Russian Journal of Applied Chemistry, Vol. 77, No. 3, 2004, pp. 380–384. Translated from Zhurnal Prikladnoi Khimii, Vol. 77, No. 3, 2004, pp. 386–390.

Electrically Conducting Formulations Based on Ultradispersed Powders of Copper, Obtained by Reduction of Its Salts with the Hypophosphite Ion

I. I. Obraztsova, G. Yu. Simenyuk, and N. K. Eremenko

*Kemerovo Branch, Institute of Solid-State Chemistry and Mechanochemistry, Siberian Division,
Russian Academy of Sciences, Kemerovo, Russia*

Received July 29, 2003

Abstract—Powders of copper were obtained by reducing its various salts with hypophosphorous acid and sodium hypophosphite. The influence exerted by various factors on the stability and electrical conductivity of composites on their base was studied.

Thanks to unique physicochemical, electrical, magnetic, and optical properties, polymeric formulations with an ultradispersed metallic filler find wide application in modern science and technology in developing current-conducting pastes, photo- and X-ray-sensitive resists, shielding coatings, and electrodes. Silver is most commonly used in electrically conducting formulations because of its high electrical conductivity and resistance to oxidation [1, 2]. Recently, steadily increasing attention has been given to development of copper-based formulations [3], whose production cost is lower. In this context, the problems associated with stabilization of ultradispersed powders (UDP) of copper and improvement of the service life and electrical conductivity of composites on their base are of current interest.

Previously, methods were developed for obtaining copper UDP with average particle size of 20–40 nm by reducing various copper salts with glycerol and making formulations on their base with epoxy and novolak resins [4–8]. The most efficient is the reduction of basic carbonate, acetate, and tartrate of copper with glycerol, and formulations on their base with novolak resin exhibit higher electrical conductivity [resistivity $\rho = (0.6\text{–}1.9) \times 10^{-6}\ \Omega$ m] and stability (more than 6 years).

In addition, it was found that, with appropriate stabilizing agents, it is also possible to prepare formulations based on copper sulfate with the electrical conductivity and stability comparable with those of pastes based on copper UDP obtained by reduction of readily decomposing copper salts. Introduction of organic acid reductants (ascorbic, citric, formic, and acetylsalicylic acids) leads to an increase in the reaction rate by a factor of 5–10, decrease in the process temperature by 20–40°C, and improvement of the stability and electrical conductivity of the pastes.

It was found that epoxy formulations with addition of stabilizers (1-naphthol and *p*-aminophenol) in amount of 1% (relative to the mass of the copper UDP) retain high electrical conductivity without changes for more than 10 years, and formulations with 1-naphthol have the lowest resistivity of $(0.8\text{–}1.2) \times 10^{-6}\ \Omega$ m, which is close to that characteristic of metals. It was also found that 1-naphthol is the best oxidation inhibitor for the novolak resin, and addition of glycerol as a plasticizer in a 1 : 3 ratio yields formulations whose electrical conductivity (resistivity $1.2 \times 10^{-6}\ \Omega$ m) is comparable with that of the best samples with epoxy resin. Pastes based on the novolak resin are only slightly inferior to the above formulations in stability, but they are less expensive and more readily available, and, therefore, primary attention will be given here to novolak formulations.

The study is concerned with reduction of various copper salts with hypophosphorous acid and sodium hypophosphite at a molar ratio $\nu(\mathrm{Cu}) : \nu(\mathrm{H_2PO_2^-}) = 1 : (1.5\text{–}4.0)$. The promise of this method is in that the reduction with hypophosphite ions is carried out under milder conditions (reaction temperature not higher than 95°C, reaction time 2–35 min) than those in reduction with glycerol (130–200°C, 15–240 min). The copper UDP obtained was used to prepare formulations with phenol–formaldehyde novolak resin. The influence exerted by various factors on the stability and electrical conductivity of the formulations ob-

1070-4272/04/7703-0380 © 2004 MAIK “Nauka/Interperiodica”

tained was studied. These materials were compared with samples obtained previously by reduction with glycerol and with industrially used pastes based on noble metals.

EXPERIMENTAL

The copper salts were reduced with sodium hypophosphite as follows: into a vessel with a solution of a copper(II) salt heated to 80–90°C, we gradually poured with continuous agitation a solution of sodium hypophosphite heated to 50–60°C. Then the reaction mixture was heated to 80–95°C [depending on a copper(II) salt used] and kept at this temperature until an ultradispersed copper powder precipitated. After that, the UDP was washed with water to neutral reaction of the washing water, treated with solutions of hydroquinone and stearic acid in ethanol, and stored under a layer of the solution of stearic acid in ethanol. According to small-angle X-ray scattering data (Fig. 1), the copper UDP obtained has particle size in the range 8–100 nm, with 45% of the particles (by mass) being less than 30 nm in size. The formulations prepared from SF-010 phenol–formaldehyde resin and copper UDP (with 80 wt % metallic phase) were kept at 140–145°C for 4 h. The dc resistance of the pastes was measured (12 V, 2.5 mA) at room temperature (20–25°C).

To improve their resistance to oxidation, all the copper UDP samples were treated with solutions of hydroquinone and stearic acid in ethanol, as suggested in [4]. The ultradispersed powders of copper obtained by reduction of copper(II) salts (and $CuSO_4 \cdot 5H_2O$, in particular) with sodium hypophosphite are highly active and are readily oxidized in air because of their increased dispersity. As a result, the formulations on their base have relatively high resistivity (10^{-2} Ω m) and are very unstable in storage (Fig. 2, curve *1*). However, it was found that treatment of copper UDP with formic acid leads to a dramatic increase in the electrical conductivity and stability of the formulations (Fig. 2, curve *2*). This is due to the fact that treatment with formic acid removes the oxide film from the surface of UDP particles and stabilizes metallic copper against further oxidation.

Inorganic (nitrate, sulfate, chloride) and organic (acetate, formate, citrate) salts of copper(II) were reduced with sodium hypophosphite. The results are listed in Table 1. It can be seen that the highest reduction rate is observed for copper nitrate, sulfate, and formate (Table 1, sample nos. 1, 2, 5, 6, 8). Copper acetate and nitrate (sample nos. 3, 4, 9) are reduced at a lower rate because of their lower solubility in water. With $CuCl_2$ used, copper UDP was formed, in contrast to the case of reduction with glycerol [8], but formulations on its base could not be obtained because of the decreased stability and increased reactivity of the powder. Before being introduced into formulations, all the copper UDP samples obtained were treated with formic acid.

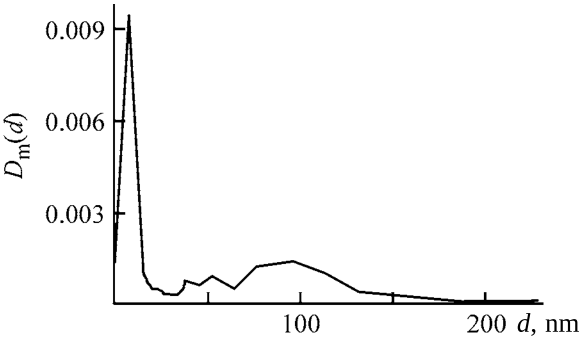

Fig. 1. Mass function $D_m(d)$ of the size (d) distribution of ultradispersed copper particles, calculated from small-angle X-ray scattering curves in the approximation of uniform spherical particles.

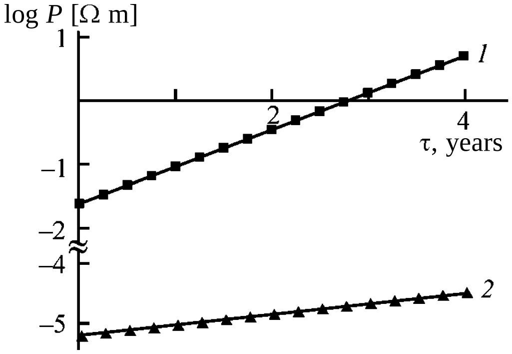

Fig. 2. Electrical resistivity ρ of the formulation (copper UDP + novolak resin SF-010) (*1*) in the initial state and (*2*) after additional treatment with formic acid, vs. the testing time τ.

The copper UDP samples obtained were used to prepare formulations with a novolak resin at a copper UDP to novolak resin ratio of 100 : 25. The highest electrical conductivity and stability were observed for a formulation based on copper formate, since in this case the reaction products (formate ion etc.) stabilize copper (sample no. 8). Only slightly inferior in electrical conductivity to this sample are formulations based on copper sulfate (sample nos. 5, 6) and copper citrate (sample no. 9), but they are unstable in storage. The formulations based on copper nitrate and acetate have even lower electrical conductivity and stability.

Apparently, the presence of an excess amount of sodium hypophosphite leads to higher electrical con-

Table 1. Reduction of copper(II) salts with sodium hypophosphite in an aqueous medium.* SF-010 novolak resin : copper UDP = 25 : 100

Sample no.	Copper salt	Cu(II) : NaH_2PO_2, mol : mol	τ_r, min	T_r, °C	$\rho \times 10^6$, Ω m, at indicated testing time, years				
					1 day	1	2	3	4
1	$Cu(NO_3)_2 \cdot 3H_2O$	1 : 1.5	7	85	11.2	15.6	22.5	31.8	40.2
2	″	1 : 2	5	85	8.5	11.8	16.9	22.4	28.2
3	$Cu(OAc)_2 \cdot H_2O$	1 : 1.5	35	90	18.2	22.6	32.4	44.2	55.8
4	″	1 : 2	30	90	10.8	14.3	19.8	27.2	34.6
5	$CuSO_4 \cdot 5H_2O$	1 : 1.5	10	85	8.2	10.6	16.8	24.4	32.6
6	″	1 : 2	7	85	6.8	8.2	12.0	16.4	21.2
7	$CuCl_2 \cdot 6H_2O$	1 : 3	10	90	–	–	–	–	–
8	$Cu(COOH)_2$	1 : 2	10	85	4.2	4.4	4.6	4.7	–
9	$Cu_2(Citr) \cdot 2.5H_2O$	1 : 3	15	95	7.4	8.6	11.8	14.5	–

* τ_r and T_r are the time and temperature of the reduction of copper(II) salt with sodium hypophosphite.

ductivity and stability of copper formulations. This is presumably due to an additional stabilizing effect of unreacted hypophosphite ions, which decompose in the course of the reaction under the action of water, to give hydrogen [9].

We also studied the influence exerted by stabilizers introduced directly into the novolak resin on the electrical conductivity and stability of copper powders. It was noted in [8] that the best stabilizer (for both epoxy and novolak resins) is 1-naphthol, and additional introduction of glycerol as a plasticizer leads to a considerable increase in the stability and electrical conductivity. In this work, we analyzed the effect of the ratio between UDP, novolak resin, 1-naphthol, and glycerol on the stability and electrical conductivity of pastes with novolak resin (Fig. 3). Ultradispersed copper powders were obtained by reducing copper sulfate with sodium hypophosphite at a ratio ν(Cu) : $\nu(H_2PO_2^-)$ = 1 : 1.5 (Table 1, sample no. 5). It was found that, after introduction of 1-naphthol and glycerol, phenol–formaldehyde novolak formulations based on copper UDP obtained by the hypophosphite method become comparable in stability and electrical conductivity with copper ultradispersed powders prepared by reduction with glycerol.

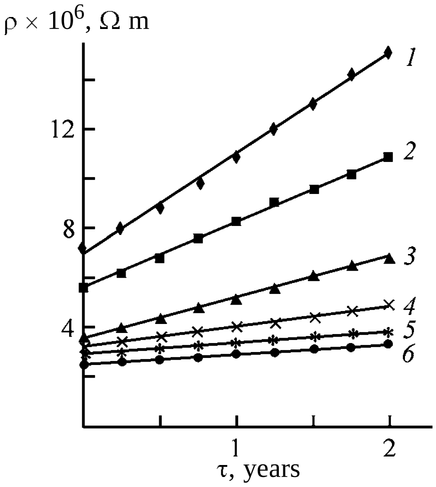

Fig. 3. Effect of stabilizers on the electrical resistivity ρ of formulations with an SF-010 phenol–formaldehyde novolak resin. (τ) Testing time. Weight ratio of copper UDP, SF-010, 1-naphthol, and glycerol (plasticizer): (*1*) 100 : 25 : 0.5 : 1.5, (*2*) 100 : 25 : 0.5 : 3, (*3*) 100 : 25 : 1.0 : 1.5, (*4*) 100 : 25 : 1.0 : 3, (*5*) 100 : 25 : 2.0 : 1.5, and (*6*) 100 : 25 : 2.0 : 3.

It can be seen that the optimal content of 1-naphthol in the formulations is 2 wt % relative to the amount of copper UDP (sample nos. 5, 6). A smaller amount of 1-naphthol is insufficient for obtaining stable formulations with nearly metallic electrical conductivity (sample nos. 1–4). As for the use of a larger amount, it is unfeasible because the electrical conductivity and stability increase in this case only slightly. Apparently, the stability and electrical conductivity also become higher as the amount of glycerol is raised (sample nos. 2, 4, 6). However, a large excess of glycerol may impair the properties of the pastes, because they show poorer hardening and become less stable in storage. Introduction of glycerol in an amount of 1.5–3% (relative to the mass of copper UDP) diminishes the brittleness of the novolak resins. The highest stability and electrical conductivity are exhibited by sample no. 6, stabilized with 2 wt % naphthol and 3 wt % glycerol. The higher optimal content of 1-naphthol in the formulations, compared to that in formulations prepared on the basis of ultradispersed copper powders obtained by reduction with glycerol,

Table 2. Reduction of copper(II) salts with sodium hypophosphite in a water–hexanol medium. SF-010 novolak resin : copper UDP = 25 : 100

Sample no.	Copper salt	Water : hexanol, v/v	Cu(II) : NaH_2PO_2, mol : mol	τ_r, min	T_r, °C	$\rho \times 10^6$, Ω m, at indicated testing time, years				
						1 day	1	2	3	4
1	$Cu(NO_3)_2 \cdot 3H_2O$	10 : 1	1 : 2	2	85	6.4	7.4	8.6	9.8	10.7
2	″	5 : 1	1 : 2	4	85	4.2	4.8	5.6	6.2	6.8
3	$Cu(OAc)_2 \cdot H_2O$	10 : 1	1 : 2	35	90	7.8	8.9	10.2	11.8	13.2
4	″	5 : 1	1 : 2	30	90	5.6	6.2	7.1	7.9	9.2
5	$CuSO_4 \cdot 5H_2O$	10 : 1	1 : 2	5	85	3.8	4.2	5.1	5.8	6.4
6	″	5 : 1	1 : 2	4	85	2.6	2.8	3.1	3.4	3.8
7*	″	5 : 1	1 : 2	4	85	2.8	3.0	3.2	3.5	–
8	$CuCl_2 \cdot 6H_2O$	10 : 1	1 : 4	4	90	–	–	–	–	–
9	$Cu(COOH)_2$	10 : 1	1 : 2	7	85	2.1	2.2	2.4	2.5	–
10	″	5 : 1	1 : 2	5	85	1.7	1.8	2.0	2.1	–

* Formulation prepared on the basis of copper(II) (sample no. 6) a year after UDP synthesis.

is due to the higher dispersity and reactivity of the UDP synthesized by reduction with sodium hypophosphite.

Copper(II) compounds were reduced with sodium hypophosphite both in an aqueous medium and in a mixture of solvents, polar (distilled water) and less polar (hexyl alcohol), at a water : hexanol volume ratio of 5 : 1 and 10 : 1. The reduction was carried out as follows: into a vessel containing a copper(II) salt solution was poured a sodium hypophosphite solution, the mixture was agitated, a necessary amount of hexyl alcohol was added, and the resulting mixture was heated to the reaction temperature of 80–90°C and kept at this temperature for 2–35 min, depending on the copper(II) salt used. Then, the hexanol layer was decanted, and the UDP formed was washed with water and treated with solutions of hydroquinone and stearic acid in ethanol. It was found that the stability of the UDP is enhanced as the amount of hexyl alcohol is increased.

The copper UDP samples synthesized were used to prepare formulations with novolak resin. The results obtained are listed in Table 2. It can be seen that all the samples prepared in the system water–hexanol have higher electrical conductivity and stability, compared to the samples synthesized in an aqueous medium (Table 1). The highest stability and electrical conductivity were observed for the UDP samples based on copper(II) formate and sulfate (even when the UDP was stored for a year). This is due to the action of hexanol, which, being adsorbed on the surface of copper UDP, prevents its oxidation and aggregation. However, the copper UDP samples obtained from copper chloride (Table 2, sample no. 10) are rather unstable, are rapidly oxidized, and formulations based on these UDP samples are not electrically conducting. This is probably due to the presence of chloride ions adsorbed on the UDP surface.

Copper(II) acetate, sulfate, formate, basic carbonate, and oxide were reduced with hypophosphorous acid in a water–hexanol medium at a water : hexanol volume ratio of 5 : 1. It was found that basic copper carbonate and copper oxide can only be reduced in the presence of excess hypophosphorous acid [$\nu(H_3PO_2)$: $\nu(Cu)$ = 4], and, being poorly soluble in water, these compounds do not react with sodium hypophosphite. The results obtained are listed in Table 3. Apparently, the reduction of copper(II) compounds with H_3PO_2 occurs more actively than that with sodium hypophosphite.

Comparison of Tables 2 and 3 shows that the highest electrical conductivity is exhibited by formulations based on copper UDP samples obtained by reduction with hypophosphorous acid. This is due to the fact that, according to the results of X-ray phase analysis, virtually no oxides could be found in the samples reduced with hypophosphorous acid even in an aqueous medium, in contrast to the samples synthesized by reduction with sodium hypophosphite. Thus, the highest electrical conductivity and stability of formulations based on copper UDP are attained in the case of reduction of copper(II) formate or sulfate with hypophosphorous acid, and also upon introduction of 2 wt % 1-naphthol and 3 wt % glycerol into the formulations.

These formulations are only slightly inferior in electrical conductivity and stability to those ob-

Table 3. Reduction of copper(II) salts with hypophosphorous acid in a water–hexanol medium. Volume ratio water : hexanol = 5 : 1, SF-010 novolak resin : copper UDP = 25 : 100

Sample no.	Copper salt	Cu(II) : H_3PO_2, mol : mol	τ_r, min	T_r, °C	$\rho \times 10^6$, Ω m, at indicated testing time, years				
					1 day	1	2	3	4
1	$Cu(OAc)_2 \cdot H_2O$	1 : 2	20	90	4.2	4.6	5.4	6.2	6.6
2	$CuSO_4 \cdot 5H_2O$	1 : 2	3	85	2.0	2.2	2.5	2.8	3.2
3	$Cu(COOH)_2$	1 : 2	4	85	1.5	1.6	1.7	1.8	–
4	$CuCO_3 \cdot Cu(OH)_2$	1 : 4	15	90	2.4	2.7	3.1	3.6	4.1
5	CuO	1 : 4	25	90	2.5	2.7	3.0	3.4	3.9

tained by reduction with glycerol and stabilized with 1-naphthol and glycerol, but their synthesis is characterized by lower consumption of energy and materials (milder conditions, low expenditure of the reducing agent, lower expenditure of a solvent for UDP washing).

Thus, it is preferable to perform the reduction of copper(II) compounds with sodium hypophosphite and hypophosphorous acid in the system water–hexanol, rather than in the aqueous medium. Adsorption of hexyl alcohol on the surface of copper particles substantially improves their stability and raises the electrical conductivity, so that formulations based on the UDPs of this kind become comparable with those prepared on the basis of UDPs synthesized by reduction with glycerol [4–8] and can compete with similar materials based on silver [1–2].

CONCLUSIONS

(1) Ultradispersed copper powders and formulations based on them were synthesized by reducing various copper salts with sodium hypophosphite and hypophosphorous acid.

(2) The ultradispersed copper powders obtained by reduction with sodium hypophosphite and hypophosphorous acid become more stable and electrically conductive upon treatment with formic acid.

(3) The ultradispersed copper powders synthesized in a water–hexanol medium show higher stability and electrical conductivity.

(4) The increased stability and low production cost of these materials make them promising for use in modern nanoelectronics instead of composites based on noble metals.

REFERENCES

1. US Patent 5 891 367.
2. US Patent 5 929 141.
3. JPN Patent Appl. 3 239 767.
4. RF Patent 2 031 759.
5. RF Patent 2 115 516.
6. Obraztsova, I.I., Efimov, O.A., Eremenko, N.K., and Simenyuk, G.Yu., *Izv. Ross. Akad. Nauk, Neorg. Mater.*, 1995, vol. 31, no. 4, pp. 798–799.
7. Obraztsova, I.I., Simenyuk, G.Yu. and Eremenko, N.K., *Inorg. Mater.*, 1999, vol. 35, no.. 8, pp. 792–794.
8. Obraztsova, I.I., Simenyuk, G.Yu., and Eremenko, N.K., *Zh. Prikl. Khim.*, 2002, vol. 75, no. 11, pp. 1772–1775.
9. Chernogorenko, V.B. and Tasybaeva, Sh.B., *Zh. Prikl. Khim.*, 1995, vol. 68, no. 4, pp. 529–533.