

Tribological Properties of Multilayer TiN and MoS₂ Thin Films

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Abstract: This paper presents tribological behavior of titanium nitride and molybdenum sulfide thin film coatings on a workpiece. The titanium nitride films were coated by RF magnetron sputtering method and molybdenum sulfide films were coated by vacuum thermal evaporation. Titanium nitride is a hard ceramic materials, which has excellent mechanical properties. However, the friction coefficient of titanium nitride is rather high. To improve the tribological properties of the titanium nitride films, a thin layer of molybdenum sulfide was coated as a solid lubricant. The results showed a substantial decrease in the coefficient of friction of dual-layered MoS₂ over TiN compared with the titanium nitride film or as-received aluminum substrate. The low coefficient of friction can directly be correlated to the MoS₂ layer whereas the TiN film acts as a robust and durable base material. The coefficient of friction was measured using a pin on a disc tribometer with a steel pin as the counter face. Our results demonstrated that the coating of MoS₂ over TiN has a low coefficient of friction. In addition, it was also found that wear resistance of MoS₂ coated TiN was better than both MoS₂ and TiN films.

Keywords: Coefficient of Friction, Titanium Nitride, Molybdenum Sulfide, Tribology

1. Introduction

Coatings are often used in manufacturing to improve mechanical, tribological, and aesthetic properties of workpieces. These coatings have several applications that range from lubrication to formation of hard protective layers. Different kinds of coatings are available depending on the applications. Hard ceramic coatings are used for coating of machine tools and protect underneath material, whereas soft lubricating coatings are employed to improve the lubricity in places where fluid lubricants cannot be used. Mechanical and tribological properties of thin films can be improved by application of multilayer coatings. Multilayer coatings have resulted in enhanced properties such as decreased coefficient of friction, increase in load bearing capacities, and wear life (durability) for different materials [1-9]. Several type of coatings such as composite, hybrid, multiphase, or gradient films have been developed for improving the tribological properties by combination of materials [1, 3, 4]. The combinations of these layers also depend on the cost and

throughput of manufacturing. Based on quality, the film surfaces can be classified into either anti-friction coatings determined by low friction or anti-wear coatings characterized by high hardness [18].

Titanium nitride (TiN) is a widely used ceramic coating due to its excellent mechanical properties and high resistance to wear and corrosion [10]. TiN is coated as thin films to improve the mechanical performance of substrates [1, 11]. Although TiN has good durability, it has a high coefficient of friction (> 0.62). It is vital to improve the frictional properties of TiN as it is mostly used in machine tools and materials having contact [11]. Molybdenum sulfide (MoS₂) is a commonly used dry solid lubricant, which has a low coefficient of friction in the range of 0.09 - 0.15 as a single layered film on the working surfaces. MoS₂ have also been used as a composite/additive to lower friction in composite or multilayer coatings [3, 14, 16]. An optimum balance of good durability and low coefficient of friction can be obtained by combining the properties of TiN and MoS₂ films.

Several studies have been conducted to study the effect of compound MoS₂ and TiN thin film coatings [1, 3, 4, 12, 17,

20]. coating of TiN + MoS composite were carried out by closed-field magnetron sputtering method and the thickness of 2 μm showed the average coefficient of friction around 0.35 [12]. The composition of MoS₂ in surface coatings showed decrease in friction coefficient from 0.3 to 0.05, but the results were irregular due to its low hardness [18]. MoS₂ coatings provided a very low coefficient of friction with an average value around 0.08 in different working environments [19].

In this study, MoS₂ were deposited on pre-fabricated TiN films. The TiN and MoS₂ films were coated separately in different processes & environments to distinguish between the layers. TiN films were coated using RF magnetron sputtering and MoS₂ films were coated using vacuum thermal evaporation technique. The friction measurements were made using a pin-on-disc tribometer with a steel counter face pin and the substrate rotating at a constant speed. The effect of wear and durability were studied by changing the applied normal loads.

2. Experimental Procedure

The TiN and MoS₂ films were deposited on the as-received Al substrates. The Al grade used was alloy 1100 as it is commonly used in general fabrication and metal spinning. The aluminum alloy 1100 had composition of 99.88% Al, 0.1% Copper and 0.02% residuals [22]. Prior to deposition, the substrates were cut into appropriate dimensions (8 cm x 8cm, thickness 0.8 mm) and cleaned with soap and water for removing grease and dirt. The substrates were then sonicated in a mixture of acetone, isopropanol alcohol and distilled water for removing surface contaminations. All components were analytical grade and were used as received. The thin films were coated on these Al substrates by physical vapor deposition techniques.

The TiN thin films were deposited by reactive radio frequency (RF) magnetron sputtering method on Al substrates. The deposition was carried out a pressure inside the chamber was maintained at 1×10^{-6} Torr with the help of a multi-stage vacuum pump throughout the deposition time. After the required pressure was obtained, the vacuum chamber was purged with argon to remove any oxygen in the chamber. Then a mixture of Ar and N₂ gases (1: 1) were introduced and pressure was adjusted to 30 mTorr. Titanium nitride was deposited for 120 min using RF power of 250 W. The average thickness of the film obtained was in the range of 325 ± 10 nm.

Vacuum thermal evaporation technique used for the deposition of molybdenum sulfide (MoS₂) films. This process provided a higher deposition rates and was suitable for depositing MoS₂. In this technique, the MoS₂ powder to be deposited was evaporated/sublimated at a temperature higher than 1185°C. The TiN coated Al substrates were coated at a pressure of 10^{-6} Torr using a Mo crucible filament. MoS₂ powder of 99.9% purity with average particle size of 44 microns was used as the source material. The average the thickness of MoS₂ films were around 350 nm.

The tribology tests were conducted on a custom-built pin-on-disc tribometer (figure 1). It measures the frictional force exerted on the surface of the substrate by deflection of the stationary pin. The coated substrates were mounted on a steel holder attached to the motor. The counter face steel pin was placed on the surface of the disc so that it touches the substrate surface. The pin was rigidly attached to strain gauges. A normal force was exerted on the pin due to its own weight and external application of applied normal force. Additional weights were used to increase applied normal force for different experiments. The applied normal load was increased by the use of static weights such that the force acts tangentially to the substrate surface. The deflection was measured with the set of strain gauges that are interfaced to a computer running LabVIEW™. Real-time deflection and frictional force data were collected via a data acquisition system and custom LabView™ software. The surface roughness of the pin was 110 nanometers. A constant speed of 150 rpm was maintained and loads of magnitude, 0.25 N, 0.375 N, and 1.1 N were used. All the readings were recorded at room temperature and ambient air-conditions (1 atm). The forces acting on the substrate during the test are illustrated in figure 1.

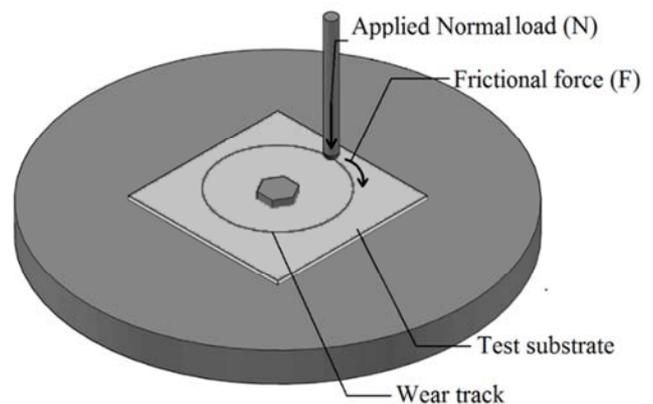


Figure 1. Schematic of pin on disc tribometer.

3. Results and Discussion

3.1. Coefficient of Friction

An overview of average coefficients of friction of coatings are presented in Table 1. The friction coefficient (μ_k) was calculated for steady states. All the frictional force measurements were recorded at constant speed of 150 rpm. MoS₂ coatings provided a better coefficient of friction as indicated from the averages in Table 1. MoS₂ films and MoS₂ over TiN films showed similar behavior and yielded similar average friction values. These results were trait of the identical MoS₂ top layer coating on both substrates. The average coefficient of friction of TiN is 0.62, which is considerably higher than coefficient of friction of MoS₂ coatings. A TiN film deposited using closed-field magnetron sputtering exhibited similar results with average coefficient of friction of 0.65 [12]. The MoS₂ film displayed low average

coefficient of friction of 0.14, which is comparable with the sputter deposited MoS₂ films, which have the average frictional value of 0.12 [12, 19].

Table 1. Average coefficient of friction of coatings at different loads.

Layer	Contact pressure		
	180 MPa	270 MPa	800 MPa
TiN/Al		0.62	
MoS ₂ /Al	0.1	0.14	0.14
MoS ₂ /TiN/Al	0.09	0.14	0.15

The comprehensive effect of friction coefficient MoS₂ over TiN coating and TiN coating is shown in figure 2. The friction coefficient of the coated substrates is plotted versus number of cycles in figure 2 and figure 3. The coefficient of friction of MoS₂ over TiN coating was significantly lower than the TiN coating as presented in figure 2. During the period of 20,000 cycles, the coefficient of friction of MoS₂ over TiN behaved consistently and displayed a low value. These measurements were recorded at applied normal load of 0.375 N on the counter face steel pin. TiN provided a good protection for the base Al but it did not demonstrate good frictional properties. The frictional coefficient of TiN remained in the range of 0.59 to 0.77. Also, the coefficient of friction of MoS₂ over TiN was in a lower range of 0.12 to 0.15 for identical speed and normal load. The MoS₂ coatings studied in several other studies exhibited similar results with low coefficient of friction of approximately 0.1 [12, 15, 16-20]. A MoS₂ film deposited by sputtering technique with film thickness of one micron showed steady state coefficient of friction of 0.08 at ambient conditions [19]. J. Haider et al [12] reported that the MoS₂ deposited by magnetron sputtering resulted in film with average coefficient of friction of 0.15. The addition of MoS₂ on the substrate improved coefficient of friction. The decreased coefficient of friction shows that the MoS₂ layer provides better lubricity in steady state conditions. Lower friction coefficients were obtained by the incorporation of MoS₂ within a hard matrix such as TiN by co-deposition, which also resulted in drop in hardness [20]. In this case, the coefficient of friction was inversely proportional to hardness of the coatings.

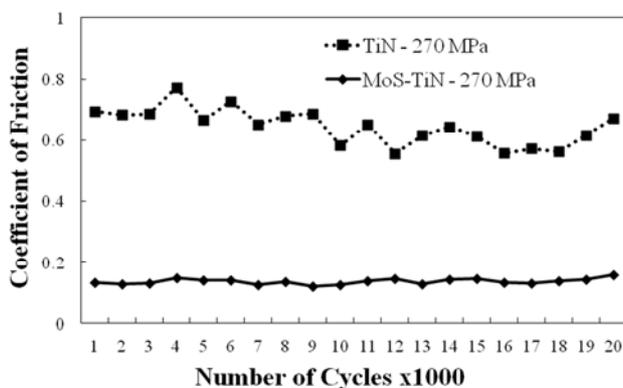


Figure 2. Coefficient of friction of TiN and MoS₂ over TiN thin films.

Single layered MoS₂ and dual layered MoS₂ over TiN provided similar coefficient of friction as shown in figure 3.

The difference in friction coefficient is low with an average of 0.14. Reduced values of coefficient of frictions were obtained (in figure 3) as the top most layer comprised of MoS₂ films. The top layer of both the substrates contained similar MoS₂ films and materials and they were deposited using identical techniques and parameters. Another study indicated that the TiN + MoS₂ composite coating exhibited an average steady state coefficient of friction of 0.32 with drastic changes throughout the testing period [18]. The films of TiN+MoS deposited by magnetron sputtering also showed a higher coefficient of friction of 0.35 [12]. These results suggest that the homogeneous MoS₂ layer proved to be suitable solid lubricant layer for reducing coefficient of friction.

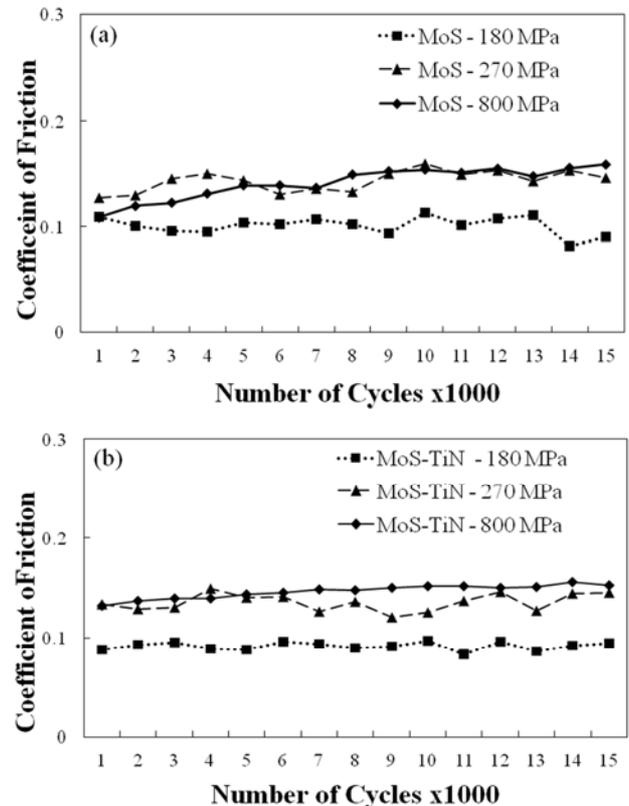


Figure 3. TiN-MoS₂ coatings vs MoS₂ coatings (a) Normal load = 0.375 N (b) Normal load = 1.1 N.

MoS₂ and MoS₂ over TiN displayed similar frictional properties (figure 3) for a limited number of cycles but the long-term performance of these two coatings was different. The differences between the single layered MoS₂ film and dual layered MoS₂ over TiN films are quite noticeable in long-term performance (figure 4). The combinations of properties of the TiN and MoS₂ thin film coatings were integrated to form durable layers with lower coefficient of friction for longer periods of use. The sturdy underneath layer of TiN enhanced the lubricating properties of MoS₂ thin film coatings for long-term applications [18]. The durability of the two films in contrast with each other is shown in figure 4. The single layered MoS₂ thin film worn out after 380 s; this was noticed by the drastic increase in the coefficient of

friction. The increased coefficient of friction value of MoS₂ film is closer to coefficient of friction of standard Al alloy 1100, which was used as the substrate material. The dual layered MoS₂ over TiN coating showed a better durability than single layered MoS₂. In the MoS₂ over TiN film coatings, the MoS₂ layer wore out after 300 s, but it still provided lubricity and displayed decreased coefficient of friction for MoS₂ over TiN film substrates.

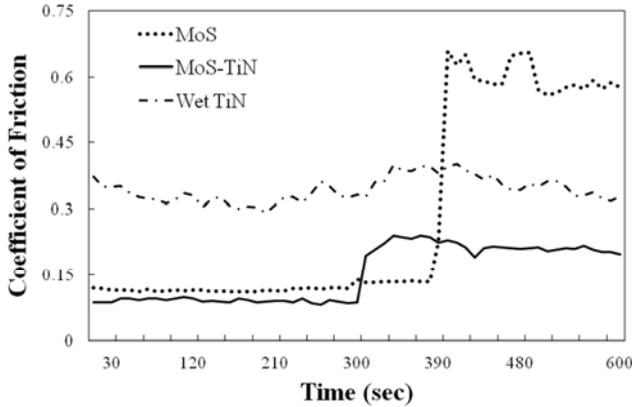


Figure 4. Wear and durability, MoS₂, MoS₂-TiN & Wet TiN.

The MoS₂ layer had positive effect over the coefficient of friction of the substrates after deteriorating. The MoS₂ debris was presented at surface interaction between pin and substrate surface. The suspended MoS₂ fragments acted as partial dry solid lubricant in this case. The average steady state coefficient of friction of plain TiN coatings was 0.62; but the average coefficient of friction of TiN layer after wearing of MoS₂ layer was found to be 0.21. This decrease in coefficient of friction indicated the effect of MoS₂ particles on the lubricity of the substrate after the MoS₂ film was scratched. The MoS₂ debris particles provided lubrication effect in the case of single layered MoS₂ film coating, as there was a considerable decrease in coefficient of friction in Al. The average coefficient of friction of as received Al 1100 was 0.7. However, the coefficient of friction of Al 1100 after the MoS₂ film was scratched was found to be 0.6. These results suggested that the interface of MoS₂/TiN has some significant effect on tribology performance. Authors plan to investigate these phenomena in the future.

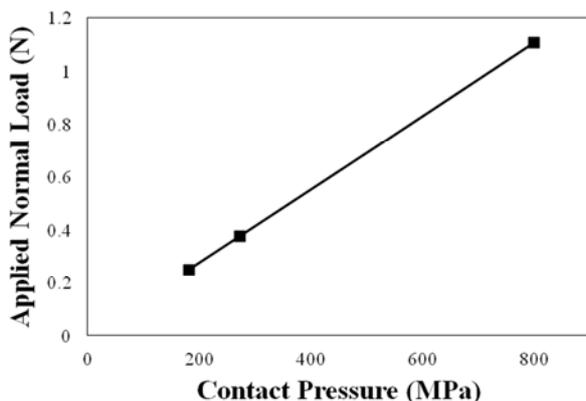


Figure 5. Relationship between applied normal load and contact pressure.

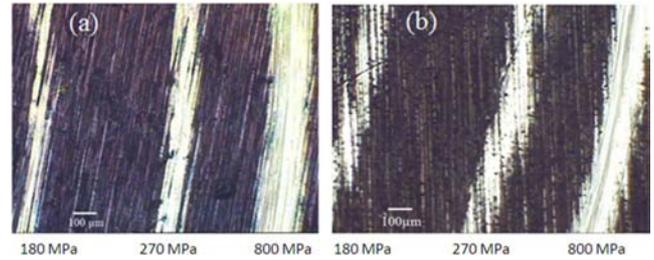


Figure 6. Surface morphology for different loads (a) MoS₂ film (b) MoS₂ over TiN films.

The effect of lubrication of MoS₂ is apparent in figure 6. The lubrication effect of water on plain TiN coatings is compared to lubricity provided by MoS₂ layer. Water acted as an effective lubricant and provided lower COF average of 0.34 compared to 0.62 of dry TiN coatings. The effect of wear was also decreased with consistent performance throughout the testing period.

3.2. Surface Interactions

The actual load acting on the substrate surface through the pin changes with different loads and this changes coefficient of friction and area of contact. This phenomenon can be explained using Hertzian contact theory and by calculating Hertzian contact pressure for the applied normal loads and geometry of the setup. Hertzian contact pressure can be calculated by using the following set of formulae [21],

$$a = \left\{ \frac{3PR}{4E} \right\}^{1/3} \quad (1)$$

where, a is contact radius, E is Young's Modulus, P is applied normal load, R - radius of the pin and ν - poisson's ratio. Maximum Hertzian contact (P_{max}) pressure is given by

$$\frac{1}{E} = \frac{1-\nu_{pin}^2}{E_{pin}} + \frac{1-\nu_{plate}^2}{E_{plate}} \quad (2)$$

$$P_{max} = \frac{3P}{2\pi a.a} \quad (3)$$

The relationship between the applied normal load and the maximum Hertzian contact pressure is linear as calculated from eq. (2). The results show a linear relationship of applied normal load and maximum Hertzian contact pressure. As the applied normal load increases the maximum Hertzian contact pressure also increases with corresponding magnitude. The change in contact pressure had direct influence on frictional coefficients and wear behavior for MoS₂ and MoS₂ over TiN film coatings. The maximum Hertzian contact pressures for 0.25, 0.375 and 1.1 N were found to be 263, 300 and 430 MPa, respectively.

The normal force acting on the surface of the thin films can also be calculated empirically by dividing the contact area with the total normal force acting on the counter face steel pin of the Tribometer (as shown in figure 1). The contact area of the steel pin is circular with 0.042 mm as the

diameter that was measured by optical microscope. The empirically calculated contact area and contact pressure acting on the surface are displayed in figure 5. The contact area of the steel pin is 0.00138 mm^2 . The contact pressures for 0.25, 0.375 and 1.1 N were found to be 180, 270 and 800 MPa, respectively.

Figure 6 shows the surface images of MoS_2 and MoS_2 over TiN after application of different loadings in tastings. The difference in width of wear tracks in figure 6 was explained by increase in contact pressure. The wear for 15,000 cycles in the dual layered MoS_2 over TiN coating was similar to the single layered MoS_2 coating as shown in figure 6.

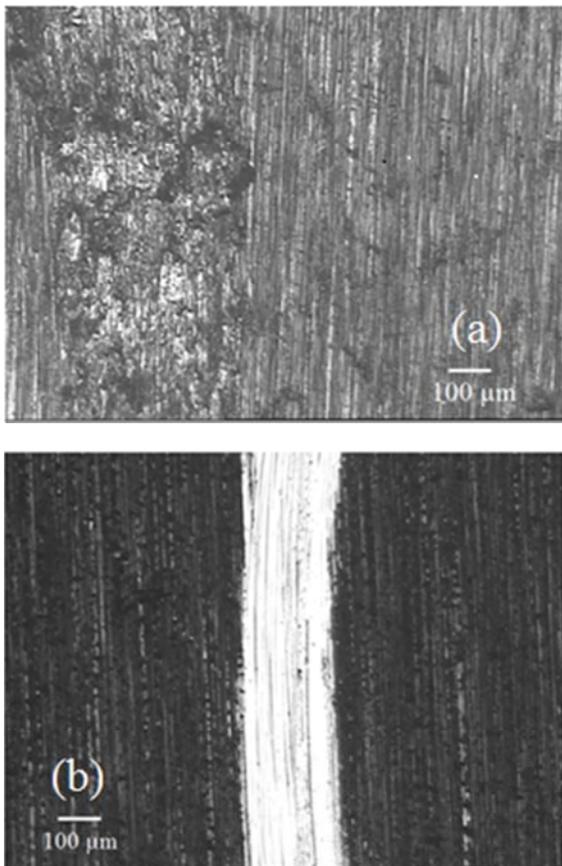


Figure 7. Wear tracks for (a) MoS_2 and (b) MoS_2 over TiN films.

Figure 7 shows the effect of wear between MoS_2 and MoS_2 over TiN films for long-term applications. The difference in wear tracks is between the two coatings subjected to identical load, speed, and other conditions. In the case of MoS_2 film, the wear was apparent and the wear track was rough exposing the bare substrate material (Al). Due to wear and tear, the width of the track was irregular on MoS_2 coated substrate. This resulted in formation of a rugged wear track with high coefficient of friction after wear. Whereas, in MoS_2 over TiN film, the TiN below the MoS_2 layer prevented the substrate from excessive damage and wear. The wear track also had uniform width and substrate material was not scarred.

The MoS_2 over TiN dual layered coatings proved to be a good option for increasing the lubricity of the TiN coatings that are often used in machine tools as hard ceramic coatings.

The MoS_2 over TiN dual layered coatings have advantages over the TiN+ MoS composite coatings. The dual layered MoS_2 over TiN films obtained in this study have lower coefficient of friction of 0.15 compared with the TiN+ MoS composite coatings that have a higher coefficient of friction of 0.35 [12].

MoS_2 has been used as a solid lubricant because it has a lamellar structure, which the layers can slide along each other. It is known that MoS_2 doesn't function very well in a wet environment and causes corrosion of metal surfaces due to galvanic corrosion between Molybdenum disulfide and metals. In this study, however; reduced friction coefficient after addition of water into the MoS_2 surface after coating on TiN. Furthermore, TiN is an anticorrosion materials and thus, its durability of MoS_2 in wet environment might be enhanced by coating dual layer of MoS_2 and TiN.

4. Conclusion

The coatings of MoS_2 films, TiN layers and MoS_2 over TiN were carried out by RF magnetron sputtering and vacuum thermal evaporation. These films were investigated for their tribological properties in sliding contact (pin-on disc tribometer) in ambient conditions by varying the applied normal load. Although the coating of TiN provided hard protective layers for the base materials, its coefficient of friction is as high as 0.6. A thin film of MoS_2 was proven a reliable and dry solid lubricant with the coefficient of friction as low as 0.14. By combining the properties of these two materials, a dual layered coating with contact layer being MoS_2 was fabricated to utilize the coefficient of friction of MoS_2 and anti-wear properties of TiN. The experimental results exhibited that the proposed novel dual layered coatings were successful with the average coefficient of friction of dual layer remained close to that of MoS_2 . Study suggested that the coating of MoS_2 over TiN was a useful self-lubricating coating for long-term applications. Thin films of MoS_2 can be deposited on TiN coated substrates and machine tools. MoS_2 over TiN dual layered coatings can also be applied in places where conventional lubrication techniques are difficult to use effectively such as in high temperature environments, space vehicles, food industry equipment, and bearings.

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