Explanation of electrolysis water utilization to PWB field which is included industrial field

～ Using as an environmental load reduction technique～

JIPCM LLC

1505aS2

Contents of the explanation

★ **Explanation of espax electrolysis water**

cf. electrolysis water = e-water

- Generation principle of e-water

★ **Characteristics of e-water(Pros&Cons)**

- Characteristics of cathode side e-water (Alkaline e-water)
- Characteristics of anode side e-water (Acid e-water)

★ **Usage of alkaline e-water**

- Usage, effect and attention points

★ **Usage of espax acid e-water(for PWB industry)**

- Characteristics of espax acid e-water
- Procedures by the PWB production process.(Results & attention points)

※ Explanation of right procedures & attention points

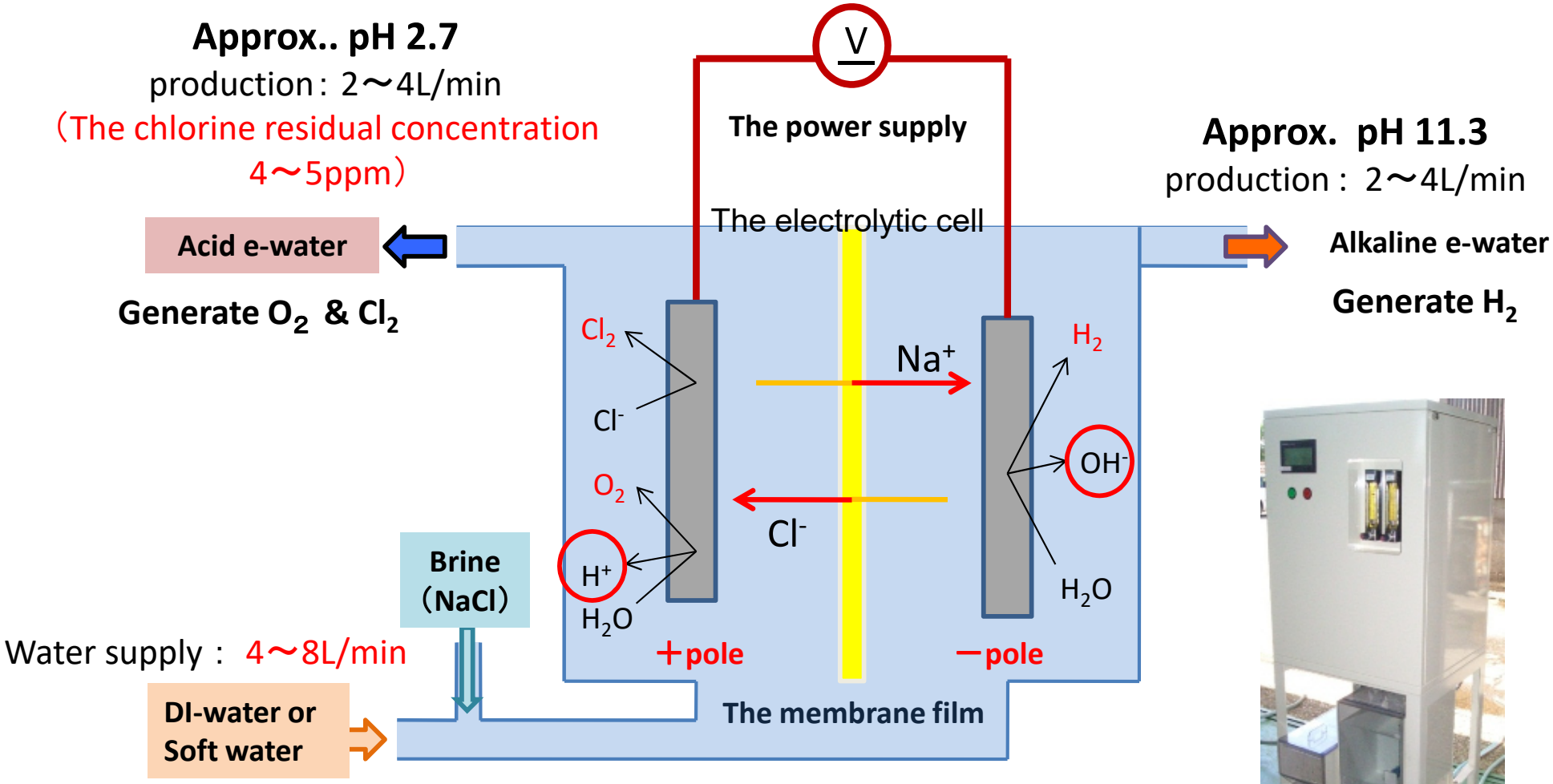
- **Data of actual effectiveness**
  - Basic conditions of using espax acid e-water
  - About running costs
  - Consideration for installation
  - Usage & maintenance note

Generation principle of espax e-water

Approx.. pH 2.7
production：2～4L/min
（The chlorine residual concentration
4～5ppm）

Acid e-water

Generate O_2 & Cl_2



Approx. pH 11.3
production： 2～4L/min

Alkaline e-water

Generate H_2

Type : J02B-GS

Water(H_2O)'s being electrolyzed

The anode reaction： $2H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$

The cathode reaction： $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Characteristics of e-water (Pros & Cons)

~ The point of difference between general e-water and espax e-water ~

Characteristics of alkaline e-water

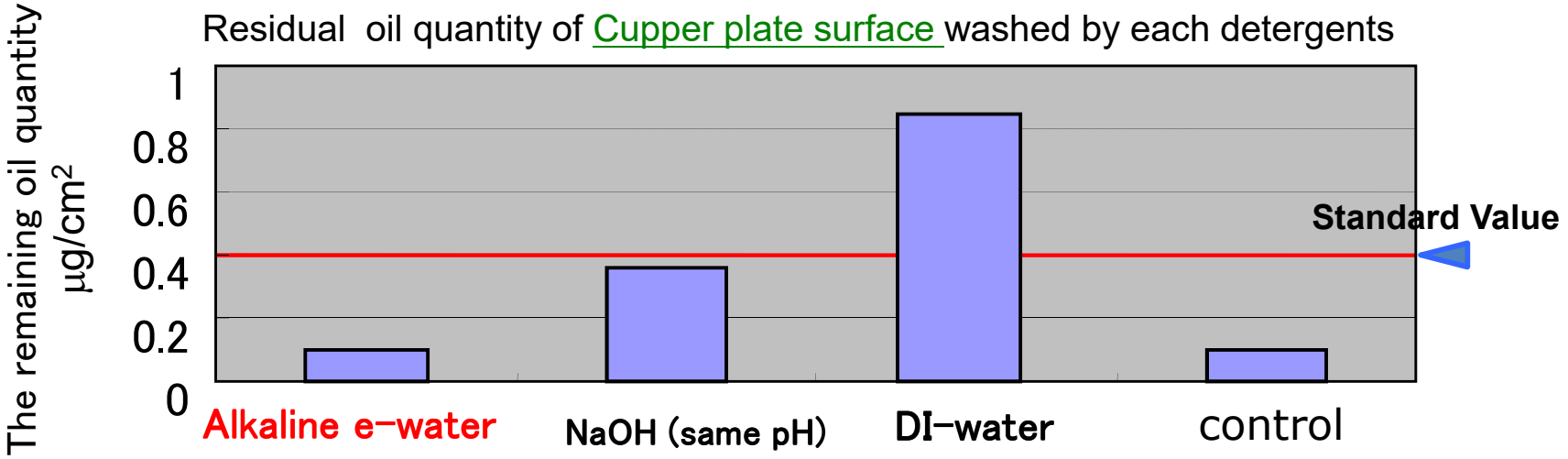
1. **Possible to remove grease.**
   （can be used for detergents）
   - P4009385（Japan-domestic/ Application Nippon Steel Co.,Ltd）
2. **Possible to use silicon processing and metal processing field.**
   - It has been developing by FUJI KIKO.
3. **Hydrogen nano bubbles exist for more than 24 hours in espax alkaline e-water.**

As the result, It is good for

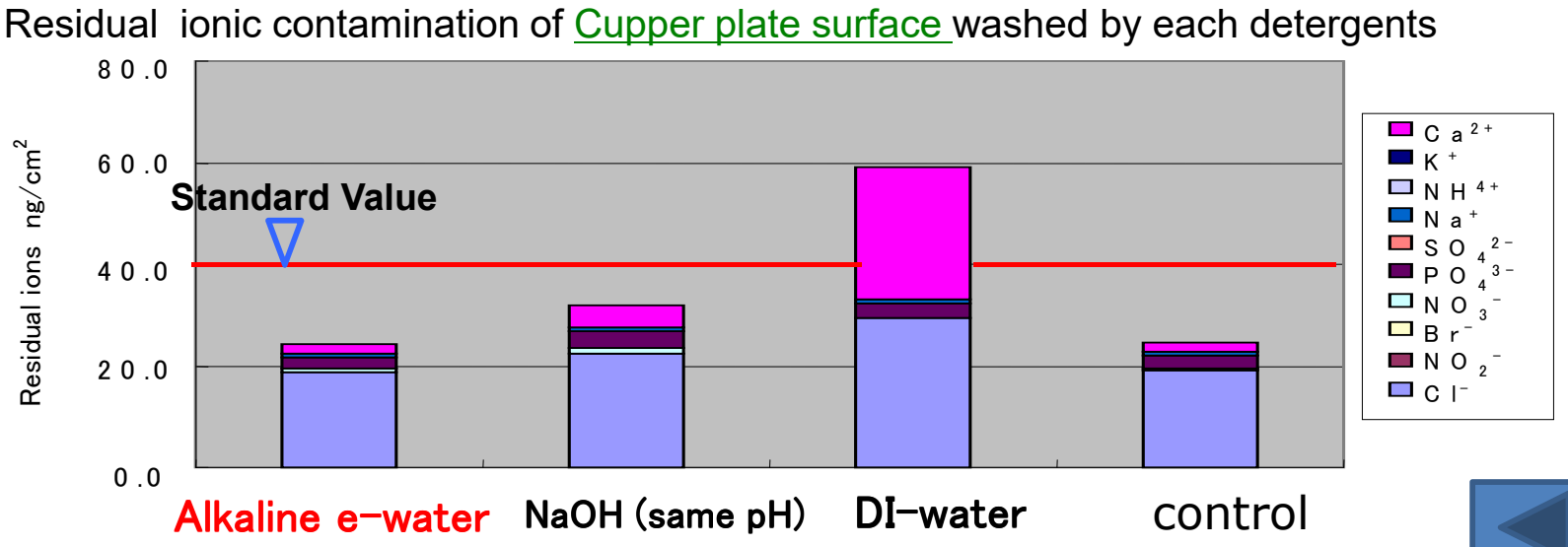
1) ion contamination removal.
2) Antirust (not strong effect)

Evaluation of espax alkaline e-water

1. Removing grease detergency evaluation



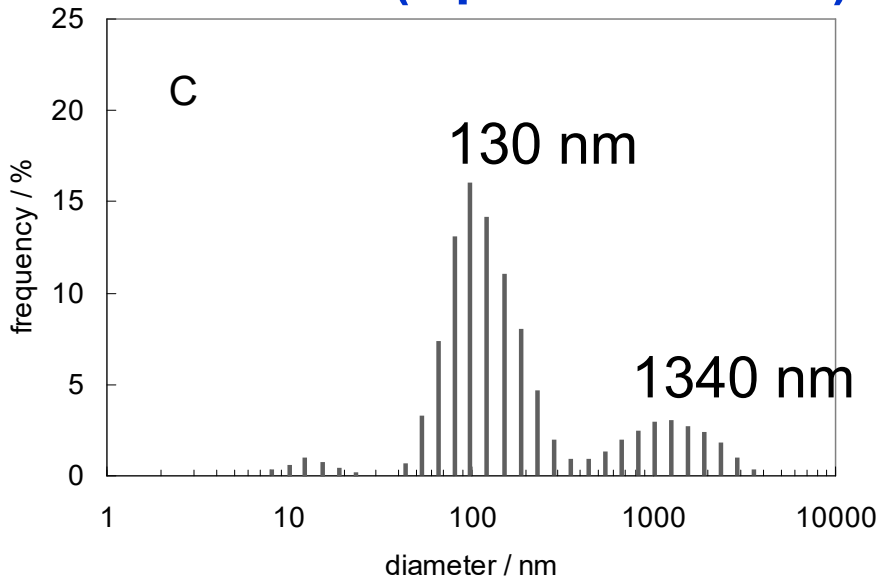
2. Evaluation of the ion residual removal effect



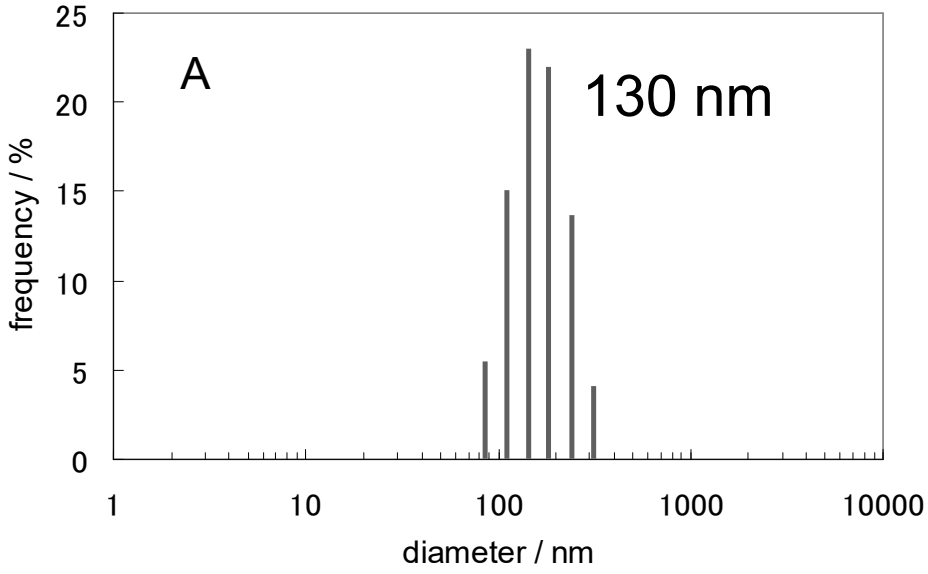
POINT **The reason why the cleaning effect is more excellent than NaOH of the same pH**

★ The nano-bubble of hydrogen exists in the espax e-water?

After 24 h(Open container)



After 5 h (Closed container)



The test cooperation ：

Professor Unkai Sato by Shinshu Unv.

The grade scale measuring machine：
Otsuka Electronics

Fiber-Optical Dynamic Light-Scattering Spectrophotometer　FDLS-3000

There is stable hydrogen nano-bublles in espax alkaline e-water.

Characteristics of acid e-water

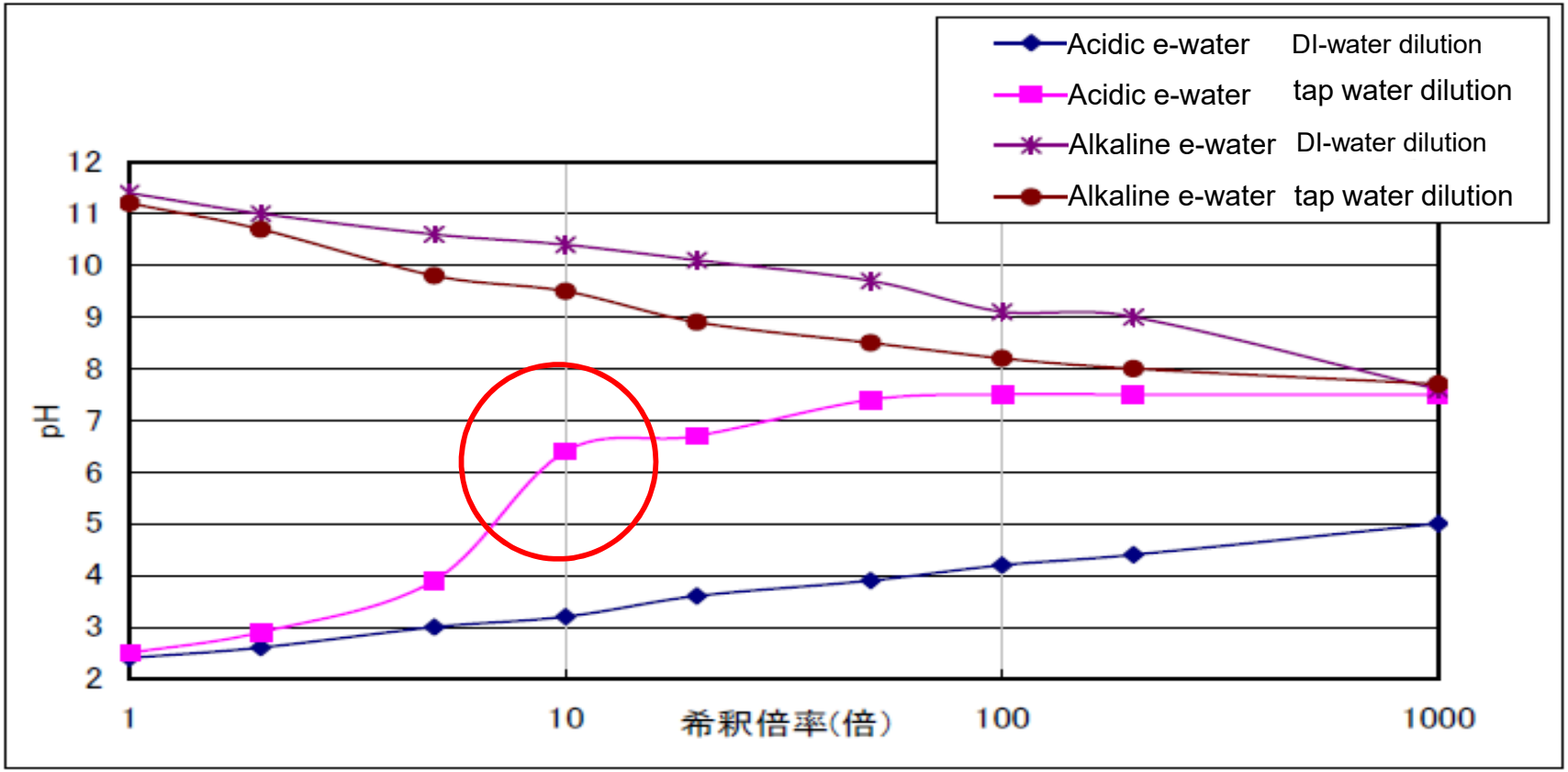
1. **High Effective in Killing bacteria**
   - 10 times of Sodium hypochlorite(NaOCl) Sol.
2. **Safe & secure : human & eco-friendly**
   - The electrolysis product is The hypochlorous acid(HClO).
3. **Can be remove oxide film of copper.**(espax)
   - Using NaCl can clean Cu surface.

＊ These effects can be used for the surface cleaning of PWB.

Why espax acid e-water is environment-friendly?

HClO disappears when it reacts to the organic matter.

＝The environmental load(BOD) reduction



★ **Easy drainage treatment = Eco-friendly.**

using e-water in the industrial field

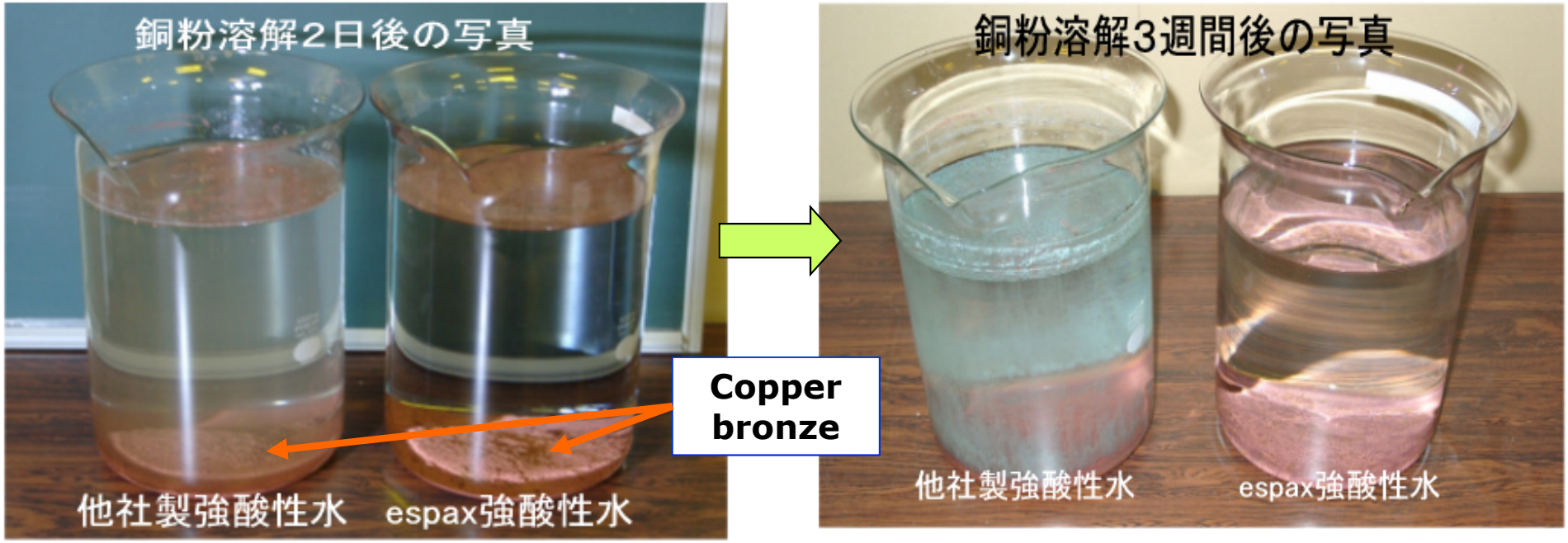
Usage of espax acid e-water

～ The main use in PWB production ～

Characteristics of espax acid e-water used in PWC

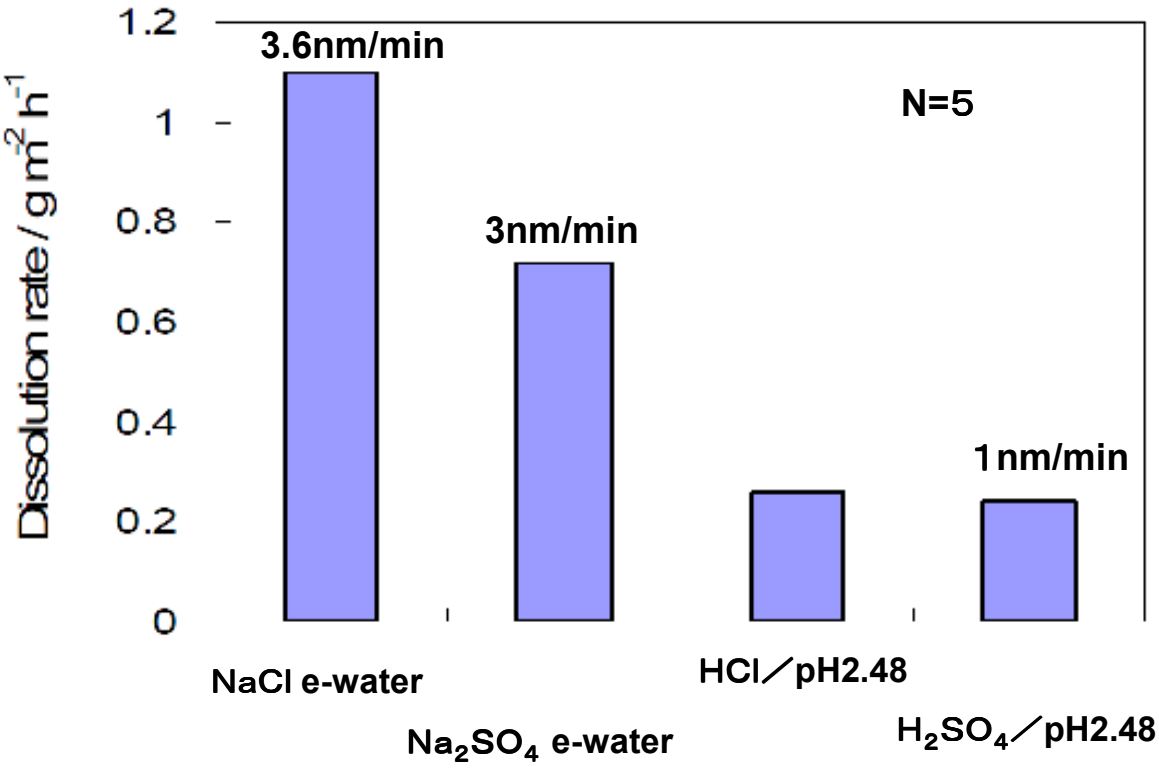
1．It doesn't form patina even if it dissolves copper.

＊Patina：$CuCO_3 \cdot 2Cu(OH)_2$ ／緑青



＊ The espax acid e-water can be recycled in washing tank.
（It is necessary to add e-water to maintain pH. : about 1L/min）

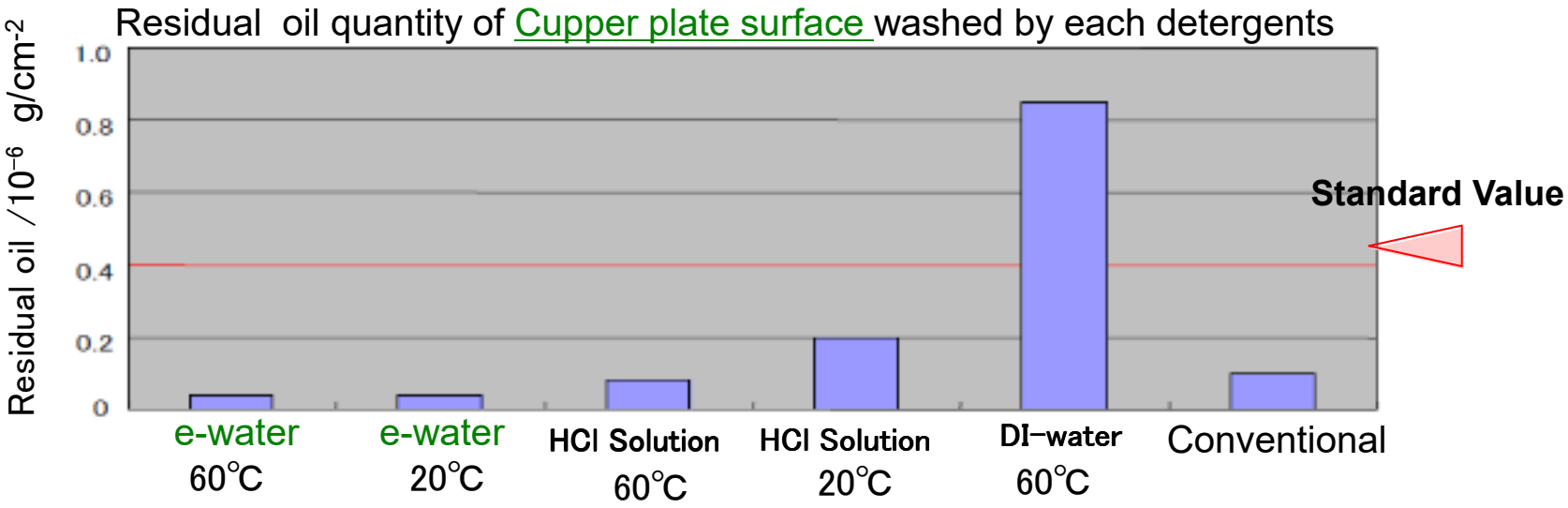
2. Copper dissolution rate of espax acid e-water is 3 – 4 times faster than same pH. chemical solution.



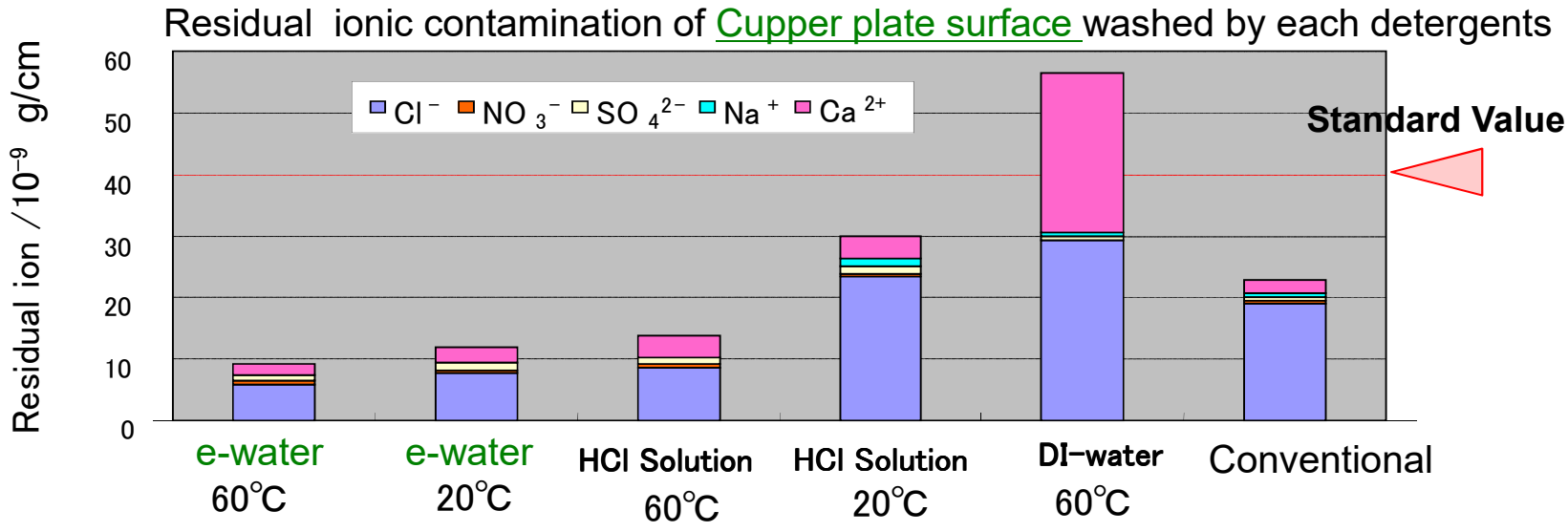
★ Attention： The espax acid e-water is not so strong like sulfuric acid/hydrogen peroxide which can dissolve metallic copper

The evaluation of espax acid e-water

1. The removing grease detergency evaluation



2. The evaluation of the ion residual removal effect



Quantification method : Ion chromatograph

Data of actual effectiveness and consideration using espax acid e-water in PWB production

The specific procedures of the espax acid e-water

(Diluted brine electrolysis)

1. Pre-treatment process

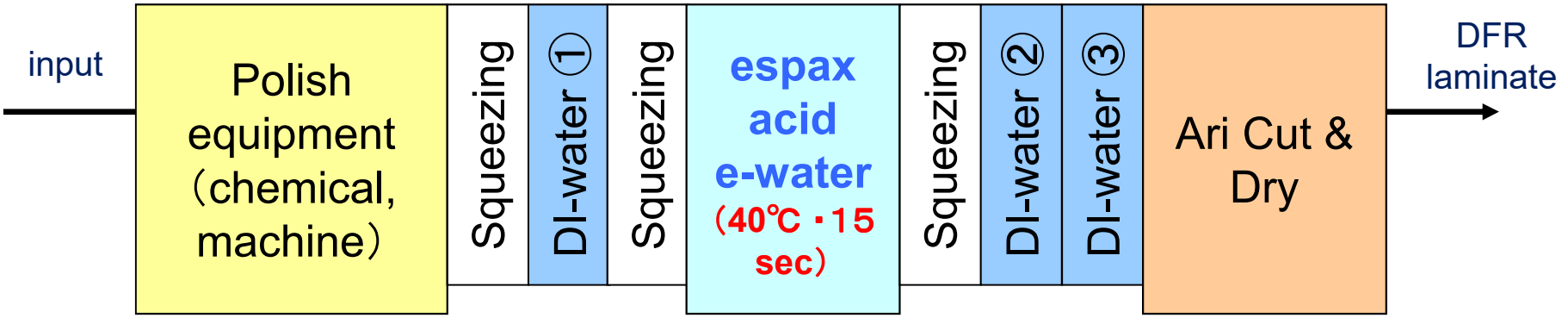
- before DFR laminate, PSR coating, Water-soluble Flux

(Dry Film Resist) (Photo Solder Resist)

1）Using espax acid e-water after polish (chemistry & physics)

- **Purpose： Remove copper dust & chemical residual**
- **Effect ： Clean copper surface⇒prevent distain**

★ **Condition：40℃(Liquid temperature) &15sec. spray rinse**



- **Experiences：CSP, FPC, Multi-PWB etc.-**

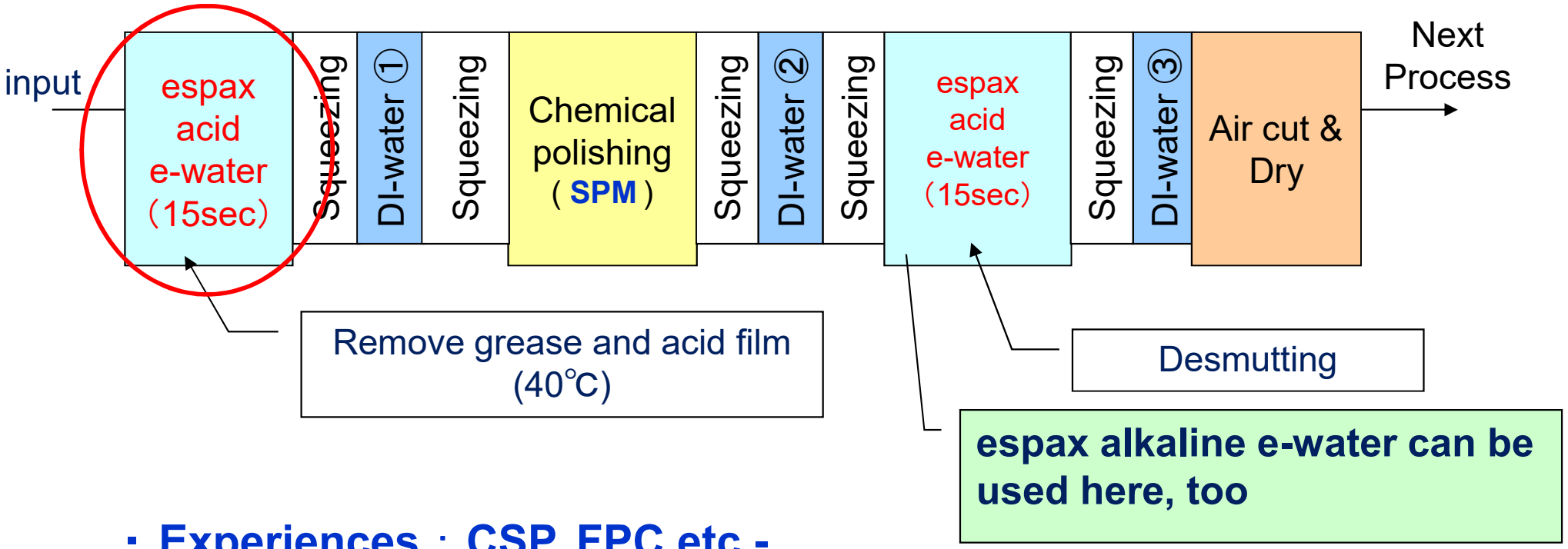
2）Using in FPC & Semi additive Process(SAP) PWB

＊ using in SPM before DFR laminate

★ Using before SPM process: Remove copper oxide film and grease

（Purpose：SPM process equalization）

★ Using after SPM process: same as above + remove smuts

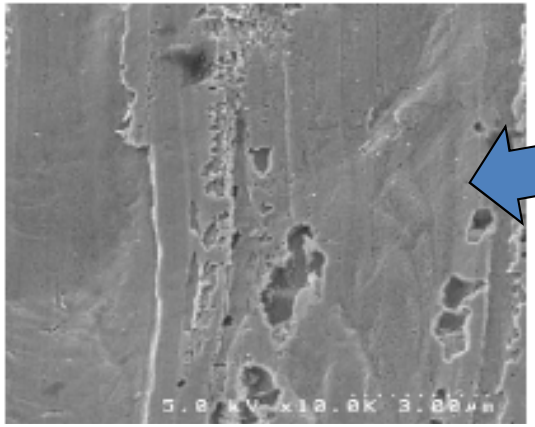


· Experiences：CSP, FPC etc.-

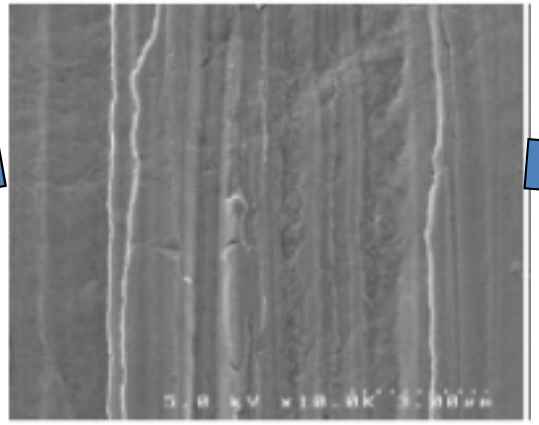
How to remove oxide film (Movie)

- Material: substrate processed by 180℃/90min.

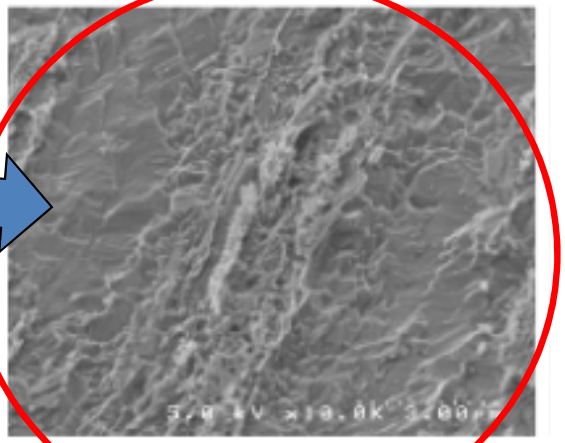
Surface condition of copper processed by espax acid e-water



The immersion in 10 min

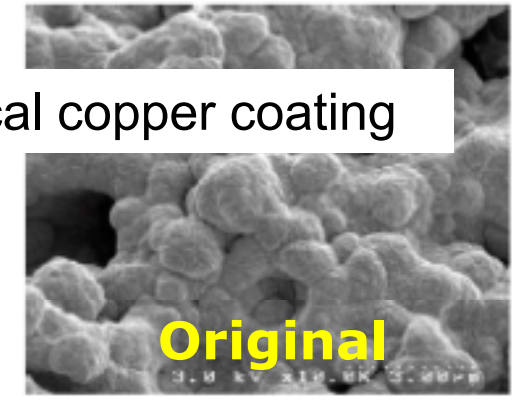


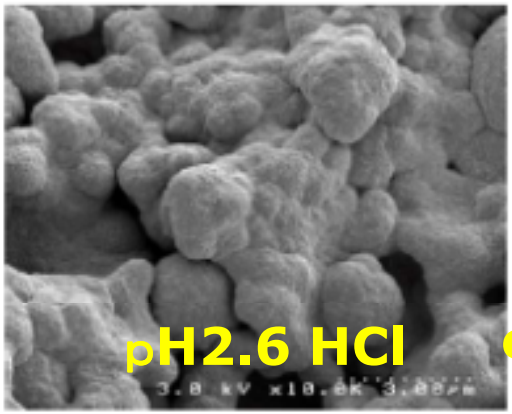
The original copper surface

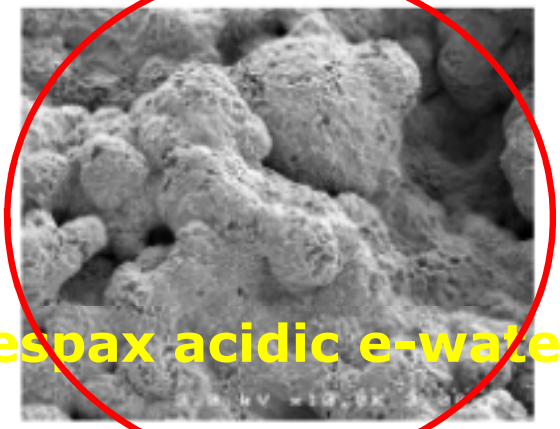


sprayed for 4 minutes.

chemical copper coating







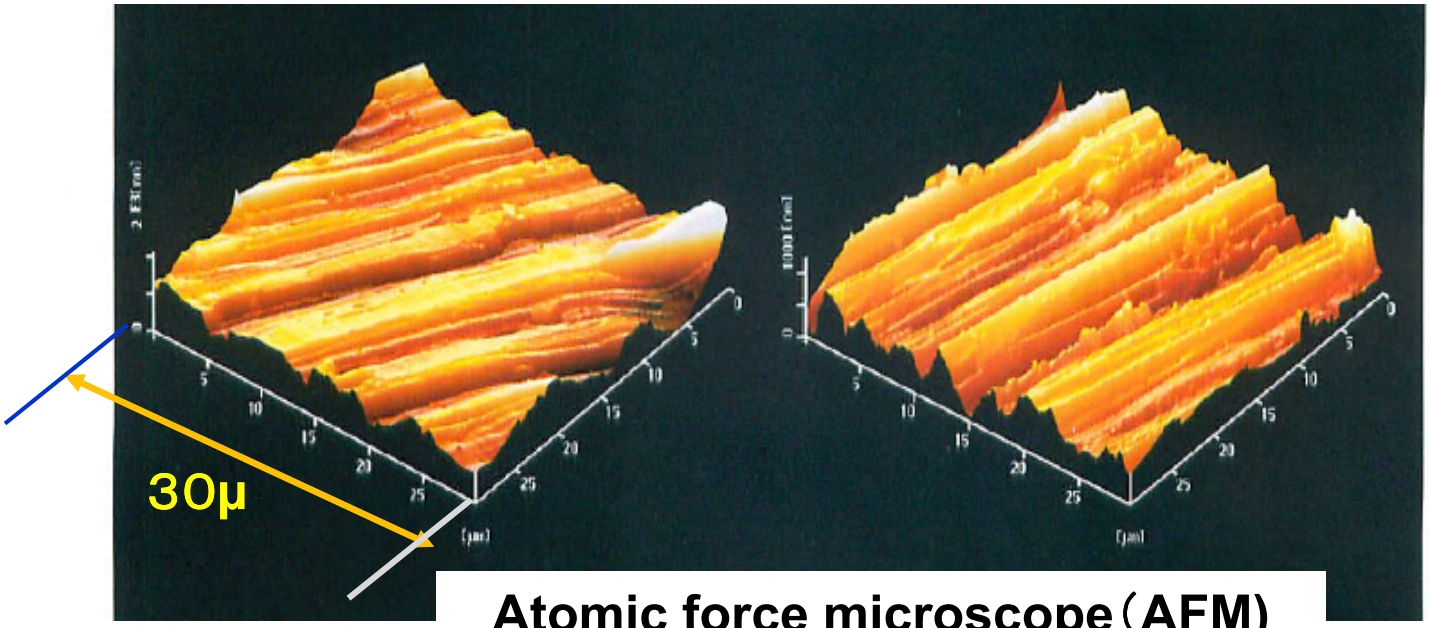
X 10000 無電解銅めっき 左:めっき後、中:塩酸浸漬後、右:酸性電解水浸漬後

espax acid e-water can achieve nano-level surface roughening by its free chloride

User evaluation data

1. espax acid e-water after buff polish (2003 data)

Buff polish＋e-water rinse　　Buff polish＋normal water rinse

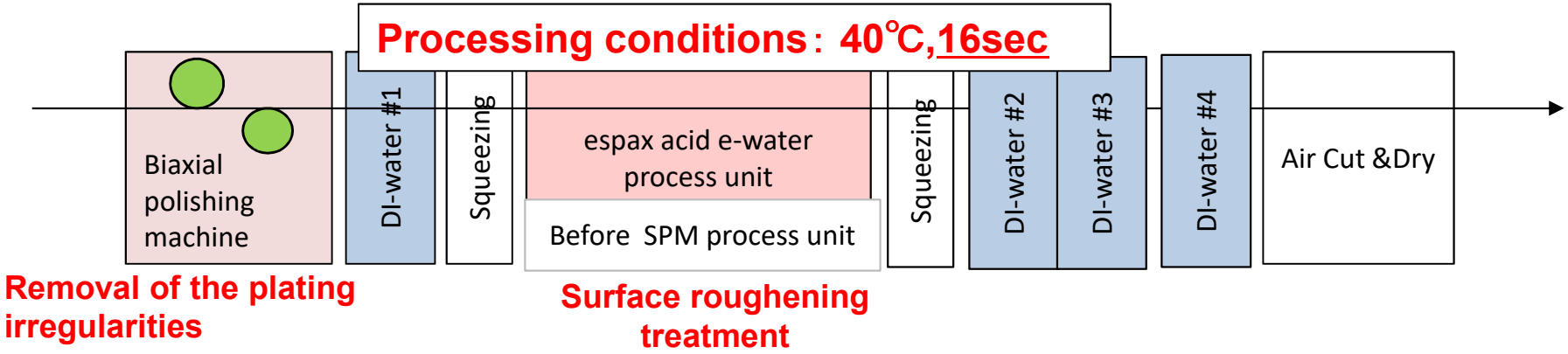


Atomic force microscope（AFM)

★ espax acid e-water can remove copper dust after buff polishing process and fine burrs.

2. SPM alternative in DFR laminate pretreatment (2014)

★ Overview of the pre-treatment line／After plating process



★ Test results／ Evaluation after etching

Pattern residual rate

研磨条件① Buffe + SPM

確認箇所 [mm]	上面 縦向き	上面 横向き	下面 縦向き	下面 横向き
0.05/0.05	0%	0%	0%	0%
0.06/0.06	80%	68%	100%	96%
0.07/0.07	100%	100%	100%	100%
0.08/0.08	100%	100%	100%	100%
0.20/0.20	100%	100%	100%	100%
集計	92.5%	91.8%	93.8%	93.5%
総計	92.9%			

研磨条件③ Buffe + e-water

確認箇所 [mm]	上面 縦向き	上面 横向き	下面 縦向き	下面 横向き
0.05/0.05	0%	0%	0%	0%
0.06/0.06	64%	64%	100%	100%
0.07/0.07	100%	100%	100%	100%
0.08/0.08	100%	100%	100%	100%
0.20/0.20	100%	100%	100%	100%
集計	91.5%	91.5%	93.8%	93.8%
総計	92.6%			

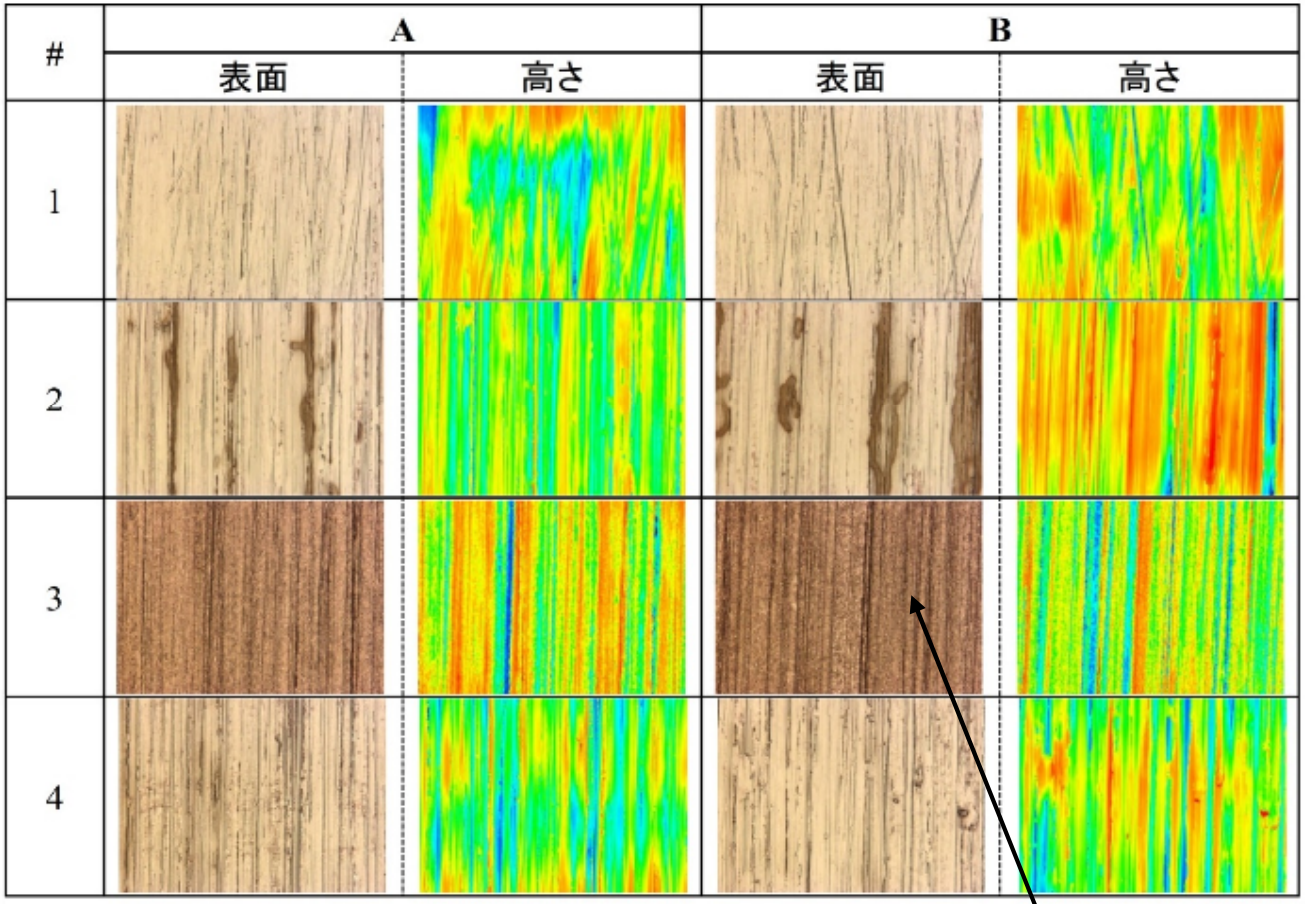
★ **According to the result, espax acid e-water rinse can be used as replacement of SPM = save costs.**

※ Reference：Surface condition after treatment (previous page)

Surface observation

1．表面観察結果（×3000倍）

Brown color means discoloration by oxidation
Red and blue color describes unevenness



#1 : Original (substrate after electrolytic copper plating)
#2 : "substrate # 1“ + Buff process
#3 : "substrate #2" + SPM(H2SO4/H2O2) rinse
#4 : "substrate #2" + espax acid e-water rinse

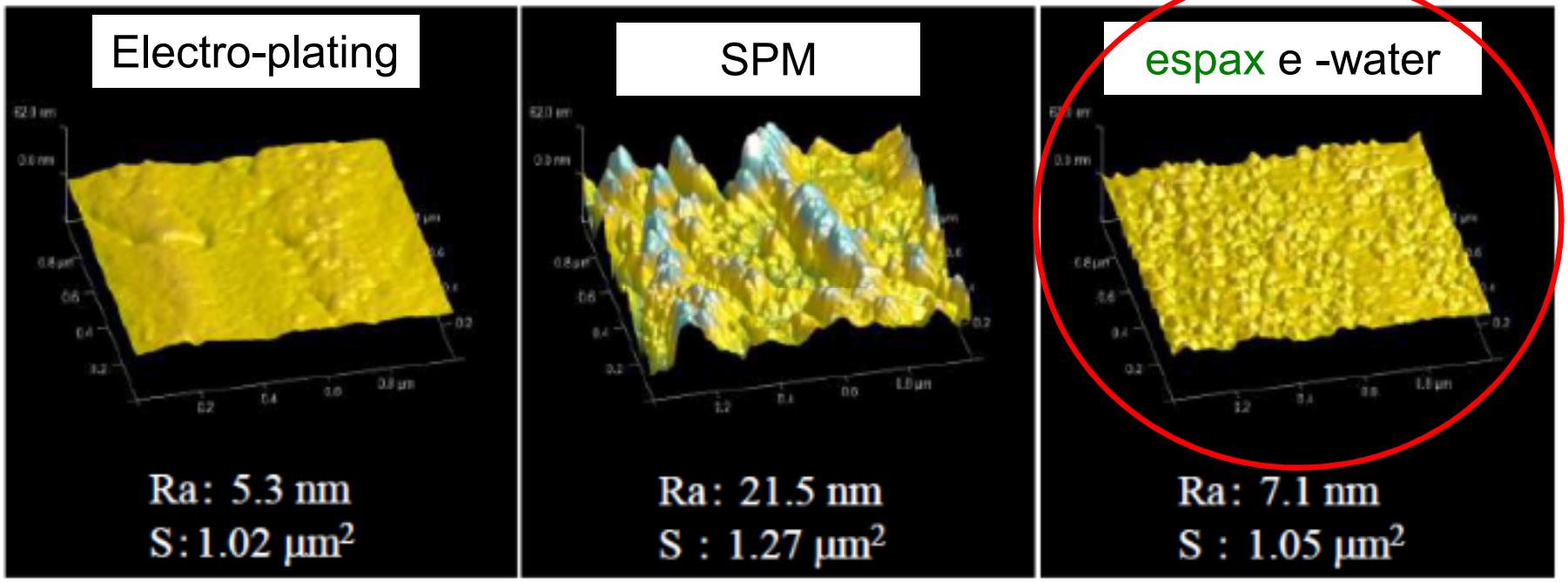
★ **Smut removal after SPM process is necessary**

Evaluation test of DFR laminate pre-treatment in SAP process

espax acid e-water can rough(nano-level) and clean board surface at the same time, so can it be used as SPM rinse in DFR laminate pretreatment process in SAP process?

1. Comparison of surface condition

★ **Internal evaluation test**

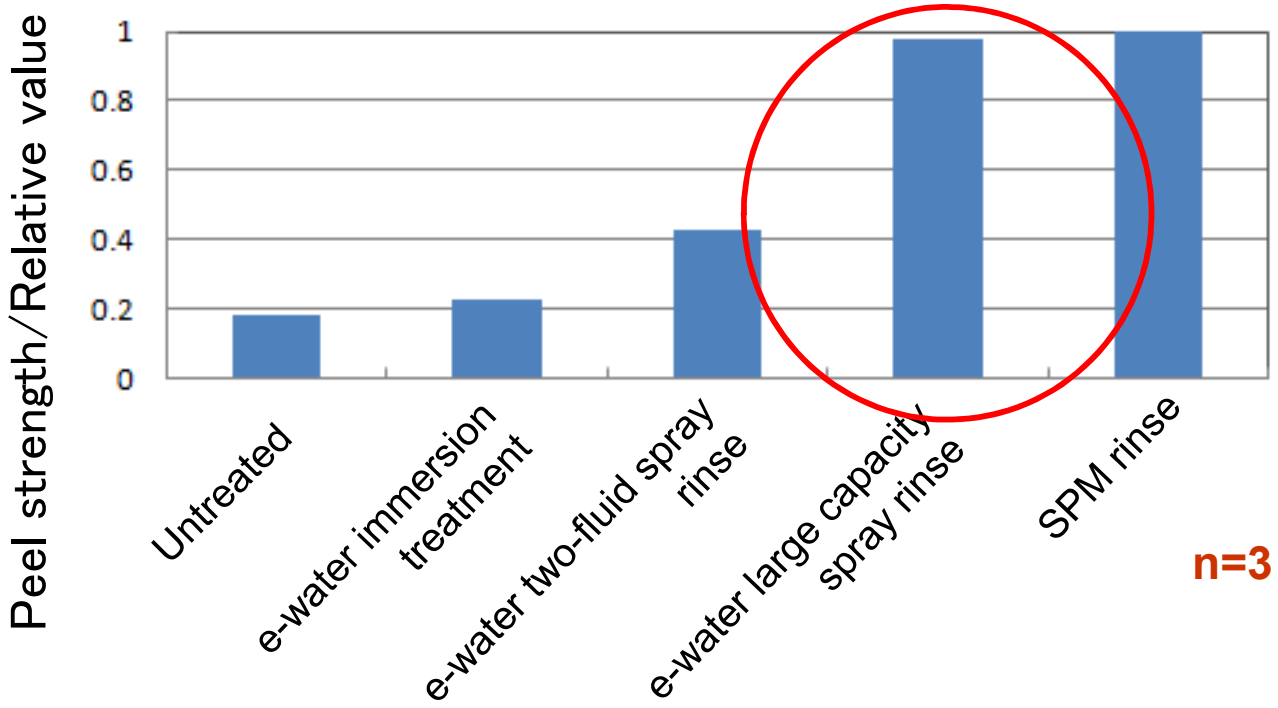


espax acidic e-water can achieve nano-level roughing.

How about DFR adhesion?

2. Comparison of adhesion with another rinsing method

＜Comparative assessment : in the case of SPM rinse =1＞



n=3 Average value

TEST CONDITIONS：**espax acid e-water、40sec、45℃**

★ **According to these test data, espax acid e-water can be said to substitute for SPM rinse in DER laminate pre-treatment in SAP process**

※ we would like to recommend you to test it in actual production line.

Considerations

In the case of evaluate espax acid e-water using existing chemical tank in your factory…..

Please be care full about following two points.

1）Wash the tank by hot water (40℃）

- **remove crystallized Cu-sulfate in the tank and pipings.**
- **how to do?：hot water cleaning (40℃/1hour）x 2times.**

2）Process condition for removal oxidized film

① **Process time：15 sec or more**

② **espax acid e-water temperature：40℃**

③ **espax acid e-water pH：< pH3.1**

＊ **espax acid e-water replenishment is needed to avoid reducing pH by water dragging out.**

④ **Quickly neutralized can prevent board oxidation and discoloration**

2. espax acid e-water & development process（DFR、PSR）

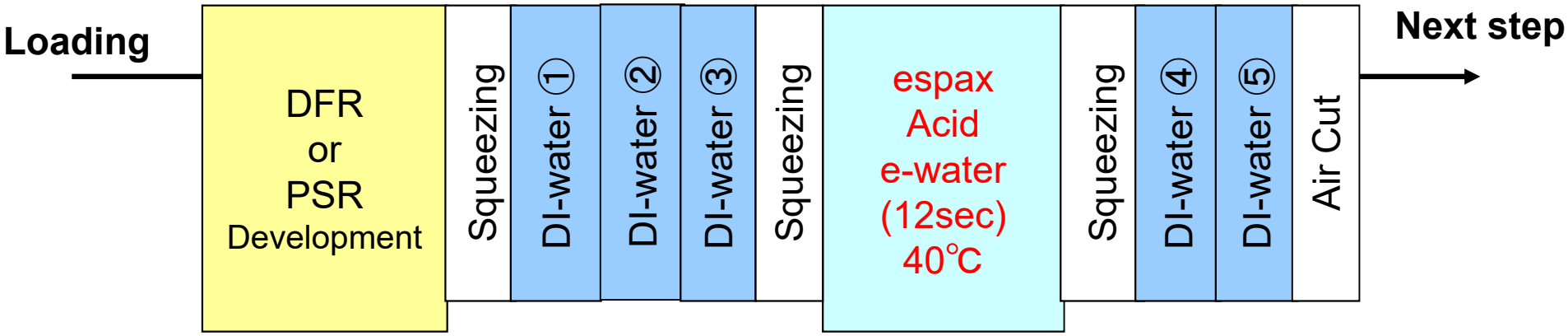
・**Purpose**：**prevent to tailing phenomenon of light-sensitive photo & remove residue (Desucm). As well as decreasing Au(gold) plating failure.**

（e-water works for fine scum removal like >10μ / evaluation by a user）

・**Process condition**：**time / at least 12 sec or more**

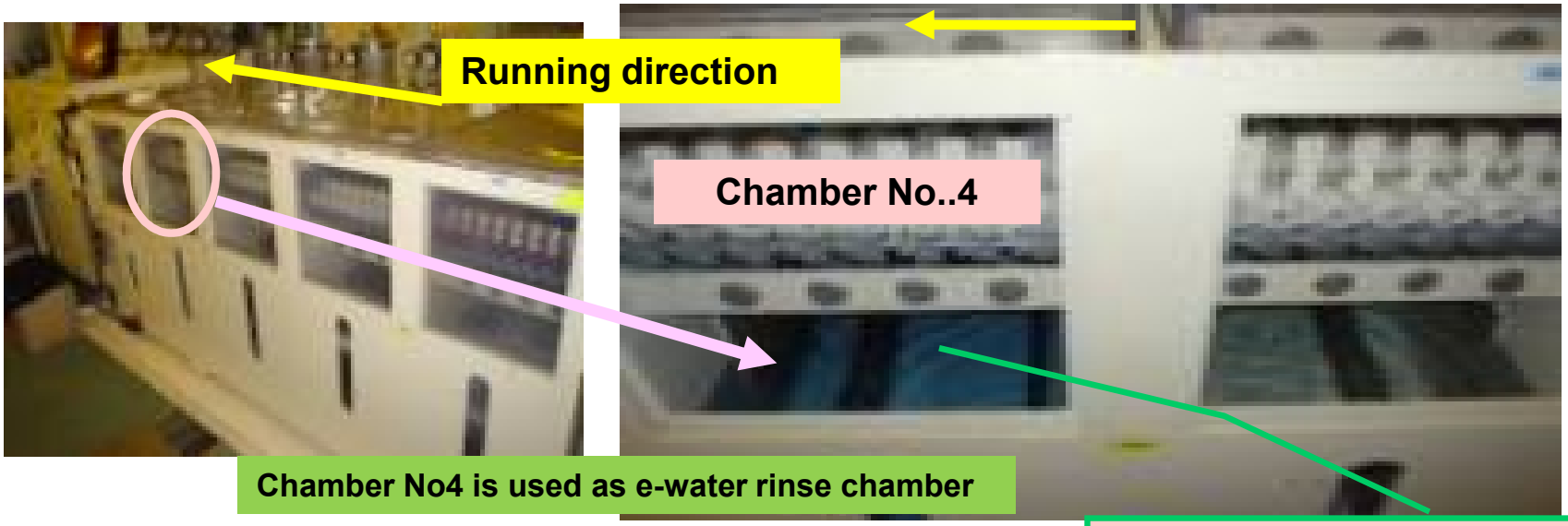
（If process time is not enough, it can't achieve expected results ）

* **Liquid temperature / 40℃**

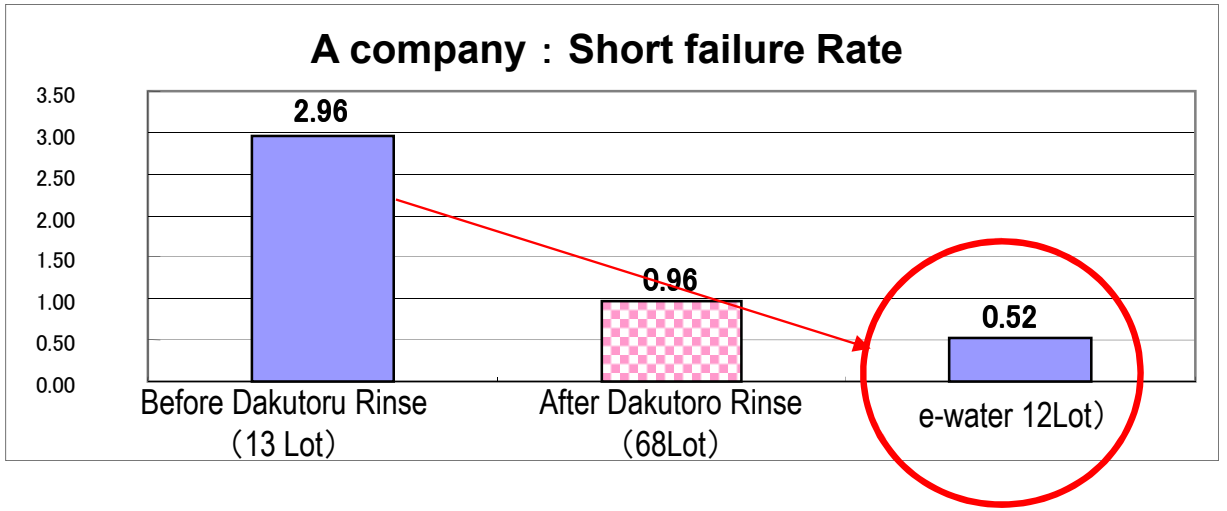


・**Experiences**： **Package substrate manufacturers**

Scum removal effect in DFR Development



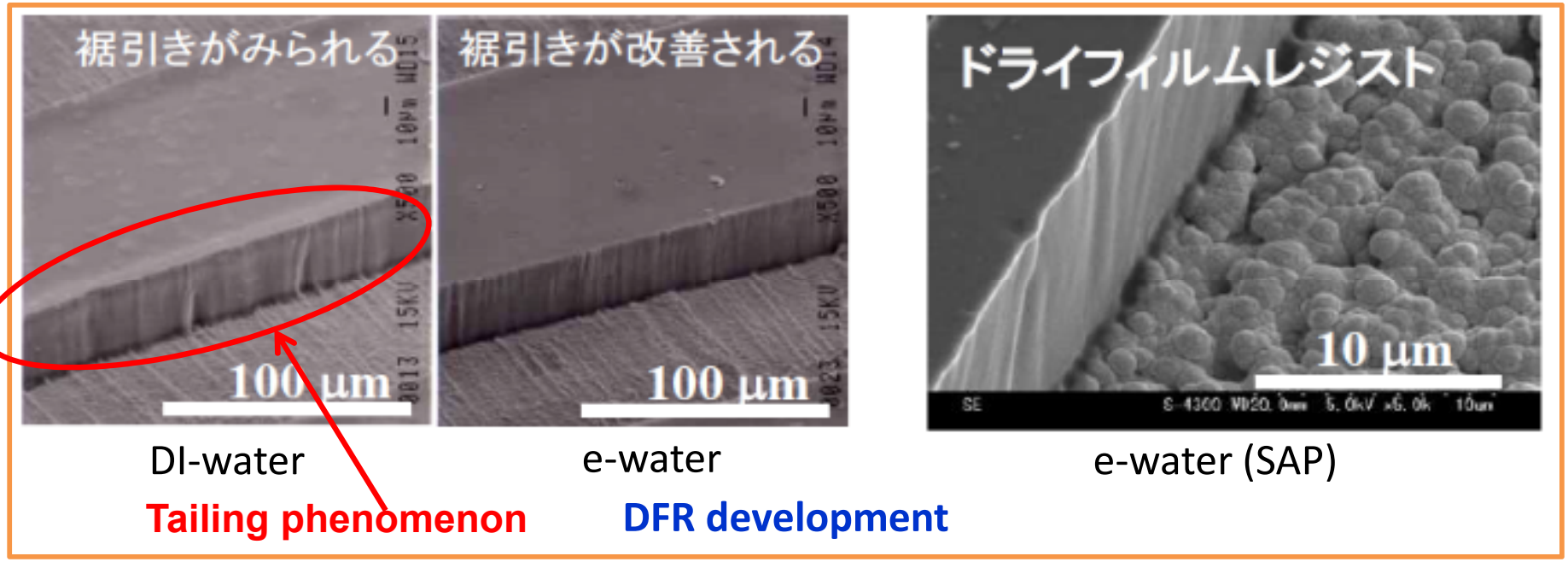
Data for one month used



In this A company, failures became ppm order from % order.
=it works <L&S135μ

Improvement of light-sensitive resin failure in developing water rinse section

★ **Improvement of tailing phenomenon⇒pattern accuracy becomes good**



- **espax acid e-water has neutralizing effect in DFR developing process. Unexposed light-sensitive resin is neutralized immediately and tailing phenomenon stops. As the result, pattern accuracy going to be improved.**

【Attention!!】 espax acid water doesn't remove light-sensitive resin tailing, it stops tailing phenomenon.

If you misunderstand it, and use e-water rinse wrong way, tailing phenomenon will occur often. → Why???

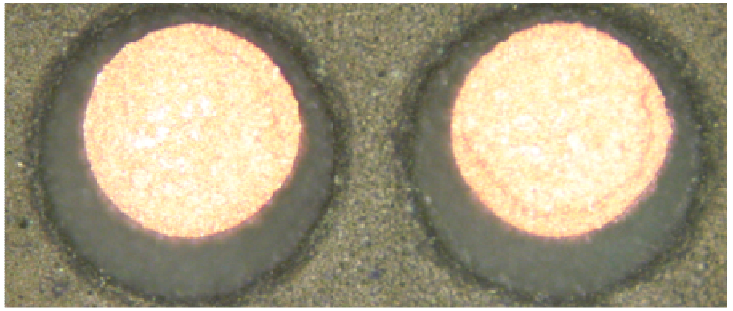
Misunderstanding e-water use in developing process

- espax acid e-water doesn't remove tailing, it can improve resolution by preventing elution of unexposed light-sensitive resin.
- If developing is not enough, it will be neutralized by espax acid e-water and tailing phenomenon will be remaining.

Developing process is carry out even it is in water rinse chamber, because alkali has already been swelling.

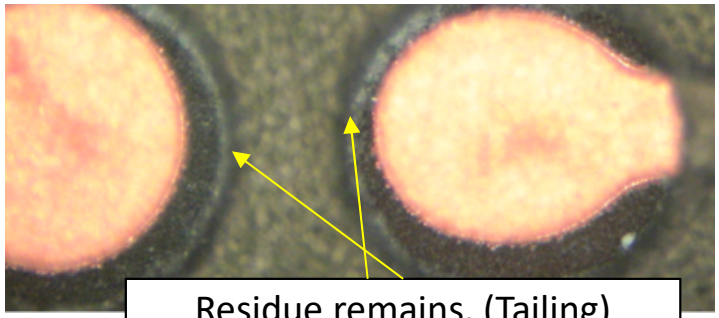
State soon after development ~ rinse

Only water rinse



Developing process stops because acid e-water neutralize soon, so it becomes residue.

Acid e-water use.



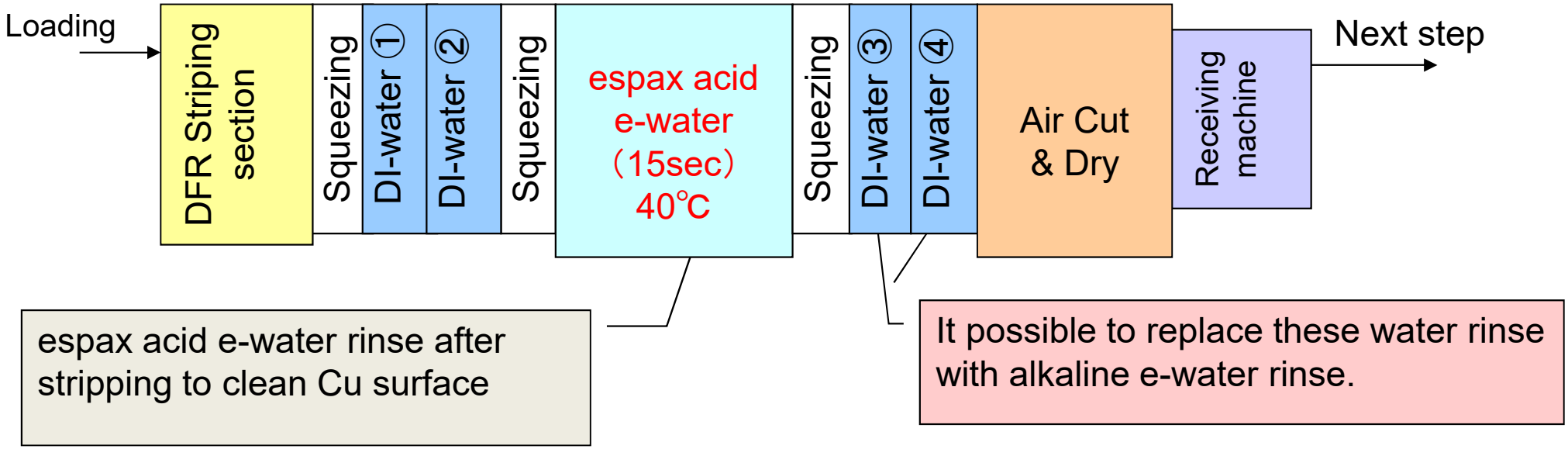
★ **It requires to confirm developing completion point.**

3. espax acid e-water & DFR striping

- **Purpose：Remove striping residue and alkali burn**
- **Effect：Prevent AOI simulated error（Antirust, not strong effect)）**

※ Unlike H_2SO_4 or SPM, there is no discoloration after treatment.

Line configuration



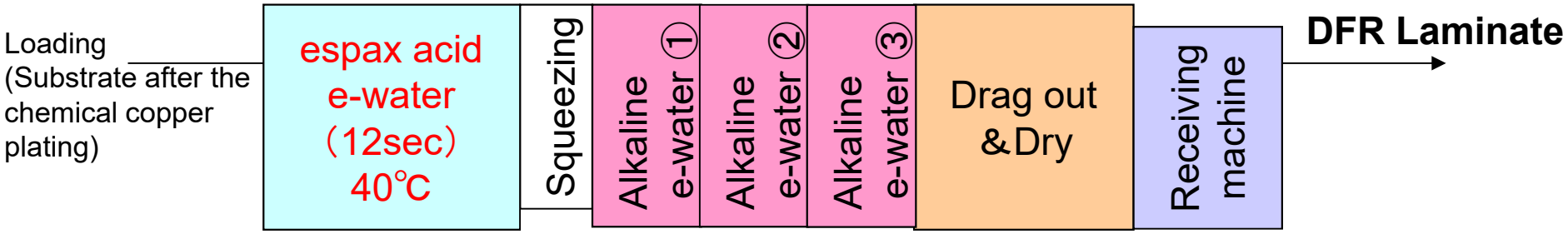
Experiences：Package substrate, FPC, Multilayer substrate, etc.-

4. Finishing process（Flux pretreatment）

- **The purpose：Abolition of SPM**

5. Acid rinse after chemical copper plating(SAP)

- **The purpose：Remove plating residue ＆ antirust (not strong effect).**



6. Acid rinse after Au- plating

Basic process conditions of espax acid e-water

- **Process time：>12sec or more（recommendation 15 sec）**

  ＊ it should be more than 40 seconds in the case of roughening treatment of the copper surface.

- **Process liquid temperature**：40℃
- **Spray pressure　：0.1Mpa or more**
- **Use nozzle　：use 5L / min type（large amount of use）**

  ＊ It is necessary to increase the pump capacity.

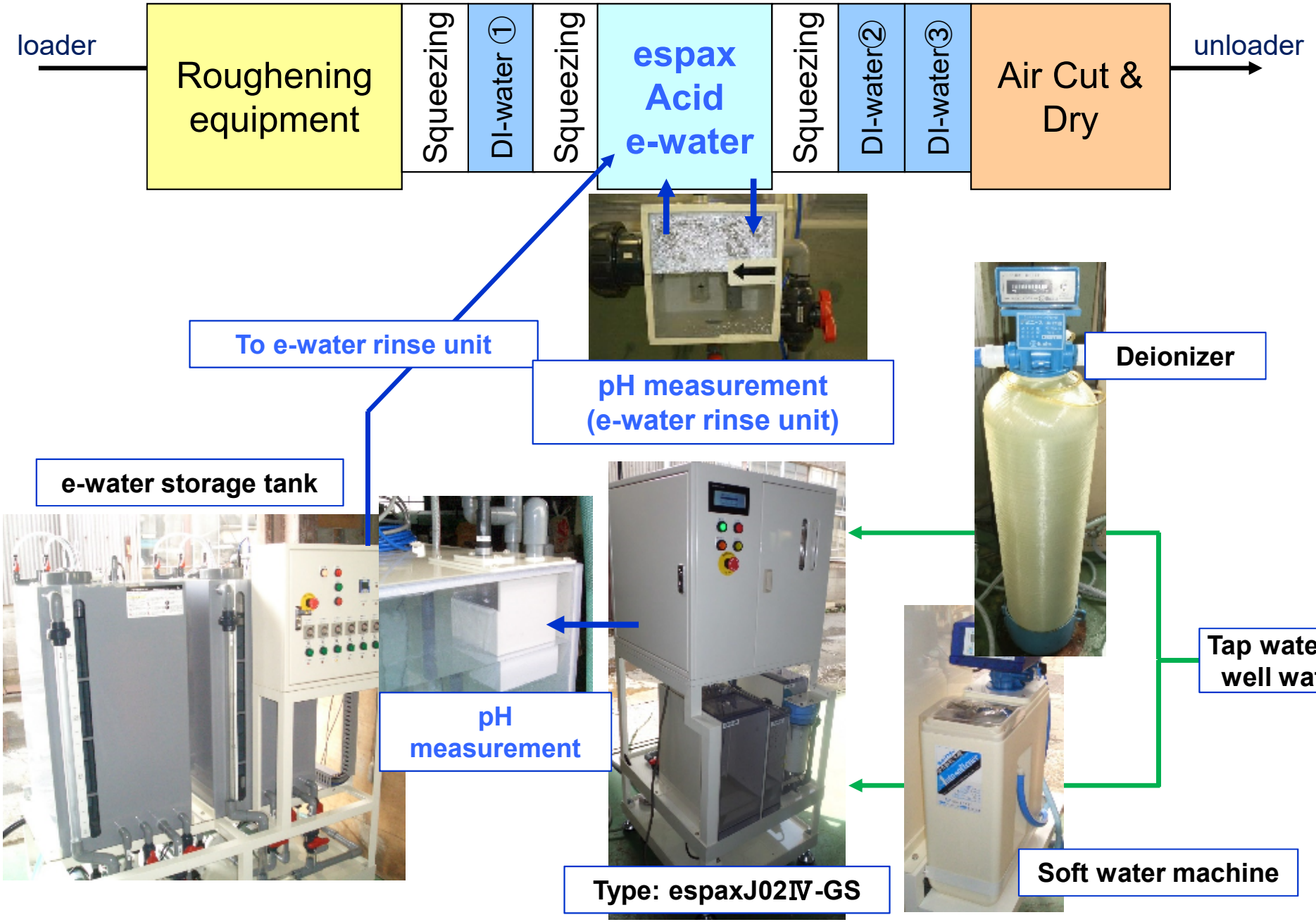
- **Management method：　< pH3.1 below**

  （Replenishment of　e-water）

- **After the treatment, neutralize first(Washed with water）**

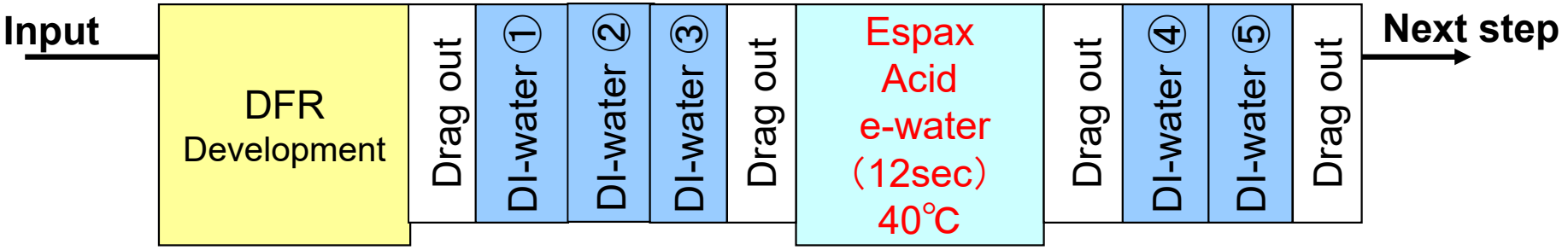
★ **If process time is not enough, it can’t work as we expected.**

Case example for Installation & Management



Cost estimation

Example : developing process



＜ 4L type espax e-water machine : 8.2hur./day for one month＞

1. Consumption amount of Tap water（use it soften）

・3,840L/Day About JPY691 / D × 30Days= JPY20,736 / Month

2. Consumption amount

1) Soft water generation : 20kg/M About JPY2,000/M
2) For electrolysis : 20kg/M About JPY2,000/M

Total About JPY25,000/M（Electricity costs excluded）

cf. TypeJ04 : Power consumption : 3.6Kwh

For further information, please contact us.

Considerations before use

1. E-water rinse is required large amount of acid e-water.
   - Nozzle : 5L/min type, Spray : >100L/min
2. Treatment time : >12sec. Recommendation>15sec.
3. E-water temperature : 40 ℃
4. If the machine drag out lot of chemical or water, it need to modify to drag out.＝Acid e-water is easily neutralized.
5. espax e-water machine must use DI water or soft water for electrolyzation. (Prevent to attach calcium compound to negative pole)
6. Replenishing amount of espax acid water is 0.8 ~ 1L / min.

   （it depends on amount of water drag out or Cu surface condition）

● Caution : if you use chamber for espax e-water treatment, which was used SPM treatment, please wash it by hot water and remove crystallized Cu-sulfate before use. (please refer to page 23)

Considerations before use in overseas countries

1. Prefer to use DI-water (prevent Ca attachment)

* Soft water can be used, but if soft water quality is no good, e-water tank might get damage.
* In the case using soft water, please do not forget add salt(common salt is OK)

2. As for salt for electrolyzation, please use sea salt, or salt which is made in Japan. (please refer to following pictures)

Considerations for evaluation test

1. espax acid e-water treatment can't work just soak test board into e-water.
   - When using the espax e-water, it requires physical force.(spray and ultrasonic)

2. espax acid e-water treatment works by water temperature 40℃. Especially, oxidized cu film removal.
   - 40℃ is optimum e-water treatment temperature.

3. espax acid e-water treatment test of DFR and PSR development should be done in your line.
   - Once scum is dried, it can't be removed. So, test should be done in developing line to keep wet condition.
   - Break point need to be confirmed.

Precaution for use in e-water machine

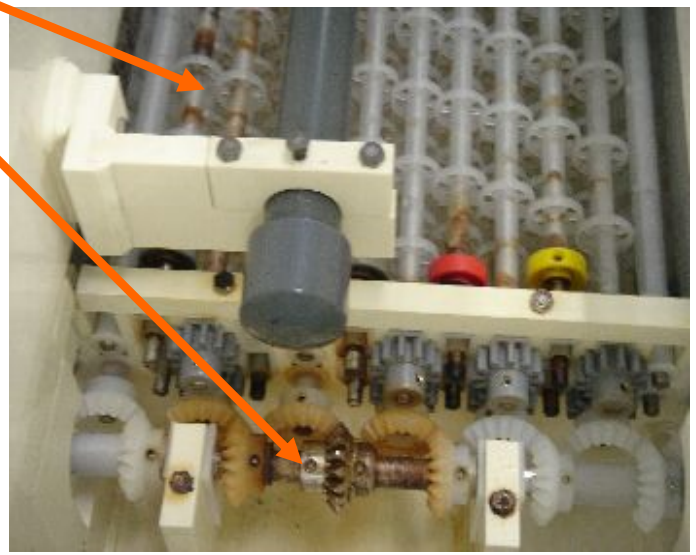
1. There is possibility that sus parts might get rusted.

Parts which are soaked or touch acid e-water are not get rusted, parts which are in e-water air layer, might get rusted. (recommend to use Ti material for metal parts.

Acidic e-water use tank

There is no rust.

Rust of Drag out part



Rust has occurred in the air layer section.

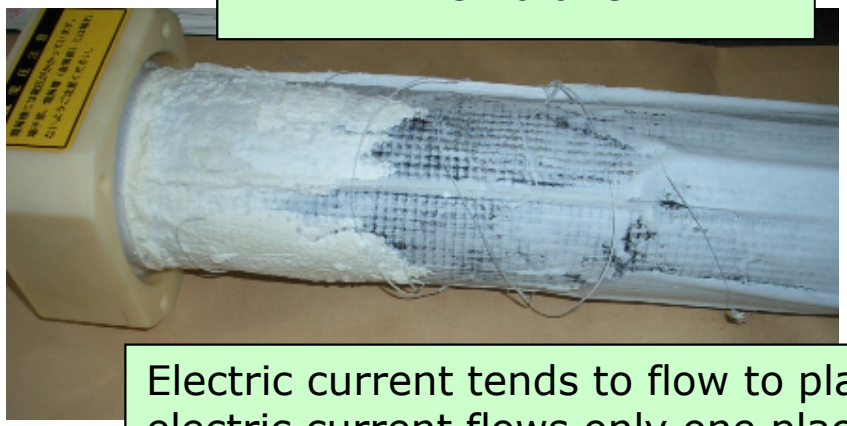
2. Maintenance

Electrolytic cell needs to be replaced every 3000 hours (depending on water quality)

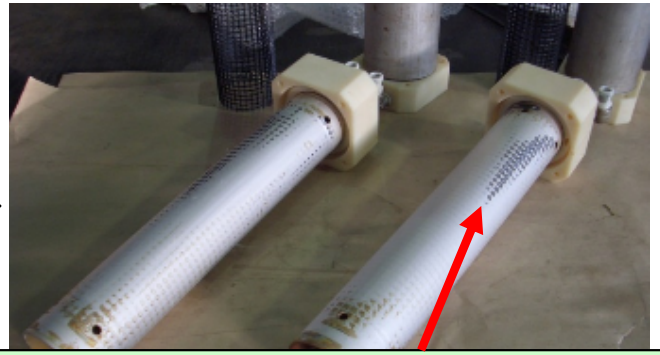
★ **prevent adhesion of Ca, it must be regularly exchanged.**

The appearance of the electrolytic cell

State of the neutral membrane



Electric current tends to flow to place where Ca is not attached, so electric current flows only one place, then makes hole on Ti tube.



Neutral membrane was broken, then electric current focuses on it and it makes platinum plating peeled off. (5400 hours after use)

Summary

We recommend to use espax e-water machine in electric device industry including PWB industry as environmental-friendly system.

＜The espax e-water is a technology which does not give burden to our environment.＞

- ⇒ **Reduction of amount of chemicals use（Alternate also possible）**
- ⇒ **Reduction of water consumption amount＝Water-saving**
- ⇒ **Reduction of waste water amount**
- ⇒ **Reduction of environmental impact**

JIPCM LLC