principal investigators, will be examined.

Fretting is defined as wear phenomena occurring between two surfaces having oscillatory relative motion of small amplitude; fretting corrosion is defined as the type of fretting damage which occurs when the debris produced is a chemical reaction product between constituents of the surface and the environment. Fretting and fretting corrosion are important problems since they involve wear, corrosion, damage, and even fatigue failures of a wide variety of mechanical systems.

The basic approach proposed here is to bring together recent advances in three areas in studying the use of polymeric films to reduce fretting damage and wear, namely, advances in (a) polymer science and technology including the tribological behavior of polymers, (b) experimental techniques for investigating tribological phenomena, and (c) methods for examining in detail the physical and chemical nature of solid surfaces and of thin films on solid surfaces.

It is proposed to carry out both oscillatory and unidirectional sliding contact experiments by using a modified ball-on-cylinder device. This system was developed originally for fundamental studies of metallic contact in the transition from hydrodynamic to boundary lubrication. In addition, a recently-developed device for fretting corrosion research using various geometries will be used. Designed experiments are planned to determine the significance of various factors (e.g., adhesion, rheological and viscoelastic behaviour, film thickness) on fretting, contact, and wear, as well as interactions among these factors. Possible relationships between physical and chemical changes in polymer films and the effectiveness of such films in preventing fretting corrosion and other tribological damage will be examined.

2. Research Results

The approach taken at VPI&SU for the study of fretting mitigation through the use of thin polymer films on metal surfaces consists of hypothesis formulation and experimental verification. In most instances, complete verification of hypotheses was not achieved and the experimental results were used to formulate new hypotheses. In addition, some experiments were performed for the sole purpose of observing phenomena such as polymer film breakdown, fretting of metals in contact with polymers and debris generation and migration. These observations then became the basis for hypotheses which require verification. Another part of the program was the development of experimental techniques such as coating preparation, dynamic measurements, and environmental control as well as the use of

statistical methods of experiment design and analysis. In this section, some of the proposed hypotheses and experimental results will be discussed.

In the initial study of the program, four polymer films were applied to the surface of 52100 steel balls and then oscillated on 1045 steel plates. The variables in the study were the polymer composition and the roughness of the steel plate. Three of the polymers, polytetrafluoroethylene, polysulfone, and low density polyethylene caused pitting of the steel surface in a ring around the contact. The fourth polymer, polyvinyl chloride did not cause any pitting. The time required for the polymer film to wear through to the metal was indicated by an electric circuit which indicated a drop in voltage when metallic contact occurred. Polyvinyl chloride films had the longest lives on polished surfaces and ground surfaces with sliding both parallel and perpendicular to the lay of the grinding marks. Low density polyethylene had the lowest average film life on all surfaces but it displayed the greatest variability in film life. Polytetrafluoroethylene had a long film life comparable to that of PVC on smooth surfaces but a short film life comparable to that of LDPE on the ground surfaces. Polysulfone film lives were the reverse of those for PTFE.

The two major conclusions from this first study were that polyvinyl chloride, the only chlorine containing polymers included in the program, did not cause pitting of the steel and that the life of the films was shortest on the ground surfaces when sliding perpendicular to the lay. Two mechanisms were postulated for the absence of steel wear in the presence of the PVC film. Both hypotheses were based on the assumption

that the chlorine was removed from the polymer chain. One hypothesis was that the chlorine reduced the magnitude of the oxygen potential in the steel and polymer interface. The second hypothesis was that the released chlorine reacted with the steel to form iron chloride which has better lubricating properties than iron oxide. To test these hypotheses, two parallel studies were performed.

In one study, two chlorine containing polymers, PVC and polyvinylidene chloride, PVDC, were coated on 52100 steel balls and then oscillated against polished 1045 steel plates. The load and film thickness were chosen so that the films did not wear down to the metal in 30 minutes. The variables were humidity and atmosphere (air and nitrogen). Tests were also run with the steel plate replaced by glass and with a thermal stabilizer added to the PVC. Chemical analyses of the coating on the ball and the plate in the area of contact were performed by ESCA. The most significant observation was the discoloration of the coating which occurred in the contact area under certain conditions.

The discoloration is associated with degradation of the chlorine containing polymers by a process called dehydrochlorination during which hydrochloric acid is formed from hydrogen and chlorine stripped from the polymer chains. The discoloration was most pronounced in the presence of air, 25 percent humidity, and iron. The thermal stabilizers decreased the degree of discoloration. No fretting of the steel was found and no iron could be detected on the polymer wear scars. Polymer transferred to the steel appeared to be deficient in chlorine when compared to the original coating on the ball. Iron chloride could not be identified because the binding energies are very close to those of iron

oxide which was ever present on the steel plates. While the evidence suggested that dehydrochlorination occurred the formation of iron chloride could not be confirmed.

In the other study, PVC coatings were applied to the steel plates, thus the sliding occurred between the coating and the 52100 steel ball. A five factor (load, frequency, amplitude, film thickness, and humidity), two level, full factorial experiment was performed with two replicates (total of 64 tests). The film life, friction, and wear of the plates and balls after film breakthrough were measured.

The most significant result was that the film life at 17 percent relative humidity was 15 times that at 58 percent humidity. One possible explanation for this result was that the higher humidity enhanced the retention of the hydrochloric acid produced during dehydrochlorination in the interface. The presence of the hydrochloric acid thus accelerated the dehydrochlorination process. An analysis of variance of the film life data showed that all main effects and 21 interactions were significant at a confidence level of 99 percent. This result is an indication of the complexity of the mechanism of film breakthrough. For example, for several variables an increase in the variable would cause the film life to increase at one level of humidity and decrease at the other level.

A study of the film life of 10 polymers with load as a variable was performed to determine the performance polymers with a wide range of properties. The films were applied to steel plates and had thicknesses which ranged from 10 to 130 μm . The average film lives varied from 15 s to over an hour. Two polymers which had long lives and did not cause

any damage to the 52100 steel balls were polyimide and polystyrene. The polyimide films were 11 μm thick and showed evidence of film transfer to the steel ball. The polystyrene films were 85 μm thick and the transferred material on the ball was finely divided and loosely attached.

As a follow-up to this study, two studies were performed: the effect of thickness of polystyrene films on the film life and the effect of humidity and load on the life of films of five polymers. In the former study, it was found that time required for the ball to wear through the film was proportional to the wear scar volume for film thicknesses from 7.9 to 40 μm . Above 40 μm the lives were much longer than predicted by the proportional relationship. The development of the wear scar was observed by optical and scanning electron microscopy, and by profile measurements. The measurements revealed that initially the wear rate was high followed by a period of lower constant wear rates, and finally a gradual increase in wear rate until the metal substrate was exposed. The photomicrographs suggested that the initial high wear rate was caused by plastic flow while the subsequent wear was dominated by the fatigue mechanism of particle formation.

In the other study, a statistically designed experiment was performed to determine the effect of load and humidity on the lives of polyvinyl chloride (PVC), polyvinylidenechloride (PVDC), polystyrene (PS), and polyimides (PI) modified with 10 and 20 percent polysiloxane films. The results indicated that film lives were significantly longer at lower humidity for all the polymers except PS, especially at the lower loads. The lives of the PVC films at the lowest loads were 10

times or more greater than those of the other films. The films of PVDC had the shortest lives.

One of the last studies looked at two elastomers, polyurethane and styrene-ethylene-butylene (SEBS). Film life was measured as a function of frequency, amplitude, and thickness. An excellent correlation was found between film life and the ratio of the amplitude to the film thickness raised to a -5 for polyurethane and -4.5 for SEBS. Photomicrographs showed that the film failed in two stages. First, debonding occurred between the elastomers and the substrate, and second, tears or cracks initiated and propagated perpendicular to the sliding direction near each end of the stroke. Eventually, the cracks opened wide enough so that the ball could touch the steel substrate. The lives of the polyurethane films were greater than those of SEBS but were not as long as those of the polymers mentioned in the previous study.

The frictional work done during a cycle of motion of the ball was recorded for many different conditions of amplitude and film thickness. Three stages were identified starting when the motion reversed direction. First, relaxation of the friction force with no significant displacement. Second, elastic shear deformation of the film, and third, sliding of the ball on the film. When the frictional work was a minimum as a function of the number of fretting cycles, the cracks in the film initiated.

The infrared microscope was modified to measure temperature in a reciprocating contact. A variety of materials in contact with sapphire have been tested. Some typical results for the average temperature rise in the center of the contact were:

<u>Material</u>	<u>Frequency (Hz)</u>	<u>Amplitude (mils)</u>	<u>Atmosphere</u>	<u>Temperature°C</u>
steel	100	6	nitrogen	4-5
steel	200	3	nitrogen	4-5
steel	50	20	nitrogen	10-11
steel	50	20	air	6
polystyrene	200	3.5	air	3

General Conclusions

1. There is a wide variety in the lives of polymeric films in a fretted interface. Polyvinyl chloride has consistently exhibited the longest film lives.
2. A polymeric film not only must have a long life, it must not damage the metal which is sliding on the surface. Polystyrene consistently showed no damage to the ball surfaces whereas polyvinylchloride caused the balls to wear.
3. Almost all solvent cast films debonded from the substrate during the fretting test. This debonding contributed to the reduction in film life, particularly for the elastomers for which debonding was a precursor for crack formation and propagation.
4. The failure mechanisms varied with the polymer composition. Polystyrene and PVC failed by plastic flow followed by wear particle formation by a fatigue process. The elastomers failed by debonding, crack initiation and propagation which exposed the substrate to the ball.
5. Temperature rises in fretting interfaces appear to be quite low and thus would not contribute significantly to film degradation or softening.

3. List of Publications

Furey, M. J., Eiss, N. S., Mable, H. H., and Sweitzer, K. A., "The Effects of Thin Polymeric Surface Films on Fretting Corrosion and Wear," Proc. Eleventh International Conference in Organic Coatings Science and Technology, Ed. A. V. Patsis, Advances in Organic Coatings Science and Technology Series, Vol. 9, Technomic Publishing Co., Inc., Lancaster, PA, 1987, pp. 110-119.

Rorrer, R. A. L., Mable, H. H., Eiss, N. S., Jr., and Furey, M. J., "The Wear and Friction of Polyvinylchloride Coatings Under Fretting Conditions," ASLE Paper No. 87-AM-2D-1.

Raciti, R., Eiss, N. S., Jr., Mable, H. H., and Furey, M. J., "The Effect of Thickness on the Lives of Polystyrene Films Subjected to Fretting Conditions," Proceedings of the International Tribology Conference 1987, December 2-4, 1987 in Melbourne, Australia.

Puzio, D., Eiss, N. S., Furey, M. J., and Mable, H. H., "A Study of Chlorine-Containing Polymer Coatings in a Fretting Interface," submitted for publication in Langmuir, a journal of the American Chemical Society.

The following Master of Science Theses were published at Virginia Polytechnic Institute and State University, Blacksburg, VA.

Sweitzer, K. A., "The Effects of Thin Polymeric Surface Films on Fretting Corrosion," September 1984 (Major Advisor, N. Eiss).

Puzio, D., "A Study of Chlorinated Polymer Coatings in a Fretting Interface," November 1985 (Major Advisor, N. Eiss).

Rorrer, R. A. L., "The Effects of Load, Frequency, Slip Amplitude, Humidity, and Film Thickness of Polyvinyl Chloride on Fretting Corrosion," December 1985 (Major Advisor, H. H. Mable).

Day, K. A., "The Use of Thin Polymeric Coatings to Prevent Fretting Corrosion and Metallic Contact in Steel-on-Steel Systems," March 1986 (Major Advisor, M. J. Furey).

Raciti, R., "The Effect of Film Thickness on the Behavior of Polystyrene-Coated Steel Disks Under Fretting Conditions," January 1987 (Major Advisor, N. S. Eiss).

Veyret-Abran, C., "Friction and Degradation of Rubber Coatings Under Fretting Conditions," October 1987 (Major Advisor, M. J. Furey).

Gaydos, P. A., "The Effects of Load and Humidity in Friction and Life of Polymeric Coatings Used to Prevent Fretting Corrosion," (expected to finish December 1987; Major Advisor, N. S. Eiss).

4. Participating Scientific Personnel

All personnel were in the department of Mechanical Engineering unless indicated otherwise.

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C. Veyret-Abran, M.S. November 1987

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