Effects of Organic and Metal Contamination on the Etch Rate of Acid Baths - Implications for Extended Acid Use

by A. Ellis, J. Deluhery & N. Rajagopalan[*]

Appreciable quantities of hazardous acid wastes are generated during electroplating operations. These acids are typically disposed of when their etching rates have dropped below some critical threshold. It has often been assumed that the acid etch rates are primarily limited by the build-up in metals concentration. In this paper, we demonstrate that acid etch rates are highly sensitive to the presence of organic/colloidal impurities. Consequently, the removal of such impurities by soluble silicates, ultrafiltration or carbon adsorption improves the etch rates of acids even in the presence of substantial metal contamination.

Introduction & motivation

Pickling, pre-cleaning and stripping operations generate large quantities of acid waste streams. The most commonly used acids are hydrochloric, sulfuric and nitric in concentrations ranging from 10% to 40%. The acid waste streams are classified as hazardous waste, and electroplating shops incur substantial costs to treat or dispose of the acids.

The primary method for treating acid wastes is neutralization to remove both metallic contamination and the corrosive nature of the acid. Neutralization is expensive because of the residual acidity of the "spent acid" baths. The disposal of the resulting sludge is also expensive. Little work has been done to extend the life of acid solutions or to recycle the acid after purification. While methods such as acid sorption, evaporative recovery and diffusion dialysis have been demonstrated to be technically and economically feasible in some specific cases, they have not been widely adopted in small to medium sized electroplating facilities because of the costs and complexity associated with such operations.[1,2,3]

It is well known that the etch rates of acids are decreased by accumulation of metals and/or organic contaminants that conceivably act as inhibitors.[4,5,6] A slow etch rate is one primary reason that acid baths are considered as spent. In this paper, therefore, we investigated the effectiveness of various treatments on improving the etch rates of acids contaminated with metals and organics. We focused specifically on a proprietary treatment based on a soluble silicate[**] product that is stated to be effective at extending the life of acid cleaners.[7] In particular, it is claimed that the use of soluble silicates decreases metal contamination by the formation of an insoluble metal precipitate. The reduction of dissolved metals would presumably allow the acid to be recovered and reused.

In the first part of this study we evaluated factors that affect the rate of etching and the response of the etch rate to various treatments. In the second part we focused on the effectiveness of silicate precipitation as a means of reducing the dissolved metal concentration in acids.

Nuts & Bolts:
What This Paper Means to You

Acid etches are often dumped and replaced when the etch rate slows down to a point where production is affected. The common thinking blames the slow down on metal build-up. But whoa! The authors here have found that organic contamination is a worse actor, and show a means of going after this contamination. The result is extended life for the etches that might have otherwise been discarded and reduced hazardous waste.

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[*] *Corresponding Author:*
Dr. N. Rajagopalan
Illinois Waste Management & Research Center
1 E. Hazelwood Drive
Champaign, IL 61821
Phone: (217) 244-8905
E-mail: kishore@wmrc.uiuc.edu

[**] *PRO-pHx®, Wagner Environmental Technologies LLC, Cornelius, NC 28031.*

Methods & materials

In the first phase, the etch tests were carried out on galvanized coupons, measuring approximately 4 × 8 cm (1.57 × 3.15 in.), which were cleaned with mineral spirits and acetone to remove any residual oils. The parts were weighed prior to immersion in a 3.96N hydrochloric acid bath at room temperature. The parts were immersed for specified time periods, removed, rinsed, dried and weighed. The weight loss was converted to a metal loss factor. Data presented on etch rates reflect the average of two or more replications.

Certified ACS Plus grade hydrochloric acid was either used as received, or with metal and organic inhibitor contamination. A spent hydrochloric acid sample from the field (labeled "Spent Acid" in the data presented) was also used for additional investigation.

Contaminated acid samples were made by spiking fresh acid with either Certified ACS grade anhydrous zinc chloride to approximately 10,000 mg/L or by adding a proprietary acid inhibitor[***] at levels of 100 to 200 mg/L.

The contaminated acids were either treated with 1% sodium silicate solution containing 14% NaOH and 27% SiO_2, the proprietary soluble silicate product[**] at 1%, or activated carbon. Following treatment with the silicates, the sample was allowed to stand for a period of one week to ensure complete precipitation of all insoluble material. It was subsequently filtered through a five-micron filter and used for etch studies. The field sample was also subject to an additional treatment of ultrafiltration through a 50,000 molecular weight cut-off membrane. The treated samples were further analyzed for metal content, and Total Organic Carbon (TOC). Metal analyses were carried out using ICP-MS or AA, as appropriate. TOC analyses were carried out on a TOC analyzer. Standard procedures such as calibration checks, spike recoveries and duplicate analyses were utilized to ensure quality control.

In the second phase of this work, extensive tests were carried out to evaluate the effectiveness of the commercial soluble silicate product in reducing dissolved metals concentration from a range of acid/metal combinations. The acids were trace metal grade hydrochloric, sulfuric and nitric acid at concentrations ranging from 50% to 5%. The salts used were reagent grade anhydrous ferric chloride, ferrous sulfate heptahydrate, anhydrous zinc chloride, zinc sulfate heptahydrate, nickel chloride hexahydrate and nickel nitrate hexahydrate. Metal concentrations ranged from 6 to 13 g/100 mL. Solutions were made up in 40 mL volumes and split in two parts. One portion was treated with the soluble silicate product and the other left as an untreated control. The solutions were sampled before and after treatment (typically after one week as suggested by manufacturer) and analyzed for acidity and metal concentrations. Filtration was performed either by first centrifuging followed by filtration or directly by filtration using a 0.45-micron filter. Metal concentrations were measured via AA[†] and all values reported were in mg/L or g/100mL. Acidity measurements were made using an auto titrator[††] and values are reported in equivalents/L or Normality (N). Some of the precipitates were analyzed and imaged using a scanning electron microscope (SEM) along with energy dispersive spectroscopy (EDS).

Results & discussion

Effect of treatments on etching rates

Figure 1 provides information on the "Spent Acid" sample from the field that was highly contaminated with both organics and metals (Table 1). Not surprisingly, the spent acid exhibited slow etching kinetics, presumably due to the presence of contaminants. Treatment of the field sample by both soluble silicate products resulted in an improvement in the etching kinetics. Analysis of the treated acids for both metals content and TOC revealed a minor reduction in zinc, no reduction in iron and a small reduction in TOC (Table 2).

Ultrafiltration, a membrane-based process that removes colloidal impurities, but not dissolved metals, was equally effective at improving the etching kinetics. As seen in Table 2, this treatment had no effect on zinc or iron content (Variations were due to experimental errors.). Treatment of the spent acid by carbon resulted in the best performance.

It is clear from the above data that the level of dissolved metals was not a significant factor impacting the etching kinetics. Reductions in TOC occurred with carbon and ultrafiltration treatment and were accompanied by an improvement in the etching kinetics. However, improvement was also noted for the soluble silicate treatment although the reduction in TOC was

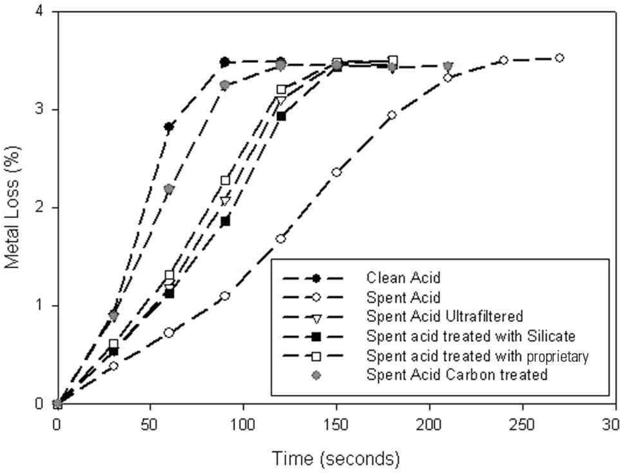

Figure 1—The etch rate of a "Spent Acid" is significantly lower than a clean acid. A number of treatments including soluble silicates, ultrafiltration and carbon are effective at improving the etch rate of the "Spent Acid".

Table 1
Analysis of Spent Acid

Anolyte	Level
Acidity	4.17 N
Zn	74,600 mg/L
Fe	24,900 mg/L
Cr, Mn, Ni, Ca	Minor amounts
TOC	3,200 mg/L

[***] *Armohib 28®, AkzoNobel Surface Chemistry LLC, Chicago, IL 60607.*

[†] *Varian SpectrAA 300 Plus, Varian Associates, Inc., Wood Dale, IL 60191.*

[††] *Orion 960 Autochemistry System, Thermo Orion, Thermo Electron Corp., Beverly, MA 01915.*

Table 2
Treatment of Field Sample

		Treatment			
Contaminant	**Spent Acid**	**1% Proprietary Silicate**	**1% Sodium Silicate**	**Ultrafiltration**	**Carbon**
Zinc (mg/L)	74,600	63,000	61,000	78,000	68,000
Iron (mg/L)	24,900	25,600	25,500	30,000	29,000
TOC (mg/L)	3,200	3,120	3,160	0.4	1500(est)
Etch Rate	Poor	Improved	Improved	Improved	Best

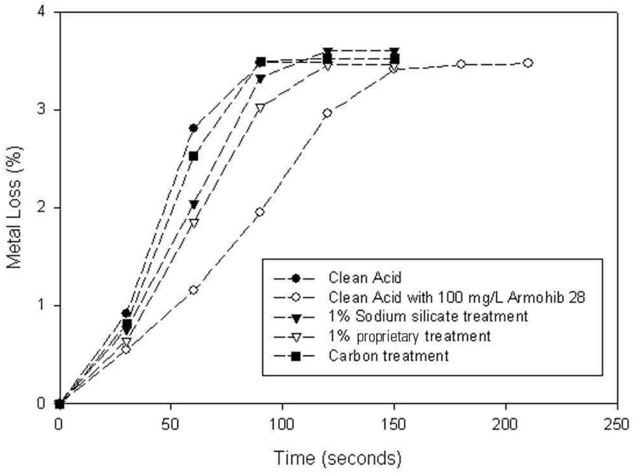

Figure 2—A small quantity of organic inhibitor (100 mg/L) significantly inhibits the etch rate. Removal by treatments such as carbon adsorption and soluble silicates improve etching kinetics.

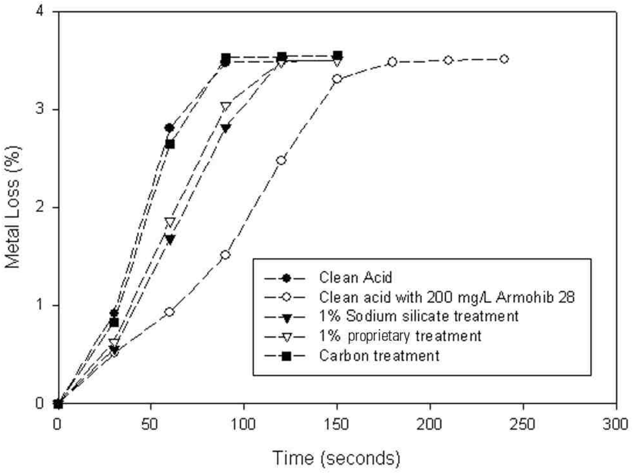

Figure 3—A small quantity (200 mg/L) of organic inhibitor significantly inhibits the etch rate. Removal by treatments such as carbon adsorption and soluble silicates improve etching kinetics.

minor. Moreover, as the TOC determinations had a relative percentage difference of about 2%, the reductions in TOC noted for the silicate treatments could have been an analytical artifact. Thus, no unambiguous conclusion could be drawn on the relative importance of organics on the etch rate. To resolve this ambiguity, further investigations were conducted with the known proprietary organic inhibitor.

Figures 2 and 3 provide data on the etch rates of clean acid and acid contaminated with inhibitor at 100 and 200 mg/L, respectively. The data for the clean acid exhibits a sigmoidal pattern, reaching a constant value after around 100 sec. By contrast, the presence of the inhibitor significantly decreased metal loss. It took approximately 180 sec for the inhibited acid to achieve the equivalent metal loss for the uninhibited acid. When the acids contaminated with the inhibitor were treated with soluble silicates (both sodium silicate and the proprietary product), the treated acid etched metal at a faster rate than the inhibited acid. However, the etch rate did not fully recover to the level of the clean acid, suggesting incomplete removal. Despite this, the positive impact of the treatment in restoring the etch capacity of the acid is evident. Both soluble silicate products were equally effective. TOC data for the treatment are presented in Table 3. It is clear that small amounts of organic inhibitor in acids had a significant impact on etching rates and that their removal is indeed possible through silicate treatment and carbon.

Figure 4 provides additional data with respect to etch rate of acids contaminated with 1% zinc. The effect of zinc, at the levels tested, was minimal at lowering the etch rate of the acid. Treatment with soluble silicates of purely metal-contaminated acids failed to produce any improvement. In fact, such treatment appeared to slightly retard the etch rate.

All of the above results allow us to conclude that the effect of residual metals (at levels comparable to those in spent acid) on etch rates was not significant. The treatments employed were primarily effective because they removed organic/colloidal contaminants. However, it is also clear from Table 2 that not all organics have a negative impact. Possibly, only those organics that can form some kind of inhibitory film appear to be implicated. These organic contaminants have a disproportionately adverse impact on etch rates at low levels. Their removal by silicates, ultrafiltration or carbon treatment resulted in improved etching rates.

Table 3
Effect of Silicate and Carbon Treatment on TOC Reduction in Acid Contaminated with Inhibitor

Contaminant	Level	TOC (mg/L) After Treatment			
		Before Treatment	1% Proprietary Silicate	1% Sodium Silicate	Carbon
Proprietary Inhibitor in HCl	100 mg/L	71	31	32	20
Proprietary Inhibitor in HCl	200 mg/L	98	41	46	26
Etch Rate		Poor	Improved	Improved	Improved

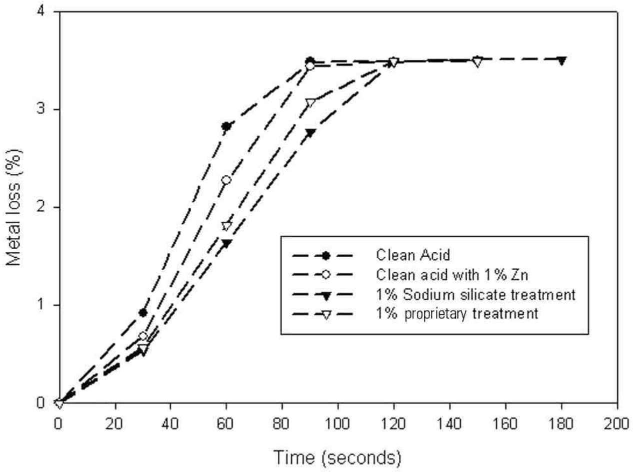

Figure 4—Contamination of hydrochloric acid with 1% zinc does not significantly retard the etch rate.

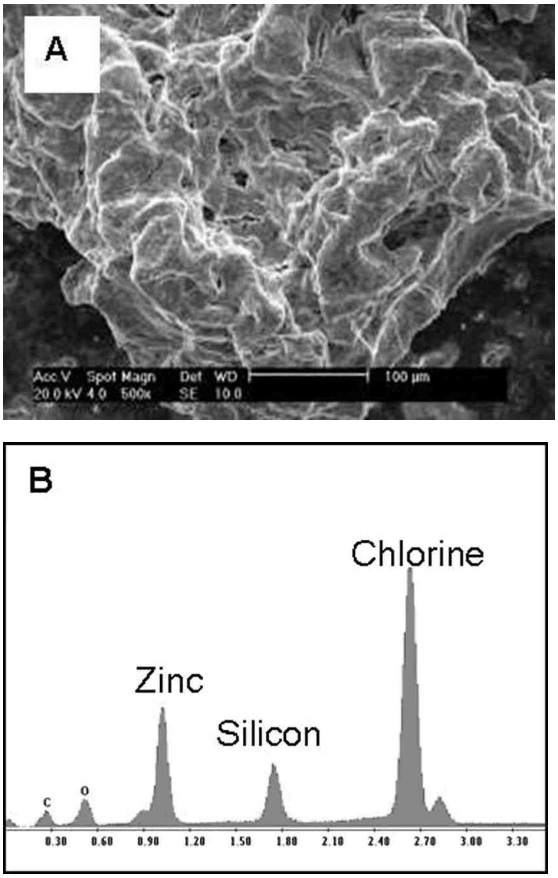

Figure 5—Precipitate from Zinc-HCl experiment: (a) SEM image at 500X; (b) for EDS spectra at 500X

Removal of metals by soluble silicates

In this section, we address the question of whether metal removal from acids can occur when they are treated with soluble silicates. The results of such treatments on a range of acid-metal combinations are presented in Table 4. All values reported have a precision (2σ) of ± 5%. Even the largest difference in metal concentration of 8.8% for nickel in hydrochloric acid is within the margin of error. The visible amount of precipitate formed was variable and similar in color and transparent to that of the solution in which it formed. Addition of the proprietary sodium silicate solution did not have much of an impact on the free acid in solution and the largest drop was about 0.5 equivalents/L.

The precipitates from most of the experiments were analyzed for the presence of the metals, the corresponding anion, silicon and oxygen using an SEM. The results confirmed the presence of metals and silicon in the precipitate. An example of the results for a zinc-hydrochloric acid system is presented in Fig. 5. Based on the spectra in Fig. 5(b), the intensity of the chlorine anion peak may indicate either the high excitation ability of the element or the relatively high concentration of chlorine. If the latter is true, it would indicate that the dissolved metals are simply trapped within the silica gel polymer rather than forming a predominantly metal silicate precipitate.

This would partially explain the low metal removal observed in this study. Thus, of the three possible mechanisms for metal removal,[8] (a) the formation of insoluble metal silicate, (b) the adsorption on the silica gel and (3) a metal-acid complex trapped within the polymer, the third mechanism (c) seems to be dominant.

Based on stoichiometric calculations of the following reaction:[8]

$2Zn^{+2} + H_4SiO_4 \rightarrow Zn_2SiO_4 + 4H^+$,

the amount of zinc removal as a silicate can be estimated. One mole of silicon will remove two moles of zinc. Assuming a 1.0-L total volume and given that the recommended dosage is 1% by volume, we would be adding the equivalent of 0.01 moles of silicon per liter (The silicon content in the proprietary product is 29 g/L.). Therefore even under conditions where the reaction goes to completion, only 0.02 mol/L or 1.35 g/L of zinc will be removed per addition the proprietary product. This is a very small amount and thus metal removal by silicate formation will not be significant.

Previous research on soluble silicates has concluded that "silica suspended in solutions of most polyvalent metal salts will adsorb the metal ions when the pH is raised to within one to two pH units below that at which the metal hydroxide will precipitate."[9,10] The acidity of the acid pickling baths is far removed from the above pH to result in large-scale adsorption of metals.

All of the above support our observations that dissolved metal removal by the proprietary soluble silicate product is unlikely to occur to any significant degree.

Conclusions

The etching properties of acids appear to be very sensitive to organic/colloidal contamination, but to a lesser degree to the dissolved metal concentration. Removal of the organic/colloidal contamination can therefore improve the etching properties of the acid. Soluble silicates appear to aid in this removal by removing the organics/colloidal material. This is probably accomplished by adsorption onto the large surface areas of the silica gels produced *in-situ* or by co-precipitation with the settling floc. However, no remarkable difference between ordinary silicate and a commercial proprietary mixture was found in our studies. Other methods of colloid removal, *e.g.*, ultrafiltration or organic removal by carbon treatment, were also found to be effective at improving the etching kinetics of acids. Dissolved metal reduction via treatment by soluble silicates from contaminated acids was insignificant across a range of acid/metal combinations, in samples generated either synthetically in the laboratory or from electroplating facilities, as well as over a range of metal concentrations.

Facilities interested in extending the life-time of their acid baths are encouraged to determine whether organic/colloidal contamination could be their current limiting factor. If so, a number of treatments identified appear to be effective at removing this limiting factor. In this event, additional means for removing metal build-up will still be required in the longer term unless a dynamic equilibrium is reached that limits the metal build-up to a level that does not lower the etching kinetics below a critical threshold. Furthermore, additional studies need to be carried out to ensure that treatments involving chemicals such as silicates have no adverse impact on subsequent plating quality.

Acknowledgements

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Table 4
Results and Experimental Details of Proprietary Silicate Bench Tests

	Initial Acidity (N)	Final Acidity (N)	Metal Concentration (Initial) (g/100 mL)	Metal Concentration (After proprietary treatment) (g/100 mL)	Metal Removal
Iron / Hydrochloric acid	12.0	11.75	13.54	12.46	7.98%
Iron / Sulfuric acid	3.5	3.5	6.96	6.50	6.61%
Zinc / Hydrochloric acid	5.25	4.75	12.50	11.84	5.28%
Zinc / Hydrochloric acid	0.95	0.95	13.98	14.76	0.0 %
Zinc / Sulfuric acid	3.5	4.0	13.56	13.20	2.65%
Zinc / Sulfuric acid	1.38	1.38	15.02	14.76	1.73%
Nickel/Hydrochloric acid	4.0	4.0	12.26	11.18	8.81%
Nickel / Nitric acid	5.25	5.25	14.24	13.78	3.23%
Nickel / Nitric acid	1.95	1.95	11.94	11.82	1.01%

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About the Authors

Andre Ellis is a Post-Doctoral Fellow in the Department of Geological Sciences at Northwestern University, Evanston, IL. His primary research interests focus on environmental geochemistry ranging from monitoring and remediation of metal contaminants to changing global climate. A part of this study was conducted during the course of his graduate study at the University of Illinois, Urbana-Champaign with a grant from the Illinois Environmental Protection Agency's Pollution Prevention Internship program.

Jennifer Deluhery currently works as a Chemist in the Pollution Prevention group at the Illinois Waste Management & Research Center, Champaign, IL. Her current research involves development of novel methods for monitoring the integrity of membranes used in drinking water treatment and processes for purifying metalworking fluids. She has previously served as an intern with the Illinois Environmental Protection Agency at the Inorganic Laboratory, Champaign, IL. Jennifer holds a B.S. in Chemistry from the University of Illinois, Urbana-Champaign.

Nandakishore Rajagopalan is a Sr. Research Engineer at the Illinois Waste Management & Research Center, Champaign, IL. He leads the technology development and demonstration team at the Center. His research is focused on separation processes, pollution prevention and waste minimization. He has several years of experience in project management and research and development across a wide spectrum of industries. He holds a B.S. in Chemical Engineering from the University of Madras, India and a Ph.D. in Food Science from the University of Illinois, Urbana-Champaign.

OSHA's Chrome PEL Proposal Will Devastate Metal Finishing Industry

Your Industry Needs Your Help Now!

Pursuant to a court order, on October 4, 2004 OSHA published in the Federal Register a proposed new standard for occupational exposure to hexavalent chromium. After several years of litigation and discussion with industry and union organizations, OSHA is seeking to lower the Permissible Exposure Limit (PEL) for hexavalent chromium and for all hexavalent chromium compounds from 52 $\mu g/m^3$ to 1 $\mu g/m^3$ as an eight-hour time weighted average.

Analysis by leading industry consultants indicates that this rule could have an impact on processes beyond traditional hard and decorative chrome plating. ***Any facility that has hexavalent chromium in their shop will have to comply with the new standard. If you have the following processes in your shop, this proposal will affect you:***

- Chromate Conversion Coatings over Zinc and Cadmium Plating
- Stainless Steel Passivation
- Plating on Plastics
- Chromic Acid Anodizing
- Welding
- Electropolishing

The proposed standard also includes a so-called "action level" of 0.5 $\mu g/m^3$ – which means that at this level, facilities would face a range of new requirements for controlling exposure, including:

- Exposure Assessments
- Respiratory Protection
- Protective Clothing and Equipment
- "Clean" Change Rooms and Showers
- Medical Monitoring
- Hazard Communication
- Recordkeeping

While OSHA's proposal states that the compliance costs for the regulation will average $15,000 per facility, initial industry estimates point toward compliance costs of approximately $300,000 per year. This could force many companies to either install expensive control measures above and beyond those that are currently in place to protect worker health or abandon the impacted finishing operations.

The Metal Finishing industry needs to correct OSHA's basis for this rule and support a protective workplace exposure standard that can be achieved without bankrupting the industry. Take the time to fill out this form and make a donation.

For more information, please contact Christian Richter (crichter@thepolicygroup.com) or Jeff Hannapel (jhannapel@thepolicygroup.com) or call (202) 457-0630.

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