

## THE EFFECT OF Cu ADATOMS UPON THE ELECTROCHEMICAL PROPERTIES OF GOLD

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### ABSTRACT

In the present study the electrocatalytic effect of Au-Cu couple upon the propanol oxidation by depositing Cu adatoms on Au substrate. Alcohol oxidation does not take place on Cu anode.

### INTRODUCTION

There is a definite relation between the electrocatalytic processes and the structure of the electrode material. The electronic character of the electrode surface was shown to change significantly by the deposition of a monolayer of foreign metal atoms (Rand and Woods, 1973). The electrodeposition of a monolayer of foreign metal atoms before the equilibrium potential is the result of the strong interaction between the band structure of the electrode metal and the adsorbed atoms. Although the nature of such layers is yet to be fully enlightened they are known to be consisted of partially charged adsorbed atoms (Schultze and Vetter, 1973). (Schultze and Koppitz, 1976). There are intensive studies currently being carried out upon this subject.

### EXPERIMENTAL

The experiments were carried out by using cyclic voltammetry.

The apparatus used in obtaining the *i*-*E* profiles was described in our previous study (Bilgiç and Kabasakaloğlu 1986). The voltage scan rate was chosen as 50 mV/s for acidic and 5 mV/s for basic media. The experiments were carried out in a three compartment cell made with pyrex glass. The reference electrode employed, was saturated calomel (Tacussel S 09405) and the working and the auxiliary electrodes were Au and Pt respectively. All the potentials measured against the calomel electrode were given against hydrogen electrode.

The electrode was pretreated as follows. In order to obtain the reproducibility of the experiments the electrode was first oxidized at 1650 mV for 10 minutes and then reduced at 300 mV for 10 minutes in 1N H<sub>2</sub>SO<sub>4</sub>. The gold electrode deposited with Cu adatoms was prepared by applying various potential various times to the pure gold electrode in a solution of 1N H<sub>2</sub>SO<sub>4</sub> + x M CuSO<sub>4</sub>. The solution was bubbled with N<sub>2</sub> for ten minutes prior to the experiment till the electrode reached the equilibrium potential in this medium. The N<sub>2</sub> gas was passed through the cell throughout the experiment.

## RESULT AND DISCUSSION

In this study first the effect of Cu adatoms upon the characteristic i-E curves of Au was investigated. As seen in Table I the potentials at which the cathodic currents begin to pass and the peak potentials are similar to those curves obtained in 1 N H<sub>2</sub>SO<sub>4</sub>.

Table I. The potential and current values obtained from the i-E curves of Au electrode in 1 N H<sub>2</sub>SO<sub>4</sub> + xM CuSO<sub>4</sub> (x= 0, 10<sup>-6</sup>, 10<sup>-5</sup>, 10<sup>-4</sup> and 10<sup>-2</sup> M).

	E <sub>p'a</sub> (mV)	E <sub>p'c</sub> (mV)	i <sub>p'a</sub> (μA)	i <sub>p'c</sub> (μA)
1 N H <sub>2</sub> SO <sub>4</sub>	1390	1290	45	180
1 N H <sub>2</sub> SO <sub>4</sub> + 10 <sup>-6</sup> M CuSO <sub>4</sub>	1370	1280	42	180
1 N H <sub>2</sub> SO <sub>4</sub> + 10 <sup>-5</sup> M CuSO <sub>4</sub>	1390	1280	45	200
1 N H <sub>2</sub> SO <sub>4</sub> + 10 <sup>-4</sup> M CuSO <sub>4</sub>	1370	1280	48	150
1 N H <sub>2</sub> SO <sub>4</sub> + 10 <sup>-2</sup> M CuSO <sub>4</sub>	1370	1290	44	156

The i-E curves obtained are plotted in Figure 1. If one choose x as 10<sup>-6</sup> M and 10<sup>-5</sup> M one can see that although the current peaks in anodic and cathodic peaks remain unchanged, there are marked changes below 650 mV as the concentration of CuSO<sub>4</sub> increases. Figure 2 shows the i-E curve obtained in 1 N H<sub>2</sub>SO<sub>4</sub> + 10<sup>-4</sup> M CuSO<sub>4</sub>.

The current-potential curve obtained in 1 N H<sub>2</sub>SO<sub>4</sub> + 10<sup>-4</sup> M CuSO<sub>4</sub> + 10<sup>-2</sup> M Prop (1) is shown in Figure 3. But curves are similar in other words there are no changes in the shapes of the curves by the addition of propanol. In fact there is no oxidation taking place in 1 N H<sub>2</sub>SO<sub>4</sub> + xM Prop(1).

Figure 4 shows the i-E profile obtained in 1 N H<sub>2</sub>SO<sub>4</sub> + 10<sup>-2</sup> M CuSO<sub>4</sub>. As seen from the potential although there are no change in the region above the equilibrium potential there are two regions (monolayer and multilayer) below this potential. Thus the increase in CuSO<sub>4</sub>

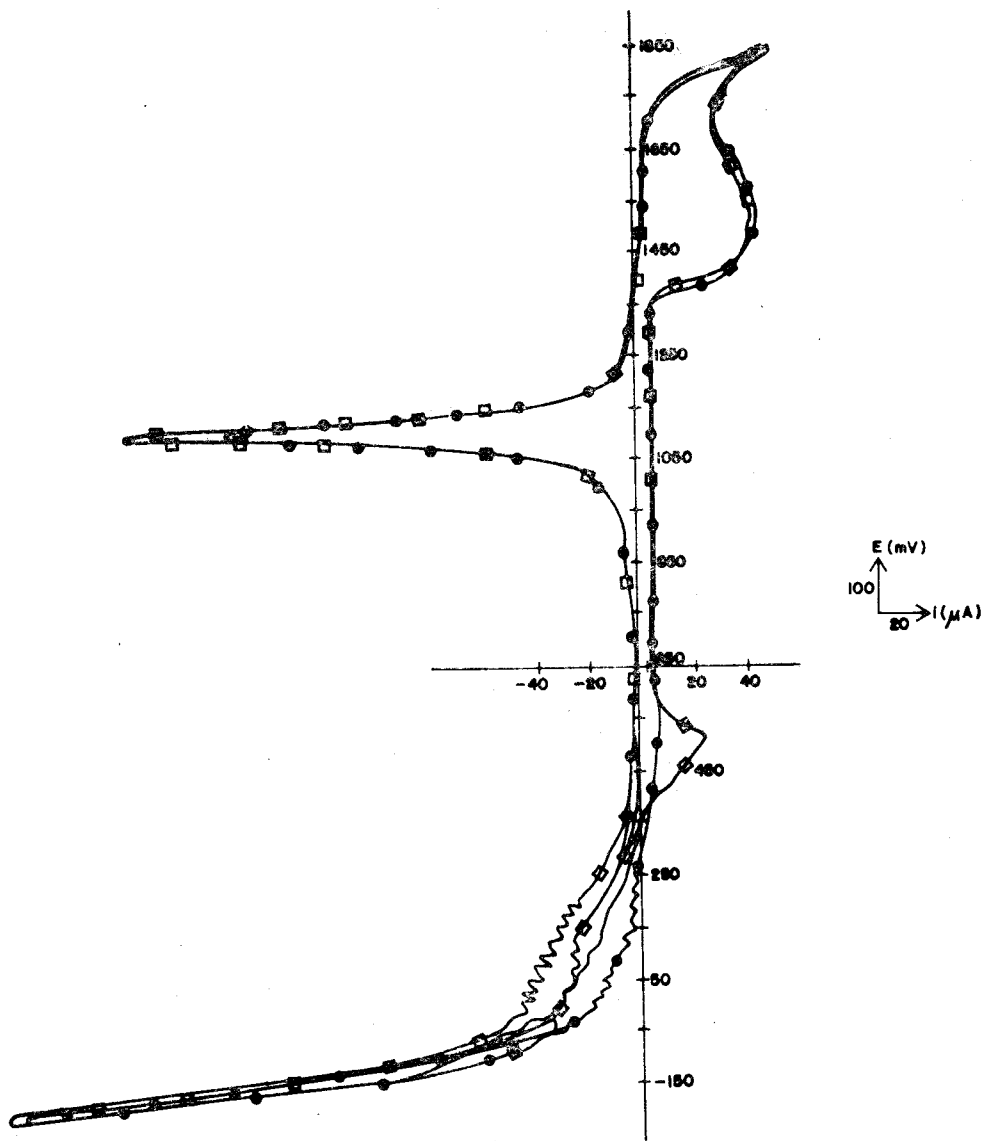


Fig. 1. The  $i$ - $E$  curves of Au electrode obtained in  $1 \text{ N H}_2\text{SO}_4 + x \text{ M CuSO}_4$ . (●)  $10^{-6} \text{ M CuSO}_4$ , (□)  $10^{-5} \text{ M CuSO}_4$

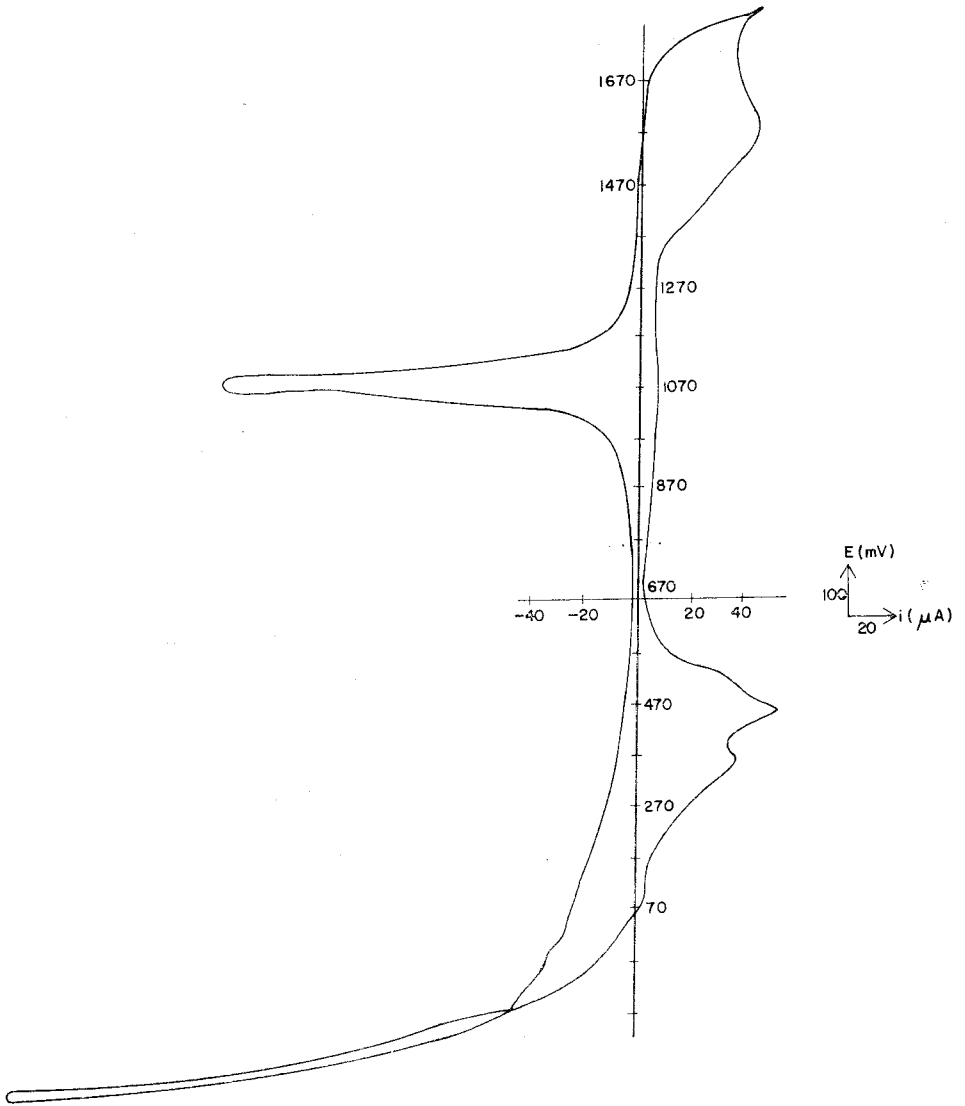


Fig. 2. The  $i$ - $E$  curve of Au electrode obtained in  $1\text{ N H}_2\text{SO}_4 + 10^{-4}\text{ M CuSO}_4$ .

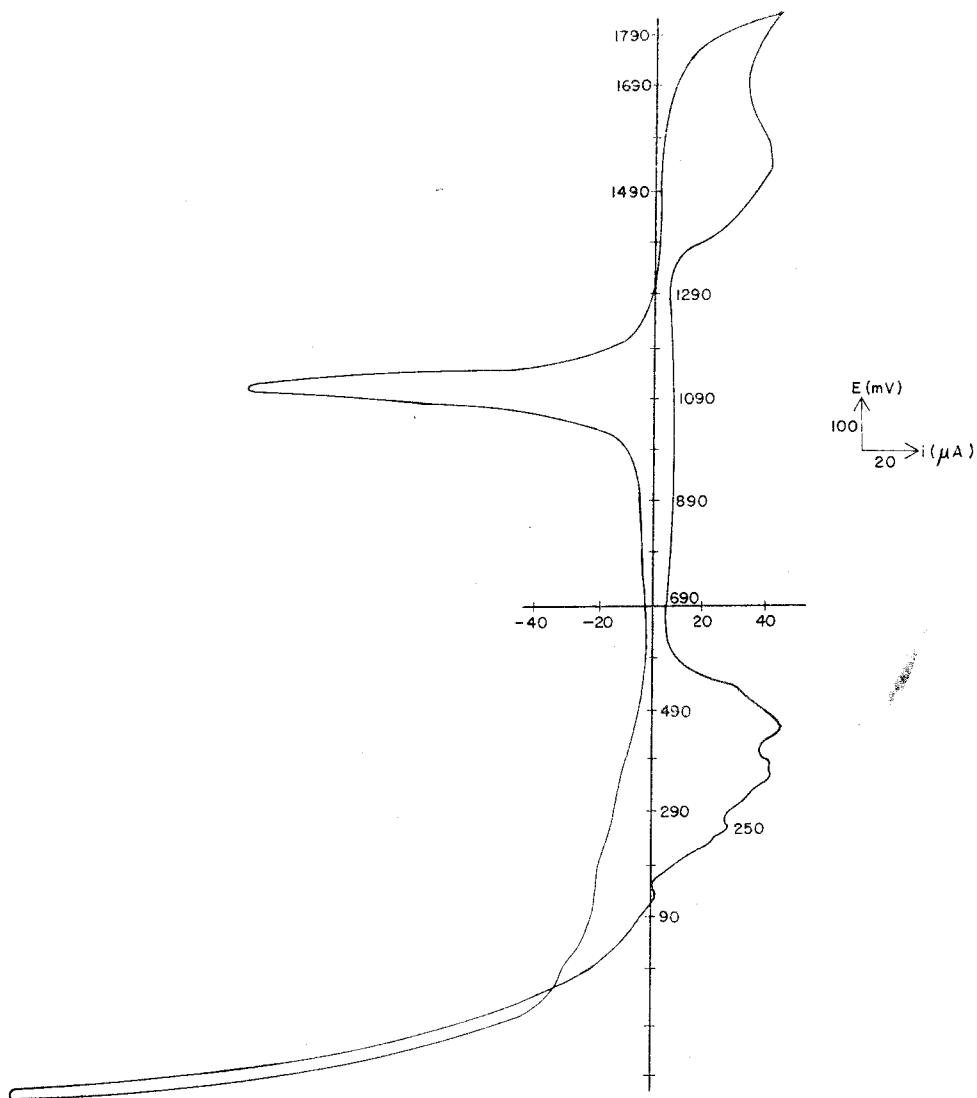


Fig. 3. The  $i$ - $E$  curve of Au electrode obtained in  $1\text{ N H}_2\text{SO}_4 + 10^{-4}\text{ M CuSO}_4 + 10^{-2}\text{ M Prop(1)}$ .

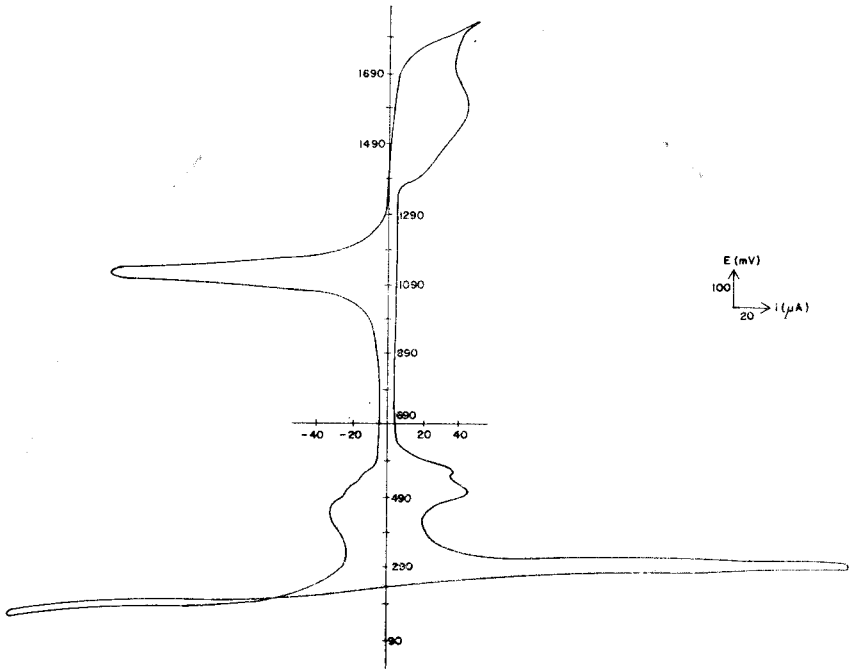


Fig. 4. The  $i$ - $E$  curve of Au electrode obtained in  $1\text{ N H}_2\text{SO}_4 + 10^{-2}\text{ M CuSO}_4$ .

concentration makes no significant difference on the shapes of the peaks in anodic region. There observed no effect of the presence of propanol in acidic medium upon the Cu deposited Au electrode. This was an expected result. Au does not show an electrocatalytic effect upon propanol oxidation in acidic media. Since Cu deposited upon Au desorbs at a potential which alcohol could give a reaction in acidic media, it has no catalytic effect upon the propanol oxidation as well. But Au shows a catalytic effect upon the alcohol electrooxidation in basic media.

The electrode used in the investigation of the electrocatalytic reactivity of Au-Cu couple was prepared as follows. The pretreated Au electrode was kept at 310 mV for 7 and 10 minutes respectively in a solution of  $1\text{ N H}_2\text{SO}_4 + 10^{-5}\text{ M CuSO}_4$  in order to deposit Cu upon the Au substrate. This electrode was then put into another cell containing  $1\text{ N NaOH} + 5 \cdot 10^{-3}\text{ M Prop}$  (1) and the  $i$ - $E$  curves were recorded (Figure 5 a and 5 b). According to these curves Cu deposited upon the Au

does not show electrocatalytic effect upon the electrooxidation of propanol (1) on the contrary it inhibits the reaction. Same situation was observed in the studies carried out at 190 mV. As seen from figure 6 the current peaks in anodic region decrease when the electrode kept in 1 N  $\text{H}_2\text{SO}_4 + 10^{-5}$  M  $\text{CuSO}_4$  for then minutes at a potential of 190 mV, is immersed into a solution of 1N NaOH +  $5 \cdot 10^{-3}$  M Prop(1).

When one compares curves obtained with Au-Cu electrode and Au electrode alone in a medium containing propanol by drawing them together in the same graph one can understand that Cu adatoms block the sites where propanol oxidation takes place.

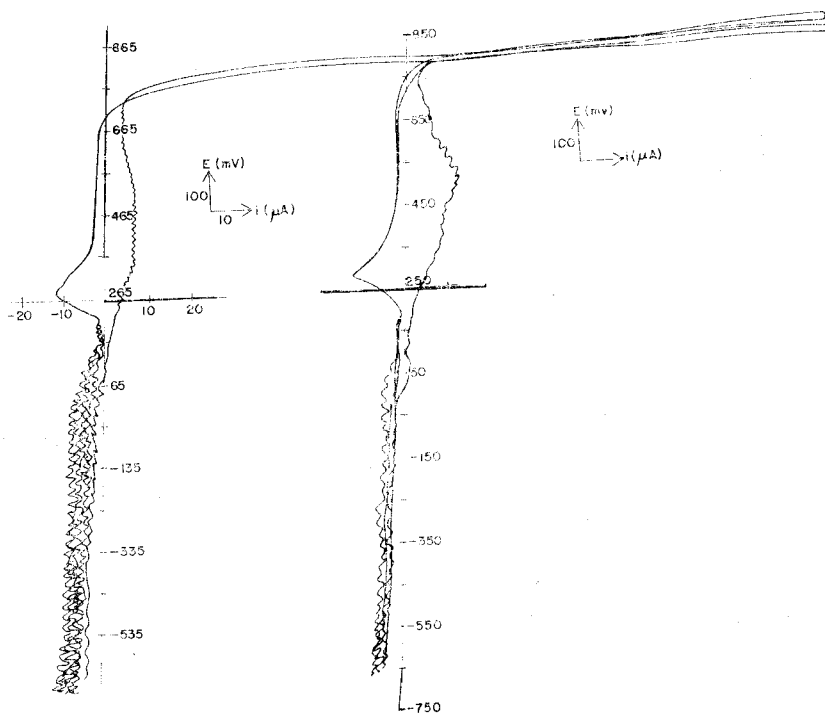


Fig. 5a. The effect of the electrode kept at 310 mV for 7 minutes in 1 N  $\text{H}_2\text{SO}_4 + 10^{-5}$  M  $\text{CuSO}_4$  on the gold electrode curve in 1 N NaOH +  $5 \cdot 10^{-3}$  M Prop(1).

Fig. 5.b The effect of the electrode kept at 310 mV for 10 minutes in 1 N  $\text{H}_2\text{SO}_4 + 10^{-5}$  M  $\text{CuSO}_4$  on the gold electrode curve in 1 N NaOH +  $5 \cdot 10^{-3}$  M Prop(1).

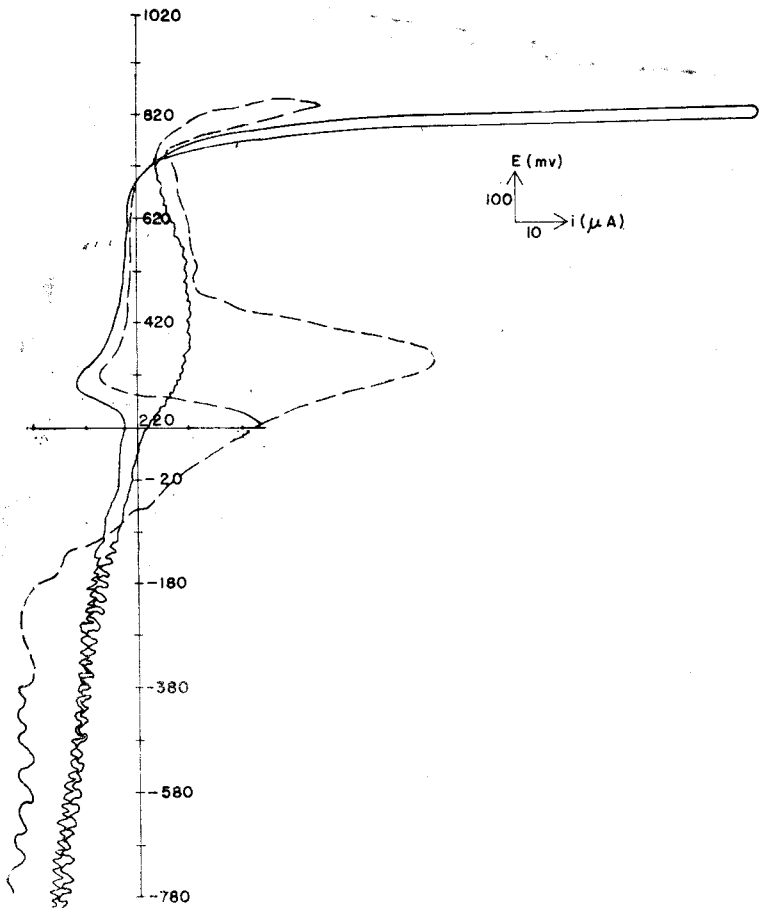


Fig. 6.—The effect of the electrode kept at 190 mV for 10 minutes in 1 N  $\text{H}_2\text{SO}_4 + 10^{-5}$  M  $\text{CuSO}_4$  on the gold electrode curve in 1 N NaOH +  $5 \cdot 10^{-3}$  M (Prop(1)).

————— The  $i$ - $E$  curve obtained in 1 N NaOH +  $5 \cdot 10^{-3}$  M (Prop(1)).

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