PERMANGANATE DESMEAR PROCESS CONTROL

by

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The alkaline permanganate process demonstrates significant advantages over other chemical methods for desmear or etchback of epoxy and polyimide printed circuit boards. However, the process control of the permanganate bath is difficult due to limited stability of the bath solution and inaccuracies in chemical analysis. This paper presents a better understanding of permanganate solution chemistry and chemical analysis, SPC process/measurement capability study, and the schemes for process/process control improvements.

As part of the circuit board plating process, drill smear deposited on the hole walls and the interconnect areas of a multilayer printed circuit board during the drilling operation must be removed prior to electroless deposition of copper in order to achieve reliable interconnections. The smear removal methods include chemical methods, mechanical methods and gas plasma. This paper will emphasize the alkaline permanganate desmear process of the chemical methods. This process is a three-step operation to remove drill smear from the hole wall and innerlayer face. It consists of an alkaline epoxy sensitizer, regenerable permanganate bath and post permanganate neutralizer. First, all drilling debris is removed and the epoxy surface is sensitized. Then the pre-sensitized dielectric surface is attacked by the permanganate oxidizer. This results in a micro-roughened, micro-porous resin hole-wall topography which provides for good adhesion of electroless copper. Finally, the hole wall surface is neutralized to remove any residual processing solutions.

The permanganate desmear process demonstrates significant advantages over other chemical methods for smear removal, such as the sulfuric acid system, chromic acid system, and strong base system[1-11]. However, the process control of the permanganate bath is difficult due to the limited stability of the bath solution and inaccuracies in chemical analysis. This paper summarizes the results of a study on the problems and improvements of the process/process control of the permanganate bath operation at Naval Air Warfare Center, Aircraft Division, Indianapolis.

CURRENT PERMANGANATE BATH OPERATION

The second step of the permanganate desmear process is an alkaline permanganate attack. The solution contains primary and secondary oxidizers plus an alkaline promoter (NaOH) for the process. The primary oxidizer ($KMnO_4$) is used to attack the dielectric material. The secondary oxidizer (NaOCl) is used to regenerate the permanganate. The permangante solution is agitated and operated at 160°F for desmear and at 180°F for etchback. Make-up solution composition and control range for desmear are given in Table 1.

Table 1
The Permanganate Bath Make-up and Control

	Make-up Concentration	Control Range
$KMnO_4$	60 g/l	55-60
NaOH (30% wt. concentration)	15 % vol.	14-17
NaClO(11% wt. concentration)	3 % vol.	0.7 A.F. min*
Water (DI or distilled)	80 % vol.	balance

* Controlled by A. F. (Activity Factor) = Active permanganate/Total permanganate. The activity factor maintained above 0.7 by adding the hypochlorite to regenerate active permanganate.

Daily chemical analysis of the bath solution is performed during the production period. Based on the analytical results, the bath is replenished with chemicals to maintain the solution within the control ranges. Production is not continuous, it is a batch operation.

Although the vendor claims the permanganate step is self-regenerating with no addition of permanganate and no build-up of manganese dioxide, the actual operation requires addition of permanganate and precipitates the dioxide. Further, the current production capacity reaches less than one-third of the claimed throughput of 20-25 m^2/L (800 - 1,000 ft^2/gal). Improvements in the process and process control were needed for higher productivity and quality with minimum additions of chemicals. The approaches for this study were:

(a) Understanding of permanganate chemical analysis and chemical reactions

(b) Process/Measurement capability study - Statistical Process Control (SPC)

(c) Process/Process control improvements

CHEMISTRY AND ANALYSIS OF PERMANGANATE/MANGANATE

For process control, a better understanding of the permanganate solution chemistry and current analytical methods is needed. The analytical methods include the chemical titration, spectrophotometry and spectroscopy. A synthetic bath solution was prepared in the laboratory and analyzed by the current titration method and a new ICP spectroscopic method. The results are summarized as follows.

Chemical Titration Method:

The current method of determining total ($KMnO_4$ and K_2MnO_4) and active ($KMnO_4$) permanganate oxidizer components is based on a chemical titration. The bath solution is reacted with an acidic potassium iodide solution and the free iodine liberated is titrated with standard thiosulfate solution for total permanganate. For determining the active permanganate component, the inactive manganate (K_2MnO_4) is removed from the solution by precipitation as barium manganate before titration. Based on the analytical results, it was concluded that the current titration method for determining total and active permanganate values is not accurate with up to 10% errors due to the following reasons:

(a) During the analytical titration, the hypochlorite (NaOCl, also $NaClO_3$ existing in basic solution) will also react with KI along with the main reactants of permanganate and manganate, resulting in higher values of total and active permanganate:

$$NaOCl + 2KI + H_2O \text{ ---> } NaCl + 2KOH + I_2 \quad (1)$$

$$2NaClO_3 + 6H_2SO_4 + 10KI \text{ ---> } Na_2SO_4 + 5K_2SO_4 + 6H_2O + Cl_2 + 5I_2 \quad (2)$$

$$Cl_2 + 2KI \text{ ---> } 2KCl + I_2 \quad (3)$$

The iodine generated in the above reactions (1), and (2) and (3), and in the main reactions from permanganate and manganate is then titrated with $Na_2S_2O_3$ to complete the titration method.

(b) Only two-thirds of the manganate is quantitatively titrated as permanganate due to a disproporationation reaction:

$$3K_2MnO_4 + 2H_2SO_4 \text{ ---> } 2KMnO_4 + MnO_2 + 2K_2SO_4 + 2H_2O \quad (4)$$

$$2KMnO_4 + 10KI + 8H_2SO_4 \text{ ---> } 2MnSO_4 + 6K_2SO_4 + 5I_2 + 8H_2O \quad (5)$$

The remaining one-third of the manganate precipitates as MnO_2 and does not react with KI during the analytical procedure.

(c) The permanganate solution has a limited stability. The permanganate decomposition can be catalyzed by light, heat, acids, bases, MnO_2 particles, nickel ion or cobalt ion[12-14]. The hypochlorite in the solution decomposes to release oxygen and chloride. Thus, a fresh bath solution prepared in the laboratory is unstable. The measured permanganate value, including the hypochlorite, decays rapidly over a period of 1-2 days, as shown in Figure 1. A similar decay of the permanganate value was exhibited in new production make-up baths in 1991 and 1992. The stability of bath solutions influences not only the accuracy, but also the precision in the chemical analysis. More detail about the precision is presented in the next section.

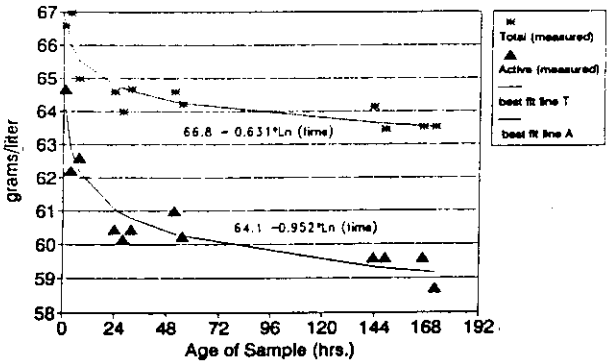

Figure 1 - Permanganate Concentrations in Bath Solution vs. Time

Spectroscopy:

A different method using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was developed in an attempt to provide a more accurate and precise method of determining total manganese. Table 2 indicates that the test data were about 1% below the true value for a pure permanganate solution, and about 4% below for the bath solution. Further development is needed to improve the method. This method could be used to determine the total manganese in both "total" permanganate solution and "active" permanganate filtrate which are prepared during the titration method.

Spectrophotometry:

The spectrophotometric method is very simple. It is based on the strong absorption of the light by permanganate at 525 nm (namometers or millimicrons) and a strong absorption of manganate at 605 nm. The sample is diluted and the absorbance measured at wavelengths of 525 and 605 nm with D.I. water as a reference. However, the method has shown to be unreliable.

Table 2 - Potassium Permanganate Concentration by ICP-AES

Sample No.	Bath Solution*	Control Solution**
1	54.63	39.58
2	58.60	39.81
3	55.12	39.58
4	57.53	39.67
5	57.99	39.87
6	55.84	39.32
7	54.92	39.93
8	55.95	40.01
9	57.68	39.73
10	55.81	30.73
Avereage =	57.455	39.72
Std. Dev. =	1.419	0.200

* The bath solution was prepared in laboratory with a make-up composition shown in Table 1.

** The control solution contained 40.09 g/l of $KMnO_4$ only (A.C.S. Reagent Grade).

PROCESS/MEASUREMENT CAPABILITY

Specification Range Estimate:

(a) A measurement capability study was conducted by duplicate measurement of ten samples taken from the permanganate production bath. The results of the study indicated that the measurement standard deviation for the total permanganate was $\sigma_m = 1.164$. A capable measurement system will have a variance that is only 5% of the total variance ($\sigma_m^2/\sigma_t^2 = 5\%$) when $\sigma_t = (USL - LSL)/8$. Following this guideline a measurement system with a standard deviation of 1.164 would be capable for this process if the specification range were 42 g/l. The range of 42 g/l was not realistic for the total permanganate. Thus, the assumption of 5% measurement variability for the permanganate operation is questionable. In some systems, it is acceptable to have a measurement variance that is 10% of the total variance. The correct assumption is unknown for the permanganate bath due to its limited stability of the solution and inaccurate titration method.

(b) A different assumption of eight sigma for the specification range was employed to re-calculate the specification range. The total or data standard deviations estimated from the above ten samples was $\sigma_t = 2.2$, which is very close to $\sigma_t = 2.19$ of the production data in 1991. The process standard deviation σ_p is calculated as

$$\sigma_p = (\sigma_t^2 - \sigma_m^2)^{1/2} = (2.2^2 - 1.164^2)^{1/2} = 1.87 \quad (6)$$

$$\text{Specification Range} = 8 * \sigma_p = 15 \text{ g/l} \quad (7)$$

$$\sigma_m^2 / \sigma_t^2 = 1.164 / 2.2 = 28\,\% \quad (8)$$

(c) The SPC control charts of X/movR for the 1991 production in Figure 2 gives the control limits UCL= 64.9, LCL= 53.2, X= 59 and movR= 2.19. A new specification range can be estimate:

$$\text{Specification Range} = (64.9 - 53.2) * 8\,\sigma_p / 6\,\sigma_p = 15.6 \text{ g/l} \quad (9)$$

$$\text{USL} = 59 + 15.6/2 = 66.8 \text{ g/l} \quad (10)$$

$$\text{LSL} = 59 - 15.6/2 = 51.2 \text{ g/l} \quad (11)$$

$$\sigma_p = \text{movR}/1.128 = 2.19/1.128 = 1.9 \quad (12)$$

(d) In conclusion, the present permanganate process is capable in a specification range of 51 - 67 g/l, and in control at the mean of 59 g/l with a process standard deviation of 1.94. Thus, the control range specified in Table 1 should be adjusted accordingly.

Precision for Total and Active Permanganate:

Based on a synthetic solution prepared in the laboratory, the permanganate concentrations change with time. As a result, the measurements taken may not be as repeatable or as reliable as desired. An exponential decay model provided a good fit to both the total and active permanganate in Figure 1 is given in Table 3.

The value for R^2 is the percent of the variation that is accounted for by knowing the age of the sample. Values greater than 80% indicate a strong correlation between time and the measurement. The standard deviation listed is with respect to the fitted curve. In other words, at a given point in time the standard deviation for total permanganate is 0.47 and for active permanganate is 0.54, resulting in the analytical precision of about 1 g/l (= 2 * std. dev.). It is interesting to note that if the measurement data were analyzed without considering the time effect, the standard deviation is 1.13 for the total permanganate which is very close to the $\sigma_m = 1.164$ from the previous measurement capability study for the production samples. Thus, the precision of 1 g/l can be reached if the time effect is considered during the sampling and analysis.

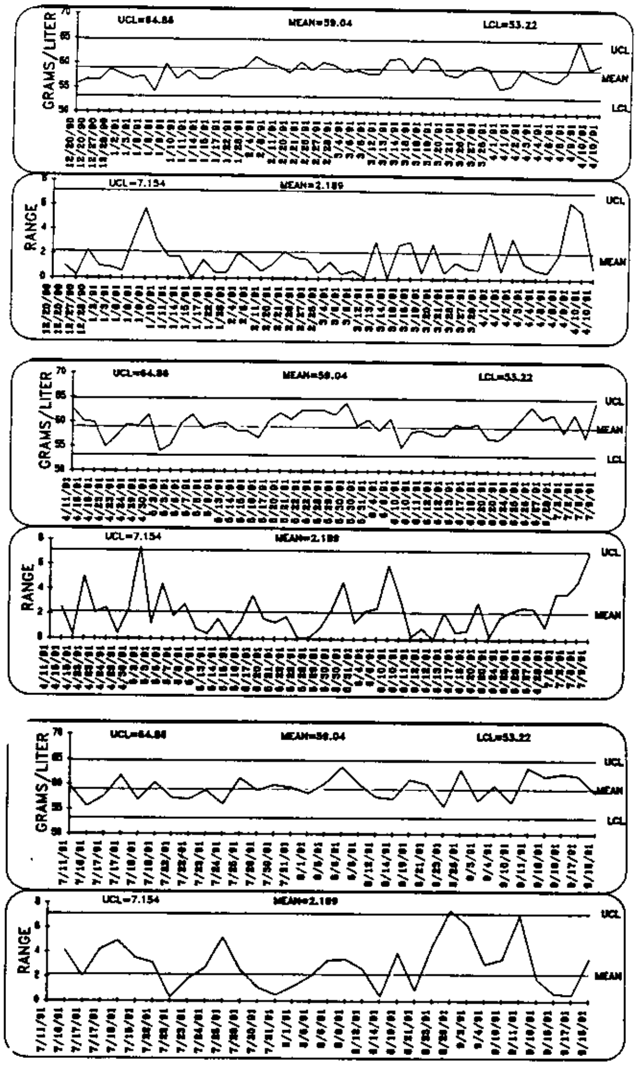

Figure 2 - Control Charts of X/movR for Total Permanganate in 1991 Production Bath

Additional measurements were taken 27 days later from the same samples. The results of this test were consistent with the predicted value according to the models. In both cases, the difference between the measurement and the prediction is within the expected error (±1 g/l) based on the standard deviation from the fitted curves.

Table 3 - Best-Fit Model for Total and Active Permanganate

Best-fit Model	R^2	Std.Dev.	27 days later Measured	27 days later Predicted
Total Permanganate = 66.8 - 0.631 * Ln(time)	82.3%	0.47	62.13	62.69
Active Permanganate = 64.1 - 0.952 * Ln(time)	89.1%	0.54	57.71	57.90

The current SPC control charts and above proposed specification range for total permanganate could be improved further by changing the procedures of sampling, hypochlorite addition, and bath make-up. Details of the process control improvements are discussed in the next section.

PROCESS/PROCESS CONTROL IMPROVEMENTS

The schemes for better process controls and process improvements are summarized as follows:

Better Utilization of Regenerator:

Problem: The current practice of batch addition of the hypochlorite (2 to 6 liters) to the bath (200 liters) at the end of the day shift does not provide an efficient chemical regeneration of permanganate due to the low ambient temperature overnight. Further, a portion of the hypochlorite is decomposed into sodium chloride and oxygen immediately, which releases to the air in form of bubbles. This hypochlorite is wasted, and its by-product increases the NaCl concentration which deters the chemical regeneration:

$$2K_2MnO_4 + NaOCl + H_2O \longleftrightarrow 2KMnO_4 + NaCl + 2KOH \quad (13)$$

$$[MnO^-_4] = \frac{[MnO_4^{-2}]}{[OH^-]} \left\{\frac{k[ClO^-]}{[Cl^-]}\right\}^{1/2} \quad (14)$$

The equilibrium equation indicates that the increase of NaCl concentration will decrease the concentration of permanganate. The k in equation (14) is the equilibrium constant.

Solution: For better utilization of the regenerator, metered addition of the hypochlorite over a few hours should be conducted at the operating temperature of 160°F to foster the permanganate regeneration[7,8,11]. In addition, other benefits of this approach are:

(a) It stabilizes the permanganate/managanate concentrations and chemical analysis to improve the analytical results.

(b) It avoids dilution due to the batch addition (up to 3% for 6 liters addition) and improve the analytical accuracy.

(c) It reduces the excess addition of the hypochlorite and slow down the build-up of NaCl concentration. This will favor the regeneration and prolong the bath life.

Periodic Removal of Manganese Dioxide[7-11]:

Problem: It has been known that the manganese dioxide precipitated during the desmearing operation will catalyze the decomposition of the permanganate solution. Thus, the dioxide particles should be removed from the solution to prevent further decomposition of the permanganate. In addition to MnO_2, trace nickel and cobalt ions in the solution will actively assist the decomposition, while the tellurate ion provides the inhibitive effect on the decomposition[12].

Solution: A filtration test for the removal of dioxide particles was conducted in one of the permanganate bath operation. After two months of regular operation, the periodic filtration (average 6 hours per week) was initiated. The results of the two months filtration showed that the bath life was doubled by increasing production from about 13m^2 to over 25m^2 of total surface area. Therefore, periodic filtration of the bath solution to remove manganese dioxide particles and sludges should be used to enhance bath life and performance. As a result, it also reduces the disposal of hazardous wastes.

Sampling:

Problem: The sampling procedure will affect the chemical analysis. The hypochlorite solution,about 2 - 6 liters,was batch-added to the bath at the end of the shift and stayed at lower temperature overnight. After the bath was heated up to 160°F next morning, a sample was taken for analysis. The regeneration reaction is not effective at low temperature and a portion of the hypochlorite is not reacted. The permanganate solution is in the metastable state. The chemical analysis of the total and active permanganate will pick up the unreacted hypochlorite and give inaccurate results. Thus, the sample does not represent the bath solution under actual production conditions.

Solutions: Meter the addition of the hypochlorite during production to reduce/eliminate unreacted hypochlorite in the bath. Take samples at end of the production run to ensure no presence of unreacted hypochloride.

Liquid Level:

Problem: The permanganate bath is operated at a high temperature 160°F that causes a high evaporation rate. If the liquid level drops 2.5 - 5 cm (1 - 2 in.), it affects the liquid volume 7.5 to 15 liters. As a result, analytical results will be 3.5 to 7% higher than the samples taken at the correct liquid level. Such analytical errors should be eliminated.

Solution: Install an automatic water feeding device to maintain the liquid level continuously.

Make-up New Bath:

Problem: The laboratory results indicate that the permanganate concentrations (Total and Active) in a fresh bath of solution will decrease with time. The most rapid changes occurred during the first 1 - 2 days after the solution was prepared as shown in Figure 1. The rapid decreases were also observed in the production baths during the first 7 to 12 days after each of the make-up baths was prepared. The initial decrease of the permanganate values may be caused by the decomposition of the hypochlorite which was present in the make-up. This hypochlorite is wasted and its by-product NaCl is harmful for regeneration of the permanganate.

Solution: The hypochlorite should not be added to the solution make-up[8,10,11]. It should be saved to use for the chemical regeneration later. Metered addition of the hypochlorite could be initiated as soon as a production run starts. The SPC control charts will be improved due to the absence of undesired data points from first few days.

Alternative Regenerators:

(a) Chemical Regenerator: Use of a different chemical (peroxodisulfate or persulfate) to replace the hypochlorite will perform more efficient in regeneration of permanganate[8,11,15]. The by-product of this generator is Na_2SO_4, which will precipitate as decahydrate crystal $Na_2SO_4 .10H_2O$ on cooling of saturated solution. Periodic removal of the crystals will provide about ten times the bath life using the hypochlorite[1]. Further, the sulfate-based generator does not require expensive titanium or Teflon tanks and auxiliary equipment.

(b) Electrolytic Regenerator: This regenerator can eliminate the need for a chemical regenerator. It regenerates soluble manganate[16-18] and insoluble manganese dioxide[19] in the bath solution back into the permanganate by electrolysis. It prevents dioxide particles from accumulating, eliminates the filtration and extends the bath life. The recent trend has been changing from chemical regeneration to electrolytic regeneration for desmear/etchback operations.

SUMMARY

The present chemical titration method for determining the total and active permanganate in desmear/etchback solutions with chemical regenerators is not reliable (up to 10% errors) due to the presence of unreacted regenerator and limited stability of the permanganate solution. The ICP-AES method appears to be more accurate, but needs further development. Understanding of permanganate chemistry and analytical procedures help diagnose problems and trouble-shooting.

The SPC process/measurement capability study has resulted in a realistic specification range for the total permanganate concentration (15 g/l) using the control charts of X/movR or eight sigma. The conventional assumption of measurement variance that is 5-10% of total variance was not applicable to the permanganate bath operation.

The schemes for various process controls for better control of the permanganate bath, along with process improvements have been summarized in this paper.

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