STANDARDIZATION OF SURFACE CONTAMINATION ANALYSIS SYSTEMS

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ABSTRACT

Corrosion products, oils and greases can potentially degrade material bonding properties. The Marshall Space Flight Center (MSFC) Surface Contamination Analysis Team (SCAT) utilizes a variety of analytical equipment to detect, identify and quantify contamination on metallic and non-metallic substrates. Analysis techniques include FT-IR Microscopy (FT-IR), Near Infrared Optical Fiber Spectrometry (NIR), Optically Stimulated Electron Emission (OSEE), Ultraviolet Fluorescence (UVF) and Ellipsometry. To insure that consistent qualitative and quantitative information are obtained, standards are required to develop analysis techniques, to establish instrument sensitivity to potential contaminants, and to develop calibration curves.

This paper describes techniques for preparing and preserving contamination standards. Calibration of surface contamination analysis systems is discussed, and methods are presented for evaluating the effects of potential contaminants on bonding properties.

BACKGROUND

Efforts are underway at MSFC to develop a robotic surface contamination analysis system that can examine space shuttle booster, nozzle and external tank surfaces for contamination which might affect bonding properties. The system will detect, identify and quantify contaminants, then make appropriate decisions regarding the need for cleaning. As part of this effort, surface analysis systems are being evaluated to determine sensitivity to potential contaminant types, and to develop data necessary for integrating decision making capabilities into the system.

SELECTION OF SUBSTRATES AND MODEL CONTAMINANTS

SCAT efforts are focused on analysis of hardware in the space shuttle solid rocket booster, nozzle and external tank; therefore, contamination standards were prepared with major material components from these systems. The substrates of interest were D6AC steel and nitrile butadiene rubber (NBR) insulation from the RSRM booster, 2219-T87 aluminum from the external tank, and 7075-T73 aluminum, carbon and glass phenolics from the RSRM nozzle.

Selection of model contaminants was based on comparison of oils and greases typically found in shuttle component manufacturing environments. The materials segregated into two general classes, hydrocarbons and silicones. Hydrocarbon greases are typically used as corrosion inhibitors during steel case processing. Hydrocarbons are also present as plasticizers in bagging materials and vinyls, and can degas from the plastics and deposit on bonding surfaces. Silicones, which are often components of mold release agents, are potentially more damaging to bond strength because a much smaller amount is required to affect adhesive properties.

Conoco HD-2 grease and paraffin were selected as model hydrocarbon contaminants for SCAT standards. HD-2 grease is currently used as a corrosion inhibitor during RSRM case processing, and is therefore a likely potential contaminant to the case/insulation bond. Paraffin is a relatively non-volatile wax which was selected because of its expected stability. CRC Industrial Duty Silicone was chosen because it represented typical mold release agents.

DEFINING ZERO FOR REFERENCE

Before examining a substrate for contamination, one must first define clean for reference. It is impractical to seek a truly uncontaminated surface, since typical production cleaning procedures leave behind small amounts of residues which do not adversely affect bonding properties. Therefore, the objective for preparing reference standards is to minimize surface chemistry differences between specimens, while achieving a level of cleanliness which is representative of that obtained during production processing.

Baselines for SCAT contamination standards were defined as the surfaces obtained with current space shuttle booster, nozzle or external tank cleaning procedures. 2219-T87 aluminum (space shuttle external tank) was cleaned in Turco 4215 and Smutgo #1 (deoxidizer) solutions. Steel substrates and 7075-T73 aluminum were vapor degreased with methyl chloroform to remove oils and greases, then grit blasted with Zirclean media to remove oxidation. OSEE analysis, which is extremely sensitive to oxidation on metal substrates, demonstrated that grit blast angle and environmental conditions affected initial instrument response. An enhanced signal was observed at low blast angles, and was believed to be due to less embedded grit on the surface. The environmental conditions affected the rate of oxidation buildup on the metals. Thus, equivalent blast angles and environmental conditioning were required to obtain consistent reference data for these samples.

As with the metal substrates, processing of insulations and phenolics was carried out to provide surfaces similar to space shuttle flight hardware. Glass phenolics were machined to a smooth finish, then degreased with methyl chloroform. Carbon phenolics and insulations were not machined, but were degreased with methyl chloroform. Mirrored surfaces for ellipsometry studies were purchased clean, and were not reused.

PREPARATION AND MONITORING OF CONTAMINATION STANDARDS

SCAT contamination standards were prepared by spray applying dilute contaminant/methyl chloroform solutions (for example, 5 mg/ml HD-2 grease) using an air brush or modified Sono-tek. The spray gun was similar to those used in the automotive industry (Graco model 1265, series B), and produced a fine mist which could be adjusted to an approximately 12-inch wide spray pattern. The Sono-tek, a modified ultrasonic spray system utilizing a 48 kHz nozzle and adjustable speed conveyer belt, was originally designed to spray flux onto printed circuit boards, but modifications were made to the nozzle to make it more suitable for spraying contaminant solutions. With both methods, coating levels were determined by measuring weight changes of aluminum foil witness samples sprayed along with the standards. Several passes were required to attain target coating levels, which typically ranged from 1-30 mg/ft^2. The Sono-tek proved to be a good tool for reproducibly applying low levels of contamination (down to 0.5 mg/ft^2), while the air brush was used for higher coating levels (up to 200 mg/ft^2). The solvent was allowed to "flash" off for 15-20 minutes before witness foils were weighed.

Standards were prepared with either one coating level per panel, or in a "step plate" fashion with 5 coating levels (plus an uncontaminated area for baseline) per panel. Step plate standards offered the advantage of several coatings to examine on a single plate, which reduced the effects of substrate processing variables on analysis results. Panels with one coating were better for evaluating coverage uniformity, and for subsequent bonding studies. Standards were preserved by storage in fall-out plates, in sealed containers purged with nitrogen gas, or at specific environmental conditions in a temperature/relative humidity controllable chamber.

Only singular contaminants were used on the panels, no mixtures. The reasons were that it would be impractical to prepare a complete range of mixture ratios for analysis, and the resulting homogenous mixture of contaminants would be unlikely to occur in nature. Also, instruments used in the robotic analysis system will be programmed to color code the contaminants it detects. For example, hydrocarbons may be blue and silicones red. If more than one contaminant type is present, the results will be presented as a color pattern containing elements of each class of material detected.

Contamination standards may change over time due to migration, diffusion or volatilization of the coatings, and therefore must be monitored. FT-IR microscopy was found to be an effective method for quantifying coating levels on most substrates of interest. The viability of this technique was demonstrated when it was discovered that Kaydol, a low molecular weight oil being considered as a model hydrocarbon, was migrating on the surface of aluminum and D6AC step plate standards. The panels showed linear correlations between coating levels and CH_2 peak heights immediately after preparation, but within 2 weeks the slopes of the plots changed and approached an equilibrium across the surfaces. This technique would also be expected to detect coating volatilization or diffusion, since peak height would be reduced.

INSTRUMENT PERFORMANCE TESTING

Prior to examining surfaces for background spectra or contamination, instrument performance was measured against reference standards to ensure that the instruments were working properly, and to adjust for signal response variations due to light source or detector response fluctuations.

The OSEE system was calibrated using polished nickel panels. Ultraviolet bulb intensity diminished with time, which caused a reduction in electron emission from panel surfaces. To achieve consistent quantitative results, the bulb current was adjusted to counteract the loss in intensity. Polished nickel did not oxidize appreciably over time and had an extremely electron emissive surface, which made it a good reference standard for this instrument.

Gold mirror reference standards were used to monitor signal-to-noise levels and optimize detector signal responses of the FT-IR microscope and NIR systems.

Performance testing for the ellipsometer involved determining the "true" azimuthal orientation of the polarizers and the effects of the signal processing electronics, and optimizing reflectance of the plane polarized light off of a smooth silica wafer surface. Silica was selected as the reference standard because the optical constants for this material were well known.

The eximer laser (UVF) was evaluated for beam intensity (which affected quantitative results) and wavelength.

RESULTS FROM ANALYSIS OF CONTAMINATION STANDARDS

The contamination standards were used to develop calibration curves for surface analysis systems, to develop methods for detecting and quantifying potential contaminants, and to determine instrument sensitivity limits for the various techniques and substrates.

Figure I shows results from OSEE analysis of D6AC step plates coated with HD-2 grease or CRC Silicone. The OSEE technique, which illuminates a surface with UV light and induces electron emission, was extremely sensitive to contamination on metal surfaces, detecting most coatings at levels down to 1 mg/ft^2. Signal response could be correlated to coating level over the range from 1-20 mg/ft^2 for hydrocarbons, and from 1-10 mg/ft^2 for silicone.

Figure I. OSEE Analysis of D6AC Step Plates With CRC Silicone or HD-2 Grease

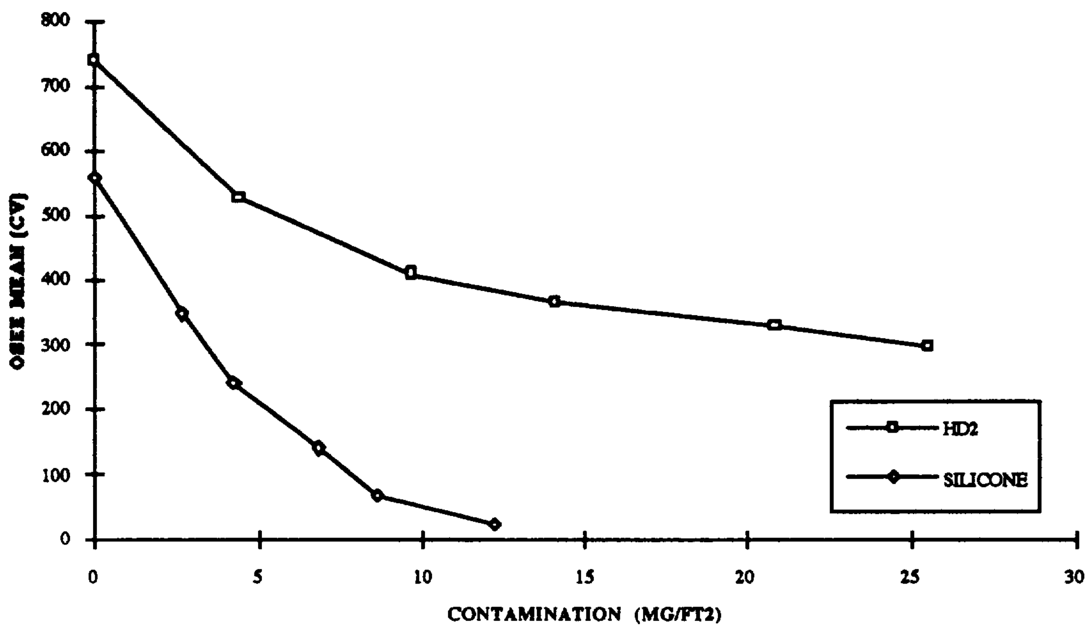
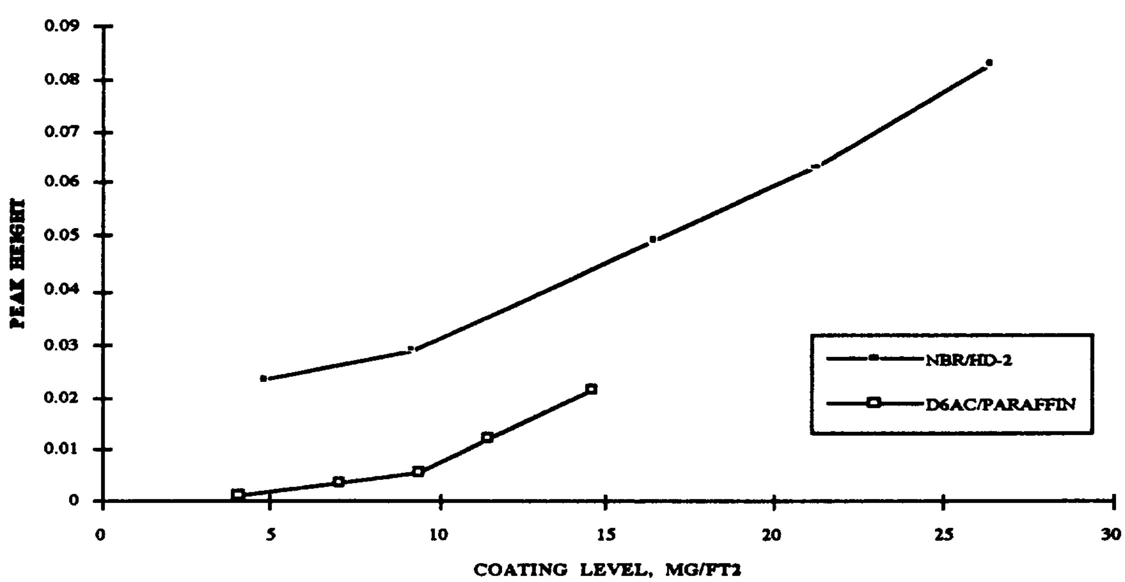


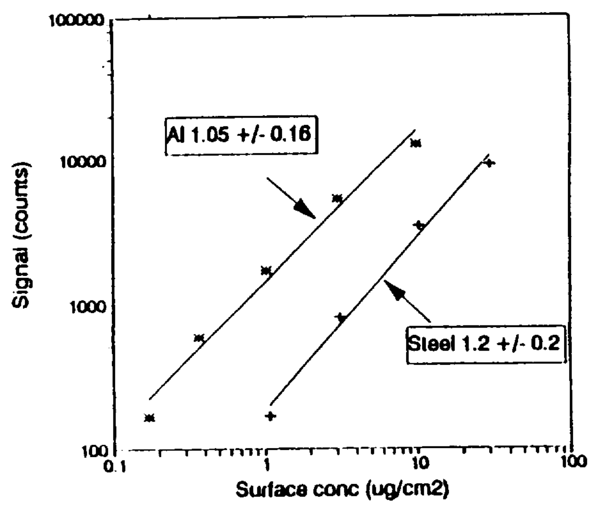
Figure II summarizes results from FT-IR analysis of NBR step plates coated with HD-2 grease, and D6AC steel coated with paraffin. The technique was acceptable for quantifying coatings above 10 mg/ft^2, but below this level peak heights approached that of baseline noise.

Figure II. FT-IR Analysis of NBR and D6AC Step plates With Paraffin



The fluorescence imaging technique illuminates a surface with a short pulse of light from an eximer laser or ultraviolet flash lamp, then captures the contaminant fluorescence with a gated image intensified camera. Figure III shows results from analysis of HD-2 grease on metallic substrates. The technique exhibited a linear response to contamination level and illumination intensity, and was independent of substrate material or shape.

Figure III. UVF Analysis of HD-2 Grease on Metallic Substrates



Ellipsometry involves measuring the change in polarization state of light reflected off of a surface, and can be used to monitor coating thickness. For example, Figure IV shows results from an experiment where baby oil was vapor deposited on an iridium surface. The technique currently works best for smooth, highly reflective materials, but methods are being developed to make it more suitable for rough surfaces.

Figure IV. Ellipsometer Measurements of Baby Oil Thickness Deposition Over Time

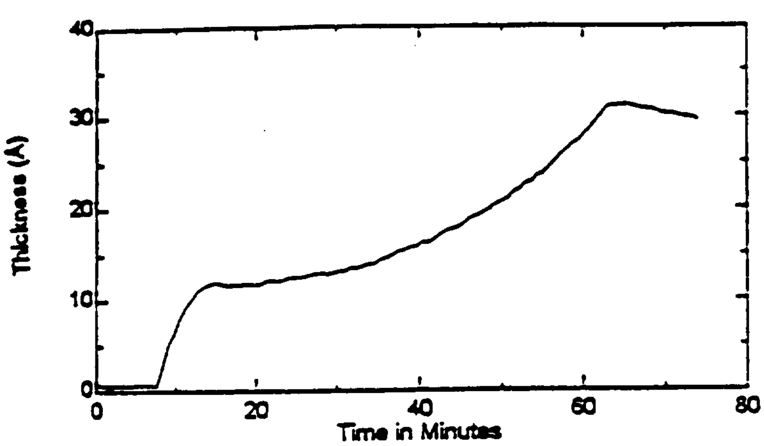
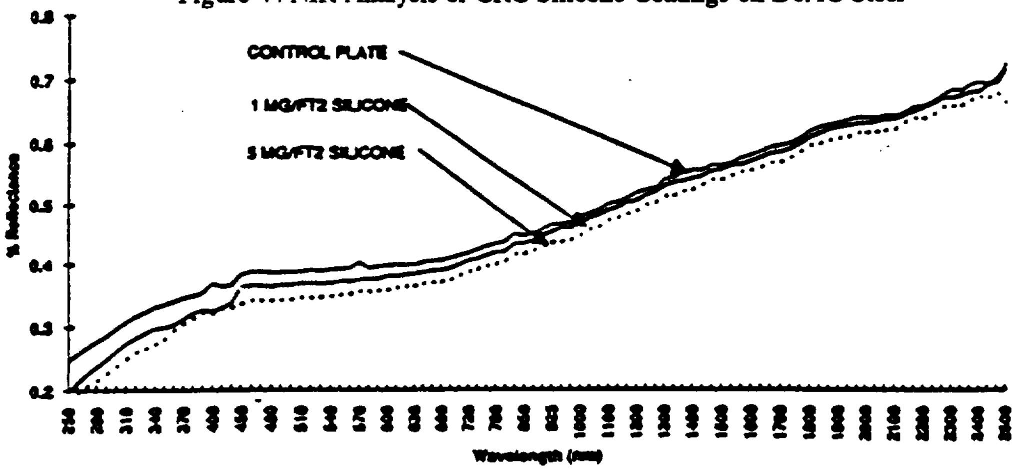


Figure V shows changes in NIR light reflectance from a D6AC panel as a function of CRC Silicone oil coating level. The technique exhibited a linear response to coating level, and could distinguish a mixture of hydrocarbon and silicone oils on metal surfaces.

Figure V. NIR Analysis of CRC Silicone Coatings on D6AC Steel



MEASURING EFFECTS OF POTENTIAL CONTAMINANTS ON BONDING PROPERTIES

Foreign material on a bonding interface is contamination only if adhesion is reduced below that of surfaces obtained with nominal cleaning procedures. Thus, if an analysis system detects potential contamination, the next step is to decide whether the material type or quantity could affect bond strength.

Peel and tensile adhesion tests are typically performed to quantify the effects of potential contaminants on bonding properties. The samples are monitored for reductions in strength, or changes in failure mode from cohesive to adhesive at the bondline.

Figure VI shows a test panel configuration typically used to measure peel and tensile adhesion of the insulation-to-case bond. Samples are pulled at a controlled rate in an Instron tester, which can be interfaced with an environmental chamber to measure temperature and relative humidity effects. Peel adhesion tests are conducted at various angles ranging from 45-135 degrees relative to the plane of the surface, while tensile adhesion is measured at 90 degrees.

Figure VI. Typical Bond Test Panel Configuration

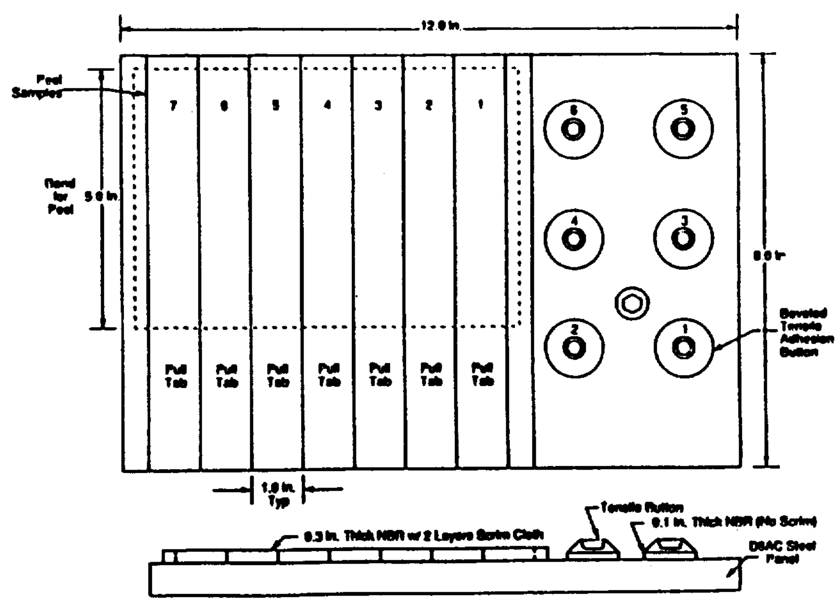


Figure VII shows results obtained from tensile adhesion testing of 2219-T87 aluminum to space shuttle external tank primer, with various levels of CRC Silicone on the substrate. Silicone acted as a contaminant to the bondline, reducing tensile adhesion by approximately 30% at a level of 1 mg/ft^2. Thus, the SCAT analysis system would be programmed to recommend cleaning of affected areas if silicone was detected at these levels.

Figure VII. Tensile Adhesion Test Results From Aluminum Coated With CRC Silicone and Space Shuttle External Tank Epoxy Primer

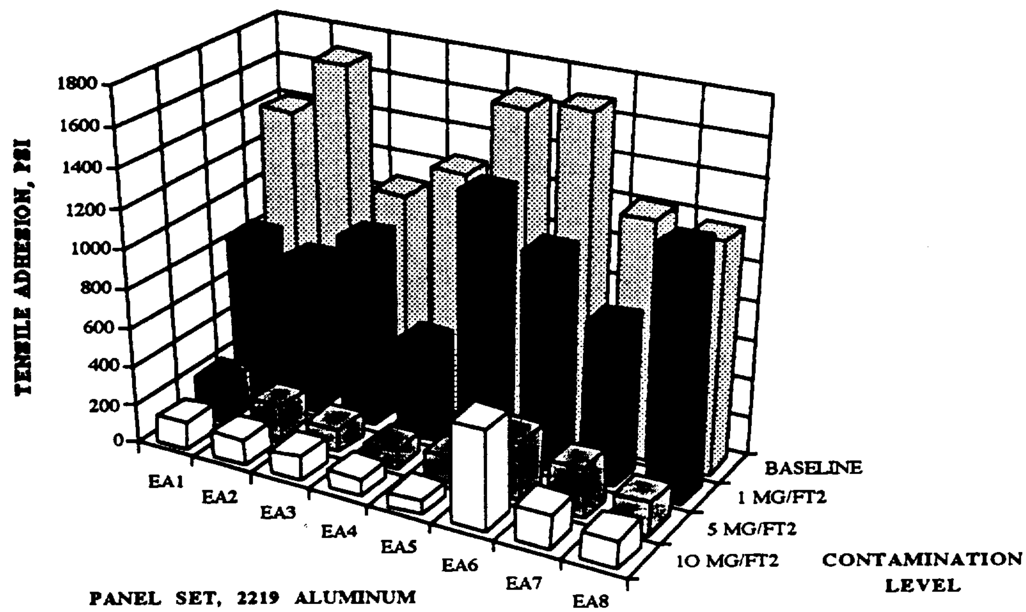


Table I summarizes results from peel and tensile adhesion testing of the D6AC steel/NBR insulation (RSRM) bondline following exposure of unprotected steel to a range of environmental conditions. The intent of the study was to determine whether the oxide formed under these conditions was a contaminant to the bond. Case-to-insulation adhesion was not affected, even after exposure to an extreme environment (29 days, 100F, 60% relative humidity). Therefore, oxidation formed under these conditions was not considered to be a contaminant to the bondline.

Table I. Effects of Environmental Exposure on D6AC/NBR Adhesion

TEMP., °F	REL. HUM., %	EXPOSURE TIME	PEEL ADHESION, PLI	TENSILE ADHESION, PSI	FAILURE MODE
-	-	-	200 TYP	700 TYP	I
50	20	3 HR	218 AVG	713 AVG	I
50	20	7 DAYS	216 AVG	759 AVG	I
50	60	3 HR	217 AVG	717 AVG	I
50	60	7 DAYS	221 AVG	742 AVG	I
100	20	3 HR	221 AVG	692 AVG	I
100	20	7 DAYS	212 AVG	668 AVG	I
100	60	3 HR	217 AVG	718 AVG	I
100	60	7 DAYS	224 AVG	802 AVG	I
100	60	29 DAYS VIS.RUST	206 AVG	697 AVG	I

CONCLUSIONS

SCAT efforts have demonstrated that a variety of analytical instrumentation is required to detect, identify and quantify contamination on space shuttle hardware bondlines. The robotic surface analysis system under development will consist of a series of instruments that can be called upon as needed to evaluate space shuttle bonding surfaces. Techniques described in this paper have proven to be effective for preparing and preserving contamination standards which can be used to evaluate instrumentation, develop analysis techniques, and establish calibration curves.

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