FUNCTIONALIZATION OF TEXTILE MATERIALS BY USING COPPER- CONTAINING COATINGS AND PIGMENTS

Huan Lu[1], Boris Mahltig[1*]

[1] University of Applied Sciences Niederrhein, Faculty of Textile and Clothing Technology, Webschulstr. 31, 41065 Mönchengladbach, Germany
[*] e-mail:boris.mahltig@hs-niederrhein.de,
ORCID ID (https://orcid.org/0000-0002-2240-5581)

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Abstract: *Copper is one of the most used industrial metals. Also, copper containing compounds have high importance in everyday life. The use of copper and its compounds for textile treatment and functionalization is possible by using a broad range of different methods; as e.g. electrodeposition, plasma deposition, spin-doping with copper containing pigment or dye applications using copper salts as mordants or complexing agents. This actual report focusses especially on the use of copper containing pigments applied as part of a coating or a print onto textile surfaces. A general introduction into different types of copper compounds is given. Examples are given for the application of coatings containing copper effect pigments, gold bronze, elemental copper pigments and copper oxide particles. Related to effect pigments, especially silver coated copper pigments are introduced. According to sol-gel applications for textile functionalization, the in-situ preparation of copper oxide nanoparticles on textile surfaces is discussed. Following an overview on possible functionalization as result of the copper application is given. Antimicrobial and antistatic properties are discussed and presented with examples. The determined effects in this field are significant but less compared to analogous functionalization using silver as functional compound. A view on optical modifications and realized UV-protective properties is given. Finally, it can be stated that copper containing materials can be helpful tools to functionalize textile materials and surfaces in a broad range.*

Keywords: copper, textile functionalization, pigment, oligodynamic effect, antistatic, coloration.

FUNKCIONALIZACIJA TEKSTILNIH MATERIJALA KORIŠĆENJEM PREMAZA I PIGMENATA KOJI SADRŽE BAKAR

Apstrakt: *Bakar je jedan od najčešće korišćenih industrijskih metala. Takođe, jedinjenja koja sadrže bakar imaju veliki značaj u svakodnevnom životu. Upotreba bakra i njegovih jedinjenja za obradu i funkcionalizaciju tekstila moguća je korišćenjem širokog spektra različitih metoda; kao npr. elektrodepozicija, taloženje plazmom, spin-dopiranje sa pigmentom koji sadrži bakar ili primena boja korišćenjem soli bakra kao jedki ili agenasa za stvaranje kompleksa. Ovaj aktuelni izveštaj se posebno fokusira na upotrebu pigmenata koji sadrže bakar naneti kao deo premaza ili štampe na tekstilnim površinama. Dat je opšti uvod u različite vrste jedinjenja bakra. Dati su primeri za nanošenje premaza koji sadrže pigmente sa efektom bakra, zlatnu bronzu, elementarne pigmente bakra i čestice bakarnog oksida. U vezi sa efektnim pigmentima, posebno se uvode posrebreni bakarni pigmenti. Prema sol-gel aplikacijama za funkcionalizaciju tekstila, razmatra se in-situ priprema nanočestica oksida bakra* *na tekstilnim površinama. U nastavku je dat pregled moguće funkcionalizacije kao rezultat primene bakra. Antimikrobna i antistatička svojstva su razmotrena i prikazana na primerima. Utvrđeni efekti u ovoj oblasti su značajni, ali manje u poređenju sa analognom funkcionalizacijom korišćenjem srebra kao funkcionalnog jedinjenja. Dat je pogled na optičke modifikacije i ostvarene UV-zaštitne osobine. Konačno, može se reći da materijali koji sadrže bakar mogu biti korisni alati za funkcionalizaciju tekstilnih materijala i površina u širokom opsegu.*

Ključne reči: bakar, funkcionalizacija tekstila, pigment, oligodinamički efekat, antistatik, obojenost.

1. INTRODUCTION

The modification of textile materials by metals and metal compounds is widely used and used in many different fields of application. Probable one of the oldest applications using metal compounds is the mordanting applied in processes of natural dyeing [1]. Here the soluble metal salts like e.g. aluminum acetate, copper sulphate or iron sulphate are used to improve the color intensity of natural dyes after application on natural fibers [2-4]. The influence of mordants on color intensity, color shade, washing, rubbing and light fastness is significant and under the demand of good fastness properties for most natural dyes an application without mordant is not possible [2-5].

Nowadays, also metals are applied on textiles in elementary form by different methods and for different functional reasons [6-8]. Textiles carrying coatings or layers of metallic aluminum are often dedicated to reflect heat radiation [9]. This reflection of heat radiation is of interest for workwear, e.g. for applications in factories where liquid metals are present. Also, applications for home textiles as window covering especially during summer season are of interest. Another very prominent example for metallized textiles are silver coating fibers and fabrics. The purpose of silver coatings is mainly to realize an effective antimicrobial effect on the textile [10, 11]. Such silver containing textiles are offered for treatment of atopic dermatitis and can be sold for reasonable high prices [12]. The antimicrobial effect of silver is related to the release of silver ions in surrounding media and by interaction of silver ions with microbes the microbes are affected and killed [13]. Several different metals and metal compounds exhibit such an antimicrobial effect and this property of metals is also named as "oligodynamic effect" [14]. Additionally to the antimicrobial properties of silver, silver is an excellent conductor for electricity. For this, silver coated fibers can be applied to reach antistatic or even electric conductive textile materials [15]. Several products are offered for the shielding of radiowaves and commercialized as materials for protection against electrosmog [16, 17].

By view on this background of broad usage of metals on textiles, it is of interest to overview the metal copper and its possible applications on textiles. Especially compared to silver, copper has a significant cost advantage. For this, the actual report supports a short overview on the usage of copper containing coatings and pigments for textile functionalization. Of course, such an overview can only cover a selection of available materials and techniques. Copper is the only red colored metal (Figure 1). It is available as pigments, which can be applied as coating additive. Also, fabrics with copper fibers are available as commercial products and offered for cleaning purposes. See examples in Figure 1.

Figure 1: Examples for copper products, from left to right: a metal copper piece, copper pigment powder and a fabric made from polypropylene fibers and copper

2. COPPER MATERIALS & APPLICATION

Copper components can be applied on textiles and fibers in totally different forms. An overview on different copper components is given in Figure 2. To support the reader a structured view on the different types of components, a categorization into four main groups is done – copper pigments, effect pigments, color pigments and electrodeposition. Copper containing color pigments are mainly dedicated to support coloration and are applied together with binder systems onto substrates. These can be inorganic pigments as malachite or spinel type pigments [18, 19]. Also, organic pigments as copper phthalocyanine should be mention. Main colorations are brown, black, green or blue [18]. While these color pigments are built up by copper compounds, also copper pigments from elemental copper can be applied. Here, a difference can be made in the size of the copper pigments – micro- or nanosized pigment particles are possible. An example for copper micro pigments applied on textiles is shown in Figure 3, presenting different microscopic images. These copper pigments are supplied under the name "Rogal Kupfer GK" by the company Schlenk GmbH. Interesting materials in the field of nanoparticles are copper oxide nanoparticles as e.g. supplied by Carl Roth GmbH (see also Figure 3). However, even if these materials are offered as nanoparticles, after application onto textiles they are forming larger agglomerates of micrometer size. Copper nanoparticles can be also deposited onto surfaces by using modified plasma polymerization processes [20]. In comparison to copper pigments with spherical shape, copper based effect pigments exhibit a flat particle shape. Please compare the microscopic images in Figure 3. The shown copper effect pigments contain an anisotropic flat structure and a shape which is also named as "corn-flake" structure [21]. Such metal effect pigments are originally dedicated to realize special optical effect containing a high reflectivity for light [22]. This reflectivity for light is also show in Figure 3 by presenting a light microscopic image recorded in reflection mode. Mostly copper based effect pigments are not built up from pure copper. Commonly they are offered as gold bronze pigments building up by an alloy containing additional to copper also other metals as e.g. zinc. Those gold bronze pigments are supplied in different colorations [22-24]. A special type of copper pigments is coated with silver and are supplied under the name eConduct by the company Eckart Effect Pigments. These products are offered for realization of conductive prints and electromagnetic shielding [25].

To protect copper pigments against corrosion and to enhance their performance in application recipe and binder, they are often coated by silicones or polymers [26]. Additionally to the application of copper as pigments, it is possible to cover a fabric or fiber completely with a copper coating by electrodeposition [27, 28]. These materials are of high interest for production of electric conductive textile useable e.g. for wearable electronics.

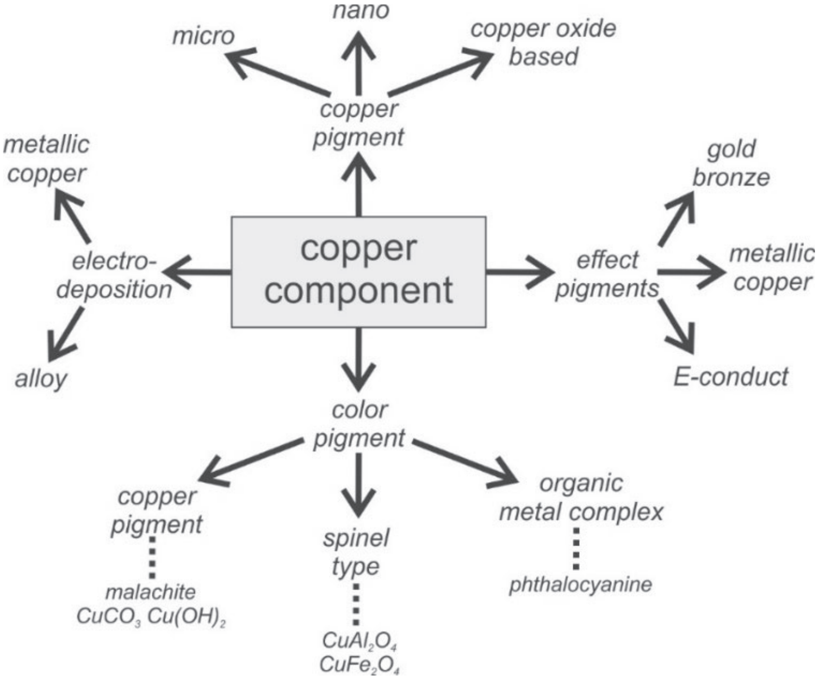

Figure 2: Overview on copper compounds applicable for the functionalization of textiles

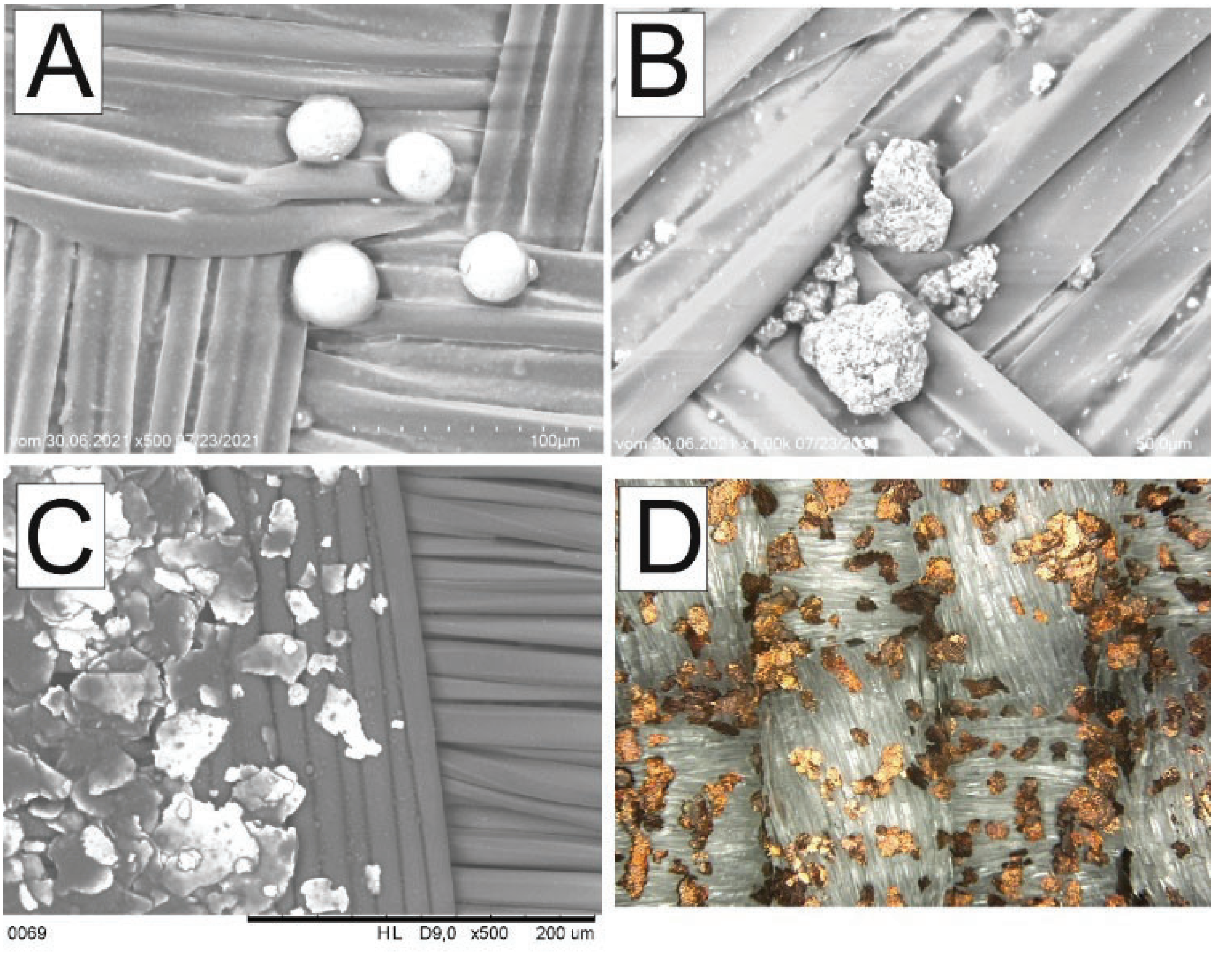

Figure 3: Microscopic images of different copper compounds after application onto textile substrates – (A) spherical copper microparticles; (B) copper oxide nanoparticles as agglomerates; (C) copper effect pigments – image taken at edge of coated area; (D) copper effect pigments – image taken by light microscopy

Textile samples treated with recipes containing spherical copper micro particles (as shown in Figure 3, Picture A) can be statistically evaluated by using a counting software analyzing microscopic images. For this, by scanning electron microscopy images with low magnification of X100 are recorded and evaluated by using the Software CountThis. Using this evaluation all copper pigments can be counted on the complete microscopic image which stands for a magnified area of 1.2 mm^2. The result of this evaluation is the determined surface concentration of copper particles on the textile surface after coating application. Figure 4 presents the results for such an evaluation, there the number of counted pigments is shown as function of pigment concentration in coating recipe. Here two types of copper pigments are used - type 1 with smaller particle size of 50 micrometer and type 2 with larger particles size of 63 micrometer. Both products are supplied under the name Rogal Kupfer GK.

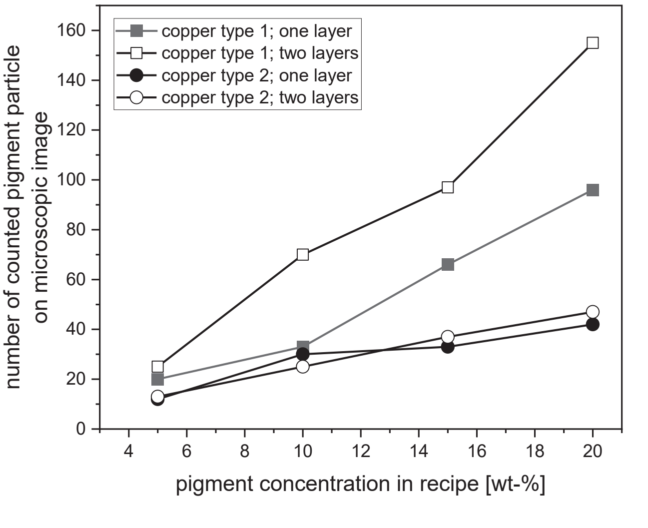

Figure 4: Surface concentration of copper particles on textile surface after coating application. The number of particles is determined from a microscopic image with total size of 1.2 mm^2

The copper particles are applied in a binder recipe in one layer or two layers application. It is obvious that with increasing copper concentration in the recipe also the amount of copper pigments is increasing on the textile surface. For the copper particles type 2 of larger size smaller number of pigments are detected, this can be explained by larger weight per particle. The application of a second layer is only increasing the number of particles for the copper type 1, containing smaller particle size. The copper particles are mainly deposited in free areas between the fibers on the textile surfaces. In application of the second layer larger particles probable do not find enough space to be deposited, so for them the number of copper particles does not increase with the application of a second recipe layer.

3. FUNCTIONAL PROPERTIES

By application of the different copper components, textile materials can be functionalized in a broad range. To structure the different functionalization in a reasonable method, they can be categorized in mainly four fields (Figure 5). The interaction with electromagnetic radiation, leading to UV-protection and shielding of electrosmog [25, 29]. The decrease of electrical resistance of a textile material, leading to anti-static or even electric conductive properties [25]. The interaction with visible light, leading to coloration effects and especially mentioned optical metallic effects [23]. Finally, the antimicrobial effectivity and for copper components in this field especially the effect against algae [25, 30-32].

To demonstrate the influence on electrical surface resistance, Figure 6 presents results gained after application of coatings containing different effect pigments [25]. Two different types of effect pigments are applied in two different coating thickness. One effect pigment is made from copper only. The second effect pigment is from the type econduct, which is a pigment with a copper core and a coated silver surface. By view on the results it is clear with increasing amount of pigments in the coating recipe the electrical surface resistance decreases drastically. In contrast, the thickness of the coating has nearly no influence. The application of the pure copper materials leads to resistance values equal to excellent antistatic properties. In comparison, by using the econduct product, even electric conductive textile materials can be realized. One explanation for this is the contact of the metal effect pigments between each other by the highly conductive silver coating on the pigment particle surface [21].

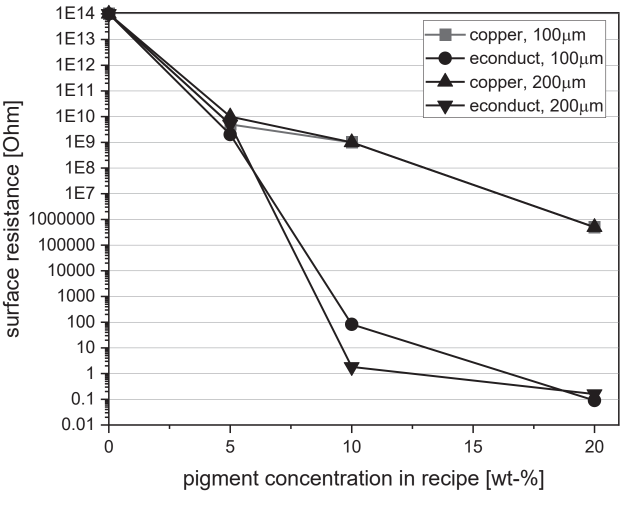

Figure 6: Antistatic properties of effect pigment containing coatings on textile fabric as function of increasing pigment concentration. Shown are two different types of effect pigments applied with two different coating thicknesses

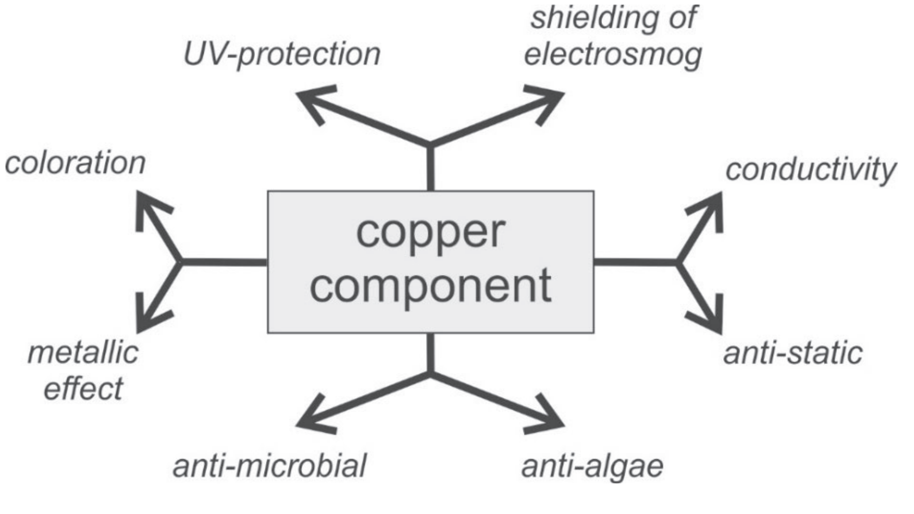

Figure 5: Overview on functionalization possible by copper containing compounds on textile substrates

The antimicrobial properties of copper particles on textiles can be demonstrated by a decrease of bacterial viability under controlled conditions (Figure 7). Figure 7 presents such results for coatings containing copper based effect pigments – pure copper pigment and one pigment of econduct type [25]. The remaining bacterial viability is determined for two different types of bacteria *E. coli* and *S. aureus*. It is obvious that the bacterial viability is decreased as function of applied pigment concentration and with applied coating thickness. Also, the silver containing pigment econduct exhibit a better performance, because silver compounds show often a better antimicrobial performance compared to copper [33].

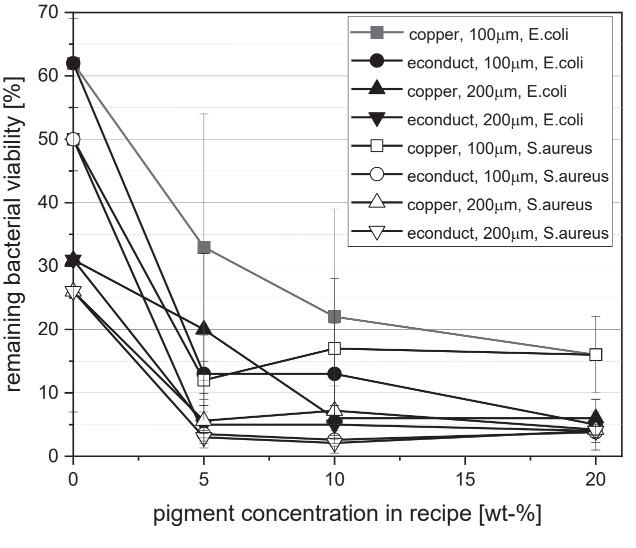

Figure 7: Antimicrobial properties of effect pigment containing coatings on textile fabric as function of increasing pigment concentration. Shown are two different types of effect pigments applied with two different coating thicknesses and tested against two different types of bacteria

4. CONCLUSIONS

In conclusion it can be stated that copper containing components can be applied on textiles and fibers in many different forms and different methods. The purpose of copper application is often to realize coloration effects and special colors. However, additional to coloration copper components can be applied on textiles for realization of a broad range of different functional properties. Nevertheless, in the field of textile functionalization, copper components have to compete with other functional additives showing similar or even better performance. Finally, the additive with the best performance under consideration of economic and ecologic concerns will be considered to realize the textile with the desired functional property.

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