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Parameters affecting the deposition of tin oxide onto glass surfaces and the function of tin oxide when overcoated with polyethylene in minimizing glass frictive damage

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(Communication of the American Glass Research, Inc., Butler, PA (USA))

(Received the 27th June, 1984)

Stannic chloride vapors were used to deposit tin oxide coatings onto glass substrates of various compositions. The microstructure of the coatings was analyzed with an SEM for coating deposition conducted under different ambient humidity levels, coating material flowrates, distances from the delivery tube to the glass surfaces, glass temperatures and carrier gas compositions. A general tin oxide coating deposition mechanism was developed. Additional tin oxide coated glass surfaces were overcoated with polyethylene. The frictive properties of tin oxide, polyethylene and a combination of these coatings were evaluated under various sliding loads and test conditions. The measured coefficients of kinetic friction were correlated with the surface topography of the coatings as observed in an SEM.

Paramètres affectant le dépôt d'oxyde d'étain à la surface du verre, rôle de l'oxyde d'étain recouvert de polyéthylène dans la diminution des détériorations du verre dues au frottement

Des vapeurs de chlorure stannique ont été utilisées pour déposer des revêtements d'oxyde d'étain sur des substrats en verre de différentes compositions. La microstructure des revêtements a été analysée avec un microscope à balayage pour des dépôts de revêtements effectués avec des niveaux différents de l'humidité ambiante, diverses vitesses d'écoulement du matériau de revêtement, des distances variables entre le tube d'alimentation et la surface du verre, différentes températures de verre et diverses compositions de gaz porteur. On a mis au point un mécanisme général de dépôt du revêtement en oxyde d'étain. Des surfaces de verre supplémentaires ont été recouvertes de polyéthylène. Les propriétés de frottement de l'oxyde d'étain, du polyéthylène et d'une combinaison de ces revêtements ont été évaluées sous différentes charges et dans différentes conditions d'essais. Les coefficients mesurés de frottement cinétique ont été reliés à la topographie de la surface du revêtement telle qu'elle a été observée au microscope à balayage.

Parameter für die Beschichtung von Glasoberflächen mit Zinnoxid und für die Funktion von Zinnoxid bei Polyäthylenüberzügen zur Minderung von Glasbeschädigungen

Es wurden Zinnchloriddämpfe zur Beschichtung von Glassubstraten verschiedener Zusammensetzungen mit Zinnoxid benutzt. Die Mikrostruktur der Beschichtungen wurde mit einem Rasterelektronenmikroskop (REM) analysiert, wobei die Beschichtung bei unterschiedlichen Bedingungen hinsichtlich der Feuchtigkeit der umgebenden Atmosphäre, der Düsenleistungen für das Beschichtungsmaterial, der Abstände von der Düse zur Glasoberfläche, der Glastemperaturen und der Trägergaszusammensetzungen vorgenommen wurde. Es wurde ein allgemeines Verfahren für die Zinnoxidbeschichtung entwickelt. Zusätzlich wurden mit Zinnoxid beschichtete Glasoberflächen mit Polyäthylen überzogen. Die Reibungseigenschaften von Zinnoxid, Polyäthylen und einer Kombination dieser beiden Beschichtungen wurden bei unterschiedlichen Gleitladungen und Testbedingungen ausgewertet. Die gemessenen Koeffizienten der kinetischen Reibung standen im Zusammenhang mit der Oberflächentopografie der Beschichtungen, wie mit dem Rasterelektronenmikroskop beobachtet werden konnte.

1. Introduction

Inorganic coatings have been applied to glass surfaces for many years. Such coatings find use as decorations on artware [1 and 2], as semi-conductive coatings in electrical components [3 to 6] and as anti-reflective coatings in optical applications [7]. In recent years tin and titanium oxide have been applied to glass surfaces in conjunction with organic coatings to maintain high percentages of pristine strengths by protecting glass surfaces from frictive damage [8 to 24]. Tin oxide used in these scratch protective coatings is inert to most chemicals [25 to 28] and is optically transparent in the visible region of the spectrum [4 and 5]. This paper summarizes an investigation into the microstructure of thin tin oxide coatings when deposited onto glasses of various compositions and the factors affecting the deposition of these coatings. The structural characteristics of tin oxide and polyethylene glass surface coatings which have been frictively loaded is discussed and the role of each coating in providing surface lubricity and preventing frictive damage is postulated.

2. Experimental procedure

2.1. Parameters affecting the deposition of tin oxide coatings and the microstructure of such coatings

The various parameters and glass substrate compositions used in the study of the deposition of tin oxide coatings from anhydrous stannic chloride are

summarized in tables 1 and 2, respectively. The coating apparatus used in this section of the study consisted of the assembly shown in figure 1. Dry nitrogen or dry oxygen was bubbled through a flask containing anhydrous stannic chloride. The gas stream containing the coating vapors was passed through a glass delivery tube and then impinged, as a collimated stream, onto the surface of the glass substrates. A second oxygen or nitrogen gas stream was either bubbled through a flask containing water or diverted to bypass the water flask completely. This second gas stream was used to effect changes in humidity levels near the substrate surfaces during coating deposition. Glass surface humidity levels of 38 and 78 %, as measured psychrometrically, were achieved by bubbling through or bypassing the water flask. The relative humidity of the ambient laboratory atmosphere was 55 %.

The glass samples to be coated were placed on a transite holder and heated in an electric muffle furnace to a temperature of 630 °C. After a 20 min soak the samples were individually removed and placed in front of the delivery tube at a specified distance. As soon as the glass temperature had cooled to the desired coating value, the carrier gas containing stannic chloride vapors and the ambient humidity controlling gas stream were allowed to impinge onto the glass surface for a constant period of time. Following coating the samples were allowed to cool to room temperature in the normal laboratory atmosphere.

The resultant tin oxide coating thicknesses were measured by two methods. For coatings in the range of 0 to 80 nm, an instrument using an infrared reflectance principle was used[1]). The thicknesses of coatings showing interference colors were evaluated by a second method described by Kim and Laitenin [29]. A value of 1,5 was used for the refractive index of the tin oxide coatings in this evaluation [10]. Microstructural details of the coatings were examined under high magnification with a scanning electron microscope (SEM). Compositional details in the coatings were identified by use of an energy dispersive x-ray spectrometer (EDX).

2.2. Frictive characteristics of tin oxide and polyethylene coatings

Soda-lime-silica glass of a composition summarized in table 2 was selected as the substrate for this study. Sections of glass 80 mm^2 and 3 mm thick were coated with tin oxide from vapors of anhydrous stannic chloride, polyethylene from a spray of an aqueous emulsion[2]), or with both coating materials. Tin oxide deposition parameters were adjusted to produce coating thicknesses of 20 nm. The polyethylene coating thicknesses were not measureable, but the deposition conditions for the polyethylene coatings were maintained constant for all samples.

An uncoated 5 mm pyrex glass sphere was frictively translated at a constant velocity of 0,5 cm/s and under normal loads of 300, 1500 and 3000 g across each coated surface and across a series of uncoated control surfaces. The sphere was firmly

[1]) American Glass Research, Inc., Hot End Coating Meter, P.O. Box 149, Butler, PA 16003–0149 (USA).

[2]) 0,1 % by weight P110, Scher Chemical Co., Cliffton, NJ 07012 (USA).

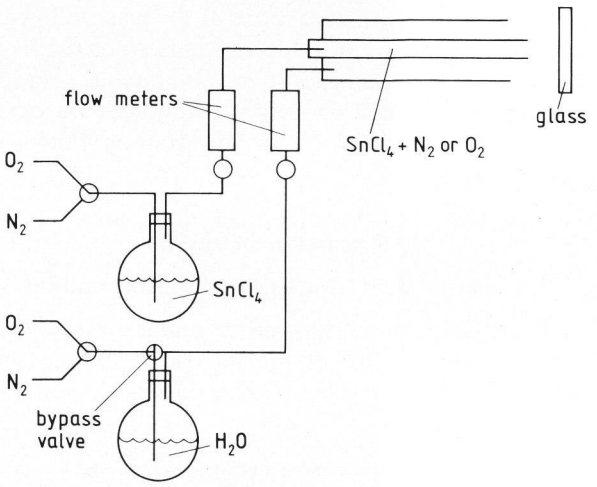


Figure 1. Coating apparatus.

Table 1. Experimental coating parameters

glass coating temperature in °C	400	500	600
carrier gas	N_2	O_2	
humidity level in % at substrate surface	38	78	
tube-to-glass distance in cm	2,5	5,0	
$SnCl_4$ material flow rates in ml/min at 20 °C	21	64	106
glass composition	soda-lime-silica	boro-silicate	fused silica

Table 2. Glass compositions (in weight %)

Glass	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	B_2O_3	Fe_2O_3
soda-lime-silica	12,8	0,44	1,83	78,27	0,36	6,99	–	0,062
borosilicate (Corning 7740)	3,8	–	2,20	80,50	0,40	–	12,9	–
fused silica	–	–	–	100,00	–	–	–	–

fixed to prevent rotation while traversing each surface. During sliding contact the surfaces were exposed to either the ambient laboratory environment (25 °C and 55 % relative humidity), hereinafter referred to as dry test conditions, or were flooded with deionized water, hereinafter referred to as wet test conditions. The pyrex sphere was replaced after each sliding contact event.

The contact areas for each load and test environment were examined in an SEM following the sliding contact described above. The contact areas were reexamined in the SEM following removal of each of the respective coatings to determine whether any observable frictive damage was present solely in the layers of the coatings or whether the damage extended down into the glass surfaces. The polyethylene coatings were removed by boiling each sample in methylene chloride, then ethylbenzene, and then passing the samples through a Bunsen burner flame. Complete organic removal was noted by the highly frictive conditions of the glass following these treatments. Tin oxide coatings were removed by subjecting the samples to a 3 % aqueous solution of hydrofluoric acid for 5 min. Complete tin oxide removal was verified by a zero coating thickness measurement.

3. Discussion of results

3.1. Parameters affecting coating deposition

The thicknesses of tin oxide coatings produced for various combinations of the deposition parameters are summarized in table 3. The data shown in this table were obtained for use of nitrogen as the carrier gas. Identical coating thicknesses were obtained for the use of oxygen as the carrier gas. This result indicates that coating deposition is independent of the composition of both the carrier and surrounding gas streams. The resultant thicknesses of deposited tin oxide coatings are also shown to be independent of glass composition.

The thicknesses of deposited tin oxide were found to be strongly dependent on the ambient relative humidity and the glass temperatures at which the coatings were deposited and less strongly dependent on the distances from the delivery tube to the glass surfaces. Coating thicknesses increased for increased glass temperatures within the temperature range studied. The effect of relative humidity levels and nozzle-to-glass distances on the resultant thicknesses of tin oxide depends a great deal on the specific combination of these two parameters. Lower coating thicknesses were observed for the combination of a 5 cm nozzle-to-glass distance and high relative humidity values as compared to a 2,5 cm nozzle-to-glass distance and/or low relative humidity values. This result can be explained in terms of the vapor delivery tube geometry and the flow parameters of the gas stream containing the coating vapors. For a given cross-sectional area of the delivery tube and for a given flow rate of the gas stream the time in which stannic chloride vapors are in contact and react with water vapors in the surrounding environment is proportional to the distance between the delivery tube and the glass surface. Therefore, increases in the tube-to-glass distance increase the reaction time

Table 3. Tin oxide coating thicknesses obtained for various combinations of deposition parameters (nitrogen carrier gas)

relative humidity	glass temperature in °C	$SnCl_4$ flowrate in ml/min	tin oxide coating thicknesses in nm for various glass compositions and nozzle-to-glass distances					
			soda-lime-silica		borosilicate		fused silica	
			2,5 cm	5,0 cm	2,5 cm	5,0 cm	2,5 cm	5,0 cm
38 %	400	21	25	20	25	23	20	18
		64	225	210	240	220	230	210
		106	625	575	650	600	640	590
	500	21	40	35	45	40	40	36
		64	370	340	365	335	370	335
		106	1 050	970	1 025	950	1 040	950
	600	21	60	55	55	48	55	50
		64	520	475	540	500	530	490
		106	1 500	1 400	1 600	1 500	1 500	1 425
78 %	400	21	225	10	250	12	225	10
		64	2 500	100	2 500	100	2 200	100
		106	6 000	280	6 500	290	6 500	300
	500	21	400	20	450	25	400	20
		64	4 000	150	4 000	170	3 500	165
		106	10 000	500	10 000	450	10 500	500
	600	21	500	28	500	30	550	25
		64	5 500	240	5 000	225	5 500	250
		106	–	650	–	700	–	710

between stannic chloride vapors and water vapors. For prolonged contact times in high relative humidity environments it is postulated that a reaction product is formed between anhydrous stannic chloride and water vapor which is unable to form tin oxide on the heated glass substrate. These results agree well with the findings of other investigators [26 and 30].

It was initially thought that maximum coating thicknesses would be obtained for short coating vapor-water vapor contact times and low relative humidities as seen by others [26 and 30]. However, maximum coating thicknesses were unexpectedly obtained for small delivery tube-to-glass distances, i.e., short coating vapor-water vapor contact times and high relative humidities near the glass surface. These results prompted additional experiments to be conducted in a tube furnace which permitted total control of the water content of the ambient atmosphere in which the coating process occurred [9]. A soda-lime-silica glass sample was placed in the furnace and an essentially water-free environment was obtained by purging the furnace system with −75 °C dew point nitrogen gas. After equilibrating the samples in that atmosphere at 600 °C, the soda-lime-silicate substrates were subjected to a stream of nitrogen gas containing stannic chloride vapors. No tin oxide was deposited in this essentially water-free environment.

Additional tests were conducted under identical conditions but with an 80 % relative humidity ambient atmosphere. This atmosphere was obtained in the tube furnace by bubbling dry nitrogen through a flask containing boiling water and then purging the furnace with this gas stream. In contrast to the results obtained in a water-free environment coatings exhibiting extremely high order interference colors were deposited on glass substrates under these high humidity conditions. In both cases the tube-to-glass distance or water vapor-coating vapor reaction time, stannic chloride flowrate and glass temperatures were constant.

The previous results may be interpreted as an indication that the degree of hydration or water content of glass substrates were significantly affecting the deposition of tin oxide. However, subjecting heated glass substrates initially to atmospheres containing high moisture contents followed immediately by stannic chloride vapors applied in a water-free environment resulted in the deposition of significantly less tin oxide when compared to the coating thicknesses obtained from the simultaneous mixing of stannic chloride and water vapors. In addition hydrated glass surfaces would be expected to affect only the first monolayer of tin oxide deposition. Further deposition of tin oxide beyond a monolayer should not be influenced by the degree of hydration of the glass substrate. These results suggest that hydration or the presence of surface hydroxyl groups on the glass surface may have some effect on subsequent tin oxide deposition but that this effect is much less significant when compared to vapor phase mixing of water and stannic chloride vapors immediately prior to their contact with heated glass substrates.

Additional studies were performed in the tube furnace under identical experimental conditions as noted before but with the substitution of isopropanol vapors for the water vapor in the ambient coating environment. In addition the effects of nozzle-to-glass distances on the thickness of deposited coatings were studied. Tin oxide coatings exhibiting high order interference colors were deposited on glass substrates in an environment of isopropanol vapors for a nozzle-to-glass distance of 2,5 cm. It is suggested that propanol vapors pyrolytically decompose into alkenes and water at 600 °C in an inert nitrogen atmosphere thus providing a certain amount of water vapor for the reaction with stannic chloride. Increasing the nozzle-to-glass distance to 10,0 and then to 20,0 cm resulted in first an increase in deposited coating thickness and then a decrease compared to the coating thickness deposited at 2,5 cm. This observation indicates that water vapor and stannic chloride vapors must be in contact for a certain optimum time to maximize the thickness of the deposited coating. Prolonged stannic chloride-water vapor reaction times decompose the coating material and result in a subsequent decrease in coating thickness. Overall, the coating thicknesses were less when compared to those coatings deposited in an 80 % relative humidity atmosphere. This result reflects the fact that the amount of water produced by the pyrolytic decomposition of propanol would be less in comparison to the water content of an 80 % relative humidity environment.

Therefore, it is postulated that stannic chloride vapor and water vapor initially react to form a product which, if caused to come in contact with heated glass surfaces, will deposit significant thicknesses of tin oxide coatings. If stannic chloride is allowed to react with water vapor for longer periods of time, a second reaction product is formed which does not contribute to the deposition of metal oxide coatings. Most likely, the second reaction product is created from the water-induced decomposition of the initial reaction product. The chemical composition of either reaction product is unknown at this time. However, an important point is that a certain level of water vapor is required to deposit tin oxide coatings onto heated glass surfaces from anhydrous stannic chloride. These results are in direct contrast to earlier work by Scholes [30] who notes that anhydrous stannic chloride vapors react with water vapor in the atmosphere to form particulate hydrates which do not promote tin oxide coating formation on glass surfaces. He cited methods to ensure that coating

operations take place in an ambient atmosphere of at least −50 °C dew point or lower. Bauer and Žagar [26] also mentioned that stannic chloride can be used to coat glass surfaces only in dry ambient air so as to prevent hydrated tin oxide formation.

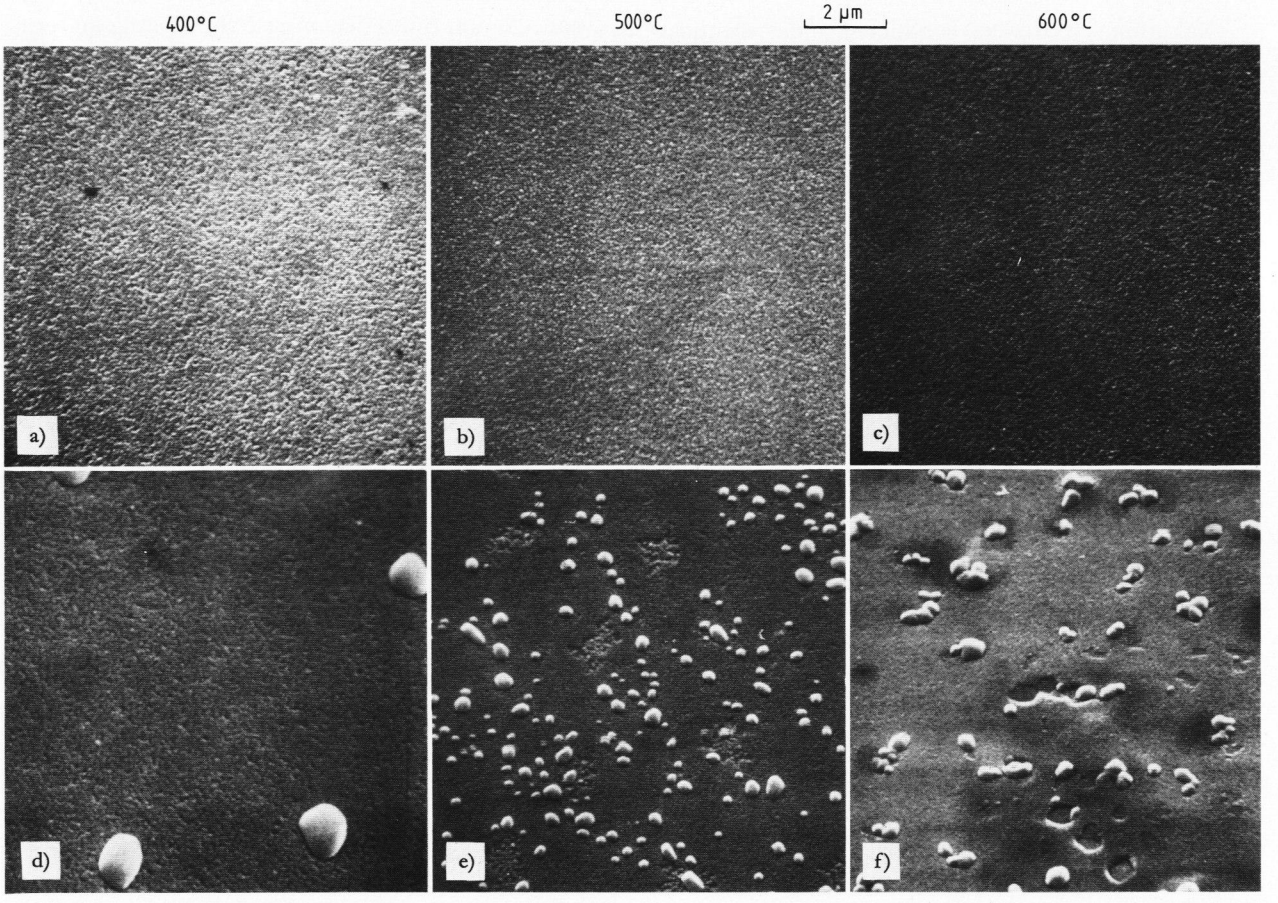
The fact that after a certain optimum time, coating deposition decreases rapidly with increasing stannic chloride - water vapor contact times indicates that the initial reaction product is very unstable with respect to water vapor contact. Therefore, stannic chloride vapors must not be allowed to react with water vapor for longer than optimum times if tin oxide coatings are to be deposited in an atmosphere containing water vapor. This effect may explain the prior inability [26 and 30] to form tin oxide coatings from anhydrous stannic chloride in the presence of water vapor if the substrates to be coated were located beyond an optimum distance from the outlet of the coating vapors.

3.2. Microstructure of tin oxide coatings

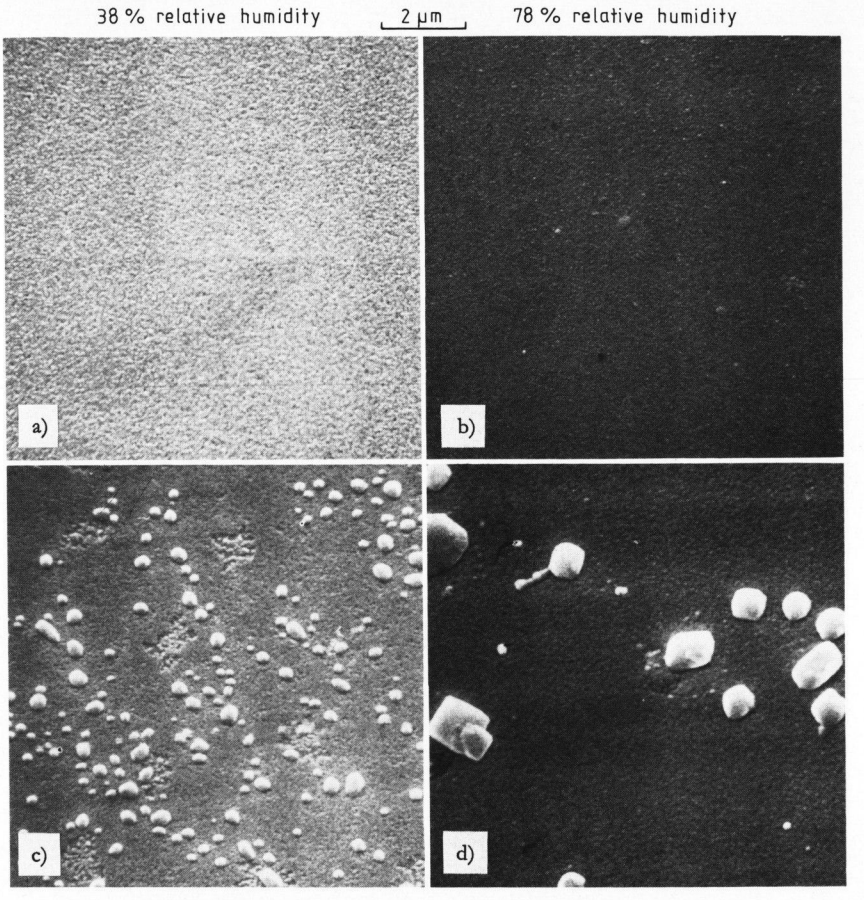
The microstructural aspects of tin oxide coatings deposited onto glass substrates of various compositions were previously presented orally by the present authors [31]. Subsequent work on soda-lime-silica surfaces by Geotti-Bianchini et. al. [32], substantiated those earlier results. Therefore, only a summary of the microstructure of tin oxide coatings deposited onto soda-lime-silica, borosilicate and fused silica surfaces will be discussed here.

Micrographs of tin oxide coatings deposited onto soda-lime-silica and borosilicate glasses under various coating conditions are shown in figures 2 through 4. The microstructure of tin oxide coatings deposited on fused silica substrates were identical when compared with the microstructure of tin oxide coatings deposited on borosilicate substrates. Therefore, only the coated borosilicate substrate samples will be discussed.

Tin oxide coatings deposited onto borosilicate glass are continuous and contain no cracks, pores or holes. However, tin oxide coatings deposited onto soda-lime-silica glass in either nitrogen or oxygen atmospheres of 38 or 78 % relative humidity exhibited crystal-like features. The composition of these features was found to be sodium chloride as determined by an EDX analysis. The maximum diameter of the sodium chloride crystals ranged in size from several hundred to several thousand nanometers. It is theorized that chloride ions from the anhydrous stannic chloride vapors react with sodium in the heated glass surface to form these sodium chloride

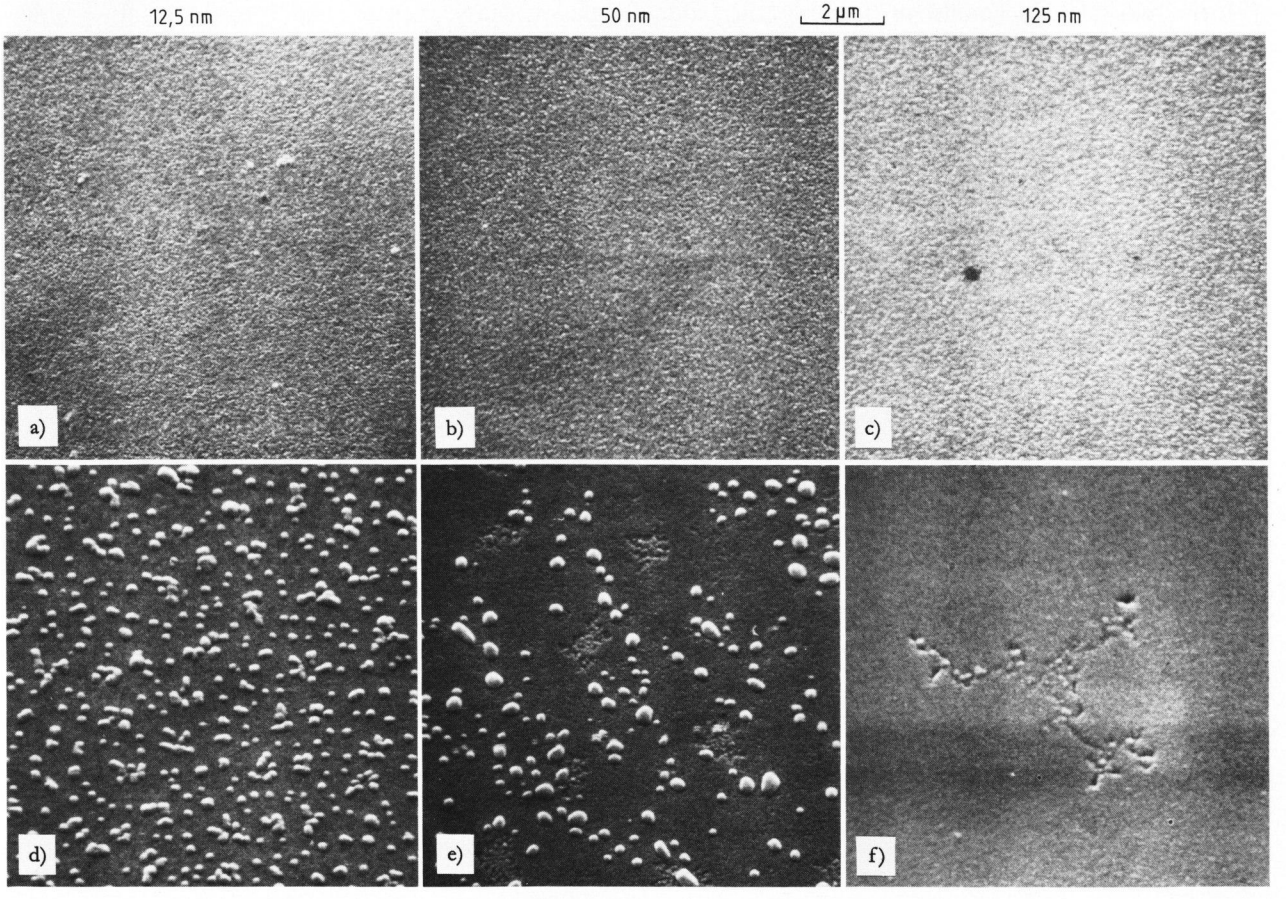


Figures 2a to f. Effect of substrate type and temperature on the microstructure of 50 nm tin oxide coatings deposited in a 38 % relative humidity atmosphere; a) to c) borosilicate glass, d) to f) soda-lime-silica glass.



Figures 3a to d. Effect of relative humidity and substrate type on 50 nm tin oxide coatings deposited at a substrate temperature of 500 °C; a) and b) borosilicate glass, c) and d) soda-lime-silica glass.

Figures 4a to f. Effects of tin oxide coating thickness deposited at a substrate temperature of 500 °C in a 38 % relative humidity atmosphere; a) to c) borosilicate glass, d) to f) soda-lime-silica glass.



crystals. No sodium chloride crystals were evident on tin oxide coated soda-lime-silica surfaces when coatings were deposited from non-halogen bearing dibutyl tin diacetate [33].

The sodium chloride crystals were removed by subjecting tin oxide coated samples to either an aqueous wash or a heat treatment in air near the annealing temperature of soda-lime-silica glass. The removal of these crystals revealed the presence of holes in the tin oxide coating as determined by EDX analyses. SEM/EDX analyses of soda-lime-silica glasses exposed to hydrochloric acid vapors under identical preparation conditions as the deposition of tin oxide coatings described above also revealed the presence of sodium chloride crystals of sizes and distributions similar to those found in the tin oxide coatings.

3.3. Tin oxide deposition mechanism

The results of the studies of tin oxide deposition parameters and tin oxide microstructure suggest that two coincident processes are occurring during deposition of tin oxide onto soda-lime-silica glass substrates from anhydrous stannic chloride vapors in the presence of water vapor. First, stannic chloride vapor hydrates or hydrolyzes in the presence of water vapor to create an unstable reaction product which undergoes a temperature dependent conversion to tin oxide at the glass surface. This reaction product decomposes rapidly with time in contact with water vapor to a form which is incapable of forming tin oxide coatings on glass substrates. Second, an exchange reaction occurs between chloride contained in the coating vapor stream with sodium either bonded directly to the glass or present on the glass surface due to a reaction involving atmospheric water vapor as mentioned by Weyl and Marboe [12]. These chloride-sodium reactions result in the formation of sodium chloride crystals distributed across the glass substrates simultaneous with the deposition of tin oxide coatings.

3.4. Frictive loading behavior of tin oxide and polyethylene coatings

The behavior of uncoated, tin oxide coated, polyethylene coated and tin oxide plus polyethylene coated glass surfaces under frictive loading conditions was determined. Only the information derived from the dry and wet tests for a 3000 g load will be discussed here in detail. Similar, but less severe, frictive characteristics were observed for 500 and 1500 g loads.

The SEM micrographs in figure 5 show the frictive damage tracks produced on uncoated glass surfaces. The coefficient of kinetic friction for uncoated glass was approximately 0,7 as tested both dry and wet which compares well with data as reported by Southwick [34] and others [35]. During sliding frictive contact numerous crescent cracks were formed behind the sliding sphere due to the combination of tensile Hertzian contact stresses developed by the loaded sphere bearing on the glass and those stresses developed by the frictive sliding action [11 and 36]. Examination of the frictive tracks revealed an area of sliding damage in the center of each track in addition to the presence of the crescent cracks.

The extent of the frictive damage was further visually developed by an HF acid etch treatment. Such treated surfaces showed no substantial difference in the extent of damage produced in the glass surfaces for tests conducted under dry or wet conditions. These results indicated that the initial appearance differences observed between the frictive tracks produced under these test conditions were due to differences occurring at the immediate glass surfaces.

It is generally accepted that freshly formed and untreated glass surfaces, when pressed together, adhere to each other due to bonding between the two surfaces [37]. During environmental exposure following surface formation contaminant adsorption by glass surfaces occurs which reduces the likelihood of such bonding. Heating glass surfaces to approximately 400 °C to 500 °C in a vacuum removes the contaminants which increases the coefficient of kinetic friction to values between 0,8 to 1,0, a range comparable to that of freshly formed glass [35 and 37]. It is evident in viewing the micrographs that glass-to-glass contact under such highly frictive conditions is quite damaging and would result in significant reductions in the strength levels of pristine glass surfaces [38].

A typical frictive track developed on glass surfaces coated only with a polyethylene compound is shown by the micrographs in figure 6. During the initial contact of the loading sphere with the coated flat plate under dry test conditions crescent cracks were produced which indicates that the translating sphere was penetrating the polyethylene coating and coming into direct contact with the coated glass plate. This effect was observed at all test loads, with the severity of the surface damage increasing at higher load levels. However, in each case, after several millimeters of travel sufficient polyethylene was transferred to the loading sphere and further frictive damage was reduced and finally eliminated.

Under wet test conditions crescent cracks were created along the entire length of the frictive track for all frictive test loads. The coefficient of kinetic friction for tests conducted on surfaces coated only with polyethylene increased from values of 0,1 to 0,3 obtained in dry tests to a value of 0,7 for the wet tests. The damage created was similar in appearance to that produced from frictively loaded uncoated glass surfaces. These results indicate that water disrupts the bonding at the glass-polyethylene interface in the

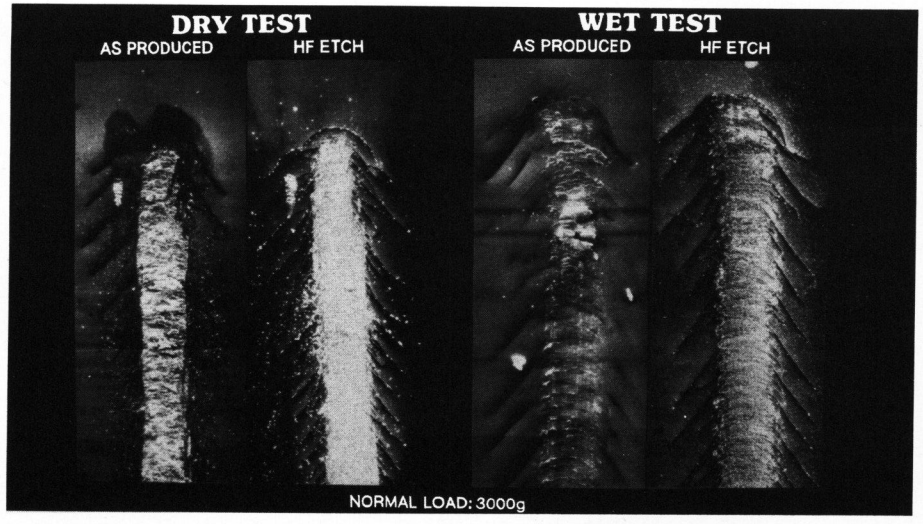


Figure 5. Micrographs of frictive track areas produced on uncoated soda-lime-silica glass.

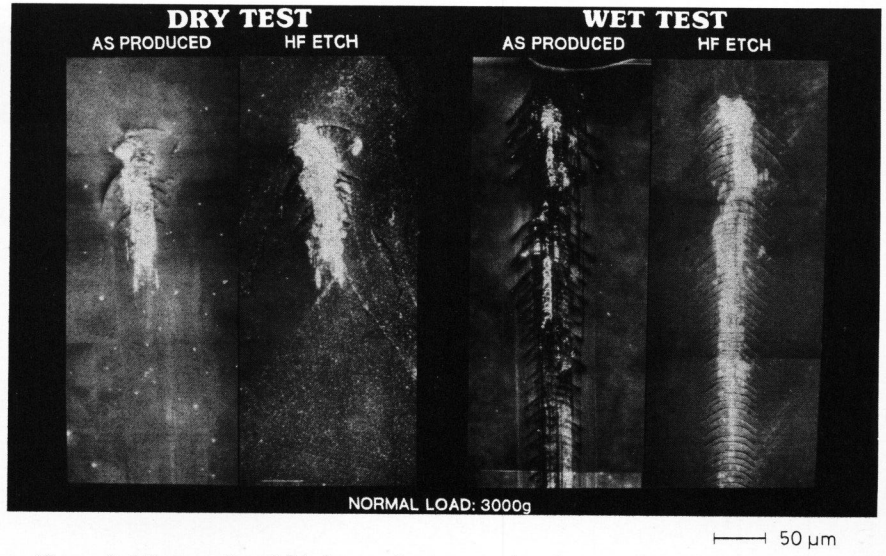


Figure 6. Micrographs of frictive track areas produced on polyethylene coated glass.

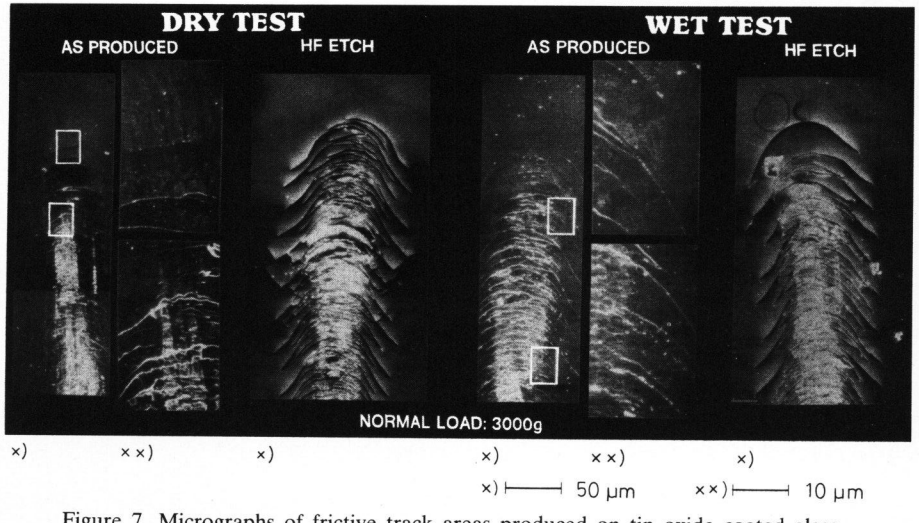


Figure 7. Micrographs of frictive track areas produced on tin oxide coated glass.

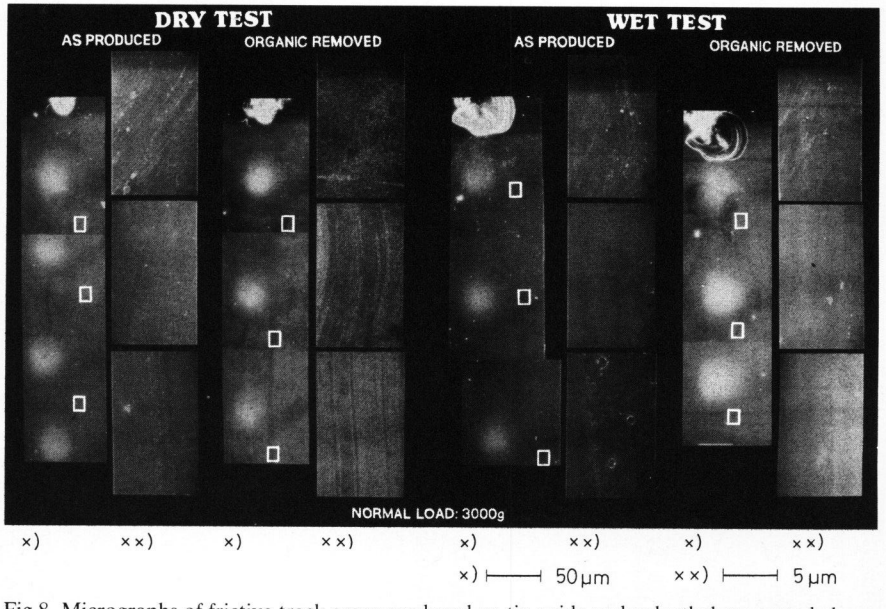


Fig 8. Micrographs of frictive track areas produced on tin oxide and polyethylene coated glass.

immediate area of frictive contact [39]. The bond disruption results in the removal of the organic coating immediately surrounding the point of loading permitting glass-to-glass contact. Such contact results in the observed increase in the coefficient of kinetic friction and the production of surface damage.

The disruption of polyethylene by water can be related to the nature of the bond formed between the organic material and the glass surface. A freshly formed glass surface possesses polar bonding characteristics due to the presence of non-bridging oxygens. This bonding character is different when compared to the more non-polar bonding nature of polyethylene. Weak bonds, therefore, are formed between the non-bridging oxygens in the glass surface and the polyethylene chain. The non-bridging oxygens, however, have a greater affinity for water and may be better screened or achieve a lower energy state [35] by forming silanol groups in reaction with water molecules. Thus under frictive loads, water is able to displace polyethylene at glass surface [39].

The frictive properties of tin oxide coated surfaces alone, as seen by the micrographs shown in figure 7, were found to be essentially the same as uncoated glass surfaces and exhibited coefficients of kinetic friction of approximately 0,7 for both dry and wet tests. The creation of frictive damage in the form of crescent cracks was also evident in both test conditions.

The mechanical bearing theory for tin oxide coatings as proposed by De Jong [25] states that metal oxide coatings are composed of discrete islands which are capable of physically deforming and smearing over the surface while under mechanical loads thus providing a certain degree of protection from frictive damage. An additional theory is offered by Dettre and Johnson [16] who concluded that metal oxide coatings are composed of hard, discrete islands which support applied frictive loads, prohibiting the breakdown of organic lubricant layers when present. The present study indicates that tin oxide coatings are continuous rather than discrete, exhibit complete surface coverage and are not deformed to any observable degree during frictive loading. The high coefficients of kinetic friction observed for tin oxide coated glass are due to glass-to-oxide contact. No inherent lubricating qualities were observed for glass surfaces coated with only tin oxide. The frictive damage produced during sliding contact on all tin oxide coated surfaces extended down into the glass surface and was not confined to the tin oxide coatings alone. This was evidenced by the presence of crescent cracks in the glass surfaces following removal of the tin oxide coatings.

Metal oxide coatings, as do other oxide surfaces, possess a certain affinity for organic substances and become easily contaminated by airborne compounds. Rawson [15] noted that the coefficient of kinetic friction of tin oxide coatings decreases rapidly upon exposure to and storage in ambient atmospheres contaminated with organic vapors. It is reasonable to expect that the scratch protection of the surface would increase corresponding to this decrease in the coefficient of kinetic friction. Previous reports by other investigators [16] of metal oxide films alone exhibiting a certain degree of lubricity and scratch protection may have been the result of using such inadvertently contaminated tin oxide surfaces in their experiments.

Other research efforts [17, 18, 40 and 41] have reported that tin oxide coatings diffuse into glass surfaces creating compressive stresses or that tin oxide coatings fill microcracks present on the glass surfaces thereby producing resultant improvements in glass strength. The results of this study indicate that glass surfaces coated only with tin oxide and subjected to frictive loads exhibit extensive frictive damage. Thus, even if the theories concerning the creation of compressive layers or the filling of microcracks are valid, those effects would be counteracted by the creation of strength reducing frictive damage for glass surfaces coated only with tin oxide.

The micrographs in figure 8 show the results of frictive testing on glass surfaces first coated with tin oxide and then overcoated with polyethylene. No frictive damage was observed for the specific loads and test conditions studied. The coefficient of kinetic friction ranged from 0,05 to 0,1 for both dry and wet tests. It is believed that tin oxide, in this application, acts as a primer or a „mordant" as described by Weyl [12] to more firmly bond the lubricious and frictive damage preventive organic coatings to glass surfaces. This increased bonding is in direct contrast to the relatively weaker bonding observed for poylethylene when deposited directly onto glass substrates.

At the glass surface non-bridging oxygens in the glass react with anhydrous stannic chloride to form strong Si - O - Sn bonds. The oxide bonding scheme is thus carried across the glass-coating interface. Due to the polarizability of the relatively large Sn^{4+} ions in the tin oxide structure the upper surface of tin oxide coatings have a more covalent-type character in comparison with the glass surfaces and result in enhanced bond strengths with polyethylene. The overall effect is to provide more adherent polyethylene coatings under both dry and wet conditions and greater degrees of frictive damage protection.

4. Conclusions

Based on the results summarized in this paper the following conclusions are offered:

a) For the coating parameters studied, neither the glass composition nor the chemical composition of the carrier gases exhibited an influence on either the

ability to deposit a coating or on the resultant thickness of the tin oxide coatings produced.
b) Humidity levels in the environment through which anhydrous stannic chloride vapors pass have a significant effect on the resultant thickness of deposited tin oxide coatings – the coating thickness increased dramatically with increased humidity levels and short contact times between the coating vapors and water vapor.
c) The presence of certain amounts of water vapor are required to deposit tin oxide coatings onto glass substrates from anhydrous stannic chloride vapors.
d) The surface temperature of the glass at the time of coating deposition had a significant effect on the thickness of the resultant tin oxide coating – coating thicknesses increased for higher substrate temperatures within the temperature ranges studied.
e) Sodium chloride crystals form on soda-lime-silica glass surfaces as a result of reactions between chloride ions in the coating gas stream and sodium ions on the glass surface. These crystals did not form on fused silica or on a chemically durable borosilicate glass surface even though the borosilicate glass used in the study contained some sodium oxide. The absence of crystals on the borosilicate glass is probably due to the increased bonding strength of sodium within the borosilicate glass matrix.
f) Tin oxide coatings produced on borosilicate and fused silica substrates were continuous, exhibited no cracks or islands and completely covered the glass surfaces. In the case of coatings on soda-lime-silica glasses, however, holes were present in the tin oxide coatings when the sodium chloride crystals were removed by sufficient heat treatments or when rinsed in water.
g) Tin oxide coatings alone did not show any observable deformation under frictive loading, offer no improvement in lubrication compared to an uncoated glass surface and are unable to prevent frictive damage from occurring on coated glass surfaces under either wet or dry test conditions.
h) Polyethylene coatings alone, when applied directly to glass substrates, provide limited lubricating qualities and prevent frictive damage only under relatively light loads and in the absence of water. The presence of water during frictive loading facilitates the disruption of polyethylene coatings in the immediate contact area resulting in glass-to-glass contact with the associated production of frictive damage and the attendant increases in the coefficient of kinetic friction.
i) The combination of tin oxide and polyethylene coatings eliminated frictive damage when loaded under wet or dry frictive conditions.
j) Tin oxide coatings increase the degree of bonding between organic compounds and glass surfaces yielding improved lubricating qualities, reduced frictive damage during mechanical contact and maintenance of these lubricating qualities under wet test conditions.

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