Surface Morphology, Appearance & Tribology of Electrodeposited Tin Films

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The appearance of electrodeposited tin has been classified as matte, satin-bright and bright. Obviously, this "appearance" classification is qualitative and subject to interpretation. It would be useful if a quantitative method could be developed, based on reflectivity (glossiness) to describe the surface appearance. Moreover, it would be fundamentally interesting to understand the relationships among surface "glossiness," surface morphology, the structure of the electrodeposited film, and its effects on tribological behavior, such as the coefficient of friction and wear resistance.

Electroplated tin and tin alloys are widely used as protective and solderable coatings in various industries.[1,2] Their visual appearance is an important physical characteristic and has often been classified as matte, satin-bright and bright, among other descriptions.[2] These qualitative appearance classifications are obviously subject to interpretation and often lead to misunderstanding.[3] A quantitative assessment based on some physical measurement would be beneficial for quality control and would provide the basis for understanding the influence of a plating process and operating parameters on the visual appearance. This analysis would be extremely useful if it could be correlated to the performance (*i.e.*, wear resistance, solderability) of the deposited films.

The appearance of an object can be described by two factors:[4] color and "geometric attributes." Color arises from the wavelength-dependent absorption and reflection of light. The "geometric attribute" is often determined by the surface "structure" of the object and is described by: gloss, lightness, haze, luster, surface uniformity and directionality.[4] A goniophotometric curve, produced by measuring reflected light at different angles of observation, and at a fixed incident angle of light, is required to fully describe the geometric attributes.

Figure 1 is a schematic representation of typical goniophotometric curves for matte and bright surfaces. A bright surface reflects a larger proportion of light specularly relative to a matte surface, where the spatial distribution of reflected light is broader. The specularly reflected light contributes to the glossiness of the substrate, while the diffuse reflection, on the other hand, leads to reflection haze. A detailed measurement of a goniophotometric curve is tedious, however, requiring rather expensive instrumentation, and therefore is not very practical.[4] An alternative method to describe the gloss of a surface is the gloss reflectance factor,[5] which measures the ratio of specularly reflected light to light reflected from a "gloss standard."

The shape of a goniophotometric curve is dependent on the type of surface under investigation and the incident angle of the light used for this measurement. This is illustrated in Fig.

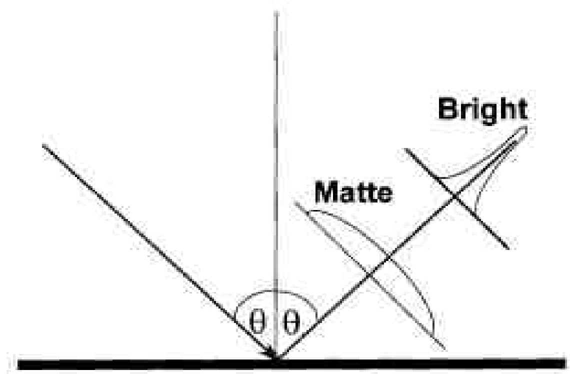

Fig. 1—Goniophotometric curves of matte and bright surfaces.

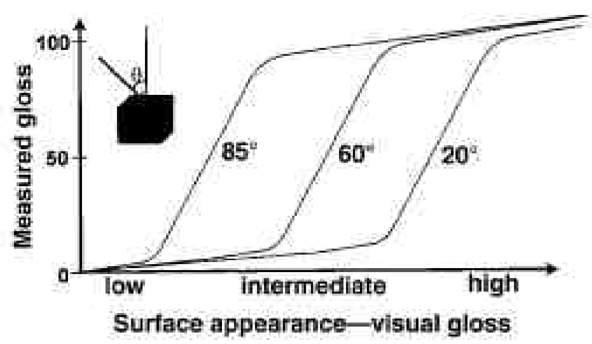

Fig. 2—Measured gloss vs. visual gloss ("appearance") at various light incident angles.

2, where the measured gloss is plotted as a function of the surface "appearance" or visual gloss at three different incident angles. As can be seen, there is a very good response between the measured gloss and the visual appearance for a highly "reflective" surface at 20°, and for a low "reflective" surface at 85°. Conversely, the measured gloss is rather insensitive for highly "reflective" surfaces when measured at 85°, and for the low "reflective" surfaces when measured at 20°C. To quantitatively describe the appearance of surfaces with high gloss, therefore, a small light incident angle (*e.g.,* 20°) should be used. On the other hand, a high light incident angle (85°) is required to distinguish surfaces with low gloss. Typical light incident angles used are 20, 60 and 85° and specific angles have also been adopted for special uses, such as 45° for ceramic and 75° for paper.[6-9]

The parameters affecting surface glossiness have not been investigated in detail; however, it is generally thought that surface morphology, surface roughness, grain size, grain structure, and orientation significantly affect surface glossiness. Sun *et al*.[10] studied the grain structure of various electroplated tin films and correlated the appearance with tin

Table 1
Gloss Reflectance Factor of Bright, Satin-bright & Matte Tin Surfaces at Various Light Incident Angles

		Light Incident Angle			
No.	**Visual**	**8°**	**20°**	**60°**	**85°**
1	Bright	77.11	1430	720	140
2	Bright	75.38	1551	769	139.5
3	Bright	78.76	1536	743	122
4	Satin	5.27	7.1	98.2	109.5
5	Satin	5.47	7.3	96.5	108.1
6	Satin	5.72	7.4	105.8	107.9
7	Matte	2.68	3	38.8	93.1
8	Matte	1.42	1.7	10	75.4
9	Matte	3.48	3.4	41.6	96.4

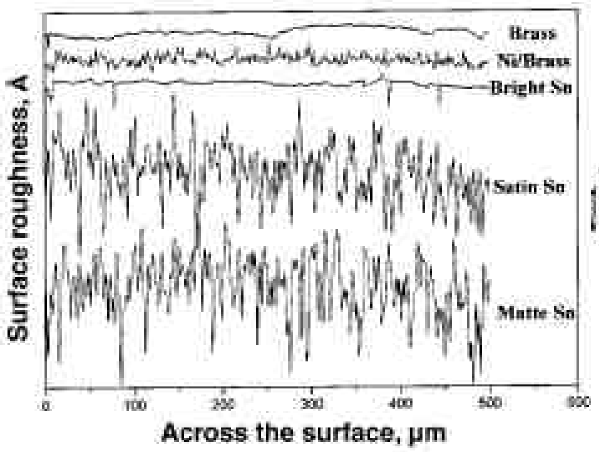

Fig. 3—Surface roughness.

crystal orientation. A Tin Gloss Index (TGI), defined as a ratio of X-ray intensity between various crystal orientations, was introduced to characterize the surface appearance of plated tin films. In this paper, we will examine how surface roughness, grain size and grain orientation affect surface appearance (*i.e.*, glossiness), and investigate its influences on tribological properties, such as coefficient of friction and wear resistance.

Experimental Procedure

Electroplated tin films classified as bright, satin-bright and matte were plated to a thickness of 3.0 µm, using a proprietary chemistry.[11,12] These films were deposited on a 2.5-µm-thick nickel underlayer plated from a proprietary semi-bright nickel process.[13]

The gloss measurements were carried out using various spectrophotometers, gloss reflectometers and haze-gloss meters. Surface roughness was measured using a surface profiler over a length of 500 µm. The arithmetic average roughness (Ra) was calculated by averaging the deviation from the mean line.

Morphology and grain size were examined using a field emission scanning electron microscope (FE SEM), that has an ultimate resolution of 2 nm. Surface texture and grain structures were studied using an X-ray diffractometer where $\theta/2\theta$ scans determined grain structure and crystal orientation parallel to the surface. Grain size was estimated using Scherrer's equation. The atomic force microscope (AFM) images were obtained with a multimode nanoscope.

Table 2
Gloss Reflectance Factor at 60° vs. Surface Roughness

Bright		Satin-bright		Matte	
Gloss	**Roughness**	**Gloss**	**Roughness**	**Gloss**	**Roughness**
720	77 Å	98.2	847 Å	38.8	872 Å
769	66 Å	96.5	868 Å	10	1222 Å
743	137 Å	105.8	793 Å	41.6	931 Å
755	94 Å	98.3	687 Å	18.8	899 Å
719	109 Å	104.7	646 Å	13.8	920 Å

Table 3
Hardness & Carbon Content for Various Tin Films

	Hardness, KHN_2	Carbon content, %
Bright	16	0.2
Satin Bright	8	0.004
Matte	8	0.01-0.02

Results

Quantification of Glossiness

Table 1 summarizes the gloss reflectance factor for bright, satin-bright and matte samples. Measurements were made at four light incident angles: 8, 20, 60 and 85°. In general, bright surfaces exhibit high, and matte surfaces exhibit low, gloss reflectance; however, satin-bright and matte surfaces have very similar gloss reflectance at light incident angles of 8 and 20°, while all three surfaces have very similar values at a light incident angle of 85°. The most significant response of gloss reflectance as a factor of the "appearance" is observed at an angle of 60°. For bright surfaces, the gloss reflectance is as high as 769 (dimensionless), while the satin-bright surfaces have a gloss reflectance around 100 and the matte surfaces are below 50. Clearly, the measurement geometry with a light incident angle of 60° provides one of the best conditions for differentiating bright, satin-bright and matte electrodeposits.

It is also interesting that one of the matte surfaces, sample No. 8, has a significantly lower (~10) gloss reflectance than the other two samples classified as "matte". Visual observation shows that sample No. 8 "appears" slightly more matte. This is a clear example of the ambiguity that arises from these subjective classifications and will be discussed in more detail in the following sections.

Glossiness & Surface Roughness

The surface roughness of the plated deposits is shown in Fig. 3, where typical 500-µm line span profiles for bright, satin-bright and matte tin surfaces are illustrated. For comparison, the line profiles for brass and Ni/brass substrates are also included. As can be seen, the bright tin plating slightly reduces the roughness of the Ni/brass substrate, showing a leveling effect, while the satin-bright and matte tin dramatically increases the roughness of the surface. In Table 2, the arithmetic average roughness (Ra) is summarized along with the gloss reflectance factor measured at a light incident angle of 60°.

As can be seen, there is a strong correlation between glossiness and surface roughness, with the smooth surface being glossier than the rough surface, as would be expected. This is clearly demonstrated in Fig. 4, where a plot of gloss reflectance shows an exponential decrease as a function of increased roughness. It is noteworthy that satin-bright is

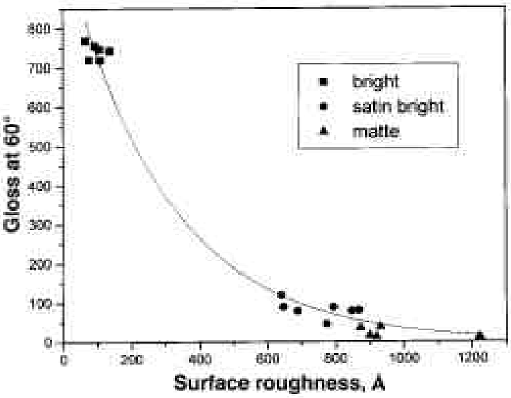

Fig. 4—Gloss at 60° vs. surface roughness measured by profilometer.

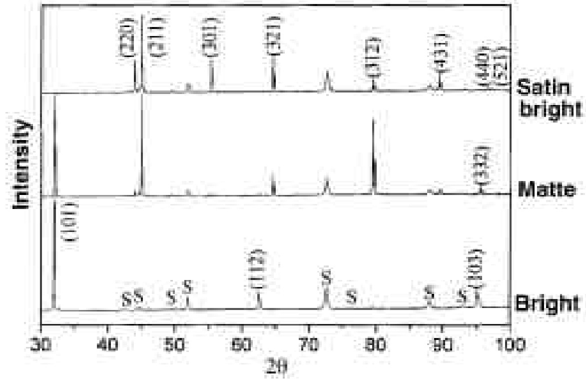

Fig. 5—X-ray diffraction spectra of electroplated tin films.

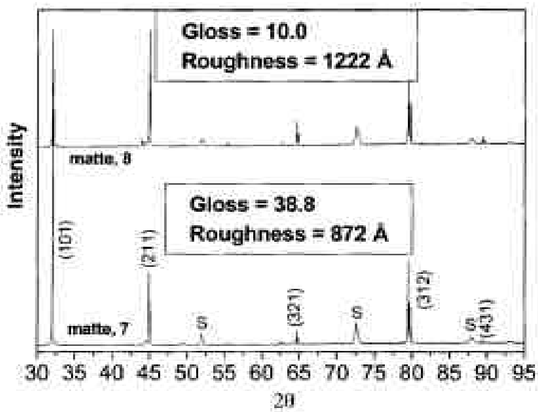

Fig. 6—Gloss, surface roughness & grain orientation of various matte tin films.

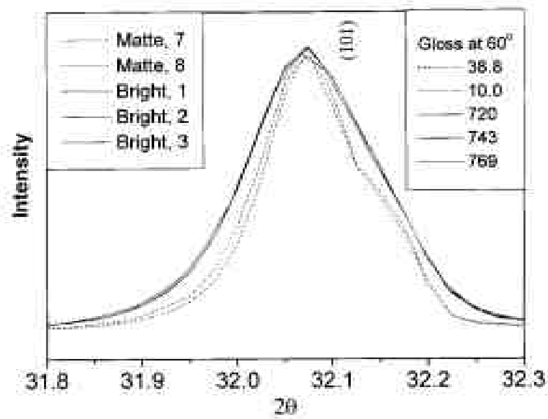

Fig. 7—Expanded view of the (101) diffraction peak.

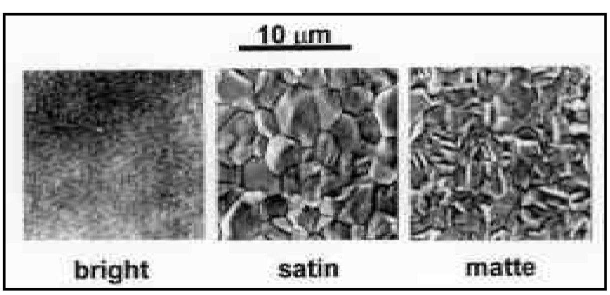

Fig. 8—SEM images of various electroplated tin films.

relatively close to matte in terms of both surface roughness and glossiness, whereas a rather large difference exists between bright and satin-bright. It would be interesting to plate tin with a surface roughness between 200 and 600 Å, which should exhibit a gloss value between 200 and 700. Moreover, it would also be useful to plate deposits with a surface roughness >1200 Å and determine whether they would fall into the categories commonly referred as "dull" or "burnt" deposits.

Glossiness & Grain Structure

The grain structure and crystal orientation parallel to the surface were studied using XRD. Figure 5 shows the θ/2θ scans for bright, satin-bright and matte films. The diffraction peaks labeled "***s***" are a result of the Ni/brass substrate. The deposits all exhibit XRD patterns typical for (β) tin; however, very different crystalline orientations are exhibited. The bright tin shows predominantly (101), (112) and (103) orientations, while the satin-bright consists of (220), (211), (301), (321), (312), (431), (440) and (521) orientations. It is interesting to note that there are no common orientations between the bright and satin-bright films. The matte film, on the other hand, is essentially a combination of the crystal faces from the other two, and exhibits a gloss lower than the satin-bright. Apparently, the addition of crystal orientations typical for bright tin to that of satin-bright tin does not increase its gloss, but rather results in a matte deposit. This indicates that there is no simple and direct correlation between specific crystal orientations, their intensity and surface appearance, as discussed by Sun *et al.*,[10] and any quantification based on these parameters could be misleading.

The data do indicate that the number of crystal orientations seems to correlate with the glossiness of the surface. The bright tin has only three preferred crystal orientations, while the satin-bright and matte films have 8 and 11 crystal orientations, respectively. This observation is consistent with the general assumption that an increase in the number of crystal faces results in a "rougher" surface and decreased gloss.

As indicated above, one of the matte surfaces (No. 8) is "duller" than the other matte samples (see Table 1), and we investigated via X-ray diffraction whether a structural difference can account for this observation (Fig. 6). The surface roughness as well as the gloss reflectance factor are included for comparative purposes. As can be seen, the two samples exhibit *identical* preferred orientations; however, the population of individual orientations, as indicated by the intensity of the diffraction peaks, is significantly different. The (101) peak is typically very intense for bright tin (Fig. 5), whereas the (211) orientation is most intense for the satin-bright tin (Fig. 5). Clearly, sample No. 8 has a lower (101) and higher (211) intensity. Reducing the population of crystal orientations typical of bright surfaces results, therefore, in a rougher deposit and a reduction in gloss. This observation supports the work of Sun *et al.*,[10] which describes the correlation of gloss and the XRD peak intensity of specific crystal orientations. This relationship is applicable, however, only for deposits with *identical* crystal orientations.

Grain size is another important parameter to be considered in this analysis. According to Scherr's equation, the width of an X-ray diffraction peak is inversely proportional to the grain size. Figure 7 shows an expanded view of the diffraction peak of grains with (101) orientation. The broader peak of the bright tin relative to the matte tin indicates a smaller grain size. Unfortunately, this methodology is limited in its ability to differentiate between satin-bright and matte depos-

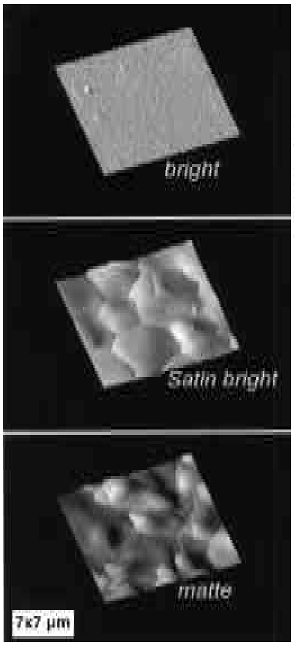

Fig. 9—AFM images of various electroplated tin films.

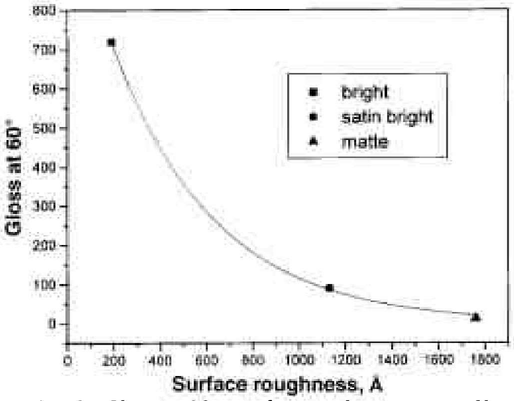

Fig. 10—Gloss at 60 °vs. surface roughness measured by AFM.

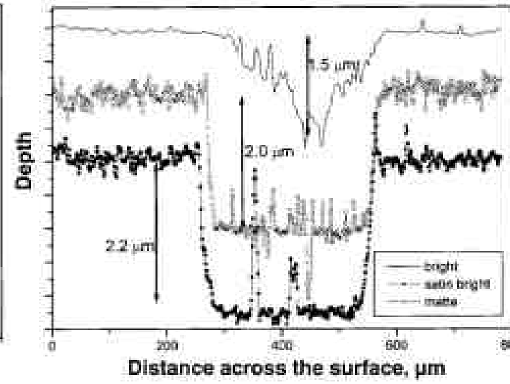

Fig. 12—Line profile of wear tracks after 300 wear cycles for various electroplated tin films.

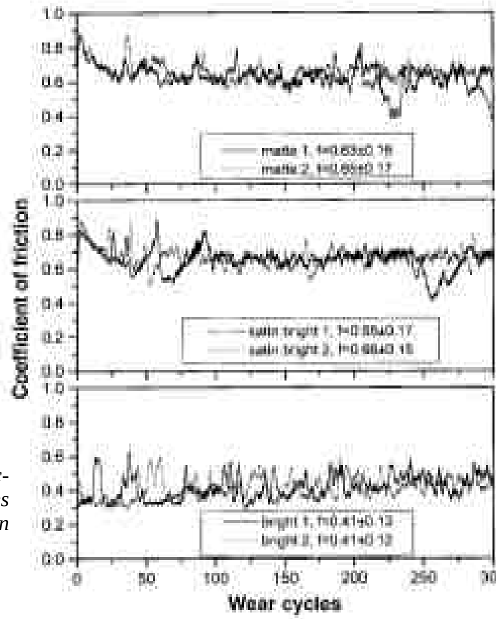

Fig. 11—Coefficient of friction at various wear cycles for various electroplated tin films.

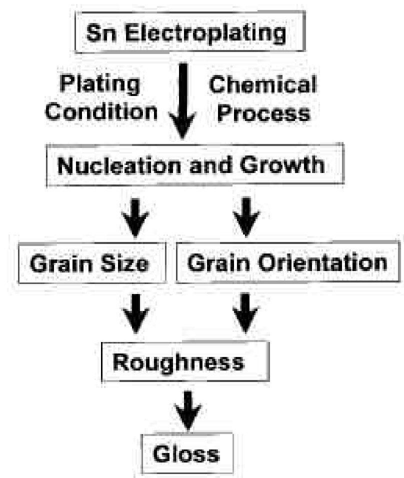

Fig. 13—Factors influencing surface appearance of electroplated tin.

its, which show a similar peak width, indicating similar grain size. Alternate methods must be employed to differentiate satin-bright and matte deposits.

SEM provides additional evidence of grain size and surface morphology and results are summarized in Fig. 8. The bright tin shows a fine structure with a much smaller grain size than either the matte or the satin-bright tin. It is very interesting to note that the matte tin has a significantly smaller grain size relative to the satin-bright tin, although its surface is less glossy. Once again, this confirms that grain size is *only one* of the parameters that affect surface appearance by modifying the surface roughness. In this regard, it is also noteworthy that the "texture" (*i.e.*, preferred orientation and surface morphology) of the matte tin is significantly different from the satin-bright tin.

AFM images were obtained and provide topographic mapping of the electroplated samples in question (Fig. 9). These measurements are inherently more sensitive because of the higher resolution (±1 Å) of this methodology relative to Dektak profilometry.

Consistent with SEM results, the AFM images show bright tin as a fine-grained structure with grain size in the range of 50 to 100 nm. The satin-bright and matte surfaces, on the other hand, have a much larger grain size of several microns. The arithmetic average roughness, calculated from AFM images over a 100 x 100-µm area, is 19 nm for bright, 113 nm for satin-bright and 176 nm for matte tin.

Figure 10 is a plot of gloss reflectance measured at 60° vs. surface roughness (via AFM). Once again, as shown in Fig. 4, there exists a strong exponential correlation between glossiness and surface roughness; however, the AFM data is better in distinguishing the surface topography of the satin-bright and matte samples. Of particular interest in the AFM view is the distinct presence of well-polygonized[11,12] and relatively smoother surface of satin-bright deposits. As discussed by Zhang *et al.*,[14] this will be a key factor in determining the propensity of electroplated tin to form whiskers.

Structure & Materials Property

The tribological behavior of electrodeposited tin deposits was studied using a microtribometer. In Fig. 11, the coefficient of friction is plotted vs. wear cycles, allowing calculation of the average coefficient of friction for the first 300 cycles. The bright tin has an initial friction coefficient of ~0.4 and remains relatively unchanged within a range of 0.3 to 0.6. Satin-bright and matte surfaces exhibit similar initial friction coefficients of ~0.65, which quickly increase to ~0.9 (within the first two wear cycles), then gradually decrease to an equilibrium value of ~0.65. The initial increase is most likely a result of removal of adventitious organics present on this surface, while the rather high friction coefficient of 0.9 is associated with the high roughness of these surfaces, which become smoother with wear and consequently stabilize.

The shape and depth of the wear track after 300 wear cycles were determined using a surface profiler and are shown in Fig. 12. The average wear track depth is 1.5 µm for bright tin, 2.0 µm for matte tin and 2.2 µm for satin-bright tin. The bright tin film, which has a low friction coefficient, exhibits a lower wear rate. On the other hand, the matte and satin-bright tin films, which have a high friction coefficient, display a relatively higher wear rate.

As discussed above, the initial coefficient of friction certainly relates to the surface roughness. However, it is worth pointing out that even deep in the wear tracks, the bright deposits show a significantly lower friction coefficient than either the satin-bright or matte films. This difference cannot be attributed solely to surface roughness and must be associated with the difference in bulk properties. There are two possible explanations: grain size and occluded organic content. The bright tin films exhibit a much smaller grain size and a higher organic content which generally result in a harder film that is more wear resistant. The trapped organic material acts as a lubricant to reduce the friction coefficient. In Table 3, the hardness and carbon content of the bright, satin bright and matte tin are summarized and clearly support this hypothesis.

Conclusions

The appearance of electroplated tin can be quantitatively described by measuring the gloss reflectance at a light incident angle of 60°. The grain structure, orientation and grain size have an indirect effect on the gloss by modifying the surface morphology (*i.e.*, roughness). The relationship of the gloss with various parameters is schematically summarized in Fig. 13.

The bright tin has a lower coefficient of friction and a higher wear resistance than the satin-bright and matte tin. The surface roughness, grain size and organic content are responsible for the observed friction coefficient and wear behavior.

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