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Effect of Chemical Modification of Ultradispersed Copper Powders on Electrical Conductivity of Formulations on Their Base

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Abstract—Ultradispersed powders of copper were obtained by reducing various copper salts with glycerol, and formulations on their base were prepared. The effect of various modifiers on the dispersity, stability, and electrical conductivity of copper powders was examined.

Synthesis and study of ultradispersed powders (UDPs) of metals and development of electrically conducting materials on their base is a topical direction of research in modern science. Recently, increasing attention has been given to copper [1, 2], which is virtually as good as noble metals as regards its electrical conductivity [3–5] and much less expensive. However, copper powders exhibit rather high activity and are oxidized in the course of time, which inevitably impairs the conductivity. This problem can be solved by optimizing the preparation process, modifying the surface of copper UDPs, and creating formulations on their base, whose electrically conducting properties are preserved for a long time. Data on the longevity of electrically conducting formulations are virtually lacking from the literature.

Previously, two methods for obtaining copper UDPs have been developed [6, 7]. These methods are based on reduction of copper sulfate with glycerol. The optimal temperature, time, and reagent concentrations were determined. Also, the influence exerted by organic acids with reducing properties (ascorbic, citric, etc.) on the reaction of copper sulfate with glycerol and on the properties of the copper powders obtained was examined. It was established that additions of these acids accelerate the reaction by a factor of 5–6, allow the process temperature to be decreased by 20–40°C, and ensure enhanced stability and electrical conductivity of the resulting copper UDPs.

It was also found that, upon an appropriate treatment with solutions of hydroquinone and stearic acid in ethanol or pentane, copper UDPs possess increased dispersity (average particle size 20–30 nm), stability, and electrical conductivity. Furthermore, powders treated with pentane can be stored for a long time not only in solution, but also in air.

In this work, we prepared UDPs from various copper(II) salts and examined the influence exerted by chemical modification of copper UDPs on the electrical conductivity and stability of formulations on their base. The data obtained in the study are compared with those published previously [8, 9]. New data on the formulation longevity are presented.

EXPERIMENTAL

Copper UDPs were prepared by reducing various copper salts with glycerol by the method described in [9]. However, it was found that complete reduction of readily decomposing salts (acetate, basic carbonate, and tartrate) requires smaller amount of glycerol, lower temperature T_r, and shorter reaction time τ_r. The results obtained at different copper salt to glycerol mass ratios A are presented in Table 1. It can be seen that the reduction of copper basic carbonate, acetate, and tartrate is the most effective, and their formulations with novolac show high electrical conductivity and are stable for a long time (more than 5 years) without addition of any stabilizers. Here, copper UDP is presumably stabilized in the course of the reaction by glycerol itself.

It also follows from Table 1 that, in reduction of copper(II) sulfate, the electrical conductivity of the resulting formulations falls dramatically when no additional stabilizers are introduced into the resin (experiment no. 1). When, however, modifiers are introduced (experiment no. 2), the formulations obtained

Table 1. Conditions of copper UDP preparation from various copper salts and resistivity ρ of novolac formulations based on copper UDPs

Experiment no.	Compound	*A*	τ_r, min	T_r, °C	$\rho \times 10^4$, Ω cm, at indicated testing time, years							
					1 day	1 month	0.5	1	2	3	4	5
1	$CuSO_4 \cdot 5H_2O$	1 : 10	300	180–190	5.4	8.0	18.2	32.4	48.4	57.6	64.8	72.6
2	$CuSO_4 \cdot 5H_2O$*	1 : 10	300	180–190	1.2	1.2	1.3	1.5	1.7	1.8	1.8	1.9
3	$Cu(OAc)_2 \cdot H_2O$	1 : 3	40	145–155	0.6	1.2	1.2	1.2	1.2	1.2	1.2	1.2
4	$CuCO_3 \cdot Cu(OH)_2$	1 : 4	14	140–145	0.6	0.8	0.9	0.9	0.9	0.9	0.9	0.9
5	$CuTart \cdot 3H_2O$	1 : 5	145	160–165	1.2	1.4	1.4	1.5	1.6	1.7	1.8	1.9
6	$Cu(NO_3)_2 \cdot 3H_2O$**	1 : 10	350	160–170	–	–	–	–	–	–	–	–
7	$CuCl_2 \cdot 2H_2O$***	1 : 10	–	–	–	–	–	–	–	–	–	–

* Formulation stabilized with 1-naphthol and glycerol simultaneously.
** Copper UDPs are rapidly oxidized by reaction products.
*** No copper powder is formed.

compare well in the electrical conductivity and stability with pastes based on copper UDPs produced by reduction of readily decomposing copper salts (experiment nos. 3–5).

In the case of reduction of copper(II) nitrate, the UDP formed is very rapidly oxidized in the course of the reaction, which markedly diminishes the yield of the metallic phase.

In reduction of copper(II) chloride, no metallic copper is formed, even upon addition of an initiator, ascorbic acid (up to 0.5 g per gram of copper). In the reaction with copper chloride, glycerol undergoes extensive tarring to give a black viscous mass solidifying on cooling.

The aforesaid suggests that it is preferable to use copper sulfate for commercial preparation of electrically conducting materials. On the one hand, other copper salts are less readily available and more expensive, and, on the other, $CuSO_4$-based formulations with various modifiers are virtually as good as pastes prepared from other copper salts, as regards their stability and electrical conductivity.

The effect of chemical modification of the surface of copper UDPs was studied in different stages: in synthesis, treatment, storage, and formulation preparation.

It was shown previously [9] that introduction of organic acids with reducing properties (ascorbic, oxalic, citric, and formic) into the reaction mixture much intensifies the reduction process. It was found here that addition of acetylsalicylic acid in amount of 5 wt % relative to copper sulfate pentahydrate makes it possible to diminish the process time even more (10-fold). Furthermore, it was found that the nature of the acid also affects the particle size. For example, the highest dispersity is observed when acetylsalicylic acid is added as initiating agent, since the major part of particles are 10–40 nm in size (according to electron microscopy). In the case when ascorbic acid is used, a minor amount of 100–200-nm aggregates are present together with the highly dispersed phase, and introduction of citric acid leads to formation of 40–300-nm particles. It was found that the dispersity grows with increasing acid concentration. This is due to the following facts: (i) particle agglomeration becomes weaker under milder reaction conditions; (ii) in some cases, introduction of acids instantaneously initiates reduction to give a large number of nuclei of the metallic phase; and (iii) organic acids may enter into the composition of intermediate reaction products, thereby changing the structure of copper UDPs formed on their base.

Prolonged storage of copper UDPs in air or in ethanol may lead to partial oxidation of the surface layer, with the electrical conductivity of formulations decreasing dramatically. It was found that the electrical conductivity can be easily restored in this case by treating the copper UDP with formic acid (1–2 ml of HCOOH per gram of copper). No UDP oxidation is observed in the case of storage in pentane.

The copper UDPs obtained were used to prepare electrically conducting formulations with epoxy or novolac resins. The formulations were cured in accordance with the polymerization mode of the resin employed. A study of the influence exerted by reduction of copper sulfate with glycerol on the electrical conductivity of the formulations demonstrated that the number of conducting chains in formulations with

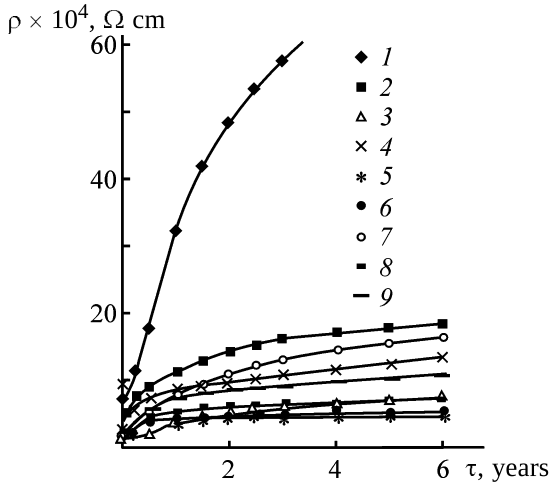

Fig. 1. Electrical resistivity ρ of formulations comprising SF-010 novolac resin, copper UDP, and organic acid vs. testing time τ. Curve nos. are sample nos. in Table 1.

epoxy resin is sufficient for stable electricity transfer even at metal concentration of 55%. In the case of novolac resin, a higher content of metal is necessary (65–70%). However, at a metal content of 75–80% the electrical conductivities of composites based on these resins become comparable.

It was established that copper formulations obtained using different methods and different modifiers markedly differ in the electrical conductivity and stability (Figs. 1, 2). Table 2 lists the results obtained in studying the influence exerted by introduction of a number of organic acids (initiating agents) at different mass ratios *B* ($CuSO_4 \cdot 5H_2O$: glycerol : initiating agent) on the parameters τ_r and T_r of the copper UDP preparation process.

As follows from Fig. 1 and Table 2, introduction of various organic acids (ascorbic, oxalic, citric, formic, or acetylsalicylic) markedly shortens τ_r of copper reduction with glycerol (by a factor of more than 10 in the case of acetylsalicylic acid) and yields formulations with novolac resin that are characterized by high stability (for more than 6 years) and low resistivity (compared to sample no. 1 prepared without introduction of initiating agents). It can also be seen that the electrical conductivity and stability of the formulations grow with increasing concentration of any of the organic acids (sample nos. 3, 5, 6, and 8).

The effect of various stabilizing additives on the electrical conductivity and stability of formulations with epoxy resin is illustrated in Fig. 2a. It can be seen that all formulations with addition of 1-naphthol or *p*-aminophenol retain unchanged high electrical conductivity for more than 10 years (curves *2*–*6*), and formulations with 1-naphthol have the lowest electrical resistivity of (0.8–1.2) × 10^{-4} Ω cm, close to that of the metal. Formulations with Diaphene (curve *7*) have high initial electrical conductivity, but, after 4 years, the properties of the formulation deteriorate dramatically. With other stabilizers (curves *8*, *9*), the longevity of formulations was even lower.

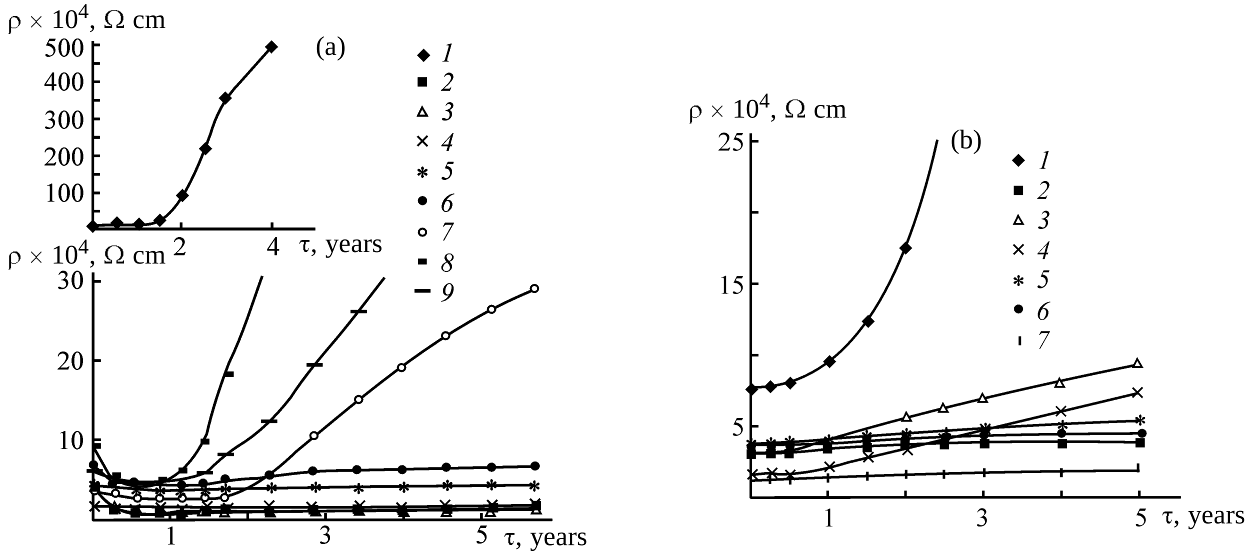

Fig. 2. Effect of stabilizers on the dependence of the electrical resistivity of formulations with (a) EDP epoxy resin and (b) SF-010 novolac resin on the testing time τ. (a) (*1*) Without stabilizer; stabilizer: (*2*–*4*) 1-naphthol, (*5*, *6*) *p*-aminophenol, (*7*) Diaphene, (*8*) *p*-phenylenediamine, and (*9*) 1-naphthylamine. Copper UDP : EDP : stabilizer mass ratio: (*1*) 100 : 40 : 0, (*2*) 100 : 40 : 1.0, (*3*) 100 : 35 : 1.0, (*4*) 100 : 25 : 1.0, (*5*–*7*, *9*) 100 : 30 : 1.0, and (*8*) 100 : 32 : 1.0. (b) (*1*) Without stabilizer; stabilizer: (*2*) 1-naphthol, (*3*) *p*-aminophenol, (*4*) ascorbic acid, (*5*) hydroquinone, (*6*) formic acid, and (*7*) 1-naphthol + glycerol (plasticizer). Copper UDP : SF-010 : stabilizer mass ratio: (*1*) 100 : 25 : 0, (*2*–*5*) 100 : 25 : 1.0, (*6*) 100 : 25 : 5.0, and (*7*) 100 : 25 : 1.0 : 3.0 (3 wt parts of glycerol).

Table 2. Effect of initiator on the conditions of preparation of copper UDPs

Sample no.	*B*	Initiator (acid)	τ_r, min	T_r, °C
1	1 : 10.0 : 0	–	300	180–190
2	1 : 10.0 : 0.003	Ascorbic	85	160–165
3	1 : 7.5 : 0.020	″	40	140–145
4	1 : 5.0 : 0.010	″	40	150–155
5	1 : 7.5 : 0.100	Oxalic	70	160–165
6	1 : 7.5 : 0.060	Citric	100	170–175
7	1 : 7.5 : 0.030	Formic	80	160–165
8	1 : 6.7 : 0.120	″	55	160–165
9	1 : 10.0 : 0.050	Acetylsalicylic	25	155–160

Thus, a conclusion can be made that the best stabilizers for epoxy formulations are 1-naphthol and *p*-aminophenol, which are known [10] to be effective inhibitors of oxidation with molecular oxygen, used to prevent aging of polymers and stabilize jet-engine fuel in prolonged storage.

For formulations with novolac resin, the effect of various stabilizers is illustrated in Fig. 2b. It can be seen that all of the modified samples have lower resistivity and are more stable than the initial sample (curve *1*), with the lowest resistivity observed for the formulation stabilized with a mixture of glycerol and 1-naphthol (curve *7*). The introduction of glycerol, presumably, makes lower the brittleness of the novolac formulations and improves their adhesion characteristics, which makes higher their electrical conductivity. In contrast to [9], where stability data were reported for a time period of only 3 months, we report here the data obtained during the last 5 years. It is clear that not all of the formulations studied possess stable characteristics, but only those stabilized with 1-naphthol (curve *2*), formic acid (curve *6*), hydroquinone (curve *5*), and a mixture of glycerol and 1-naphthol (curve *7*). As in the case of epoxy formulations, the best oxidation inhibitor is 1-naphthol, and addition to this compound of glycerol in 1 : 3 ratio yields formulations comparable in electrical conductivity (resistivity 1.2×10^{-4} Ω cm) with the best samples with epoxy resin (Fig. 2a) and novolac formulations with addition of organic acids (Fig. 1) or those obtained from readily decomposing copper salts (Table 1).

CONCLUSIONS

(1) Ultradispersed powders prepared from readily decomposing copper salts and formulations synthesized on their base retain high electrical conductivity for more than 5 years.

(2) The best stabilizer for ultradispersed copper powders obtained from copper sulfate is 1-naphthol or its mixture with glycerol.

(3) Chemical modification of ultradispersed copper powders results in that epoxy formulations prepared on their base retain their high electrical conductivity for more than 10 years.

(4) The enhanced stability and low cost of these copper-based materials makes them promising for use in modern nanoelectronics instead of composites based on noble metals.

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