COPPER ETCHING IN AIR REGENERATED CUPRIC CHLORIDE SOLUTION

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ABSTRACT

One of the most important steps in the world of printed circuit board manufacturing (PCB) is the copper etching process. Because of its low cost, environment aspects, and simple regeneration techniques, cupric chloride was chosen to be the most attractive etchant.

Etching of copper from standard single-sided copper boards used usually for printed circuit board fabrication was conducted in a cell containing cupric chloride solution. Average etching rates were recorded as a function of time, etchant specific gravity, free acid concentration, and temperature. Air was injected continuously in the etching cell during the process enabling mixing and solution regeneration. It is found that best operating conditions to obtain maximum etching rate is at 45-55°C, specific gravity of 1.3-1.4, and free acid concentration of 1.3-1.4 M.

KEYWORDS

Etching, chemical machining, cupric chloride, regeneration, PCB.

الخلاصة

ان التأكل الموجّه للنحاس يعد احد العمليات المهمة في عالم صناعة الدوائر الالكترونية المطبوعة (PCB). وانتخب محلول كلوريد النحاس ليكون احد اهم المحاليل المسببة لعملية التأكل الموجه نظراً لرخص ثمنه، وسهولة استرجاع فعاليته بعد استعماله، ولاعتبارات بيئية.

دُرس تأكل النحاس عبر عينات قياسية لالواح نحاس ذات وجه واحد تستخدم عادةً للطباعة الالكترونية في خلية تحوي محلول كلوريد النحاس، وسُجلت معدلات التأكل للعينات بالنسبة للزمن، ولدرجة الحرارة، وكثافة المحلول، وتركيز الحامض الحر. حُقن هواء بشكل مستمر في داخل الخلية بهدف مزج المحلول واسترجاع فعاليته. وجد ان افضل الظروف لتحقيق اعلى المعدلات للتاكل تكون بدرجة حرارة 45–55°م، وكثافة نوعية بحدود 1.3–1.4، وتركيز الحامض الحر بحدود 1.3–1.4 مولاري.

INTRODUCTION

Etching can be defined as a machining technique, in which, controlled corrosion process was applied on selected areas of the metal part. This is usually occurring in the presence of a corrosive media, called *etchant*. The process was used by ancient Egyptians to make copper jewelries when they etched copper with citric acid around 2500 BC. Etching, nowadays, is extensively used to manufacture geometry complex and precision parts for electronic, aerospace, automotive, medical, decorative, and microcomponent production industries (O. Cakir *et al*, 2007; O. Cakir, 2007).

One of the most important steps in the world of printed circuit boards fabrication is the copper etching step from circuit boards. Circuit boards are usually fabricated from glass fiber reinforced epoxy

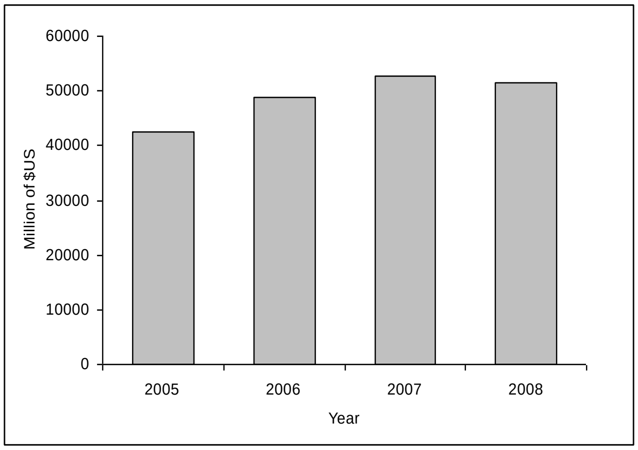

Fig.1 World PCB production (WECC reports)

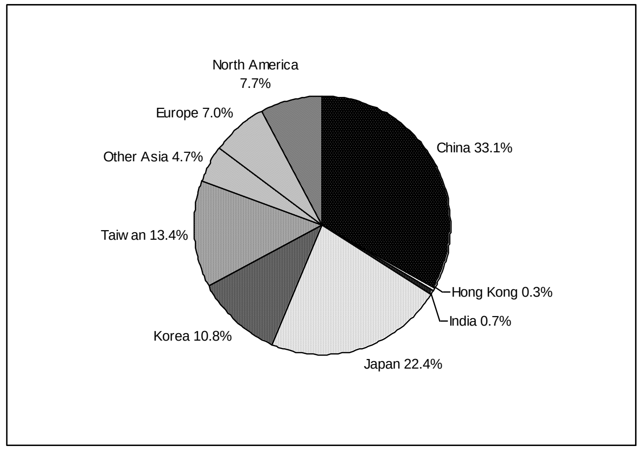

Fig. 2 Countries sharing PCB production for the year 2008 (WECC report)

with copper layers of 25 to 50 μm thick (Xingsheng Liu, 2001). There are three basic varieties of printed circuit boards: single-sided, double-sided, and multi-layered. The spatial and density requirement and circuitry complexity determine the type of board produced. **Fig. 1** Show the world PCB production estimates from 2005 till 2008, and **Fig. 2** show the major countries that share the production for the year 2008 (WECC – World Electronic Circuits Council, 2009).

Copper was commonly etched with alkaline ammonia and cupric chloride (continuous operation). Less common etchants include peroxide-sulfuric acid, persulfates, and ferric chloride (batch operation). The selection of etchant has been limited by economic, operational, and environmental concerns (Clyde F. Coombs, Jr, 2008). For single-sided boards, cupric chloride is the most suitable etchant even for large scale production lines (O. Cakir, 2006). It offers some distinct advantages like: simple regeneration of spent solution, no waste disposal problems, low cost, simple process control, and no sludging problem (Stephen D. Kasten, 1983).

Chemistry of Copper Etching with Cupric Chloride and the Regeneration Process

Cupric chloride is a yellow-brown solid with the formula $CuCl_2$ in its dehydrated state. It is sold usually in its hydrated state ($CuCl_2.2H_2O$) with a blue-green color as it absorbs moisture from the ambient. Cupric chloride reacts with copper to form cuprous chloride:

$$Cu + CuCl_2 \rightarrow 2CuCl \tag{1}$$

As the reaction proceeds, cupric ions will deplete and the reaction goes to slowdown (i.e. etching rate decreased). To obtain a constant etching rate and makes copper continue to dissolve from the metal surface, cuprous chloride should be returned back or regenerated to cupric chloride again. This can be accomplished by providing an oxidizing agent that oxidizes cuprous ions Cu^{+1} to cupric ions Cu^{+2}. Many oxidizing agents can be used for this purpose, commonly used includes chlorine or air, sodium chlorate ($NaClO_3$), or hydrogen peroxide (H_2O_2). Regeneration process by oxygen was done chemically according to the reaction:

$$2Cu^{+} + O + 2H^{+} \rightarrow 2Cu^{++} + H_2O \quad (2)$$

Reaction (2) consumes hydrogen ion, so that, hydrogen ions should by supplied to the reaction. Addition of hydrochloric acid (HCl) in excess amount to the reaction vessel was suggested to be a good source for H^+ ions and chloride balance was maintained. Also, it removes any traces of copper oxide from the surface of copper metal being etched (Chemcut Corp., 2002). It is clear that the original solution volume grows up during the regeneration process in this way. To overcome this problem, one should remove a portion of the etchant from time to time to keep a fixed reaction volume (P. Adaikkalam *et al*, 2002). The overall reaction of the regeneration process is:

$$2HCl + 2CuCl + O \rightarrow 2CuCl_2 + H_2O \quad (3)$$

In this study, copper from single-sided boards was etched with cupric chloride and the effected parameters on the average etching rate were studied. Regeneration of the solution was done by continuous injection of air to the etching cell.

EXPERIMENTAL WORK

The Etching Cell

Etching of copper from single-sided boards with cupric chloride solution was accomplished in a cell designed to meet the necessary requirements needed to study the parameters affecting etching process.

The cell shown in **Fig**. **3** was made from a glass material with dimensions of 27 cm height × 19 cm width × 3.5 cm depth, filled with 1 liter of cupric chloride etchant during each run. It holds an electrical heater used to maintain the solution at the desired temperature fixed by a contact thermometer within ±0.5°C. At the bottom of the cell, an air distributor was installed enabling air bubbles to spread along the cell. The air was injected to the cell at a fixed flow rate of 0.5 liter/min. This flow rate was selected to be the maximum flow rate allowable to prevent the solution from spilling out of the cell. Air function as a source of oxygen required to regenerate the etchant and as an agitator.

Average etching rate was recorded as a function of etching time, etchant density, free acid concentration, and temperature. Etching was monitored by visual inspection of a 2 x 4 cm circuit board sample hanged at the center of the

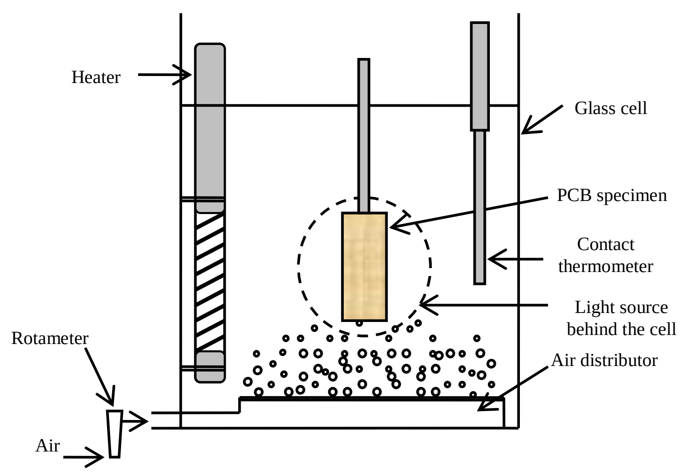

Fig. 3 Etching cell

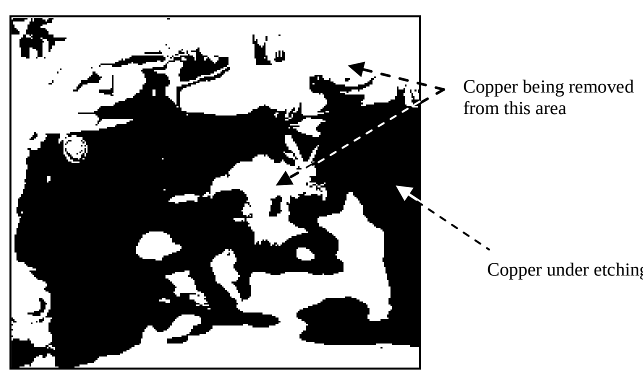

Fig. 4 Typical circuit board sample under etching

cell below the etchant surface level by about 4 cm. Samples are cleaned and polished well to obtain a scratch-free surface before dipping into the etching solution. Because the etchant become darker as its density increases, light source was installed behind the cell enabling best view of sample etching details instead of sample monitoring outside the cell from time to time.

The term '*average etching rate*' was used in this study because etching of the sample is not uniform. In other word not all the copper removed evenly from the sample sheet at the same time as shown in **Fig. 4**. Instead, pits start to appear (white area) and spread in all directions until the copper (black area) was removed completely. At this point, time was recorded and etching rate was calculated from the equation:

$$\text{Average Etching Rate} = \frac{\text{Copper Thickness}}{\text{Total Etching Time}} \tag{4}$$

Solution specific gravity was adjusted between each run after etchant was completely regenerated to its original state by a hydrometer. Leaving the solution about half-hour under air bubbling was considered to be sufficient time to return back the solution nearly to its initial state.

Free acid concentration was measured and adjusted using 37% hydrochloric acid of 1.19 specific gravity. Measurement of the free acid concentration was done by titration with NaOH solution. The amount of acid required to adjust the etchant can be calculated from:

$$y = \frac{x(a-b)}{(c-a)} \tag{5}$$

where y is the volume of acid required to adjust the etchant to the acid concentration required concentration *a*, *x* is the etchant volume (i.e. 1000 ml), *b* is the measured acid concentration by titration, and *c* is the concentration of the hydrochloric acid being added.

Note that the addition of HCl should be the last step in solution adjustment process because small amount of HCl is needed usually to bring the solution up to the desired acid concentration without changing the specific gravity of the solution appreciatory.

RESULTS AND DISCUSSION

Effect of Etching Temperature

In general, increasing the temperature tends to increase the etching rate as shown in **Figs. 5-9**. It is desired usually to select a temperature range which should give a relatively acceptable etching rate for practical purposes. Temperatures below 40°C takes long etching times (i.e. low etching rate) with low HCl fumes and above 55°C, etching rate increases many times but causes too much HCl fumes to start also. Under air regenerated cupric chloride etchant, it is observed that temperature range between 45°C and 55°C is the suitable working range depending on the air flow rate because oxygen solubility decreases with increasing temperature (i.e. to work at elevated temperature range to obtain higher etching rates, one should distribute much more bubbles - in the maximum allowable flow - to maximize the rate of solubility of oxygen to the maximum one).

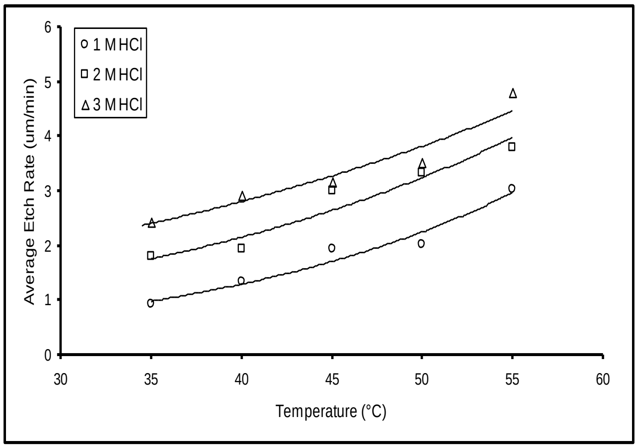

Fig. 5 Average etching rate versus etchant temp. at different free acid conc. and 1.1 sp.gr.

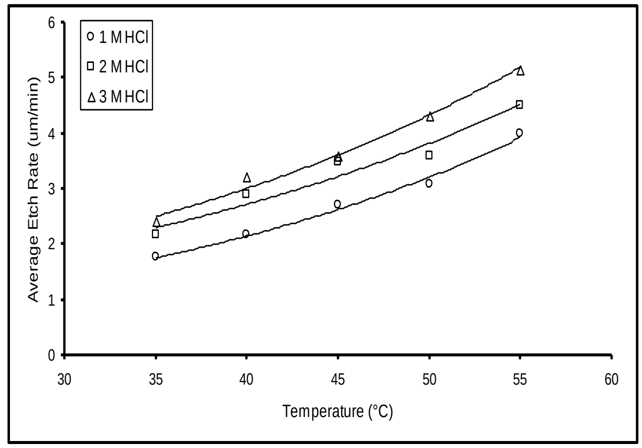

Fig. 6 Average etching rate versus etchant temp. at different free acid conc. and 1.2 sp.gr.

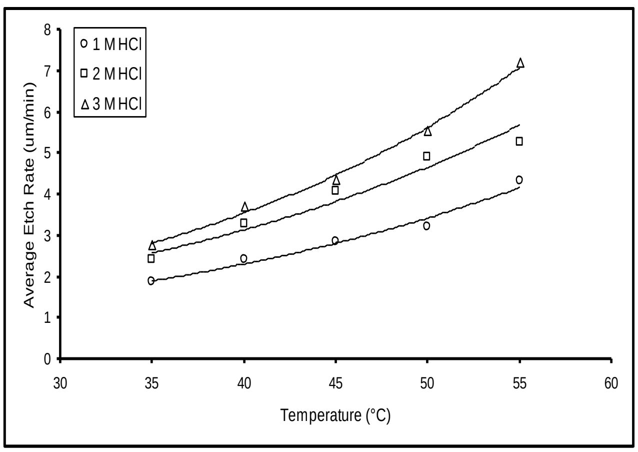

Fig. 7 Average etching rate versus etchant temp. at different free acid conc. and 1.3 sp.gr.

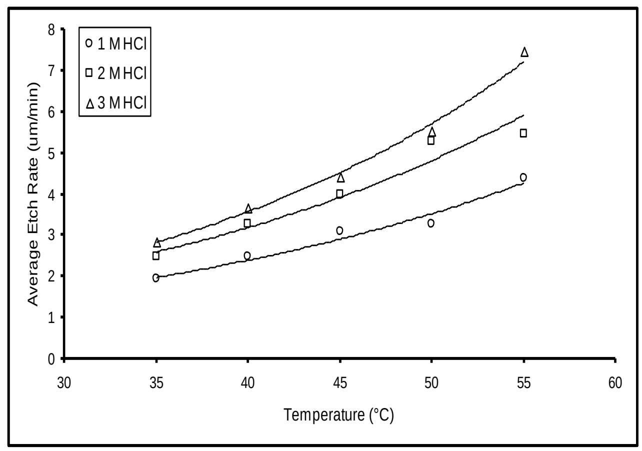

Fig. 8 Average etching rate versus etchant temp. at different free acid conc. and 1.4 sp.gr.

Effect of Etchant Specific Gravity

As copper continue to dissolve and water evaporates, specific gravity of the etchant will increase also and the etchant become a dense solution. At some point, this will cause average etching rate to slow down because the movement of cuprous ions away from the copper surface become more difficult and may initiates sludges to be formed.

Figs. 10-14 shows the effect of etchant specific gravity change on average etching rate at different temperatures. It is clear that maximum and nearly constant etching rate occurs between specific gravity of 1.3 and 1.4 as it does not change significantly within this range. Average etching rate decreased below specific gravity of 1.3 and above

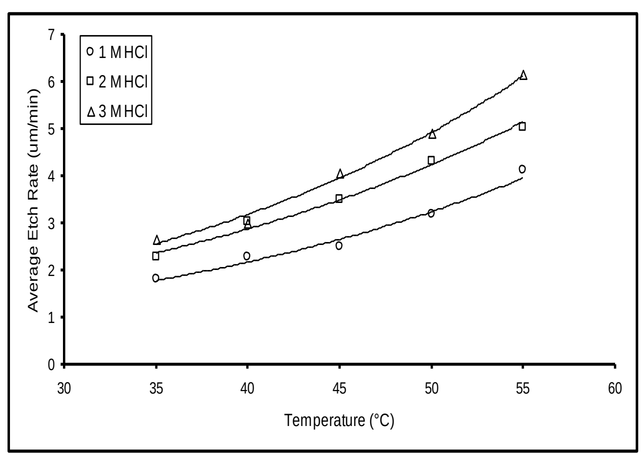

Fig. 9 Average etching rate versus etchant temp. at different free acid conc. and 1.5 sp.gr.

1.4. So that, it is desired to control the specific gravity within this range.

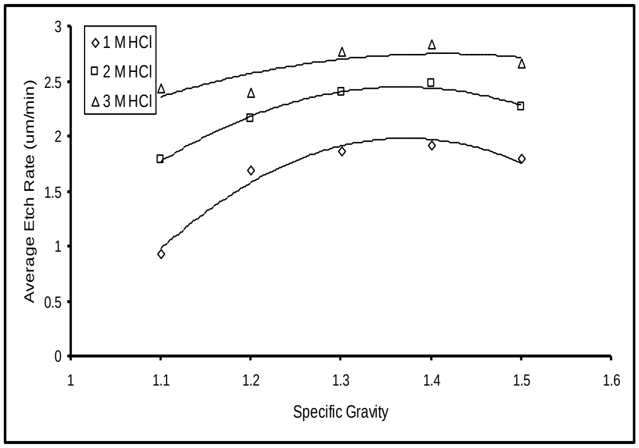

Fig. 10 Etchant specific gravity versus average etching rate at different free acid conc. and 35°C

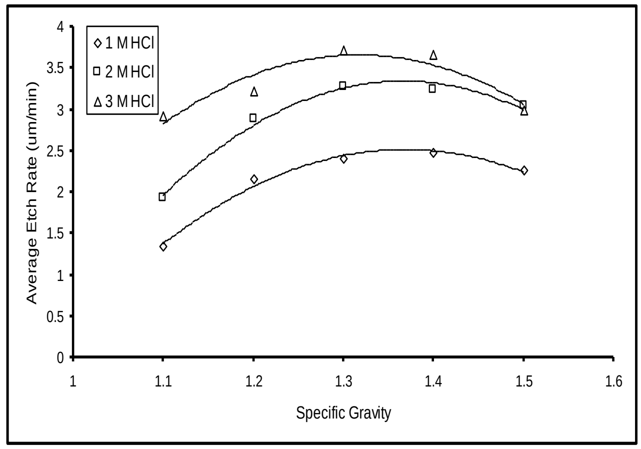

Fig. 11 Etchant specific gravity versus average etching rate at different free acid conc. and 40°C

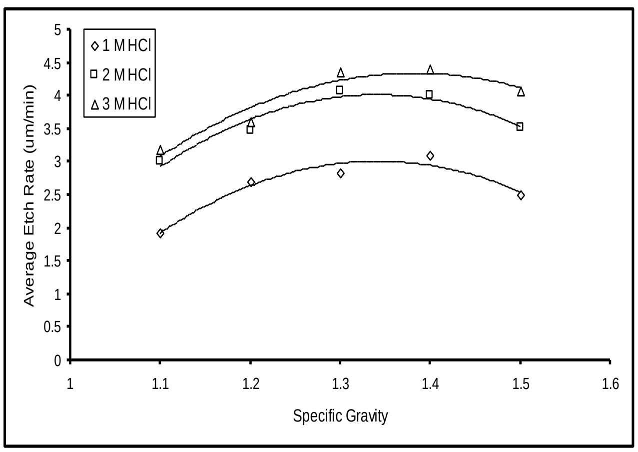

Fig. 12 Etchant specific gravity versus average etching rate at different free acid conc. and 45°C

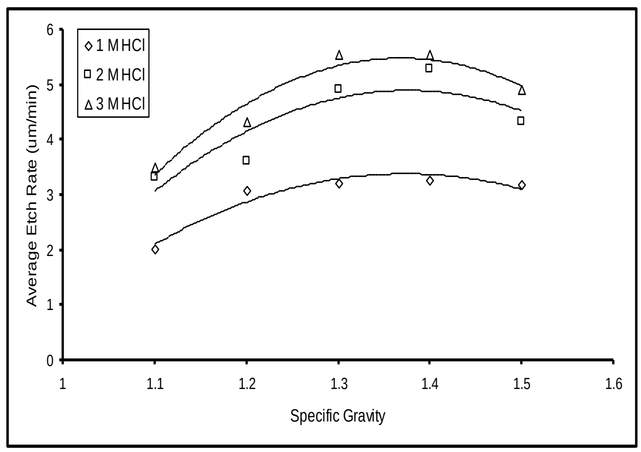

Fig. 13 Etchant specific gravity versus average etching rate at different free acid conc. and 50°C

Effect of Etchant Free Acid Concentration

From the previous figures (**Figs. 5-14**), it is clear that increasing the free acid concentration in the solution is proportional with the average etching rate. Low etching rate were observed at 1 M HCl with low fuming in all temperature range studied, at 2 and 3M HCl, higher etching rates were obtained but the rate of fuming increases also especially at elevated temperatures when 3 M HCl were used. So that, the selection of HCl concentration should be contributed with the working temperature and the allowable limit of fuming. The best operating free HCl level was suggested to be between 2 and 3 M HCl.

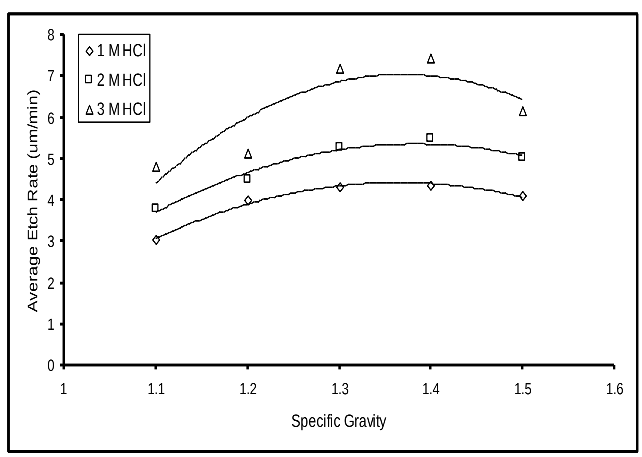

Fig. 14 Etchant specific gravity versus average etching rate at different free acid conc. and 55°C

CONCLUSIONS

- Single-sided circuit boards can be etched with different etchants but cupric chloride is the most suitable one even for large production lines.
- Cupric chloride can be regenerated using many oxidants even oxygen from air and the parameters affecting etching rates should be contributed together in order to maximize the etching rate.
- It is found that controlling temperature within the range of 45-55°C, etchant specific gravity of 1.3-1.4, and free acid concentration of 1.3-1.4 M would provide the best etching results.

NOMENCLATURE

a	Free acid required concentration, M
b	Measured free acid concentration, M
c	Acid concentration being added, M
x	Etchant total volume, ml
y	Etchant volume required to adjust the etchant to the desired level, ml

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