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Glibrite GB-4300R40

Copper roughening solution designed for Solder Mask preparation

1. GENERAL INFORMATION

Glibrite GB-4300R40 is an additive for copper roughening solution based on hydrogen peroxide and sulfuric acid, which is designed for solder mask preparation, in order to give the best adhesion with lower etching amount.

2. FEATURES

1) Clean copper oxidation thoroughly, and make dense and uniform copper surface topography with lower etching amount, in order to give the best adhesion of solder mask
2) Lower etching amount is essential for fine pattern copper circuit and high frequency requirement of the next generation PWBs.
3) Stable etching speed makes easy maintenance.
4) Applicable by either spray or dip system
5) Stable etching amount even in case of higher copper ion concentration could last the solution longer.
6) Easy waste treatment based on hydrogen peroxide and sulfuric acid solution.

3. PHYSICAL PROPERTIES

Appearance:	Transparent or light yellow aqueous solution
pH:	3 - 5 (20°C)
Specific gravity:	1.0(20°C)
Others:	Refer to MSDS for transportation and handling

4. PACKAGING

20 liter net weight in PE container

5. BATH MAKE-UP

Make-up composition should be determined by the process conditions such as required etching amount, process time and temperature, number and pressure of spray nozzle, etc. However, the typical content of hydrogen peroxide is 3-4 vol%, and the others to make up 100 liter are shown as follows.

	Make-up content	Amount
35wt% hydrogen peroxide	3.5 (vol%)	3.50 liter
98wt% sulfuric acid	2.5 (vol%)	2.50 liter
GB-4300R40	3.5 (vol%)	3.50 liter
Water	90.5 (vol%)	90.50 liter

Mixing procedure

1) Add required amount of DI water first.
2) Add required amount of 98 wt% of sulfuric acid H_2SO_4 slowly with attention to exothermic reaction. Diluted sulfuric acid 50-70 wt% may be used instead for safety.
3) Make sure of the solution temperature below 40°C, and then add GB-4300R40. GB-4300R40 does not accelerate the exothermic reaction.
4) Add required amount of hydrogen peroxide H_2O_2.
5) Stir the solution thoroughly more than 15 minutes.

The quantity of 50 and 70wt% sulfuric acid instead are given for reference.

(L)

98 wt%	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
50 wt%	2.58	5.15	7.73	10.30	12.88	15.46	18.03	20.61	23.18	25.76
70 wt%	1.59	3.18	4.77	6.36	7.95	9.54	11.13	12.72	14.31	15.90

The quantity of 50 and 60wt% hydrogen peroxide instead are given for reference.

(L)

35 wt%	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00	10.00
50 wt%	0.66	1.32	1.98	2.64	3.30	3.96	4.61	5.27	5.93	6.59
60 wt%	0.53	1.06	1.59	2.13	2.66	3.19	3.72	4.25	4.78	5.32

6. OPERATING CONDITIONS

The optimum operating conditions and the maintenance of GB-4300R40 are given as follows.

Items	Lower limit	Upper limit
35 wt% Hydrogen peroxide (vol%)	3.0	4.0
Acid content (vol%)	2.0	4.0
Copper concentration (g/L)	5	45
Etching amount (um)	0.3	0.7

Remark: in case of more than 45 g/liter copper content, a part of solution in the sump should be dumped and made-up.

1) 35 wt% Hydrogen peroxide H_2O_2
   This is the most important item to control the etching amount and copper surface topography. Lower content makes less etching speed and uneven surface. Higher content makes excess etching amount, then improper copper surface topography and poor solder mask adhesion.

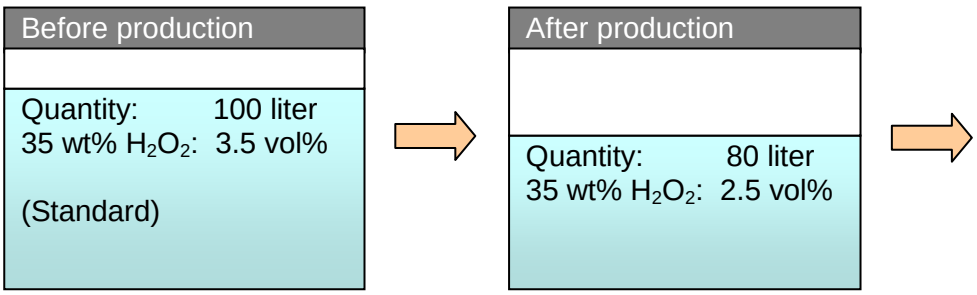
2) Acid content
Acid content gives an influence to etching speed and copper surface topography. Lower content makes less etching speed and would make the copper surface dark-reddish color. Higher content makes more flat copper surface and poor solder mask adhesion.

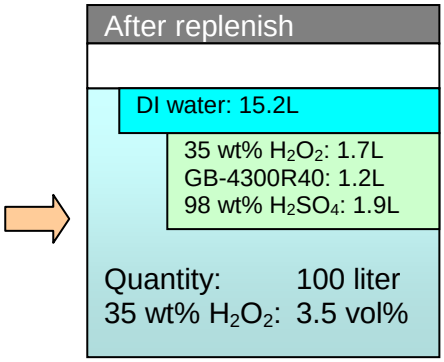
3) Copper content
Usually this tends to be higher by dissolving the copper of PWBs. In case of too high content, copper sulfate would be crystallized in the solution. A part of solution in the sump should be made-up in case of more than 45 g/liter.

4) Etching amount
This is important to affect an adhesion of solder mask with copper. Less etching amount would not give good copper surface topography to give good adhesion. Excess etching amount also would not give good topography (too flat) and make adhesion worse.

7. BATH MAINTENANCE

The example of daily bath maintenance is shown as follows.





The replenishment of 35 wt% hydrogen peroxide to adjust to the standard condition before production is calculated as follows.

(100 liter x 3.5 vol% - 80 liter x 2.5 vol%) / 100 liter = 1.7 liter

The replenishment of GB-4300R40 is 0.68 times of 35 wt% hydrogen peroxide replenishment.

1.7 liter x 0.68 = 1.2 liter

The replenishment of 98 wt% of sulfuric acid is 1.1 times of 35 wt% of hydrogen peroxide replenishment.

1.7 liter x 1.1 = 1.9 liter

Then fill the rest (100 – 80 - 1.7 – 1.2 - 1.9 = 15.2 liter) with DI water.

8. GB-4300R40 PROCESS CONDITIONS

A typical process condition of GB-4300R40 is shown as follows.

	Process	Conditions		Note
1	Degrease		Spray	W40 or DG series
2	Water rinse		Spray	At least 3 cascade
3	Air knife			
4	GB-4300R40	30 +/- 5 °C	Spray: 10 - 40 sec. Dip: 20 - 80 sec.	0.5 +/- 0.2 µm etch rate
5	Water rinse			
6	HCl acid clean		Spray	3-5 wt% HCl aq. solution
7	Water rinse		Spray	
8	Air knife			
9	Dry	80°C	60 sec.	

- Degrease is recommendable to remove oily material to make sure of GB-4300R40 process.
- In case of dip mode, dip spray in the solution from the top and bottom is recommendable to circulate the solution adequately.
- Water rinse should be done immediately after GB-4300R40 process.
- **3-5 vol% HCl aq. solution is necessary after GB-4300R40 process.**
- Use cartridge filter for GB-4300R40 to remove foreign materials from PWBs.
- Prevent HCl ion contamination into GB-4300R40 sump as much as possible.

9. MATERIALS FOR EQUIPMENT

GB-4300R40
Materials compatible with GB-4300R40 sump is shown as follows.

- Tank body: Hard PVC, Hard PE, Hard PP
- Transport rings and rolls: Hard PVC, Hard PE, Hard PP, Teflon
- Transport shaft: Carbon fiber, Stainless (SUS304, 316 or 316L)
- Squeezing rollers: PE, PP (sponge)
- Heater: Quartz, Stainless (SUS304, 316 or 316L), Teflon

Precautions

1) No other metals except stainless
   - SUS304, 316 or 316L are recommendable.
   - No titanium must be used.
2) No rubber materials basically, but only Teflon base rubber, if necessary
3) No soft plastic material is recommendable.
4) Fluorine base plastic may be used.

Compatible
Hard PVC, Hard PE, Hard PP, Acrylic resin, Carbon fiber, Teflon, SUS304 / 316 / 316L

Incompatible
Titanium, Soft PVC, Soft PE, Polycarbonate, ABS, Silicone rubber, Neoprene rubber, PVA

HCl acid clean
No stainless must be used, but only Titanium for metal parts.

10. ANALYTICAL METHOD

35 wt% Hydrogen peroxide

Cerium method

1) Take 1ml of sample solution precisely into 200 ml beaker, and add 100 ml of DI water.
2) Add approx. 3 ml of 50% sulfuric acid solution [a)].
3) Add 5 drops of ferroin indicator [b)].
4) Titrate with 0.1N Cerium standard solution [c)] and measure the amount (A ml) to change color from red / orange to light blue as the end point.
5) The content can be calculated as follows.

   35 wt% hydrogen peroxide (vol%) = 0.428 x A (ml)

   a) 50% sulfuric acid solution (1 liter)
      Add 98% sulfuric acid into 400 ml of DI water slowly with attention to exothermic reaction. After cooling down to room temperature, add DI water to 1 liter.
   b) Ferroin indicator (100 ml)
      Dissolve 0.49 gram of 1,10-phenanthroline and 0.23 gram of ferrous sulfate heptahydrate with water.
   c) 0.1N Cerium standard solution (1 liter)
      Add 50 ml of 98 wt% sulfuric acid into 500 ml of DI water slowly, and dissolve 63.25 grams of Ammonium cerium (IV) sulfate dihydrate completely. After cooling down to the room temperature, add DI water to 1 liter.

KMnO4 method

1) Take 1ml of sample solution precisely into 200 ml beaker, and add 100 ml of DI water.
2) Add approx. 3 ml of 50% sulfuric acid solution [a)].
3) Titrate 0.1N- KMnO4 standard solution with using magnetic stirrer. The content can be calculated as follows.

   35 wt% hydrogen peroxide (vol%) = 0.428 x A (ml)

   a) 50% sulfuric acid solution (1 liter)
      Add 98% sulfuric acid into 400 ml of DI water slowly with attention to exothermic reaction. After cooling down to room temperature, add DI water to 1 liter.
   b) 0.1N-potassium permanganate standard solution (1 liter)
      Add 3.16 g of potassium permanganate into 500 ml of DI water slowly, and dissolve completely. After dissolving completely, add DI water to 1 liter.

Acid content

1) Take 1 ml of sample solution precisely into 200 ml beaker, and add 100 ml of DI water.
2) Add 5 drops of methyl orange indicator [d)].
3) Titrate with 0.1N sodium hydroxide standard solution and measure the amount (B ml) to change color from red to yellow as the end point.
4) The content can be calculated as follows.

   Acid content (vol%) = 0.27 x B (ml)

   d) Methyl orange indicator
      Dissolve 100 mg of methyl orange into 100 ml of DI water.

Copper concentration

1) Take 1 ml of sample solution precisely into 200 ml beaker, and add approx. 5 ml of pH 10 buffer solution [e)], followed by 100 ml of DI water. The solution becomes blue purple by pH buffer solution.
2) Add 5 drops of PAN indicator [f)].
3) Titrate with 0.05M EDTA standard solution [g)] and measure the amount (C ml) to change color from blue purple to yellow green as the end point.
4) The content can be calculated as follows.

   Copper concentration (g/liter) = 3.18 x C (ml)

   e) pH 10 buffer solution
      Dissolve 61.4 gram of ammonium chloride in 500 ml of 25% ammonia solution and add DI water to 1 liter.
   f) PAN indicator
      Dissolve 100 mg of 1-(2-pyridylazo)-2-naphthol into 100 ml of ethanol.
   g) 0.05M EDTA standard solution
      Dissolve 18.61 gram of disodium ethylenediamine tetra acetic acid dihydrate in 500 ml of DI water and add DI water to 1 liter.

Etching amount

1) Weigh appropriate size (10 cm^2) of bare copper plate by electrical balance with 1 mg accuracy. (W_1)
2) Etch the bare copper plate, water rinse and dry completely.
3) Weigh the bare copper plate (W_2)
4) The etching amount can be calculated as follows.

   Etching amount (um) = (W_1 - W_2) x 1117 / S

   W_1: Weight before etching
   W_2: Weight after etching
   S: Copper surface area (cm^2)

11. WASTE TREATMENT

Since the waste of GB-4300R40 solution contains hydrogen peroxide, sulfuric acid and copper ion, etc., please do not discharge it into the river without treatment. Ask the waste treatment company, otherwise follow the proper treatment as follows.

1) Add 1-2% of the decomposing agent for hydrogen peroxide such as sodium hydrogen sulfite to GB-4300R40, and stir thoroughly.
2) Increase pH more than 13 by adding NaOH carefully, and stir it for 30 min.
3) Filter out the precipitation containing copper compound. The content of copper ion in the solution should be reduced below 10 ppm.
4) Neutralize the solution by acid such as sulfuric acid, followed by biological treatment or dilution with water to comply with local waste standard.

12. HANDLING PRECAUTIONS

1) Read MSDS carefully.
2) Do not return the used GB-4300R40 solution into the container.
3) Keep container tightly closed and dry in a cool, well-ventilated place without sunshine.
4) Do not dispose spill and waste of GB-4300R40 solution into river without treatment.