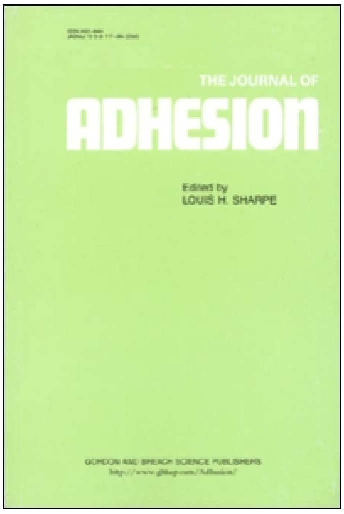

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Frictional Properties of a Composite Surface: Titania on Glass

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ABSTRACT

Partial coatings of titania (anatase) on glass, at surface coverages as low as 10%, can significantly reduce the surface damage which occurs when glass surfaces are rubbed together. The effectiveness of the coating depends upon the presence of a boundary lubricant on the uncoated portions of the glass surface. It is proposed that increased resistance to surface abrasion is obtained because the titania-coated regions support the rubbing surfaces and thereby prevent the pressure on the uncoated areas from becoming great enough to break down the boundary lubricant layer.

INTRODUCTION

THE SURFACE damage or scratch which occurs when two glass surfaces are rubbed together is caused by the formation and subsequent shear of glass-glass junctions as one surface moves over the other [1, 2]. Damage of this type can be significantly reduced by covering the glass surface with a monolayer of long-chain organic molecules which acts as a boundary lubricant [3]. Silicones and various waxes and resins have also been used as boundary lubricants. Recently, coatings of titanium dioxide and stannic oxide have been found to impart scratch resistance to glass [4, 5]. The effectiveness of these coatings is increased considerably when a boundary lubricant is also used [5, 6]. Moreover, the combination of oxide coating and lubricant is more effective than either one alone.

In the present paper we describe the frictional properties of well-characterized titania coatings on glass. A mechanism consistent with these properties is proposed to explain the improved abrasion resistance provided by the coatings.

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EXPERIMENTAL

Materials and Surface Preparation: Polydibutyl titanate (Du Pont Tyzor® PB organic titanate) was used to obtain titania coatings. The organic titanate was deposited on soda-lime glass microscope slides (A. H. Thomas Red Label brand; 2.5x7.6 cm) from solutions (1 to 7 wt %) in reagent grade carbon tetrachloride. The coatings were obtained either by withdrawing the slides from the solution using a Fisher-Payne Dip-Coater, or by spreading the solution over the slides using a second slide as a doctor blade. After evaporation of the solvent the slides were heated to 550°C for about 90 minutes. Electron diffraction and x-ray measurements showed that the residue on the glass after heating was primarily anatase, the low-temperature form of titanium dioxide.

Some of the slides were treated with an aqueous solution of trimethyloctadecylammonium chloride immediately after cooling to 25°C. This compound was obtained from Armour Industrial Chemical Co. as Arquad® 18-50, a 50% solution in an isopropanol-water mixture. The slides were immersed in a 2% solution of the quaternary ammonium salt (pH = 5 to 6) for about one minute and then rinsed with distilled water for 10 to 15 seconds. During rinsing the slides became hydrophobic; i.e., the water drained from the surface with a finite receding contact angle. This indicated that an adsorbed monolayer of the surfactant was retained on the surface [7].

Apparatus and Methods: Figure 1 is a diagram of the apparatus used to

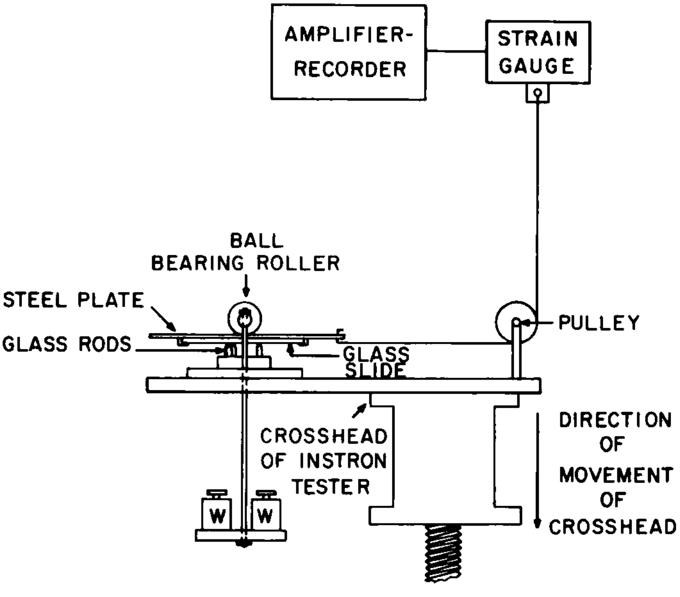

Figure 1. Friction apparatus.

produce surface abrasion under controlled loads and to measure the frictional force between sliding glass surfaces. A supporting platform for the glass surfaces was attached to the crosshead of an Instron tester. A glass slide, mounted on a steel plate, was drawn over the hemispherical ends of three fire-polished, soda-lime glass rods (6-mm diameter) as the crosshead moved down. To stabilize the steel plate, the three rods were arranged in a triangle. The plate was connected to the Instron strain gauge by a nylon cord and the load was applied to the plate through a roller bearing attached to a pan containing weights (W). The plate velocity was 2.5 cm/min. All friction and abrasion measurements were carried out at 25°C and 50% relative humidity. A different portion of surface was used for each measurement.

The ratio of the frictional force to the applied load was taken as the kinetic coefficient of friction, μ_k. For those surfaces which showed stick-slip motion [8], μ_k was calculated from the average frictional force. Since rolling friction at the pulley and roller bearing contributed to the total frictional force, the measured coefficients of friction were probably slightly higher than the true values.

After the friction measurement the regions of glass-glass contact on each slide were examined for cracks and scratches using a microscope with dark field illumination (magnification 60 to 100x). Surface damage was also detected using a more sensitive, ion-exchange method. In this method existing surface flaws are first removed by etching the glass slide in 5% HF at 25°C for 6 minutes [9]. After deposition of the titania coating the slide is covered with a eutectic mixture of KNO_3 and $LiNO_3$ (60 mole % KNO_3) at 190° to 200°C for 45 to 60 minutes. Under these conditions the sodium ions in the glass are replaced by the smaller lithium ions thereby producing tensile stresses in the surface [9, 10]. Any subsequent surface damage resulting from glass-glass rubbing causes propagation of cracks from the points of damage. These cracks are readily visible in the microscope under dark field illumination. The same results are obtained when the ion-exchange is deferred until after the surface has been damaged.

The titania-coated surfaces were also examined using an electron microscope. Carbon surface replicas, shadowed with Pt-Pd alloy, were obtained from nitrocellulose impressions of the surfaces. The details of the technique are described elsewhere [7].

Average coating thicknesses were determined by ellipsometry [7, 11].

RESULTS

Previous work [7] showed that titania coatings obtained by the method described here are incomplete and cover the glass surface in discrete patches. Patch width, surface coverage and average coating thickness were found to

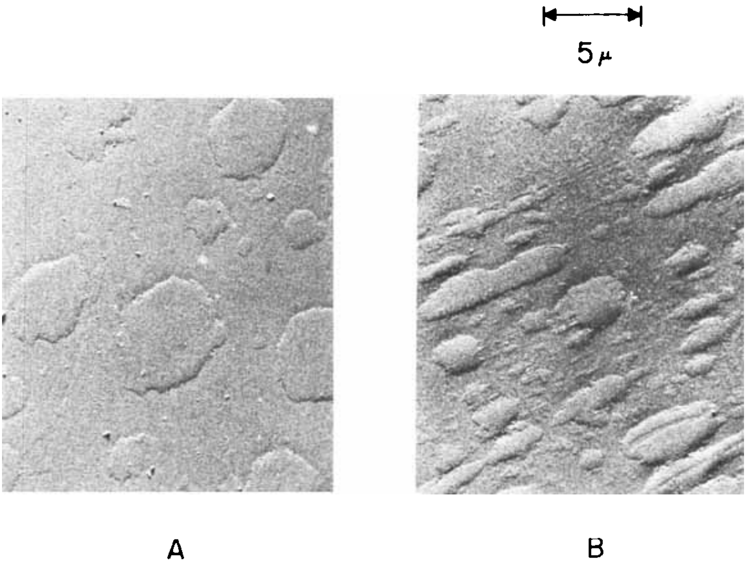

Figure 2. Surface replicas of titania-coated glass before (A) and after (B) friction measurement on surfactant-treated surface.

increase with the concentration of organic titanate in the coating solution [7]. In the present work, patch widths varied from 30 millimicrons to 5 microns. Surface coverage ranged from 10 to 30% and average coating thickness from 5 to about 30 millimicrons. The maximum patch height was no greater than about 150 millimicrons. The electron micrograph in Figure 2A shows these patches on a glass surface before a friction measurement.

Immediately after cooling from 550° to 25°C, μ_k values for both titania-coated glass and uncoated glass were about 1.0. However, μ_k decreased on standing in the laboratory atmosphere. The rate of decrease was much greater for the titania-coated glass. This is shown in Figure 3 for a constant load of 600 gm. After ageing (i.e., standing in the laboratory) for about 8 hours, μ_k for both coated and uncoated surfaces attained a constant value of 0.20 ± 0.02.

The effect of ageing on the relative scratch resistance of coated and uncoated glass is shown in the photomicrographs of Figure 4. After cooling to 25°C, a half-coated slide was subjected to sliding abrasion by lightly drawing a thin, flexible, fire-polished glass rod over the surface under a constant, reproducible pressure (A, B and C in Figure 4). Both coated and uncoated glass showed surface damage even after 15 minutes standing. However, after 25 minutes there was no detectable surface damage on the coated glass and none on the uncoated glass after 90 minutes. A heavier glass rod and a greater sliding pressure were required to produce the scratch shown in photomicro-

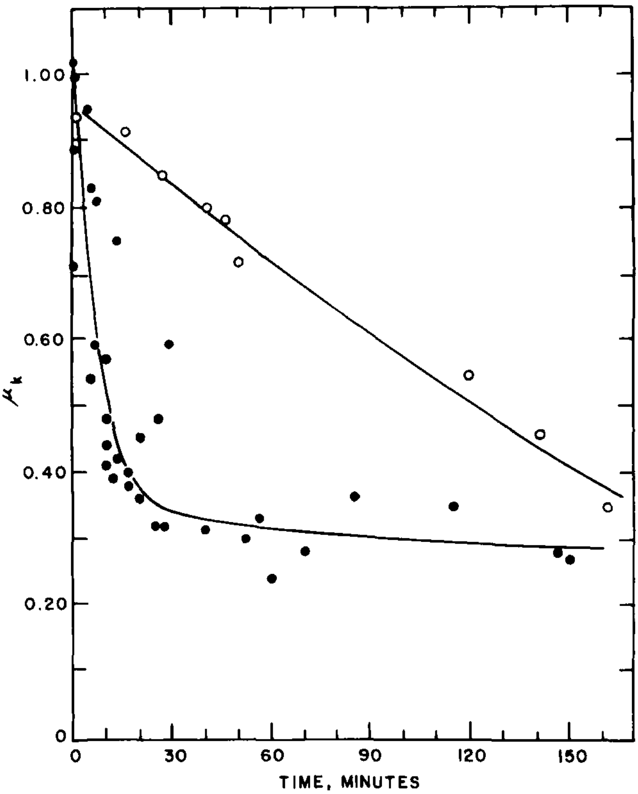

Figure 3. Coefficient of friction for glass on uncoated glass (open points) and on titania-coated glass (solid points) as a function of time. Load = 600 gm.

graph D. The cracks extending from the abrasion tracks in Figure 4 appeared after the sodium-lithium ion exchange.

When coated and uncoated surfaces were isolated from the laboratory atmosphere during cooling and for several hours thereafter, μ_k remained relatively high and scratch resistance was low. The surfaces were isolated under vacuum, in dry nitrogen, or in a mixture of water vapor, nitrogen and oxygen. After exposure to the laboratory atmosphere, μ_k decreased and scratch resistance increased.

Figure 5 compares the frictional force on coated and uncoated surfaces. An aged slide, half coated with titania, was used. Only the uncoated surface showed extensive stick-slip motion and scratches. Behavior similar to that shown in Figure 5 was observed when the surfaces were treated with a solution of trimethyloctadecylammonium chloride instead of allowing them to age. The surfactant-treated surfaces had lower μ_k values and were more

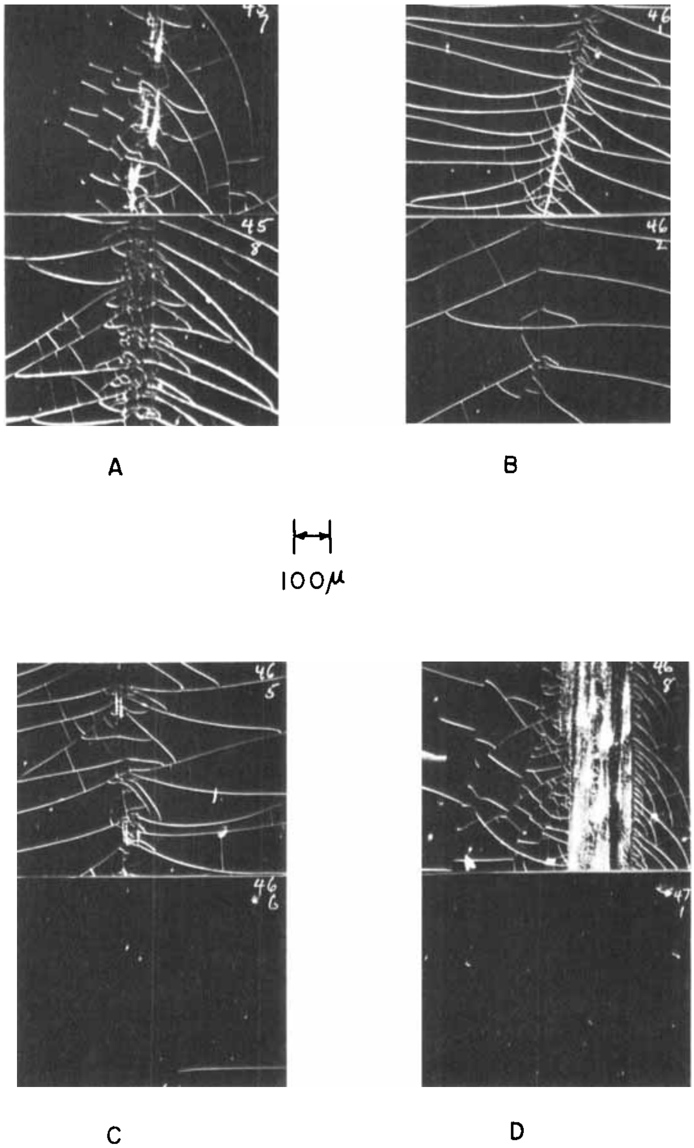

Figure 4. Surface abrasion of titania-coated glass and uncoated glass as a function of time. Uncoated glass is in the upper portion of each photomicrograph. Direction of sliding is from top to bottom. (A) 0 minutes; (B) 15 minutes; (C) 60 minutes; (D) 90 minutes.

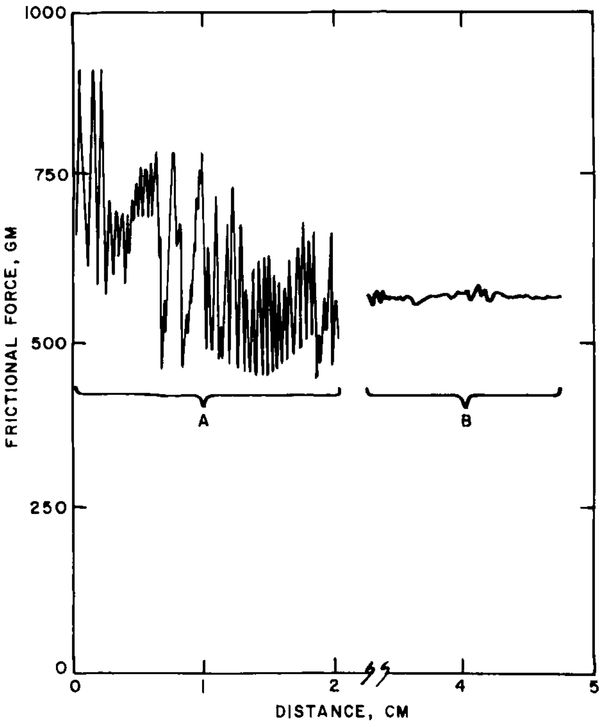

Figure 5. Frictional force for glass on aged surfaces of uncoated glass and titania-coated glass. (A) all three glass rods on uncoated surface; (B) all three glass rods on titania-coated surface. Load = 2600 gm.

resistant to surface abrasion than the aged surfaces. This is shown quantatively in Table 1 for coated and uncoated glass. Here abrasion resistance is expressed in terms of the load, W_s, necessary to produce noticeable scratches on the surface as determined by microscopic examination. The surfactant-

Table 1. Scratch Resistance of Titania-Coated Glass and Uncoated Glass

Surface Treatment	*Titania-Coated* μ_k[a]	*W_s, kg.*	*Uncoated* μ_k[a]	*W_s, kg.*
Aged[b]	0.45 ± 0.05	0.6	0.40 ± 0.05	0.6
Aged[c]	0.22 ± 0.01	6.6 ± 0.5	0.22 ± 0.01	2.1 ± 0.5
Aged[c]	0.19 ± 0.01	7.9 ± 0.6	0.17 ± 0.01	3.0 ± 0.5
$C_{18}H_{37}N(CH_3)_3Cl$	0.15 ± 0.01	11.7 ± 1.1	—	—
$C_{18}H_{37}N(CH_3)_3Cl$	0.13 ± 0.01	14.5 ± 1.0	0.13 ± 0.01	3.9 ± 0.3

[a] μ_k was determined at loads less than W_s

[b] Surface age was about 15 minutes for titania-coated glass and 150 minutes for uncoated glass

[c] Surface age was greater than 8 hours for both surfaces

treated, coated glass with $\mu_k = 0.13$ had considerable scratch resistance at pressures as high as 4×10^4 kg/cm^2.

A slight decrease in frictional force, usually observed during the initial movement of an aged or surfactant-treated slide (see Figure 5), was probably due to transfer of boundary lubricant from the slide to the glass rods [12].

Electron micrographs of coated surfaces after the friction measurement revealed that the titania patches were deformed and spread out in those regions which had been in contact with the glass rods. This is shown in Figure 2B.

Washing of aged or surfactant-treated coated glass with an aqueous solution of an anionic surfactant, such as sodium lauryl sulfate, produced water wettable surfaces which, immediately after drying, had reduced scratch resistance. On standing in the laboratory or after treatment with the quaternary ammonium surfactant solution, hydrophobicity returned and scratch resistance increased.

Both coated and uncoated glass followed Amonton's law [13]. An increase in load from 0.6 kg to 15 kg did not significantly change μ_k.

The abrasion resistance of glass is lower in water than it is in air [14]. This was also observed in the present work with both coated and uncoated glass. For example, W_s for a surfactant-treated coated surface was reduced from 12 kg in air to 4 kg in water.

DISCUSSION

The change in μ_k shown in Figure 3 for uncoated glass is almost identical to that observed by Langmuir [15]. He attributed this behavior to surface contamination from the atmosphere. Apparently, certain atmospheric components can act as boundary lubricants on the glass surface. Boundary lubrication due to adsorption of atmospheric components is also suggested by the curve in Figure 3 for titania-coated glass.

Contact angle studies on incomplete titania coatings on glass [7] have shown that adsorption from aqueous solutions of trimethyloctadecylammonium chloride (pH = 5 to 6) occurs on the uncoated portions of the glass surface and not on the titania-coated regions. The high abrasion resistance of coated glass after treatment with this surfactant (Table 1) must, therefore, be due primarily to the presence of a boundary lubricant on the uncoated portions of the glass. Presumably, this is also the important factor in the scratch resistance of aged coated glass.

The deformation of the titania patches observed after a friction measurement (Figure 2B) indicates that much of the applied load is supported by these patches. Apparently, they give sufficient support to prevent the pressure on the uncoated regions from becoming great enough to break down the

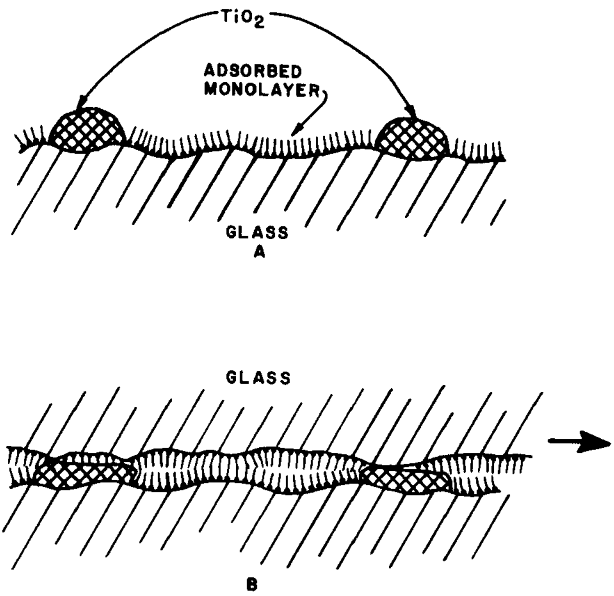

Figure 6. Mechanism of abrasion resistance. Surfactant-treated, titania-coated glass before (A) and during (B) sliding contact with an uncoated glass surface.

boundary lubricant layer. This is shown schematically in Figure 6. In Figure 6B, it is assumed that a boundary lubricant monolayer has transferred from the lower to the upper surface during the initial movement of the surfaces. This load supporting mechanism is similar to one proposed by Wells [16] to explain an increase in the hydrodynamic lubricating capacity of kerosene between steel and bronze obtained when the steel was impregnated with inert diamond "pads".

Titania-coated glass shows a more rapid decay in μ_k than does uncoated glass because less of the glass surface needs to be covered by boundary lubricant in order to reduce the number of glass-glass junctions which form during sliding.

The data in Table 1 show that greater abrasion resistance is obtained when μ_k is lower. This should be true for a given boundary lubricant since a lower μ_k indicates greater surface coverage by the lubricant monolayer. However, different lubricants having the same μ_k can vary considerably in their durability [12].

The relatively low water contact angles previously observed [7] for a trimethyloctadecylammonium chloride monolayer deposited on glass by the aqueous method used in the present work, indicate less than complete surface coverage by the monolayer. For this reason, the μ_k values in Table 1 for surfactant-treated glass are somewhat higher than the value of 0.05 one should expect for a complete monolayer [12]. This difference is greater than can be accounted for by rolling friction in the friction apparatus. The titania itself probably also contributes to the comparatively high μ_k observed on coated glass. This is indicated by the very high scratch resistance observed for coated glass having μ_k values as large as 0.19 (Table 1).

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