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The Electrodepositions of Copper and Nickel from Their Trifluoroacetate–*N,N*-Dimethylformamide Baths

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This paper will deal with the electrodepositions of copper and nickel from $Cu(CF_3COO)_2$–$HCON(CH_3)_2$, $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–citric acid, $Ni(CF_3COO)_2$–$HCON(CH_3)_2$, and $Ni(CF_3COO)_2$–$HCON(CH_3)_2$–additives baths. The properties of these baths and the mechanism of the electrodeposition of copper from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–citric acid bath were studied. The solubility of $Cu(CF_3COO)_2$ in 100 g of $HCON(CH_3)_2$ was 180 g at 20 °C. The specific conductances of the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ and $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ baths were lower than those of the $Cu(CF_3COO)_2$–$HCONH_2$ and $Ni(CF_3COO)_2$–$HCONH_2$ baths. Cu_2O was electrodeposited at the cathode, while copper was not easily obtained from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath. By dissolving citric acid in the bath, copper electrodeposition was made easier. Bright and smooth copper deposits were obtained at current densities in the range of 2.0—11.0 A/dm^2 from the $Cu(CF_3COO)_2$ 500 g/l–$HCON(CH_3)_2$–citric acid 200 g/l bath at 60 °C, the current efficiencies for cathode and anode being about 75% and above 100% respectively. The cross-section of the copper deposits showed that the deposits have a granular structure. The rate of the electrodeposition of copper from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–citric acid 200 g/l bath at current densities ranging from 1.0 to 3.5 A/dm^2 was found to be controlled by the charge-transfer reaction. A black powder nickel deposit was obtained from the $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ bath. By dissolving NH_4Cl, H_3BO_3, sulfamic acid or CCl_3COOH in the bath, adherent bright and smooth nickel deposits were obtained. While the cathode current efficiency was lower in the bath containing sulfamic acid, the anode current efficiency was lower in the bath containing H_3BO_3 or CCl_3COOH. NH_4Cl and $AlCl_3$ have the disadvantage that they are dissolved in $HCON(CH_3)_2$ only with difficulty. Since the bond between the metallic ion and the solvent in the $HCON(CH_3)_2$ bath is stronger than that in the $HCONH_2$ bath, and since dielectric constant of the solvent in the former is lower than that in the latter, metal electrodeposition from the former is more difficult.

Few fundamental data have been reported on the metallic electrodeposition from non-aqueous solutions, in addition, the electrode reaction is not clear in many respects.

The present author previously described[1] the electrodeposition of copper and nickel from the $HCONH_2$ bath, a polar proton solvent.

On the other hand, $HCON(CH_3)_2$ is a polar aprotic solvent; it has a comparatively low melting point and a comparatively high boiling point among the amide solvents. It can be expected that this solvent would also be useful for the electrodeposition of very base metals, because the solvent, lacking in active hydrogen, does not evolve H_2 simultaneously with the metallic electrodeposition from this solution.

The electrodeposition of metal from the $HCON(CH_3)_2$ solution has,. however been investigated only by Baba *et al.*,[2] and the present author cannot find any data fully examining the influence of the electrolysis conditions on the electrodeposit, the mechanism of the electrodeposition reaction, or the properties of the solution.

In the present experiment, the author investigated the properties of the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath and the $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ bath, the electrodepositions of copper and nickel from these baths, and the mechanism of the electrodeposition of copper from the former bath. The author then compared the previously described electrodepositions,[1] of copper and nickel from the $HCONH_2$ bath with those in the present experiment from the $HCON(CH_3)_2$ bath.

Experimental

Reagents. *$HCON(CH_3)_2$*: A reagent grade containing about 0.003% moisture was used.

$Cu(CF_3COO)_2$ and $Ni(CF_3COO)_2$: These were[1] prepared by the neutralization method from $Cu(OH)_2$ and $Ni(OH)_2$ with CF_3COOH.

Other Chemicals: Phosphoric acid and acetic acid of the reagent grade were used. Citric acid (anhydride) and other chemicals of a special grade were used.

Electrodeposition. The electrodepositions of copper and nickel from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ and $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ baths, or from these baths with additives, were carried out at a current density of 0.5—14.0 A/dm^2, using an apparatus already described,[1] at 40—60 °C, while the bath was being stirred at a definite rate.

The thickness of the electrodeposited layer was made about 5 μ, this thickness being calculated from the amount of electricity consumed during the deposition.

Observation of the Electrodeposited Surface and the Electrodeposited Layer. The electrodeposited surfaces and electrodeposited layers were observed by means of a metallurgical microscope. To observe the layers in particular, their thickness was made about 30 μ and they were buried in resin and etched.

Measurement of the Solubility. The solubility of $Cu(CF_3COO)_2$ in $HCON(CH_3)_2$ was obtained by determining quantitatively with oxine (gravimetric method) the copper in a definite amount of a saturated solution of $Cu(CF_3COO)_2$ at 20 °C.

Measurement of the Electrolytic Conductance. The $Cu(CF_3COO)_2$–$HCON(CH_3)_2$, $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–citric acid, and $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ baths were kept at 50 °C for about one hour before the measurement, and their electrolytic conductance was measured by means of a Yanagimoto electrolytic conductometer Model MY-7.

Measurement of the Ultraviolet Absorption Spectrum. A sample of a 0.10 mol/l $Cu(CF_3COO)_2$–$HCON(CH_3)_2$– 0 to 0.30 mol/l citric acid bath was placed in a quartz cell with a 2-mm light-pass length, and the ultraviolet absorption spectrum was measured by means of Hitachi recording spectrophotometer, Model EPS-3.

Analysis of Gas and Bath. The composition of the gas evolved during the electrolysis of a 100 g/l $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–0 to 200 g/l citric acid bath and the change in the composition of the bath itself were determined by a method previously described.1)

Polarography. With a Yanagimoto polarograph, Model PA-102, DC and AC polarograms of a 1.0×10^{-2} mol/l $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–0 to 3.0×10^{-2} mol/l citric acid bath were recorded at 25 °C, using 0.1 M sodium perchlorate as the supporting electrolyte.

Elementary Analysis. Elementary analyses were carried out on the yellowish brown substance produced at theca thode by the electrolysis of a 100 g/l $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath and on the precipitate produced after the heating, at about 90 °C for 2 hr, of a 0.1 mol/l $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–0.2 mol/l citric acid bath. H and C were determined by the Pregl method for microanalysis, N, by the Dumas method, and Cu, by the oxine method (gravimetric method).

X-ray Diffraction. The yellowish-brown substance produced at the cathode by the electrolysis of the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath was X-ray diffractometrically determined by means of a Geiger-Flex Model CN2035 manufactured by Rigaku Denki Co. Ltd., using copper as the target.

Measurement of the Overvoltage. The overvoltage of the copper electrodeposition from a $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–200 g/l citric acid bath was measured at 40, 50, and 60 °C by the current interruptor method1) for baths containing $Cu(CF_3COO)_2$: 100 g/l (35×10^{-2} mol/l), 150 g/l (52×10^{-2} mol/l), and 200 g/l (70×10^{-2} mol/l) respectively.

Results and Discussion

Electrodeposition. *Nickel Electrodeposition*: Table 1 shows some results obtained on nickel deposition from $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ baths with additives. The additives chosen were such that could dissolve the anode (Ni plate) and/or form a metal complex ion with the metal ion in the bath.

Table 1. Electrodeposition of nickel from $Ni(CF_3COO)_2$ 20.0 g/l-$HCON(CH_3)_2$ bath with additives at 40 °C

Additive (g/l)	Current density (A/dm^2)	Current efficiency (%)		Deposit
		Cathode	Anode	
No addition	0.5—1.0	56—95	12—65	black
NH_4Cl 4.0	0.5—2.0	28—78	100—110	bright
H_3BO_3 4.0 —22.0	1.0	92—42	31—62	bright
Sulfamic acid 4.0—16.0	1.0	17—9.7	16—18	bright
Citric acid 4.0	0.5—1.0	10—16	5.6—3.1	grey
Tartaric acid 4.0	0.5—1.0	3.6—22	3.6—4.3	grey
LiCl 4.0	0.5—1.0	60—6.3	104—103	black
$AlCl_3$ 4.0	0.5—2.0	59—91	105—107	bright
CCl_3COOH 2.0—6.0	0.5—2.0	65—63	6.7—12	bright
Salicylic acid 2.0	2.0	67	3.0	black
Hydroxylamine Hydrochloride 2.0	0.5—2.0	29—47	14	bright
Oxalic acid 2.0	1.0	49	5.4	bright
Lactic acid 10 ml	2.0—4.0	30—39	20—8.0	black
Glycolic acid 2.0	0.5—1.0	41—63	6.1—4.2	bright
Phthalic acid 2.0	1.0	41	10	bright
H_2SO_4 10 ml	1.0—2.0	27—51	23—23	bright

The deposit obtained from the $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ bath was a black powder; bright and smooth nickel deposits were obtained from this bath containing NH_4Cl, $AlCl_3$, H_3BO_3, sulfamic acid, H_3BO_3–NH_4Cl, saccharin–NH_4Cl, CCl_3COOH, hydroxylamine hydrochloride, glycolic acid, H_2SO_4, or phthalic acid. The deposit obtained from the solution containing $AlCl_3$ was particularly bright.

Among these baths, those containing NH_4Cl, H_3BO_3, sulfamic acid, H_3BO_3-NH_4Cl, saccharin-NH_4Cl, or CCl_3COOH gave adherent nickel deposits.

While the cathode current efficiency was lower in the bath containing H_3BO_3 or CCl_3COOH, NH_4Cl and $AlCl_3$ have the disadvantage that they are dissolved in $HCON(CH_3)_2$ only with difficulty.

From these results it is apparent that the nickel electrodeposition from a $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ bath is promoted by adding NH_4Cl, sulfamic acid, H_3BO_3, or CCl_3COOH to the bath. It would improve not only the anode current efficiency but also the adhesion of electrodeposit on the substrate if we could find a chloride highly soluble to $HCON(CH_3)_2$.

It appears that, on the anode in the $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ baths containing additives (except chloride), another reaction occurs (such as the electrolysis of the solvent).

It can be concluded that chloride is dissolved in $HCON(CH_3)_2$ with more difficulty than in $HCONH_2$: also, both nickel deposition and anode dissolution are more difficult in a $HCON(CH_3)_2$ bath than in a $HCONH_2$ bath.

Copper Electrodeposition: A bright and smooth copper deposit can be obtained from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath only if the electrodeposition is carried out in a 20 g/l $Cu(CF_3COO)_2$ concentration at 60 °C for a 1.0 to 3.0 A/dm^2 current density. Under such electrolysis conditions, the anode current efficiency is about 100%, while the cathode current efficiency is about 75%.

Figure 1 shows an example of the anode and cathode current efficiencies for copper deposition from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath.

The anode current efficiency was always about 100%, irrespective of the $Cu(CF_3COO)_2$ concentration and the bath temperature. On the other hand, while the cathode current efficiency was also scarcely affected

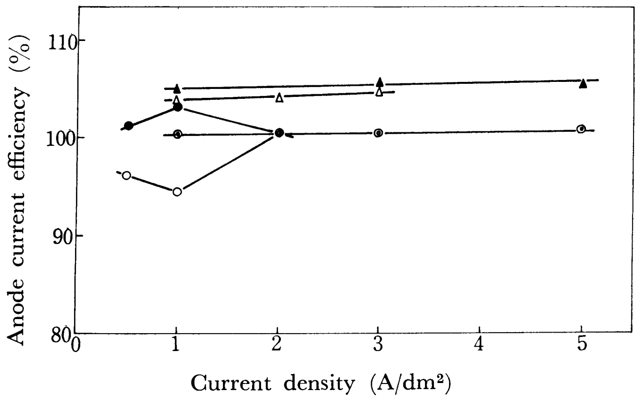


Fig. 1-1. Anode current efficiency as a function of current density for $Cu(CF_3COO)_2$-DMF bath
$Cu(CF_3COO)_2$ 20 g/l, —○—: 40 °C, —●—: 50 °C, —△—: 60 °C
$Cu(CF_3COO)_2$ 100 g/l, —◎—: 40 °C, —▲—: 60 °C

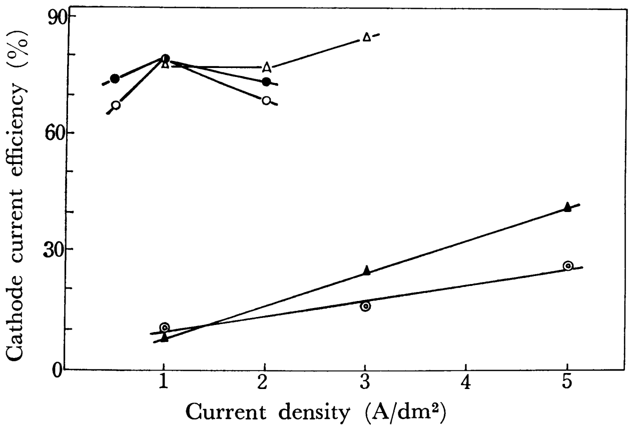


Fig. 1-2. Cathode current efficiency as a function of current density for $Cu(CF_3COO)_2$-DMF bath
$Cu(CF_3COO)_2$ 20 g/l, —○—: 40 °C, —●—: 50 °C, —△—: 60 °C, $Cu(CF_3COO)_2$ 100 g/l, —◎—: 40 °C, —▲—: 60 °C

by the bath temperature, it was decreased down to about 10% at a low current density with an increase in the $Cu(CF_3COO)_2$ concentration.

No gases evolved from the anode and cathode, but during electrolysis a yellowish-brown precipitate was produced at the cathode. Elementary analysis of this precipitate showed C: 6.89%, H: 1.56%, N: 0.88%, and Cu: 55.0%; X-ray diffraction showed that it was mainly composed of Cu_2O.

Moreover, gas chromatographic analysis of the cathode solution proved the existence of $(CF_3CO)_2O$. Therefore, the following reaction (1) can be said to have occurred at the cathode, resulting in a decrease in the cathode current efficiency:

$$2Cu(CF_3COO)_2 + 2e^- \rightarrow Cu_2O + 2(CF_3CO)_2O + 2CF_3COO^- \quad (1)$$

In view of this fact, it seems that it is difficult for copper electrodeposition to occur from a $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath because the copper ion forms a stable complex with $HCON(CH_3)_2$ if the $Cu(CF_3COO)_2$ concentration is high.

The present author has assumed that, if this stable copper complex were broken or if such a substance as forms a more unstable copper complex than the above-mentioned complex were added to the $HCON(CH_3)_2$ bath, it would be possible to facilitate the copper electrodeposition from the bath; the author thus tentatively added citric acid, a complexing agent, to the bath.

Fig. 2 shows an example of the influence of citric acid addition on the anode and cathode current efficiencies. The increased addition of citric acid increases the cathode current efficiency.

While the copper electrodeposition from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath is difficult because of the strong bond between the copper ion and $HCON(CH_3)_2$, it appears that the addition of citric acid fa-

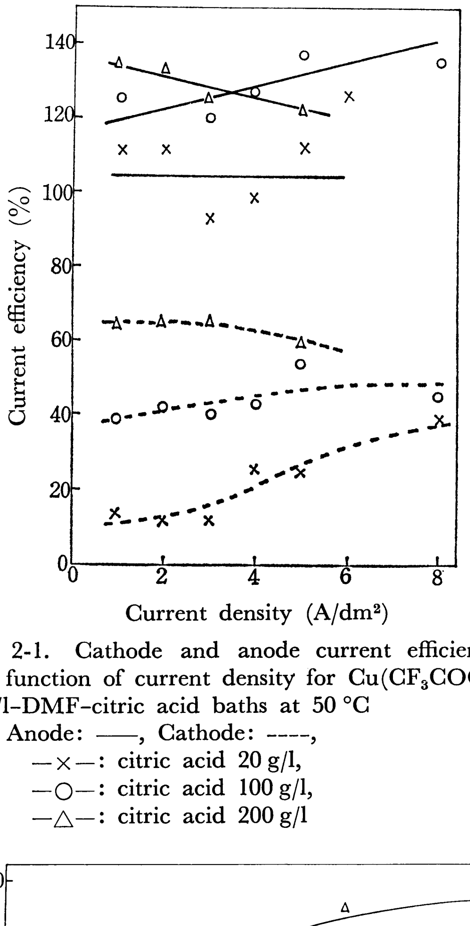


Fig. 2-1. Cathode and anode current efficiencies as a function of current density for $Cu(CF_3COO)_2$ 100 g/l-DMF-citric acid baths at 50 °C
Anode: ——, Cathode: ----,
—×—: citric acid 20 g/l,
—○—: citric acid 100 g/l,
—△—: citric acid 200 g/l

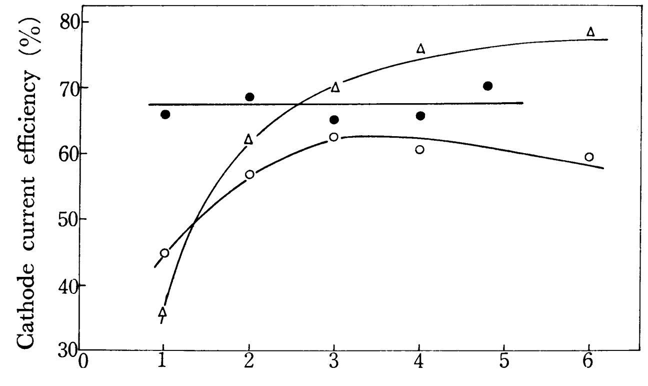


Fig. 2-2. Cathode current efficiency as a function of current density for $Cu(CF_3COO)_2$ 300 g/l-DMF-citric acid 200 g/l bath
—○—: 40 °C, —●—: 50 °C, —△—: 60 °C

cilitates the copper electrodeposition because it alters, as will be described later, the solution's property to weaken the influence of the solvent on the copper ion.

While the anode current efficiency was higher than 100% irrespective of the $Cu(CF_3COO)_2$ concentration and the bath temperature, the cathode current efficiency was affected by the $Cu(CF_3COO)_2$ concentration; it amounted to 75% in 100 to 500 g/l $Cu(CF_3COO)_2$ baths and to 85% in the bath with a $Cu(CF_3COO)_2$ concentration lower than 100 g/l at 60 °C for a high current density.

It seems that the anode current efficiency exceeds 100%, because the anode is also chemically dissolved in the bath's acid (citric acid). The evolution of hydrogen gas from the cathode lowered its current efficiency.

Figure 3 shows the range of current density within which a bright and smooth copper deposit can be obtained from a $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–200 g/l citric acid bath. At each bath temperature, an increase in the $Cu(CF_3COO)_2$ concentration contributes to the tendency for good deposits to be obtained within a wider range of current densities.

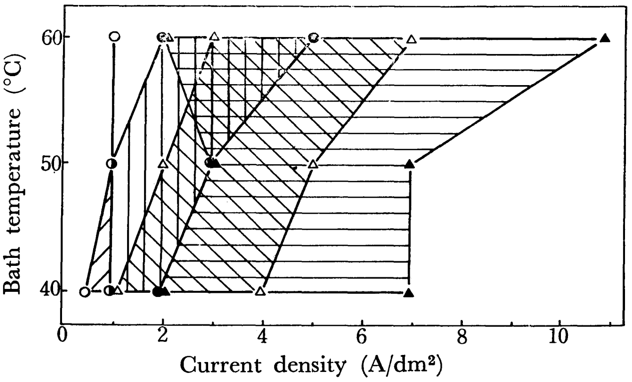


Fig. 3. The range of current density for bright and smooth copper deposit from $Cu(CF_3COO)_2$-DMF-citric acid 200 g/l bath
○: $Cu(CF_3COO)_2$ 20 g/l, ●: $Cu(CF_3COO)_2$ 100 g/l,
△: $Cu(CF_3COO)_2$ 300 g/l, ▲: $Cu(CF_3COO)_2$ 500 g/l

These ranges are remarkably wider than those in the case of the bath without citric acid and are almost equal to those in the case of the formamide bath[1]) with the same $Cu(CF_3COO)_2$ concentration.

From the above-mentioned results, it is apparent that the addition of citric acid is effective on the copper electrodeposition from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath, while the anode-current efficiency in the bath containing citric acid exceeds 100%. The cathode current efficiency reaches a remarkable level of 90% at 50 °C if more than 100 g/l of citric acid is added to a 20 g/l $Cu(CF_3COO)_2$ bath, and it is about 75% at 60 °C if 200 g/l of citric acid is added to a 100—500 g/l $Cu(CF_3COO)_2$ bath. Moreover at 60 °C from a 500 g/l $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–200 g/l citric acid bath, a bright and smooth deposit can be obtained within a current density range of 2.0 to 11.0 A/dm².

Appearance of the Deposited Surface and the Structure of the Deposited Layer. *Nickel Deposit*: A representative nickel deposited surface is shown in Fig. 5. The deposited surfaces obtained from all the baths investigated in the present experiment consist of fine grains; those obtained from the baths containing H_2SO_4, $AlCl_3$, or hydroxylamine hydrochloride consist of very fine grains. A cracked deposited surface is obtained from the bath containing $AlCl_3$ or CCl_3COOH.

Since the deposited surfaces consist of grains, it can be assumed that the deposited layer has a granular structure.

Copper Deposit: Figure 6 shows as an example of the deposited surface and the deposited layer of the copper deposit obtained from the bath containing citric acid.

The deposited surface consists of fine grains, and the deposit becomes more compact for higher concentrations of the copper salt and at high bath temperatures. Moreover, the deposited layers have a granular structure irrespective of the bath temperature, the current density, and the $Cu(CF_3COO)_2$ concentration.

It appears that, since the copper and nickel ions form a complex in the $HCON(CH_3)_2$ bath, the ligands are adsorbed on the electrode during electrodeposition, thus suppressing any surface diffusion of the adatom; the growth in the vertical direction is thus prevented, increasing the frequency of nucleus formation, and fine grains are produced to form a granular structure.

Solubility. In 100 g of $HCON(CH_3)_2$, 180 g of $Cu(CF_3COO)_2$ were dissolved at 20 °C.

After several days, crystals were precipitated in an $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ saturated solution at 20 °C.

The solubility of $HCON(CH_3)_2$ in $Cu(CF_3COO)_2$ is lower than that of $HCONH_2$.

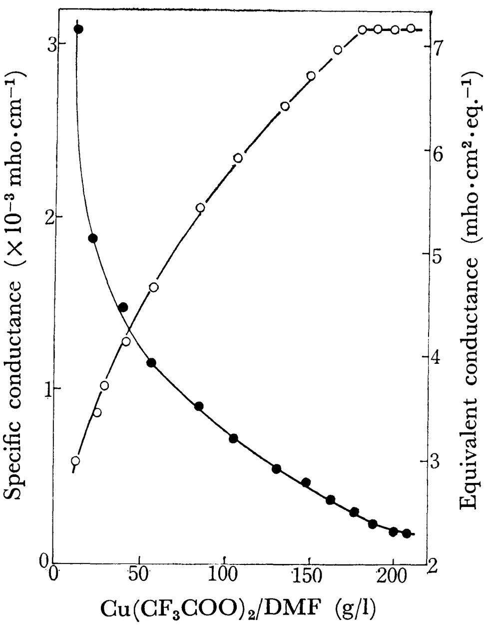
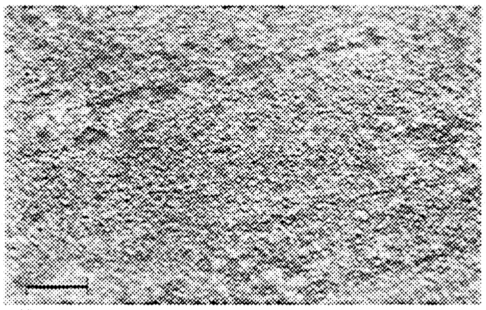
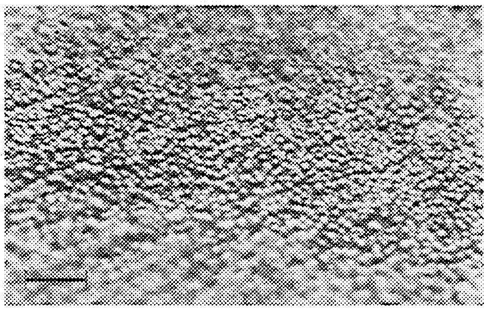


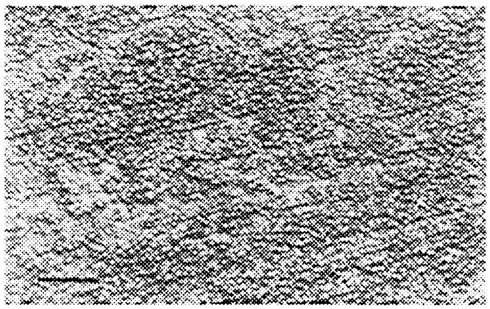
Fig. 4. Specific conductance and equivalent conductance of $Cu(CF_3COO)_2$-DMF solutions at 50 °C
—○—: Specific conductance,
—●—: Equivalent conductance

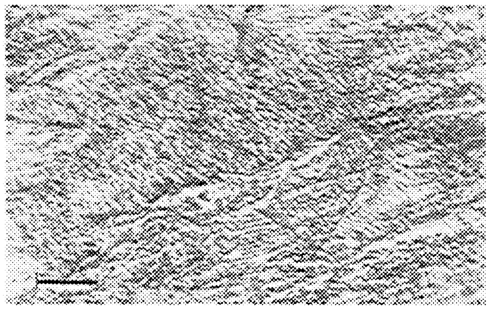
Specific Conductance. Figure 4 shows the specific conductance of the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath. The specific conductance of the $Cu(CF_3COO)_2$–

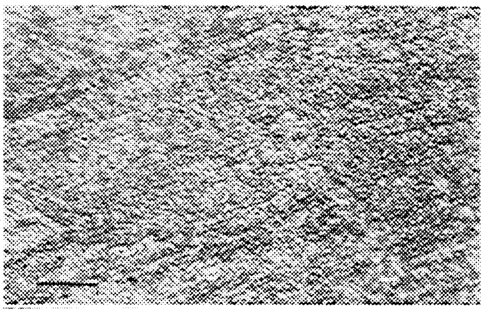

1) No additive bath, at 0.5 A/dm^2

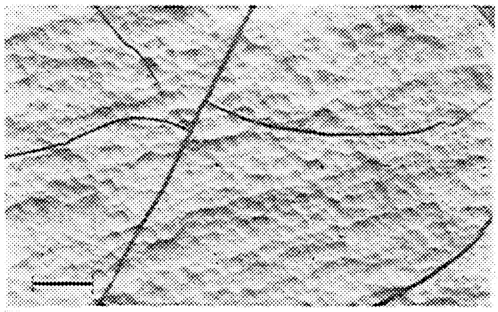

2) NH_4Cl (Saturated) bath, at 0.5 A/dm^2

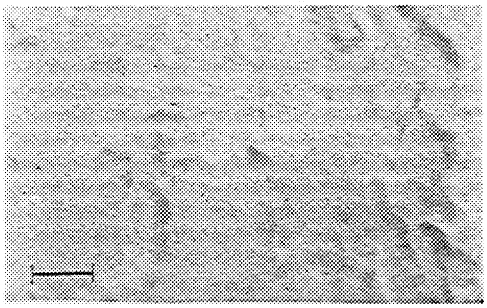

3) H_3BO_3 (22 g/l) bath, at 1.0 A/dm^2


4) Sulfamic acid (4.0 g/l) bath, at 1.0 A/dm^2


5) Citric acid (4.0 g/l) bath, at 0.5 A/dm^2


6) Tartaric acid (4.0 g/l) bath, at 1.0 A/dm^2


7) $AlCl_3$ (4.0 g/l) bath, at 1.0 A/dm^2


8) Hydroxylamine hydrochloride (2.0 g/l) bath, at 0.5 A/dm^2


9) H_2SO_4 (10 ml/l) bath, at 1.0 A/dm^2

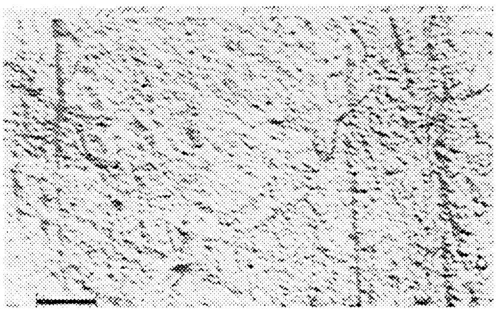

10) CCl_3COOH (6.0 g/l) bath, at 0.5 A/dm^2

Fig. 5. Surface of nickel deposit obtained from $Ni(CF_3COO)_2$ 20 g/l-DMF bath with additives at 40 °C (|——| 23 μ).

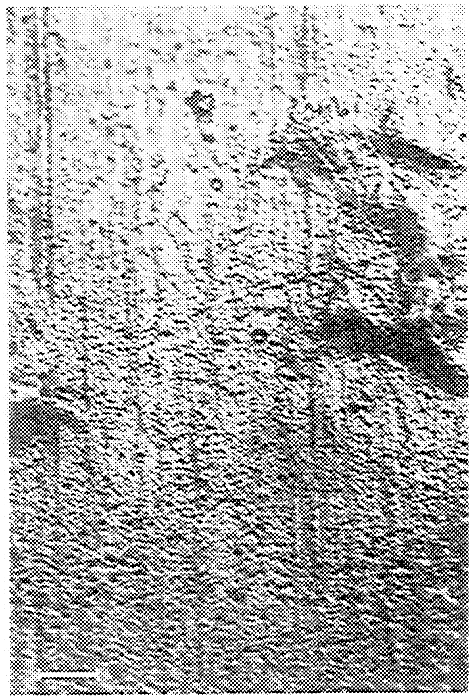


Fig. 6-1. Surface of copper deposit obtained from $Cu(CF_3COO)_2$ 500 g/l-DMF-citric acid 200 g/l bath at 8.0 A/dm^2 at 40 °C (|——|: 23 μ).

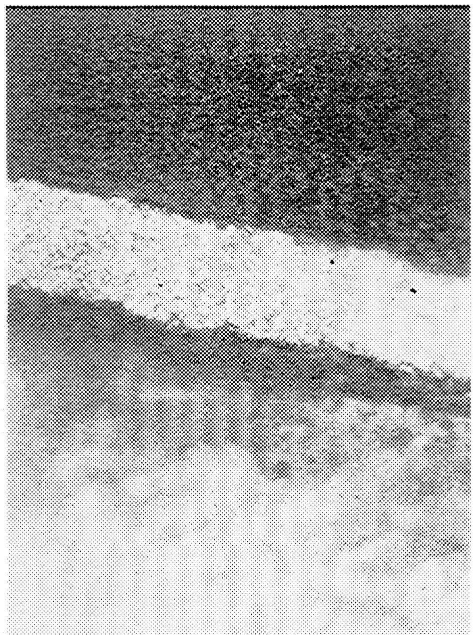


Fig. 6-2. Cross-section of copper deposit obtained from $Cu(CF_3COO)_2$ 300 g/l-DMF-citric acid 200 g/l bath at 2.0 A/dm^2 at 60 °C (|——|: 23 μ).

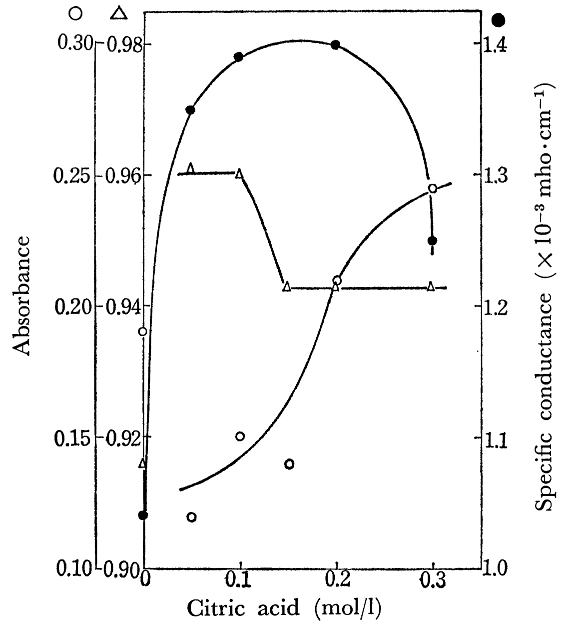


Fig. 7. The properties of $Cu(CF_3COO)_2$ 0.1 mol/l-DMF-citric acid solutions
—○—: absorbance at 1950 mμ
—△—: absorbance at 810 mμ
—●—: specific conductance at 50 °C

$HCON(CH_3)_2$ bath was almost the same as that of the $Ni(CF_3COO)_2$-$HCON(CH_3)_2$ bath. They are both about 1/4 of those [1] of the $Cu(CF_3COO)_2$-$HCONH_2$ bath and the $Ni(CF_3COO)_2$-$HCONH_2$ bath.

It seems that more viscous $HCONH_2$ bath has a higher electrolytic conductance than the less viscous $HCON(CH_3)_2$ bath, mainly because the dielectric constant of $HCONH_2$, 110, is about three times that of $HCON(CH_3)_2$, 37.

$Cu(CF_3COO)_2$-$HCON(CH_3)_2$-Citric Acid Solution. Figure 7 shows the specific conductance of a 0.10 mol/l $Cu(CF_3COO)_2$-$HCON(CH_3)_2$- 0 to 0.30 mol/l citric acid bath and the absorbance of its ultraviolet absorption spectrum.

At citric acid concentrations of from 0.1 to 0.2 mol/l the conductance has its maximum, while inflexion points appear at the absorbances of 810 and 1950 mμ. It appears that these inflexion points change the condition of the solution surrounding the copper ion. The present author believes that, in the $Cu(CF_3COO)_2$-$HCON(CH_3)_2$-citric acid bath, coordination perhaps occurs in a ratio of 1 mol of $Cu(CF_3COO)_2$ to 1 mol of citric acid.

Both AC and DC polarograph of 1.0×10^{-2} mol/l $Cu(CF_3COO)_2$-$HCON(CH_3)_2$-0 to 3.0×10^{-2} mol/l citric acid baths show a reduction wave at -0.20 V *vs.* Hg A and -0.36 V *vs.* Hg B of the average half-wave potential. A wave is a clear peak in the AC polarogram, but an ill-defined wave in the DC polarogram.

The following results were obtained by AC polarography. While the wave height of A is increased with an increase in the amount of citric acid added, it becomes constant at amounts more than 2.0×10^{-2} mol/l. On the other hand, the wave height of B is constant, irrespective of the amount of citric acid added. Moreover, the wave heights of A and B coincide with each other for amounts of more than 2.0×10^{-2} mol/l.

It appears that the A wave is a reduction wave corresponding to the valency decrease of the copper-citric acid complex from 2 to 1, while the B corresponds to the reduction of the latter to copper. Moreover, judging from the wave height, it is apparent that the addition of citric acid is effective for efficient copper electrodeposition in the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath and that the best amount of citric acid to be added is in a ratio of 1 mol of $Cu(CF_3COO)_2$ to more than 2 mol of citric acid rather than in a ratio of 1 mol of $Cu(CF_3COO)_2$ to 1 mol of citric acid, which corresponds to the amount of citric acid necessary for the formation of a copper-citric acid complex. This fact coincides well with the results of electrodeposition.

Activation Overvoltage of Copper Electrodeposition from the $Cu(CF_3COO)_2$*–*$HCON(CH_3)_2$*–Citric Acid Bath.*

From the decay curve of the overvoltage 4 ms after the interruption of the electrolytic current, the resistance polarization was subtracted. The remainder was assumed to be the activation overvoltage. Figure 8 shows an example of the current density-activation overvoltage relation during the deposition of copper from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–citric acid 200 g/l bath. Such ranges of current density as to make the activation overvoltage, η_c, related to the logarithm of the current density, log i_c, in a direct proportionality are 1.0 to 3.0 A/dm^2 at a bath temperature of 40 °C, 1.0 to 3.5 A/dm^2 at 50 °C, and 1.0 to 4.1 A/dm^2 at 60 °C; it appears that in such ranges of current density Tafer's formula is valid—in other words, the charge-transfer process is rate-determining.

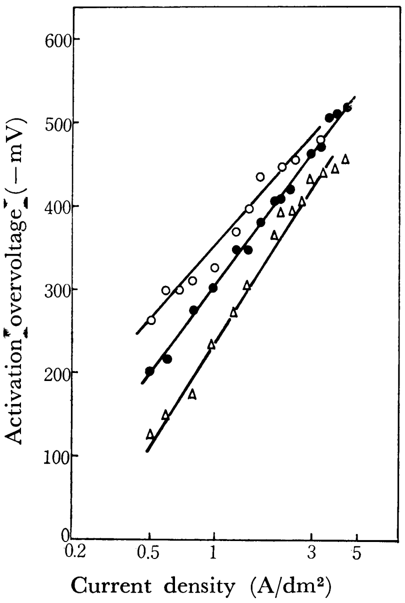


Fig. 8. Current density-activation overvoltage relation during the deposition of copper from $Cu(CF_3COO)_2$ 100 g/l-DMF-citric acid 200 g/l bath
—○—: 40 °C, —●—: 50 °C, —△—: 60 °C

This η_c value is very much larger than that[1)] in the $Cu(CF_3COO)_2$–$HCONH_2$ bath.

Table 2 shows the apparent exchange-current density, i_{oc}, the apparent transfer coefficient, α_c, and the apparent valency, n, for copper deposition, all obtained by a method previously described.[1)]

While the obtained value of i_{oc} is higher than that[2)] obtained by measuring the polarization potential with a potentiometer in a 0.1 M $CuSO_4$–$HCON(CH_3)_2$–0.1 M $NaClO_4$ bath, the former is slightly lower than that[1)] obtained from the $Cu(CF_3COO)_2$–$HCONH_2$ bath.

Also, the obtained values of α_c, n and the slope of the Tafel line, b_c, are, in the average, as follows:

$$\alpha_c = 0.20,\ n = 0.960 \text{ and } b_c = -0.336\,\text{V}.$$

Within a range of current density of about 1.0 to 3.5 A/dm^2, the copper electrodeposition reaction from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–200 g/l citric acid bath proceeds as in the following equations:

$$Cu^{2+} + e^- \rightarrow Cu^+ \qquad (2)$$

$$Cu^+ + e^- \rightarrow Cu^0 \qquad (3)$$

Moreover, it appears that Reaction (2) is rate-determining.

On the assumption of a linear relation between log i_{oc} and the reciprocal of the bath temperature, T, that is, $1/T$, the apparent activation energy, E_c of copper electrodeposition is calculated from the relation's slope; this results in values of 8.45, 8.61, and 9.10 kcal/mol E_c for the baths, the $Cu(CF_3COO)_2$ concentrations of which are 100, 150, and 200 g/l respectively.

Comparison between the Properties of a $Cu(CF_3COO)_2$*–*$HCONH_2$ *or* $Ni(CF_3COO)_2$*–*$HCONH_2$ *Bath and a* $Cu(CF_3COO)_2$*–*$HCON(CH_3)_2$ *or* $Ni(CF_3COO)_2$*–*$HCON(CH_3)_2$ *Bath and between Copper and Nickel Electrodepositions from Those Baths.* 1) While solvolysis occurs in the $HCONH_2$ bath, it does not occur in the $HCON(CH_3)_2$ bath. A complex is formed in each bath.

2) Since the bond between the metallic ion and the solvent in the $HCON(CH_3)_2$ bath is stronger than that

Table 2.

$Cu(CF_3COO)_2$ (mol/l) $\times 10^{-2}$	Bath temp. (°C)	i_{oc} (A/dm^2)	α_c	$\alpha_c n$	n	b_c (−V)	Current density of linear part (A/dm^2)
35	40	0.120	0.194	0.189	0.975	0.330	0.9—2.6
	50	0.170	0.201	0.179	0.890	0.360	0.9—2.8
	60	0.285	0.215	0.168	0.782	0.395	0.9—3.5
52	40	0.162	0.194	0.164	0.850	0.380	1.0—3.0
	50	0.240	0.201	0.172	0.859	0.375	1.1—3.5
	60	0.380	0.215	0.222	1.03	0.300	1.0—4.0
70	40	0.200	0.194	0.223	1.15	0.280	1.2—3.2
	50	0.320	0.201	0.214	1.07	0.300	1.2—4.0
	60	0.490	0.215	0.222	1.03	0.300	1.2—5.0

in the $HCONH_2$ bath, and since the dielectric constant of the solvent in the former is also lower than that in the latter, is difficult to electrodeposit metal and Cu_2O is formed at cathode in the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath.

3) The specific conductance in the $HCON(CH_3)_2$ bath is lower than that in the $HCONH_2$ bath.

4) It is possible to obtain a better copper electrodeposit over a wider range of current density in the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath containing citric acid than in the same bath containing no citric acid. This range almost coincides with that in the $Cu(CF_3COO)_2$–$HCONH_2$ bath.

While it is possible to obtain better nickel electrodeposit in $Ni(CF_3COO)_2$–$HCONH_2$ and $Ni(CF_3COO)_2$ $HCON(CH_3)_2$ baths containing appropriate additives, the range of current density which permits one to obtain a superior electrodeposit in the latter bath is narrower.

The electrodeposit of nickel or copper obtained from the $HCONH_2$ and $HCON(CH_3)_2$ baths has a granular structure.

5) The values of η_c, E_c, and b_c in the copper-electrodeposition reaction from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–200 g/l citric acid bath are higher than those in the same reaction from the $Cu(CF_3COO)_2$–$HCONH_2$ bath, while the values of i_{0c} and α_c are lower, so the electrodeposition of copper from the former can be said to be more difficult. On the other hand, the value of n is always about 1 for both the baths.

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