ABSTRACT

STEEL SURFACE OXIDATION AFTER PICKLING

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Oxidation of colled rolled steels panels after pickling in different acids and rinsing with tap water and in a beaker was investigated by Optically Stimulated Electron Emission technique. Exposed to ambient air steel surface after pickling, rinsing and blotting gains very quickly oxide film.

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Oxide film, which is present at normal conditions on the steel surface, prevents the achievement of good adhesion between the substrate and protective metal coating (zinc, nickel, copper and so on). For example, electro- or electroless plating and hot dip coating of steel surfaces. Usually oxides are removed by pickling, fluxing or annealing in furnace in a vacuum. After pickling, steel surface is rinsed by water sprays or immersed in tank with flowing water prior to transfer to the coating stage - plating or fluxing before hot dip coating. On high speed continuous strip, tubing or wire lines, the rinse time does not exceed several seconds. If the line speed is not high enough, growth of oxide film can occur prior to coating. This is also true for batch processes if the time interval between exit from the pickling tank and immersing in a coating (fluxing) solution is too long. The most favorable conditions for rapid oxide film growth exist when the steel surface is spray rinsed. The growth of oxide film thickness can reach a substantial value in 10 - 15 seconds, in some cases even red rust can be seen on the steel surface.

Oxidation of steel surface has not been studied sufficiently. The lack of such studies may be due to experimental difficulties in fast and accurate measurement of very thin oxide films, which at the initial stage is not more than tenths and hundreds of angstroms.

The study of oxidation kinetics has been made possible with the availability new instrumentation based on photo-emission technique (also known as Optically Stimulated Electron Emission OSEE) [1]. The sensitivity of the this method is very high and films from a partial monolayer to up to 7,500 angstroms can be measured. The films attenuate or enhance the OSEE signal. The level of change in the OSEE signal is proportional to the thickness of the attenuating film.

EXPERIMENTAL TECHNIQUE AND PROCEDURES

Optically Stimulated Electron Emission technique [1] was used for studying oxide film formation after pickling. Surface Quality Monitor model OP1010 with a standard vertical sensor (Photo Acoustic Technology, Inc.) was used. The aperture 6 mm diameter was installed on the sensor, amplifier gain switch was set in the 5 position, which corresponded to a gain of 16. Distance between studied surface and the sensor was 4 mm. Peak detector was switched on and maximum value of applied signal was recorded. To avoid signal decay during experiment time which was up to 30 min. the tested panel was shielded between measurements.

Steel panels of cold rolled steel 0.2*50*150* mm were used. After cleaning by brushing in alkaline cleaner at 80° C, a panel was rinsed with tap water, pickled, rinsed in different manner, blotted by filter paper and put under probe. Time between blotting and first measurement was 3 sec. The steel surface was shielded by a piece of paper with duct tape over it, all the time except during measurements. Steel surface oxidation at elevated temperature was made in electric oven with automatically controlled temperature level. At least three panels were tested for each set of experimental conditions and 10 readings were taken from each panel. All solutions for pickling and rinsing had ambient temperature.

EXPERIMENTAL RESULTS AND DISCUSSION

Steel panels after cleaning and rinsing for 2-3 sec by tap water demonstrated photo current (PC) of approx. 400 units, which during 10 sec dropped to 260-280 and then became stable up to 30 min. (curve 1, Fig. 1). This drop in signal is normal for the photo emission process. When any surface is exposed to ultra violet light for extended period of time, the PC from the surface drops due to the interaction that goes on in the air gap between the sensor and the sample surface. This drop in signal can be prevented by introducing argon into the air gap between the sensor and the sample surface[1]. This article discusses the reletive change of PC , the absolute value of the PC was not derived and is only meaningful for comparison purposes.

After cleaning and pickling during 30 sec in 10% HCL, steel surface becomes very active and PC reaches 570 units. Then it goes down (curve 2, Fig. 1), though within 30 min it stays higher, than for unpickled panel. Similar behavior is observed for 10% solution of sulfuric acid and phosphoric acids (Fig. 1). This reduction of PC is likely caused by FeO/Fe_2O_3 formation while pickled panel is exposed to air. These oxides with p-type conductivity and very high electrical resistance ($2.7*10^4$ - 10^{11} Ohm*m) considerably attenuate electron emission. It should be pointed out that instant activity of steel surface after pickling is much higher, since first measurements were made only three seconds after blotting.

Steel panels dipped in nitric acid exhibited unusual behavior. Pickling in 2% HNO_3 significantly increases PC, though in 5% solution this effect is not very pronounced (curve 5 and 6 Fig. 1). Steel surface passivated by nitric acid does not seem to readily oxidized during 30 min.

Rinsing with tap water after pickling reduces PC (Fig. 2). A 30 sec rinsing, besides reducing the electron emission, a rusty yellow-orange film can be observed on steel surface. Keeping steel panel for 10 min in a beaker of water after pickling does not reduce PC as much as using the tap water does (curve 4, Fig. 3).

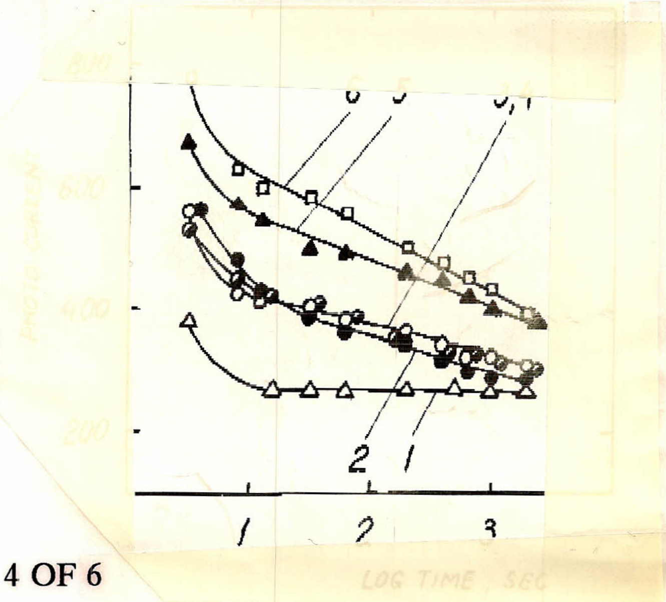
Panels pickled in 10% HCL with 2 g/l of organic inhibitor produces a very high electron emission (curve 1, Fig. 4), which after 30 min gives same electron emission as the one on which no inhibitor is used. Rinsing the sample for 15 sec with tap water somewhat reduces the protective action of inhibitor against oxidation (curve 2, Fig. 4). A 60 sec rinse almost totally eliminates the protective action of inhibitor against oxidation. However when inhibited steel sample is kept in a beaker of water, inhibitor molecule desorption does not occur even after 30 min period. (curve 2, Fig. 5)

Since PC reduction after pickling is attributed to iron oxide emerging, it was interesting to find out how artificially created oxide film will influence electron emission, A steel panel after cleaning and rinsing, which gave a PC of 250-280, was heated in the oven to 220^0 C. Heating the steel panel to this temperature produced a light yellow oxide film, approximately 4,000 Angstrom thick [3], on the surface. The electron emission from this surface dropped to 100 - 120 units. Another panel was heated to 300^0 C. This panel appeared blue in color and had an oxide film approximately 7,000 Angstroms thick [3]. Pc from this panel increased to 650 -700 units. It is possible that Fe_3O_4 oxide, which emerges at this temperature [2] is responsible for high electron emission. This oxide has n-type conductivity and its electrical resistance does not exceed $5.2*10^{-5}$ Ohm*m [4].

EXPERIMENTAL RESULTS
Photo current Verses Time
Cold Rolled Steel ; Sensor Gain = 5

Time , sec.	3	8	13	30	60	180	360	600	900	1800
Cleaning	390	-	270	272	272	274	270	272	274	275
Pickling 10% H_2SO_4	570	483	433	391	359	350	319	298	288	283
Pickling 10% HCL	562	431	411	405	392	363	355	334	320	309
Pickling 10% H_3PO_4	533	449	422	408	389	358	352	330	312	305
Pickling 5% HNO_3	672	571	552	501	489	459	445	420	403	382
Pickling 2% HNO_3	791	634	604	585	557	502	474	450	431	390

FIG. 1 Dependence of photo current on time after cleaning - 1. cleaning & pickling: 2- 10% H_2SO_4: 3- 10% HCL: 4- 10% H_3PO_4: 5- 5% HNO_3: 6- 2% HNO_3 .




800


1000

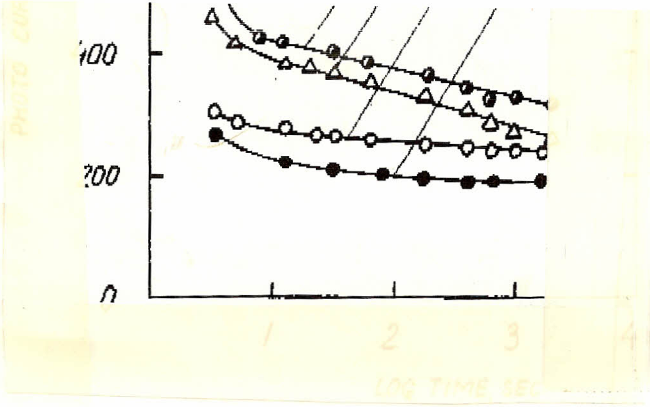


FIG. 2 Dependence of Photo current on time after pickling in 10% HCL and rinsing with tap water: 1-2; 2-5; 3-15; 4-30 sec.

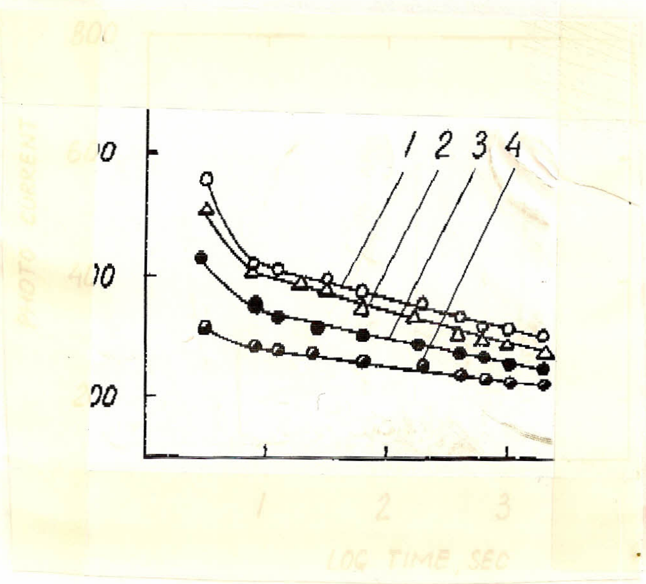


FIG. 3 Dependence of Photo current on time after pickling in 10% HCL and rinsing in beaker: 1-2Sec; 2-2; 3-5; 4-10 min.

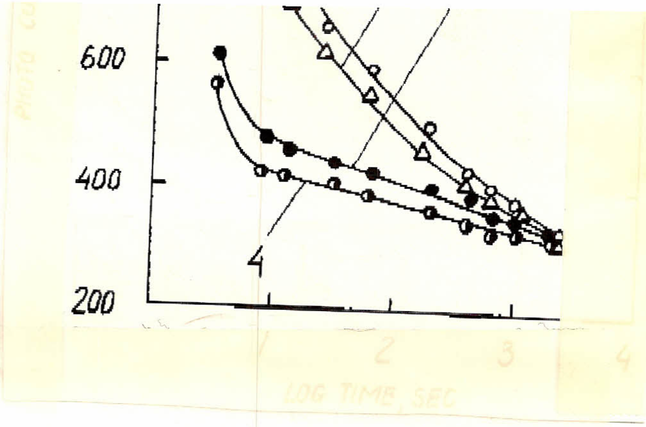


FIG. 4 Dependence of Photo current on time after rinsing with tap water: 1-2; 2-15; 3-60 sec. (pickled in 10% HCL and 2g/L inhibitor) and 2-4 sec (pickled in 10% HCL)

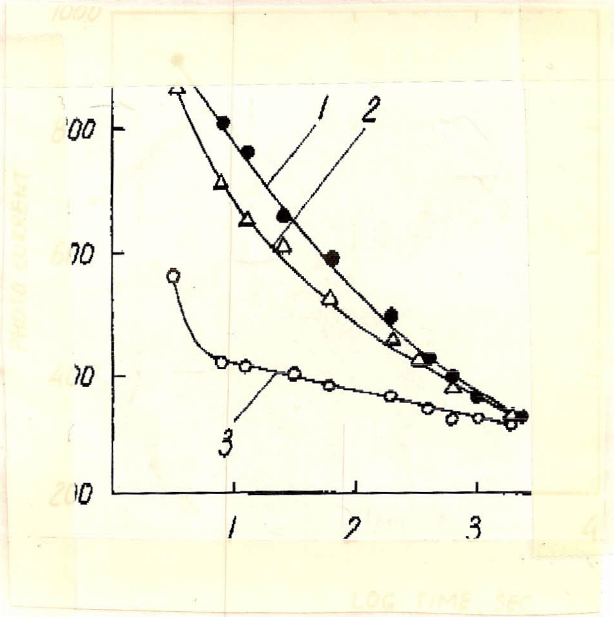


FIG. 5 Dependence of Photo current on time after rinsing in beaker: 1-2 sec; 2-30 min (pickled in 10% HCL and 2g/L inhibitor) and 2-3 sec (pickled in 10% HCL)

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