

pally by the electrode material, an area in which they have considerable expertise.

In addition to its use as a possible battery separator, the honeycomb structure can also be used for the construction of a fuel cell. The material from which the honeycomb is made need not be ceramic (although the ceramic allows high temperature processing of the electrode materials on the honeycomb before use) but must be an insulator, resistant to acid or base, and the walls must be porous. It is thought that the use of the honeycomb structure could reduce the cost of fuel cell construction.

Because the pore structure of the walls is small ( $\sim 10\mu$ ) in size (1) the wicking action of the walls will cause the electrolyte to fill the pores.

In fuel cell use, each alternate passageway of the honeycomb would contain either fuel or oxidant. A plastic header attached to one end of the honeycomb is necessary to distribute the fuel and oxidant to the required passageway. The walls of the passageway would have to be coated with a catalytic material to promote the electrode reactions. This can be done by a simple dip procedure such as is used in applying a catalytic washcoat to the honeycomb for auto exhaust service. For the fuel cell, a washcoat would be a conductive electrode catalyst. If necessary, a different washcoat could be applied to different channels by the use of a suitable plug to block off alternate passageways.

In the case of fuel cells, however, the particle size of the washcoat as compared to the honeycomb pore size is quite critical. If the washcoat particle size is too small, it will penetrate from one side of the passageway wall to the other through the pores. Since the electrode catalyst must possess electrical conductivity, it may give a partial short to the fuel cell. If the washcoat particle size is too large, it may not adhere well. This problem can be alleviated by applying a coarse particle washcoat to the honeycomb of the honeycomb material and resintering to give a passageway wall of dual pore size, the outer layer having the larger pores to accommodate and hold a large particle size electrode catalyst.

It is necessary to make electrical contact to the washcoat by means of a small metal wire inserted into each

opening with every other wire connected together. If the electrode catalyst is poorly conducting, a highly conductive washcoat would have to be applied before applying the electrode catalyst. In this case electrical connection need only to be made at one end of the passageway.

*Fuel cell.*—Two adjacent honeycomb cells, 1.1 mm inside size, of a Corning corderite honeycomb of  $\sim 47$  openings per  $\text{cm}^2$  with a 250 micron wall thickness, and a length of 3.8 cm were sealed with collodion and coated with a slurry of Ni powder (Sheritt NF-1M-P240) in water, and sintered in  $\text{H}_2$  at  $850^\circ\text{C}$  for 1 hr. This gave an adherent, porous, and very conductive Ni coating to the inside of the passageways. NiO powder would be just as effective as Ni since it reduces to Ni. A mixture of NiO + MgO could also be used so that after reduction the MgO could be leached out with acid to give a more porous Ni coating. The honeycomb structure withstands the high temperature exposures without any difficulty.

A chloroplatinic acid solution ( $8\text{ mg/cm}^3$ ) was added to the Ni containing honeycomb until the honeycomb walls were wet and then the honeycomb was dried at  $110^\circ\text{C}$ .

$\text{H}_2$  was passed through one passageway and air in the surrounding passageways. The electrolyte was 25% NaOH solution in the passageway walls. The open-circuit voltage was  $\sim 1\text{V}$  and the short-circuit current was  $\sim 19\text{ mA}$ .

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Note Added in Proof: It has been brought to the authors attention that a somewhat similar structure for a Zn-AgO and a Zn-air battery has been proposed by F. C. Arrance and C. Berger (USP 3647 542 and 3661 644).

## An Electrochemical Control System for Electroless Copper Bath

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Electroless deposition of copper was studied from the chemical (1-3), electrochemical (4-7), kinetic (7, 8-16), and mechanistic (4-7, 17-22) aspects. The subject was reviewed in a number of articles (23-26) and books (27, 28). The number of chemical and electrochemical publications on electroless deposition of copper is relatively small (about twenty-two papers in the period 1948-1979) The number of publications is even smaller when automatic analysis and control of a production electroless copper bath is considered.

So far, as we know, there is no published paper describing a complete control system (an automatic analyzer) for the analysis of the composition and performance of the production electroless copper bath. The published papers on this subject describe only control of limited number of variables, the rate of

deposition (29-31), and concentration of some reacting components (32). However, more complete control systems have been described at the fall meetings of The Electrochemical Society, 1976 (32, 33), and 1978 (34-36), and a brief description of these systems is available in the form of extended abstracts.

The subject of this paper is the application of electrochemical methods of analysis in study and control of the electroless copper bath. Duration of an electrochemical analysis is in the range of milliseconds, or seconds. This short time of analysis makes these methods very attractive.

Chronopotentiometry (37, 38), voltametry (4, 19, 20, 22, 38-40), and polarography (32) can be used to analyze (manually or automatically) an electroless copper bath. Polarographic method has been applied successfully for analysis of copper, formaldehyde, and cyanide (32, 34). This paper describes the applications of chronopotentiometry and voltametry (developed

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Key words: copper, formaldehyde, electroless plating, chronopotentiometry, sodium 2-mercaptobenzothiazole

1968-1971) in the study and control of the electroless copper bath. The same techniques can be used to analyze electroless deposition of other metals.

### Experimental

An all-glass, two (or single) compartment cell with three electrodes was used. Platinum sheets of 1.1 cm<sup>2</sup>, electroplated with copper, served as cathode and anode. Plating was done in an acid copper solution (CuSO<sub>4</sub> · 5H<sub>2</sub>O-188 g/liter, H<sub>2</sub>SO<sub>4</sub>-74 g/liter) at 10 mA/cm<sup>2</sup> for 5 min. A saturated calomel electrode (SCE), in a separate reference electrode compartment (at room temperature), was employed as a reference electrode. A platinum sheet electroplated with copper in a single compartment cell can be used as a reference electrode.

An EDTA (ethylenediaminetetraacetic acid) type electroless copper bath was used for these studies. This bath (41) contained: Na<sub>4</sub>EDTA-52 g/liter, CuSO<sub>4</sub> · 5H<sub>2</sub>O-9-12 g/liter, CH<sub>2</sub>O-5-10 ml (37%)/liter, NaCN-1-30 mg/liter, and NaOH to the desired pH. The solutions were prepared with analytical grade reagents and deionized water.

The mixed potential was measured with a vacuum tube voltmeter (pH meter) using the SCE as a reference electrode.

The voltammograms were obtained with a PAR (Princeton Applied Research, Princeton, New Jersey) Model 174A Polarographic Analyzer, and the current-voltage curves recorded on a Houston Instruments (Austin, Texas) Model RE0074 X-Y Recorder.

The chronopotentiograms were obtained with a transistorized constant current power supply, made in this laboratory. The potential-time curves were recorded on the Tektronix 564B storage oscilloscope. Oscilloscope traces were photographed with a Polaroid Camera C-27.

### Results and Discussion

**Chronopotentiometric determination of cupric ions.—Chronopotentiograms.**—A typical chronopotentiogram for the reduction of cupric ions in the EDTA bath is shown schematically in Fig. 1. The starting potential of the chronopotentiogram is the mixed potential,  $E_{mp}$ . The current is switched on at the time  $t = 0$ . Reduction of cupric ions with measurable rate starts at the potential  $E_{t=0}$  (defined according to Fig. 1). At the transition time  $\tau$  the concentration of cupric ions at the electrode equals zero and the potential is  $E_{\tau}$ .

After the elapse of time  $\tau$  a part of the current at the test electrode is used for charging the double layer until the potential reaches the value when water is reduced.

The characteristic potentials of a chronopotentiogram at 20 mA/cm<sup>2</sup>, 68°C, pH 11.90, 9.0 g/liter CuSO<sub>4</sub> ·

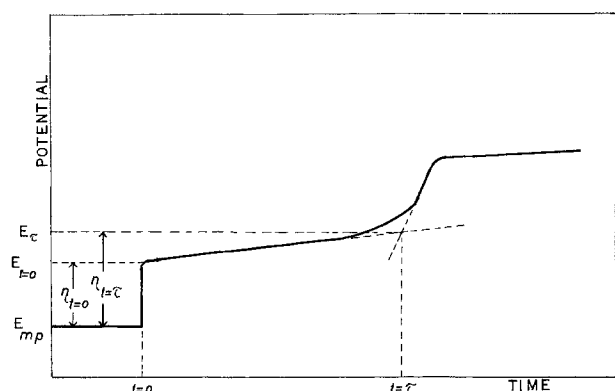


Fig. 1. Variation of the potential of the test electrode with time in cathodic chronopotentiometry of the EDTA electroless copper bath.

5H<sub>2</sub>O, 5.5 ml/liter CH<sub>2</sub>O are:  $E_{mp} = -0.78$ ,  $E_{t=0} = -1.06$ , and  $E_{t=\tau} = -1.24$  V vs. SCE.

**Reproducibility of transition time measurements.**—Change of potential in the vicinity of transition time is fast and large. This large increase of potential allows very precise determination of the transition time. The reproducibility studies on 27 chronopotentiograms show that the transition time of 0.87 sec can be reproduced with a  $\pm 0.02$  sec deviation from the mean value.

**Transition time as a function of cupric ion concentration.**—Dependence of the transition time on the concentration of CuSO<sub>4</sub> was studied at pH 11.70, 11.80, and 11.90. When the concentration of CuSO<sub>4</sub> · 5H<sub>2</sub>O varies from 9 to 12 g/liter, the transition time varies from 0.38 to 0.84 sec. The plot of  $\tau^{1/2}$  vs. the concentration is shown in Fig. 2. It is seen from Fig. 2 that  $\tau$  depends considerably on pH.

**Chronopotentiometric determination of formaldehyde.—Chronopotentiograms.**—Anodic chronopotentiogram at 4.5 mA/cm<sup>2</sup> at a copper anode exhibits two steps. A typical chronopotentiogram is shown schematically in Fig. 3. The starting potential of a chronopotentiogram is the mixed potential of the copper electrode,  $E_{mp}$ . The transition time  $\tau_2$  is measured from the first transition time,  $\tau_1$ , to the second inflection point. Oxidation in the first step starts at the potential  $E_1$  which is about +0.13V with respect to the mixed potential at the bath composition given for the cathodic chronopotentiograms. At the transition time  $\tau_1$  and  $\tau_2$  the potential is +0.21 and +0.33V with respect to the mixed potential, respectively. It is seen that there is a clear distinction between these two steps.  $E_2$  is +0.22V with respect to the mixed potential.

**Transition time as a function of formaldehyde concentration.**—The dependence of transition time on the

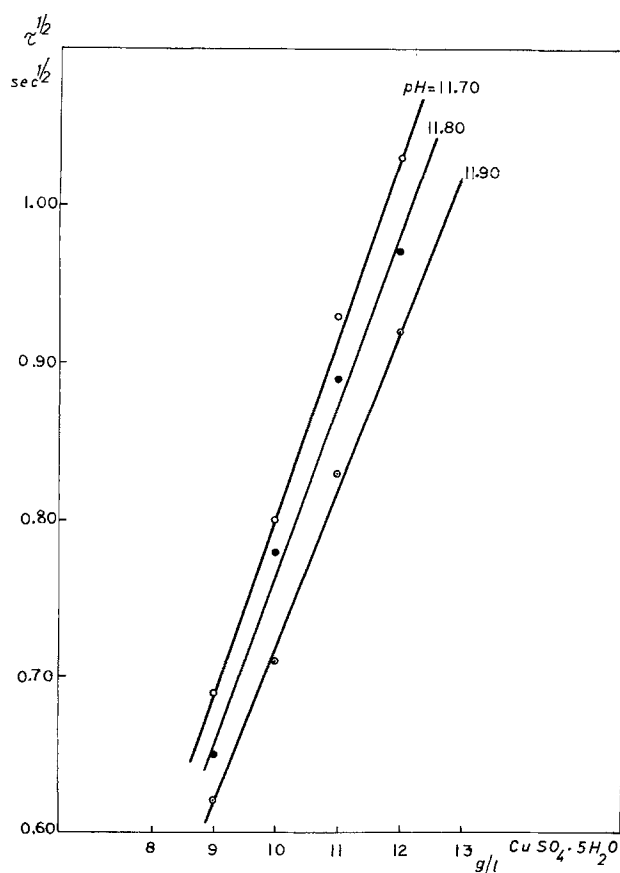


Fig. 2. Variation of  $\tau^{1/2}$  with CuSO<sub>4</sub> · 5H<sub>2</sub>O;  $i = 20.0$  mA/cm<sup>2</sup>, 68°C.

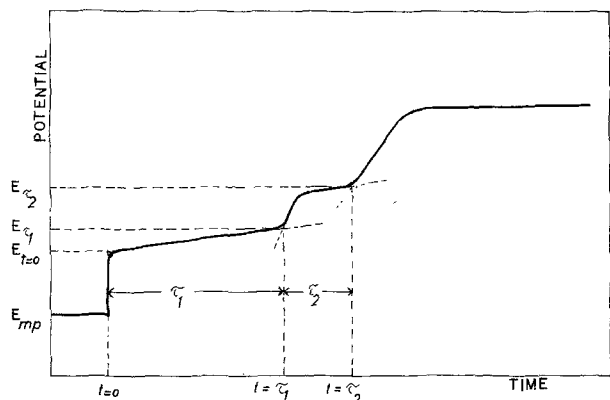


Fig. 3. Variation of the potential of the test electrode with time in anodic chronopotentiometry of the EDTA electroless copper bath.

concentration of formaldehyde in the bath is shown in Fig. 4. It is seen that for constant conditions when only the formaldehyde is a variable,  $\tau_1^{1/2}$  and  $\tau_2^{1/2}$  are proportional to the concentration of formaldehyde in the solution. Transition times  $\tau_1$  and  $\tau_2$  show differences in the following properties: the transition time  $\tau_1$  depends, and  $\tau_2$  does not, in practical limits, on the concentration of other components of the bath; the rate of change of the transition time  $\tau_1$  with the concentration of formaldehyde,  $\Delta\tau_1/\Delta C$  ( $\text{CH}_2\text{O}$ ) is faster than that for  $\tau_2$ ;  $\tau_2^{1/2}$  is proportional to the concentration of formaldehyde in the bath, irrespective of the concentration of additives (in practical limits) and  $\tau_1^{1/2}$  is proportional to the formaldehyde concentration only if other components of the bath are constant.

On the basis of the above observations, our present interpretation is that the first step in the anodic chronopotentiogram ( $\tau_1$ ) is due to oxidation of adsorbed species ( $\text{H}$ ,  $\text{CH}_2\text{O}^-$ ), or simultaneous oxidation of adsorbed and diffusing species (since the first step is sloping and not horizontal); the second step ( $\tau_2$ ) is due to oxidation of diffusing species. If the value of  $\tau_1$  depends on the amount of adsorbed formaldehyde, or adsorbed and diffusing formaldehyde, it could be a measure of the activity of the bath. The transition time  $\tau_1$  reflects the status of the competitive adsorption between additives, fragments of the dissociative adsorp-

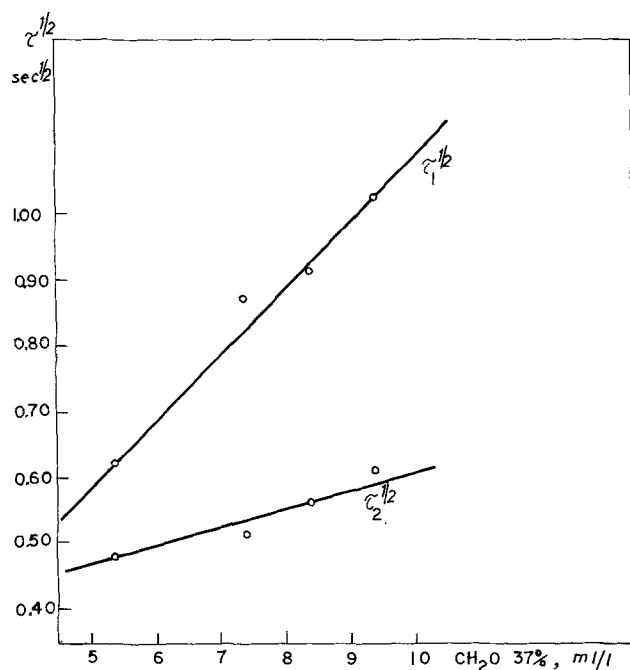


Fig. 4. Chronopotentiometric  $\tau^{1/2}$  function for the first and second transition time;  $i = 4.5 \text{ mA/cm}^2$ ,  $68^\circ\text{C}$ .

tion of formaldehyde ( $\text{H}$ ,  $\text{CH}_2\text{O}^-$ ),  $\text{OH}^-$ , ligand, complexed copper ions, and water. Situation at the electrode is even more complicated due to the partial oxidation of formaldehyde,  $\text{Cu}$  to  $\text{Cu}_2\text{O}$ , starting at  $-0.54 \text{ V}$  vs. SCE. Since  $E_2$  is about  $-0.45 \text{ V}$  vs. SCE, it follows that oxidation of formaldehyde in the time interval  $\tau_2$  occurs at the partially oxidized surface.

**Adsorption effects.—Absence of additives.**—At  $20 \text{ mA/cm}^2$  and higher current densities chronopotentiograms show only one transition time due to the anodic oxidation of formaldehyde. This transition time will be called  $\tau$ . The two transition times,  $\tau_1$  and  $\tau_2$ , are recorded at current densities lower than  $20 \text{ mA/cm}^2$ .

Variation of  $\tau$  with the current density  $i$  can be used to estimate the amount of the adsorbed electroactive species (37). The transition time  $\tau$  varies from 5 to 41 msec when the current density varies from 20 to  $87 \text{ mA/cm}^2$ . The linear relationship was obtained for the plot of  $i\tau$  vs.  $1/i$  and  $i\tau$  vs.  $\tau^{1/2}$ . Since both functions yield a straight line, it is not possible to make a conclusion on the mechanism of reactions, but it is possible to estimate the surface concentration of formaldehyde,  $\Gamma$ , from the intercepts (42).  $\Gamma$ , estimated from the intercepts, as a function of pH is shown in Fig. 5.

**Presence of additives.**—Effect of additives can be studied by recording potential time curves in the milliseconds (msec) or microseconds ( $\mu\text{sec}$ ) range. In the msec range the usual chronopotentiograms exhibit the transition time, whereas in the  $\mu\text{sec}$  range the linear relationship, with the slope characteristic of the double layer capacity, is obtained.

**Chronopotentiograms.**—The partial coverage of the electrode by the adsorbed addition agents that are neither reduced nor oxidized at the electrode causes an increase in the actual current density  $i$  due to a decrease in the available surface area  $A$  ( $i = I/A$ , where  $I$  is the current). An increase in current density causes a decrease in  $\tau$ . This change in the available surface area and the resulting change in the transition time is

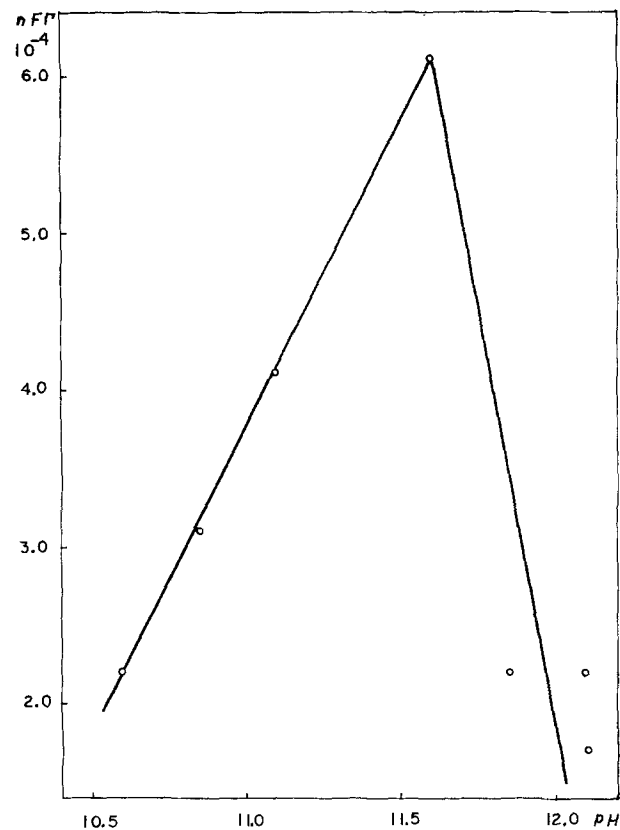


Fig. 5. The surface concentration of formaldehyde ( $\Gamma$ ) as a function of pH.

a function of the bulk concentration of the addition agent. Thus, by determining the change in the transition time  $\Delta\tau = \tau^\circ - \tau$ , where  $\tau^\circ$  is the transition time in the absence, and  $\tau$  in the presence of the adsorbed additive, one can obtain information on adsorption conditions at the electrode and, under certain conditions, the bulk concentration of the addition agent (43).

The difference  $\Delta\tau$  caused by 30 mg/liter of NaCN, in the absence of other additives, at pH 11.60 and 12.10 is 51 and 9 msec, respectively. The difference  $\Delta\tau$  caused by the adsorption of sodium 2-mercaptobenzothiazole as a function of pH is shown in Fig. 6.

**Double layer capacity.**—Galvanostatic potential time curves in the microseconds range can be used to estimate level of additives in an electroless bath (38). The slope of the recorded linear potential-time relationship is related to the electrode double layer capacity,  $C_{dl} = i(dt/dV)$ . Double layer capacity for the EDTA electroless copper bath varies from 200  $\mu\text{F}/\text{cm}^2$ , for the bath in the absence, to 100  $\mu\text{F}/\text{cm}^2$  in the presence of additives. Double layer capacity for the supporting electrolyte and the ligand only, e.g., 0.01M  $\text{Na}_2\text{SO}_4$ , and 0.01M EDTA at pH 13.0 and 70°C, is 58.8  $\mu\text{F}/\text{cm}^2$ .

**Polarization resistance.**—The current-potential relationship in the range of the mixed potential (e.g., from  $/E_{mp}/-50$  to  $/E_{mp}/+50$  mV) can be used for testing of the presence of impurities or general activity of the bath. In the vicinity of the mixed potential, the current-potential relationship is linear. The slope of this linear plot (44), the polarization resistance ( $R_p = (d\eta/di)_{i=0}$ ), can be used as a characteristic parameter of a bath. An EDTA electroless copper bath plating at the mixed potential of  $-530$  mV vs. SCE had the polarization resistance of 128 $\Omega$ . The same bath after contamination showed the polarization resistance of 4200 $\Omega$ . The potential sweep in these measurements was 1 mV/sec.

### Summary

The data presented in this note show that the chronopotentiometry and voltametry can be used to analyze and control the operation of an electroless copper bath.

In our preliminary investigations the complete chronopotentiograms have been recorded. However, in the analytical applications this is not necessary. It is sufficient to detect the transition time only. This can be done automatically (45) by introducing a time interval counter into the electrolysis circuit. In automatic determination of the transition time, the electrolysis and the counter are started simultaneously by means of a switch. Electrical signal for the counter, to terminate counting, can be the potential of the test

electrode at which the transition time is measured or the peak value of the first derivative curve at the transition time. The reading at the counter directly gives the transition time. The scale of the timer can be calibrated directly in concentrations of the species being determined.

An instrument based on the above-presented principles was constructed and used in the control of the production electroless copper bath. This control system is applicable to other electroless and electroplating baths.

It was shown that the transition time values for a specific bath component depend on pH and the concentration of other components of the bath. For this reason, it is necessary to have for each component a family of curves corresponding to the specific set of other parameters. A microprocessor, or a computer, can select the correct value of the observed component and use this value for the bath control instructions.

### Acknowledgments

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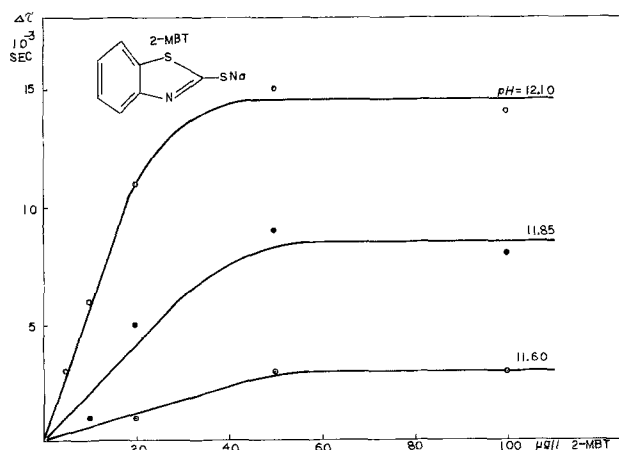


Fig. 6. Change of  $\Delta\tau$  with the concentration of sodium 2-mercaptobenzothiazole (2-MBT).

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