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Coatings with metallic effect pigments for antimicrobial and conductive coating of textiles with electromagnetic shielding properties

Kristin Topp, Hajo Haase, Christoph Degen, Gerhard Illing, Boris Mahltig

Abstract Effect pigments were originally developed to realize advanced optical effects by coating on several types of material surfaces. However, metallic effect pigments are expected to be valuable for many other applications, such as antimicrobial effects, electrical conductive coatings, or shielding against radio waves (electromagnetic shielding). Accordingly, the aim of this article is to evaluate the advanced properties which can be realized by application of coatings containing metallic effect pigments onto textile materials leading to new functional textiles. In total, four different metallic effect pigments were investigated and compared to silver and graphite pigments. By application of coatings with copper- or silver-containing effect pigments significant antibacterial properties against *E. coli* and *S. aureus* can be realized. To achieve electric conductive textiles, which also enable effective shielding against radio waves, a copper pigment carrying a silver coating leads to the best properties. Altogether, an effective coating method is presented to achieve functional textiles that offer a broad range of possible applications.

Keywords Metal pigments, Antibacterial, Conductive coating, Silver, Copper

K. Topp, B. Mahltig (✉)
Faculty of Textile and Clothing Technology (FTB), Hochschule Niederrhein – University of Applied Sciences, Webschulstr. 31, 41065 Mönchengladbach, Germany
e-mail: boris.mahltig@hs-niederrhein.de

H. Haase
Institute of Immunology, Medical Faculty, RWTH Aachen University, Pauwelsstr. 30, 52074 Aachen, Germany

C. Degen
Faculty of Electrical Engineering and Computer Science, Hochschule Niederrhein – University of Applied Sciences, Reinarzstr. 49, 47805 Krefeld, Germany

G. Illing
Faculty of Technik, Hochschule Emden-Leer - University of Applied Sciences, Constantiaplatz 4, 26723 Emden, Germany

Introduction

Through the use of effect pigments as coating additives, various kinds of advanced optical properties can be realized by coating on different types of materials.[1,2] Those advanced optical properties result from effective reflection of light. One reason for this extraordinary reflection characteristic is the anisotropic shape of the effect pigments. This anisotropic shape can be described as plain geometry which can be seen as little mirrors leading to a stronger reflection of light in comparison to isotropic spherical pigment with identical material composition.[3,4] The anisotropic geometry is also described as flake, platelet, or lamellar shape.[5] In addition to the particle shape, other parameters are discussed which have an influence on the optical effect of effect pigments, such as, pigment surface, embedding in a coating, or scattering effect between different pigments.[6] The main advantages of effect pigments are described for a various kind of different optical effects, as for example the illusion of optical depth, eye-catching color effects, or the imitation of natural pearls.[7] Nowadays, many different types of effect pigments are on the market, for example, those commercialized for coatings and paints in the automotive field. Applications are also reported for security features on paper money, quality enhancement of printing papers, modification of infrared reflection, and for special optical effects introduced to plastic substrates.[8–10] Roughly, these pigments can be distinguished by their composition in two main groups. First, there are mineral effect pigments, consisting, e.g., of

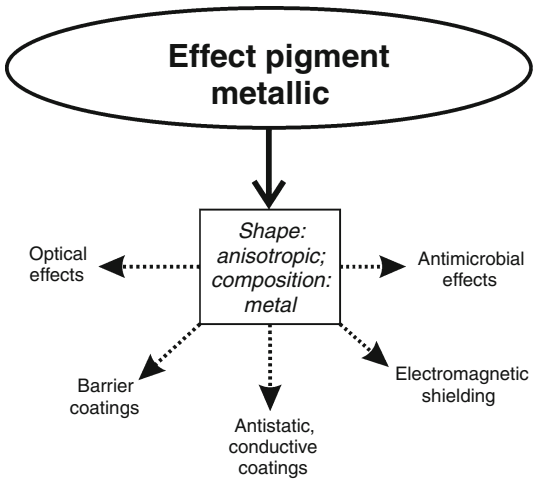
different metal oxides such as titania, ceroxide, or mica.[11–13] Second, these are metallic effect pigments, e.g., from the metals copper, iron, or aluminum. This second group also includes pigments made of alloys as steel or gold bronze.[2,14] In addition to the realization of optical effects, recently the use of effect pigments for other properties has been the focus of current research. Effect pigments with titaniumoxide compositions are used to apply photocatalytic active properties and, by this, also antimicrobial properties onto material surfaces.[15,16] Applications are also reported for the realization of barrier coatings achieved by multilayer application of effect pigments and corrosion protective applications.[17,18]

Metal surfaces, metal particles, and metal compounds are known for their antibacterial properties. Of especially high antibacterial effectiveness are silver materials. However, the anibacterial effects of copper and zinc compounds are also reported in the literature. These reports are mostly related to particular or even nanoparticular materials, probably because nanotechnology and nanoparticles have become buzzwords in recent years.[19–27] For stability reasons, the silver nanoparticles are also reported to be combined with star-like polymers (dendrimers). The dendrimers are useful for controlling the preparation and growth of silver nanoparticles and are reported to have an influence on the antimicrobial properties of silver particles.[28,29] Beside nanoparticles and dendrimers, carbon nanotubes CNT are also discussed intensively in the actual literature and experiments have been performed to apply them onto fibers and textiles.[30,31] Surprisingly, by coating with CNT or the other carbon modification of grapheme, antimicrobially functionalized materials, e.g., paper, can be realized.[32,33]

In addition, effect pigments consisting of anisotropic particles with sizes of several micrometers are expected to contain antimicrobial properties. One aim of this study is to investigate, if antibacterial properties on textile fabrics can be realized by coatings containing metallic effect pigments. Antimicrobial textiles are of high interest, because they offer a broad range of different applications. The use of such textiles can decrease the danger of spreading of harmful and antibiotic-resistant germs. Also they can be used to support the therapy of neurodermatitic skin or the diabetic feed.[34–38] Often they are used as antimicrobial barrier dressing in wound healing applications.[39,40]

Of course, the most significant properties of metals are their heat conductivity and conductivity for electricity. By coating of metal components onto normally nonconductive textiles, the conductive properties of the metal can be transferred to the textile material.[41,42] These applications are important for the preparation of antistatic textiles working under conditions of low humidity of air.[43] Conductive textiles are also of interest for the preparation of so-called smart textiles combining the cloth with computer technology and for preparation of textiles used for shielding against radio waves and microwaves.[44–47] Especially effective textile functionalization for electromagnetic shielding purposes is reported for metallized polyester covered with metal alloy multilayers. These multilayers consist of copper, nickel, and phosphorous and in addition to shielding properties, provide sufficient corrosion resistance.[48] A certain influence on a functionalization of wool on the shielding of electromagnetic radiation is reported for the application of nanoscaled zirconia particles.[49] By this nanozirconia application, the electromagnetic reflection is enhanced, so a certain shielding property should be expected. In addition to the use of metal or metal oxide materials for functionalization of textile for electromagnetic shielding, the application of different carbon modifications need to be mentioned. Several types of carbon modifications are the object of intensive investigations for shielding purposes.[50–52] Reported carbon types are multiwall carbon nanotubes, carbon nanotubes CNT, carbon nanofibers CNF, grapheme, or carbon black pigments. Al-Saleh et al.[50] reported that the anisotropic types CNT and CNF lead to better shielding properties compared to the isotropic carbon black.

It is the second aim of this study to describe the use of coatings containing anisotropic metallic effect pigments for the realization of conductive textile fabrics, which are able to shield radiowaves in an extraordinarily effective way. It can be stated that metallic effect pigments combine two main properties—their anisotropic shape and their composition of metal (Scheme 1). Their advantageous potential applications are mainly determined by these both properties. Advanced optical effects and barrier coatings are related to the anisotropic shape. Antimicrobial effects are mainly related to their metallic nature. Finally, conductive properties and application for electromagnetic shielding are related to the combination of both anisotropic shape and metallic composition. To investigate metallic effect pigments for those purposes, five different types of metal pigments and, for comparison,



Scheme 1: Overview of special properties of metallic effect pigments and related advantageous applications

a graphite pigment are investigated. All preparations are performed with two different types of binder systems applied in two different coating thicknesses. All investigations compare different coating thickness and pigment concentrations to lead the reader to optimal preparation conditions for each type of desired property. The prepared coatings are investigated using different analytical methods, such as microscopy, antibacterial tests against *E. coli* and *S. aureus*, measurement of electrical surface resistance, and shielding properties against radio waves.

In the course of research on light emitting textiles, it has been demonstrated that the performance of effect pigments can be significantly enhanced by addition of polyaniline in the coating recipe. This polymer is capable of conducting electrons and belongs to the group of the so-called ''intrinsically conductive polymers'' ICP. Their properties not only depend on chemical structure but also on factors such as polyanionic structure and morphology.[53] Polyaniline is a conjugated polymer which consists of coupled aniline monomers. To induce conductivity, polyaniline can be doped with anions. In optoelectrical applications, polyaniline is used to enable thin and transparent multilayer-structures in order to generate high electric fields. Furthermore, a broad variety of effects have been demonstrated, such as anticorrosive, catalytical and storage of electricity, shielding against electromagnetic waves, storage of electricity in batteries or capacitors, or use as a catalyst.[54–58] The high diversity of properties and derived applications thereof make polyaniline interesting as an additive for functionalization of textiles. Therefore, in the present study the combination of metallic effect pigments and the conductive polymer polyaniline in the same coating formulation are investigated and the performance of the coated textile materials is discussed.

Experimental

Materials

As substrate for all coatings, a polyester filament fabric with a specific weight of 180 g/m^2 was used. As acrylate binder the type ''Printperfekt 226 EC'' supplied by the CHT Beitlich GmbH (Tübingen, Germany) was used. This is a white acrylate screen printing paste in an aqueous solution based on a dispersion of polyacrylates. It was used as a base for pigments, for reference measurements, and as a binder for the polyaniline. The pH of this Printperfekt-type is 7.5–9 and the solid content is 10%. The polyaniline used in these experiments as additive to the acrylate binder was kindly supplied by Hochschule Emden/Leer. Reported investigations concern four different metallic effect pigments supplied by Eckart GmbH (Hartenstein, Germany), one silver pigment supplied by Doduco GmbH and one graphite pigment from NGS Naturgraphit GmbH. The corresponding trade names and particle sizes, as given by the suppliers, are mentioned in Table 1.

Sample preparation

The coating pastes based on polyacrylate and polyaniline was prepared by mixing the acrylate binder Printperfekt, water, and polyaniline under constant stirring in a weight ratio of 71.25%:25%:3.75%. For paste preparation, a VMA-Getzmann Dispermat LC30 with a dissolver disk of 40 mm was used. The stirring duration was set to 1 h. For preparation of the pure acrylate coating paste, the binder Printperfekt was used without any further dilution. After preparation of the coating paste, the pigments were dispersed for another 30 min into the paste in concentrations of 5, 10, or 20 wt%. The coating paste was applied onto the polyester fabrics by means of a spiral hand laminator (K-Hand-Coater 620 from Erichsen). This coating device is used for application of wet coatings in a thickness of 100 or 200 μm. After coating, the samples were dried at 90°C for 3 min in a drying chamber.

Analytical methods

The readily prepared pigment-containing coatings were investigated to get deeper insight into their physical properties, structure, and morphology and to get information about their antibacterial properties. By light microscopy, the distribution of the pigments and the binder on the polyester fabric was investigated. For this, an optical light microscope VHX-600 from Keyence was used. The actual zoom lens was a VH-Z250R with a magnification of 250–2500. A profile measurement unit VHX-S15 was used to generate profile pictures. 3D structures of textiles require this device for sufficient depth of focus. All samples were investigated with a magnification of 250×. At this setting, the single fibers were visible as well as single pigment particles and their distribution as a representative image for the whole coating. For higher magnifications, a scanning electron microscope SEM was used. These measurements were performed with a TM 3000 Tabletop microscope from Hitachi. For all SEM measurements, the acceleration voltage was set to 15 kV. This SEM device is equipped with an energy dispersive spectroscopy (EDS) unit Quantax 80 from Bruker, which enables the determination of the elemental composition on sample surfaces. The electrical resistance of the coated samples was determined by using two different devices, a MR-1 from Schuetz and an MGT-3 from Meco. In order to investigate the shielding against radio waves, two different experimental set-ups were used. First, an arrangement of transmitter and detector was used with a measurement frequency of 868 MHz. In this arrangement, the transmitter was a T868-K2. As detector, an Aaronia

Table 1: Overview of used pigments with particle sizes as given by the suppliers

Material	Trade name	Supplier	Particle size (μm)		
			D10	D50	D90
Copper	Copper E900	Eckart GmbH	4–7	15–19	34–40
Copper/coated with silver	eConduct Copper 421000	Eckart GmbH	16–19	38–44	66–72
Iron	Stapa IL Ferricon Resist 200	Eckart GmbH	8–12	15–21	24–32
Steel	STAY Steel 316L Flake Standard Grade	Eckart GmbH	8–14	30–40	62–70
Silver	Silver B190	Doduco GmbH	<1	4–6	66–72
Graphite	MF5	NGS Naturgraphit GmbH	3	5	10

Spectran HF6085 V4X equipped with an OmniLOG antenna was used. The distance between the antenna and the tested textile sample was set to 1 cm. The measurement time was set to 10 min and reference measurements were performed without any fabric. The second measurement arrangement used a Rohde & Schwarz ZVB Vector Network Analyser. In this arrangement, the textile samples were placed between horn antennas and the measurements were performed in a frequency range of 6.5–15 GHz. The network analyzer was used as signal source and receiver. With the transmit antenna, an electromagnetic field was generated which is assumed to be a plane wave at the position of textile sample. Transmit and receive antenna were perfectly oriented to each other with respect to the polarization of the transmitted and received electromagnetic wave.

Antimicrobial testing was done by a viability assay. It was performed with two types of bacteria, *E. coli* and *S. aureus*. Glycerol stocks (10 μl) were grown over night in 75 mL LB medium. For testing their impact on viability, textile samples (squares of 5 mm edge length) were placed in sterile 96-multiwell cell culture plates together with 200 μl bacterial suspension (diluted 1:250 in LB medium) per well and incubated for 3 h at 37°C, rotating at 120 rpm in an orbital incubator. Subsequent to treatment with the fabric samples, cellular viability was tested by measuring the reduction of methylthiazolyldiphenyltetrazolium bromide (MTT) as described elsewhere.[59,60] Briefly, cells were incubated with 0.01% (w/v) MTT in culture medium, followed by lysis in isopropanol and determination of the absorption at 570 nm (reference wavelength 700 nm). Data are shown as % viability relative to bacteria in the absence of fabric samples. For each textile sample, the measurement was conducted three times with different cutouts from the same sample.

Results and discussion

This section of results and discussion is divided into four parts to structure the results for the reader in a convenient way. First, material properties of the coated samples are reported. This is an introduction into sample properties but is also the basis for the discussion performed in the following sub-chapters. Second, the antimicrobial properties of the samples are reported. Finally, two chapters are related to the electrical properties and the ability to shield against electromagnetic radiation.

Material properties of pigment containing coatings

To first gain information on the properties of the pigment-containing coatings on polyester fabrics, microscopic methods, and the EDS method were used. The aim of the light microscopic investigations (Figs. 1 and 2) was mainly to determine the pigment distribution in the coating. As representative examples in Figs. 1 and 2, microscopic images of samples with copper pigments or silver-coated copper pigment were reported. The images represented coatings with increasing pigment concentration from 5 to 20 wt%. The effect pigments were regularly distributed on the textile surface. The anisotropic plain pigments were mainly arranged in plain direction parallel to the textile surface and by this, acted as small mirrors reflecting the light back to the microscope. This reflection was seen visually by using the light modus of the light microscopy. The planar arrangement of these anisotropic pigments is an inherent property of pigments with such a charge and was explained earlier with a self-arrangement of these pigments during the drying of the coating.[61] It is clearly seen that with the lowest investigated pigment concentration of 5 wt%, no closed pigment layer can be realized on the textile. The pigments are at that concentration mostly separated from each other placed in the binder coating. Different results were gained with the next higher investigated concentration of 10 wt% pigment. In this case, the pigments covered almost the whole surface of the fabric and the textile fiber surface was only visible in a few areas. At these areas, the textile is only coated by the binder layer but not by pigment. By using the 20 wt% pigment concentration, the pigment coating was complete and no part of the textile remained uncoated by pigments. An enhanced magnified view on the surface of coated sample was done by SEM (Fig. 3). As can be seen, the size distribution of the pigments given by the supplier of the pigments is confirmed (Table 1). Also, the ''cornflake'' structure is observed for the copper-containing effect pigments,

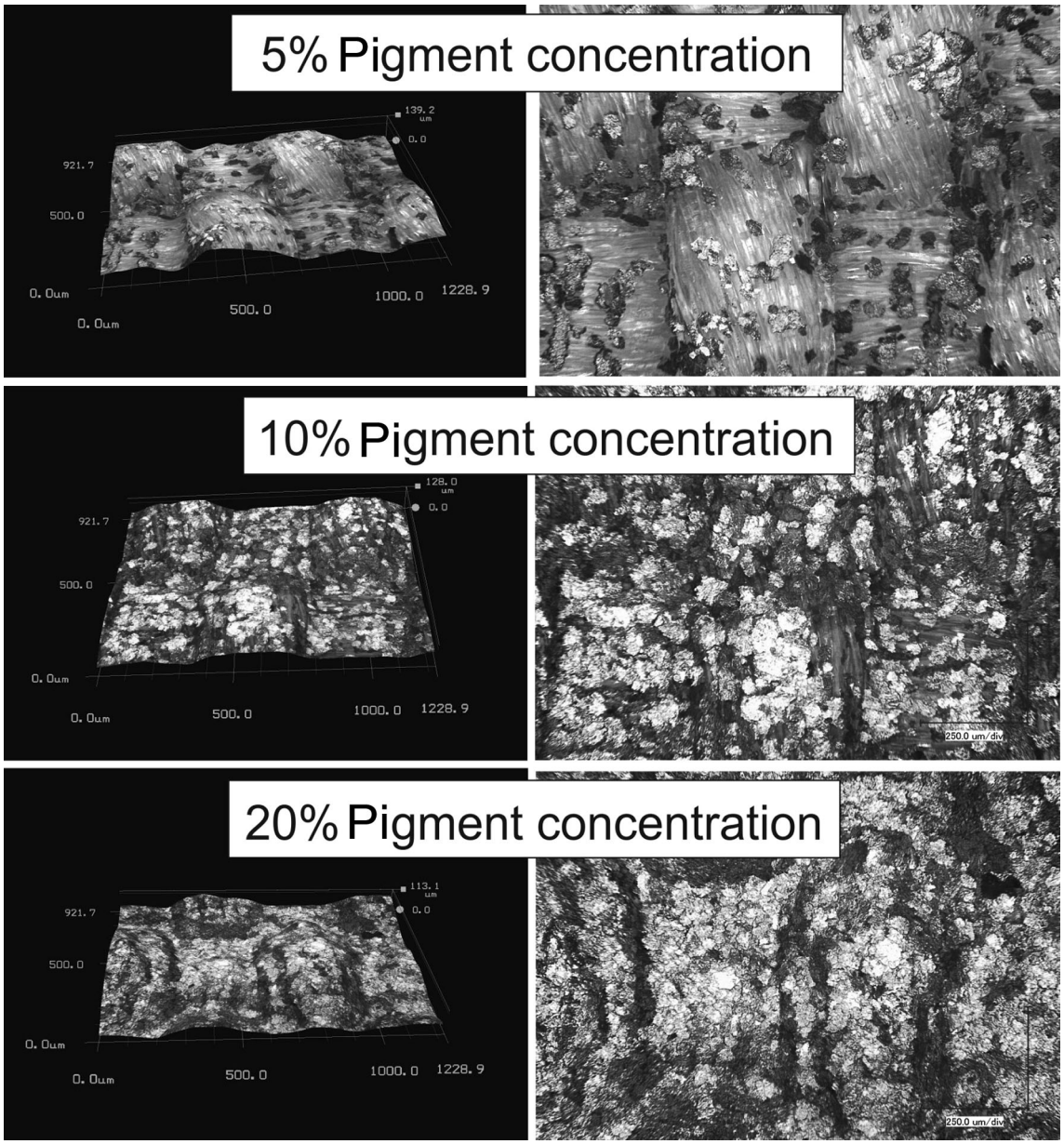


Fig. 1: Light microscopic images of acrylate coatings containing copper pigment of increasing concentration. The coating thickness is 100 μm

which is one typical shape of metallic effect pigments.[2] By SEM investigations, it can be also stated that not all pigments were placed on the surface of the coating, which means at the coating/air interface. The pigments were partially covered by the binder. The SEM device enables different types of measurement modes. The chosen mode (COMPO mode) enables the measurement of the sample surface topography, as well as a certain material contrast at the sample surface, depending on different element composition at different areas on the sample surface. For this, in SEM images the metallic pigments and the acrylic binder contain a different contrast, so the pigments appear brighter. If a pigment is depicted with decreased brightness, the amount of binder coating which covers the pigment is increased. For this, the thickness of the binder layer covering the pigments in the coating can be roughly estimated. Another method to determine the amount of metal at the coating surface is by EDS (Table 2). In comparison to the surface element composition determined by EDS, the composition of the whole coating can be also estimated from the contents used for coating preparation, as the binder or pigment concentration. In the used coating agent, the solid content of the pure acrylic binder was 10%. In the case of the preparation with the highest pigment

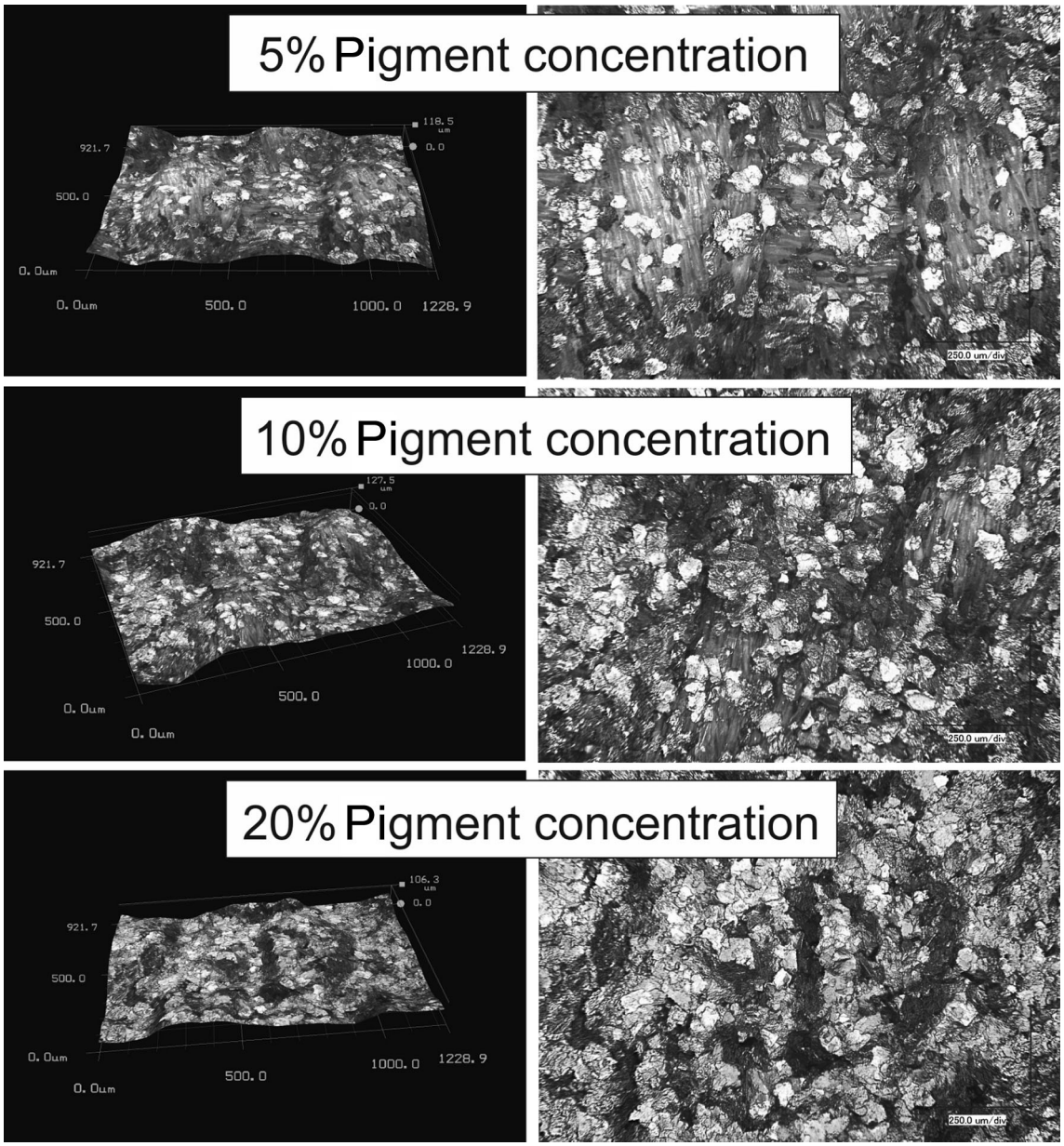


Fig. 2: Light microscopic images of acrylate coatings containing silver-coated copper pigment of increasing concentration. The coating thickness is 100 µm

concentration of 20%, the elementary ratio in the coating of carbon from binder to metal from pigment should be therefore around 1:2, if the content of oxygen and hydrogen is not taken into account. This rough estimation is the element ratio carbon:metal 1:2 in the whole coating from estimated preparation composition. By the EDS method, the elementary composition near the surface/air interface was determined and, in the case of the copper-containing pigment, a carbon content compared to the copper content is determined that is higher than expected from the preparation recipe (Table 2). With this background, an enrichment of the binder on the coating surface also placed on top of the pigments can be estimated. The same observation can be done also with coatings containing the other four metal pigments embedded in the acrylate binder coating (Table 2) under consideration that the element in the pigment is silver or iron, respectively. A different element composition on the sample surface is observed for coatings from acrylate and polyaniline (Table 3). In those cases, the detected metal content on the pigment/binder coating is significantly higher than the carbon content. For this acrylate/polyaniline coating,

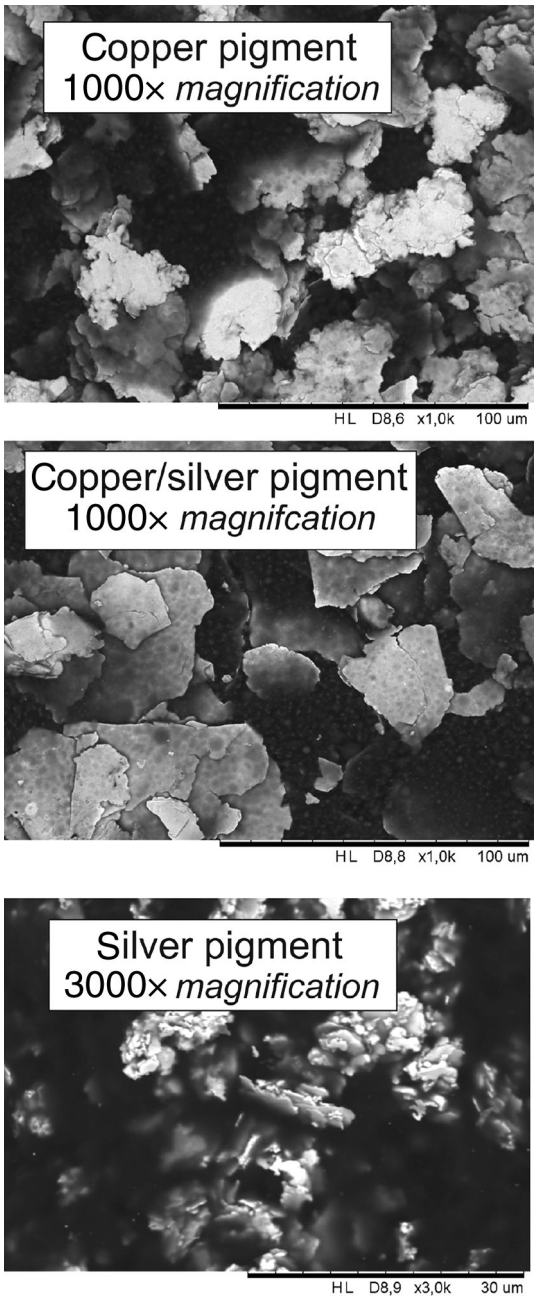


Fig. 3: SEM-images of metallic pigments in acrylate binder on polyester fabric. Pigment concentration 20%; 200 μm coating thickness—images in different magnifications of 1000× or 3000×

therefore, less enrichment of the binder at the surface/air interface can be expected. A possible explanation of such a result could be a certain dewetting behavior of the polyaniline in the current coating recipe. These reported tendencies of element distribution are also observed for coatings containing lower pigment concentrations of 5 or 10 wt% (Fig. 4). In addition, it can be stated that with increasing pigment concentration in the coating recipe, the content of metal on the coating surface detected by EDS is increased.

Antimicrobial properties

The antimicrobial properties of all coated samples were determined against the bacteria *E. coli* and *S. aureus*. Before starting the investigation of the pigment-containing samples, it was absolutely necessary to have a view of the bacterial growth measured in the presence of the nonpigment-containing reference samples (Fig. 5). As reference samples, the uncoated polyester fabric and the different binder coatings on polyester fabric but without any pigment were used. Compared to the bacterial growth in the medium without addition of any textile sample, in the presence of these reference textile samples, the bacterial viability was significantly decreased (Fig. 5). Only with the uncoated polyester fabric tested with *E. coli*, the bacterial viability was near 100%, which is the value determined without the presence of textile. With other samples, with increasing acrylate content coated on the polyester, the bacterial viability of *E. coli* decreased. One possible explanation for such an observation could be biocidal residues from the former binder recipe. Often biocides are added to water-based coating systems to prevent fungal growth on that coating paste. Residues of such a biocidal component could also be present in the coating after deposition onto the textile. In comparison, there is a certain difference in the remaining bacterial viability if the coating is prepared from pure polyacrylate or the polyacrylate/polyaniline mixture. Coating samples prepared with the addition of polyaniline led to higher remaining bacterial viability. For this, it can be stated that, in contrast to earlier reported values, in the present coating system, the polyaniline component did not lead to an additional antimicrobial effect.[62,63] Compared with the reference measurements with *E. coli*, the reference measurements with *S. aureus* led to lower values for the remaining bacterial viability in the range of 30–40% and no significant difference between the five different reference samples could be observed. The bacterial germ *S. aureus* seemed to be more sensitive in the used testing arrangement compared to *E. coli*. The antibacterial activity of investigated pigment-containing acrylate coatings on polyester is reported in Fig. 6 (for *E. coli*) and in Fig. 7 (for *S. aureus*). It is clearly seen that the addition of metallic pigments had a significant influence on the viability of *E. coli* bacteria (Fig. 6). Copper- and silver-containing pigments led to a biocidal effect which increases with the amount of pigment applied on the fabric. That means high pigment concentration but also higher coating thickness leads to decreased bacterial viability. This relation is easy to understand, because with increasing content of the antimicrobial acting pigments, obviously the antimicrobial effect of those coatings increases. Thicker coatings contain a better antimicrobial activity than thinner coatings of the same composition. These results are a hint that not only the pigments at the surface of the coating contribute to the antimicrobial effect. The pigments deposited deeply under the coating surface can also enhance the antimicrobial effect, leading to the

Table 2: Element composition on the surface of the acrylate coatings, with 200 μm coating thickness and addition of 20% pigment

Embedded pigment	Detected element (wt%)							
	Carbon	Oxygen	Copper	Silver	Iron	Silicon	Chromium	Nickel
Copper	50 ± 5	11 ± 1	39 ± 1	–	–	–	–	–
Copper/coated with silver	51 ± 5	13 ± 1	32 ± 1	3 ± 1	–	–	–	–
Silver	38 ± 4	19 ± 2	–	42 ± 1	–	–	–	–
Iron	47 ± 6	17 ± 2	–	–	33 ± 1	3 ± 0.1	–	–
Steel	45 ± 5	10 ± 1	–	–	32 ± 1	1 ± 0.1	8 ± 0.3	4 ± 0.2
Graphite	90 ± 9	9 ± 1	–	–	–	1 ± 0.1		

The element detection is performed by EDS-measurements while SEM measurements of 250× magnification. Only elements with a detected element content of 1 wt% or higher are presented

Table 3: Element composition on the surface of the acrylate/polyaniline coatings, with 200 μm coating thickness and addition of 20% pigment

Embedded pigment	Detected element (wt%)							
	Carbon	Oxygen	Copper	Silver	Iron	Silicon	Chromium	Nickel
Copper	32 ± 3	5 ± 1	63 ± 2	–	–	–	–	–
Copper/coated with silver	43 ± 5	9 ± 1	43 ± 1	4 ± 1	–	–	–	–
Silver	26 ± 3	15 ± 2	–	58 ± 2	–	–	–	–
Iron	38 ± 5	13 ± 2	–	–	46 ± 2	4 ± 0.2	–	–
Steel	30 ± 4	5 ± 1	–	–	46 ± 1	1 ± 0.1	10 ± 0.4	7 ± 0.2
Graphite	73 ± 13	27 ± 8	–	–	–	1 ± 0.1		

The element detection is performed by EDS-measurements while SEM measurements of 250× magnification. Only elements with a detected element content of 1 wt% or higher are presented

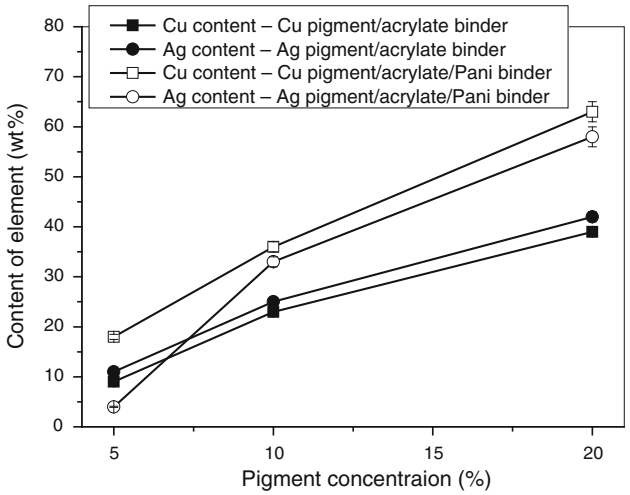


Fig. 4: Element content on coated surfaces determined by EDS. Data are given for copper and silver containing coatings as function of increasing pigment concentration

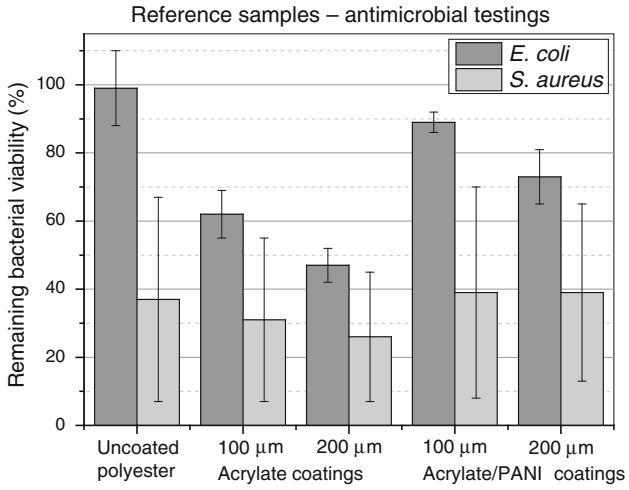


Fig. 5: Remaining bacterial viability of *E. coli* and *S. aureus* after contact with different reference sample, which do not contain any metal pigment or other pigment. The first reference material is an uncoated polyester fabric and other references are polyester fabrics carrying an acrylate binder coating or a coating of acrylate with polyaniline (PANI)

suggestion that antibacterial acting metal ions released from those pigments are able to pass through the binder layer to come into contact with the bacterial on the surface of the coated textile. The antimicrobial effectiveness of these pigments against *E. coli* can be set in the following order of pigment composition: copper < silver-coated copper < silver. This order is in good accordance with the oligodynamic order, indicating for silver a better antibacterial effect compared to the effect of copper.[64] Compared with this significant antibacterial

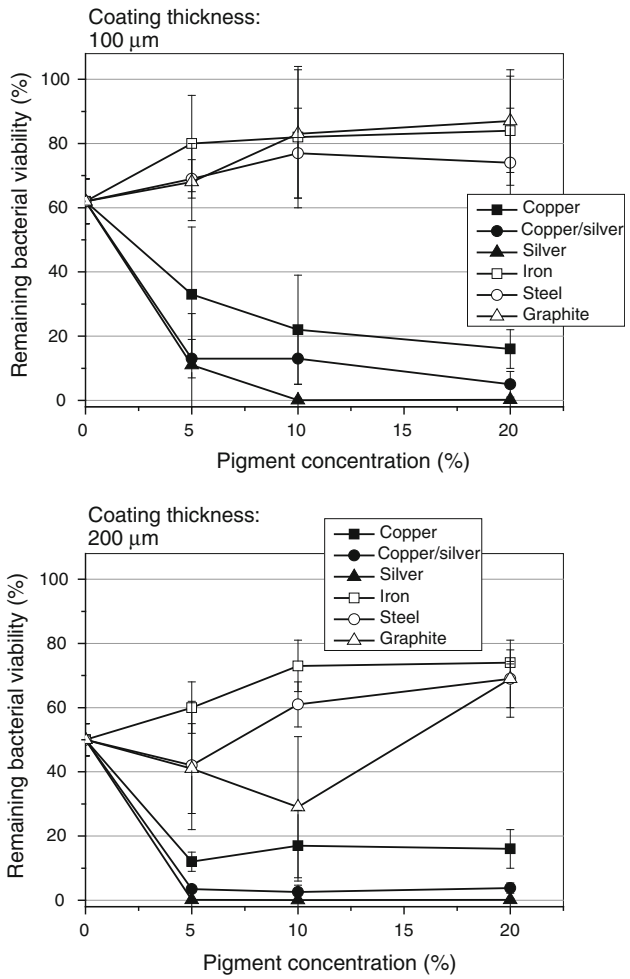


Fig. 6: Remaining bacterial viability of *E. coli* bacteria after contact with the acrylate-coated textiles. The data are shown as a function of the concentration of pigments added to the coating. Comparison of effects resulting from different coating thickness (above, 100 μm; below, coatings with 200 μm). Values are reported for all six investigated types of pigments

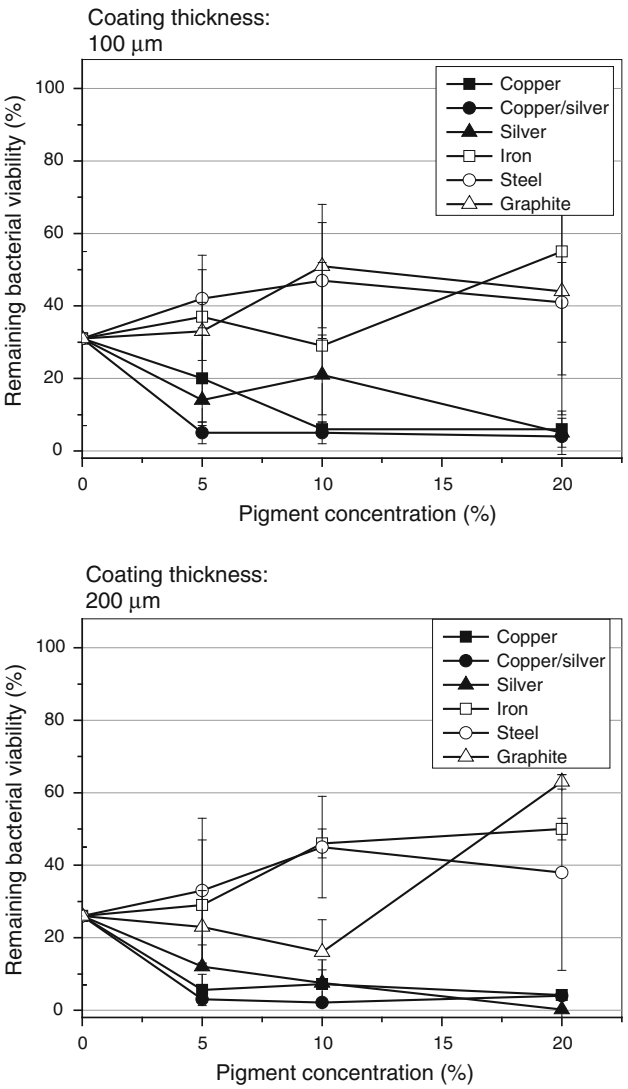


Fig. 7: Remaining bacterial viability of *S. aureus* bacteria after contact with the acrylate-coated textiles. The data are shown as a function of the concentration of pigments added to the coating. Comparison of effects resulting from different coating thickness (above, 100 μm; below, coatings with 200 μm). Values are reported for all six investigated types of pigments

effect, the addition of steel, iron, or graphite pigments led to no decrease in bacterial viability or, in a certain range, even to an increase in bacterial viability. An explanation for such an increase could be a higher surface roughness caused by adding the pigments to the acrylate coating. A rougher surface should be a better support for growing bacteria. Another possible explanation is that by addition of the nonantibacterial metal pigments, the antimicrobial acting binder system was diluted in the coating, so the antimicrobial effect from the binder as proposed from the reference measurements was diluted by the addition of the steel, iron, and graphite pigments. Compared with the results with *E. coli*, the remaining viabilities observed with *S. aureus* are generally lower (Fig. 7) and have to be set in relation to the equally lower reference values for the coatings without pigment content. From this tendency, the results gained with *S. aureus* are similar to those gained with *E. coli*. However, to a certain degree, the *S. aureus* germs seem to be more sensitive against copper-containing pigments compared to the pure silver pigments. The pigment-containing coatings based on acrylate/polyaniline composition led, in principal, to a similar antibacterial activity as the analogous acrylate-based coatings (Figs. 8 and 9). For this, for the polyaniline component of the coating, no antibacterial effect should be stated. However, in the case of testing with *E. coli* for these acrylate/polyaniline coatings, the effects of the pigment addition are more clearly observed (Fig. 8). This is mainly because the reference bacterial viability of the pigment-free coating is high, with values around 80%. The increasing antibacterial effect as a function of

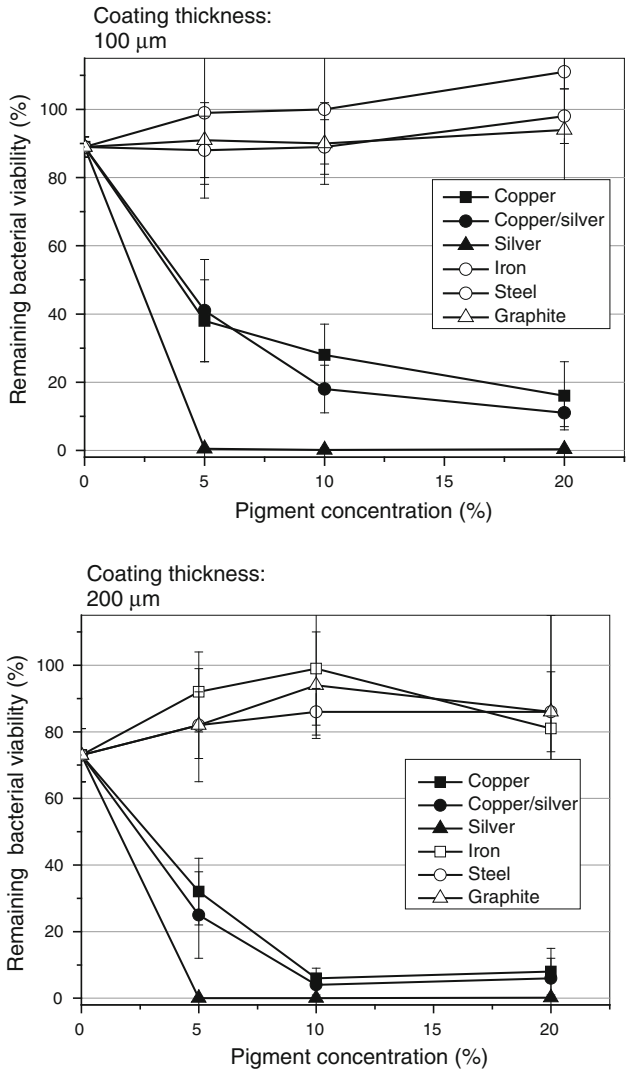


Fig. 8: Remaining bacterial viability of *E. coli* bacteria after contact with the acrylate/polyaniline-coated textiles. The data are shown as a function of the concentration of pigments added to the coating. Comparison of effects resulting from different coating thickness (above, 100 μm; below, coatings with 200 μm). Values are reported for all six investigated types of pigments

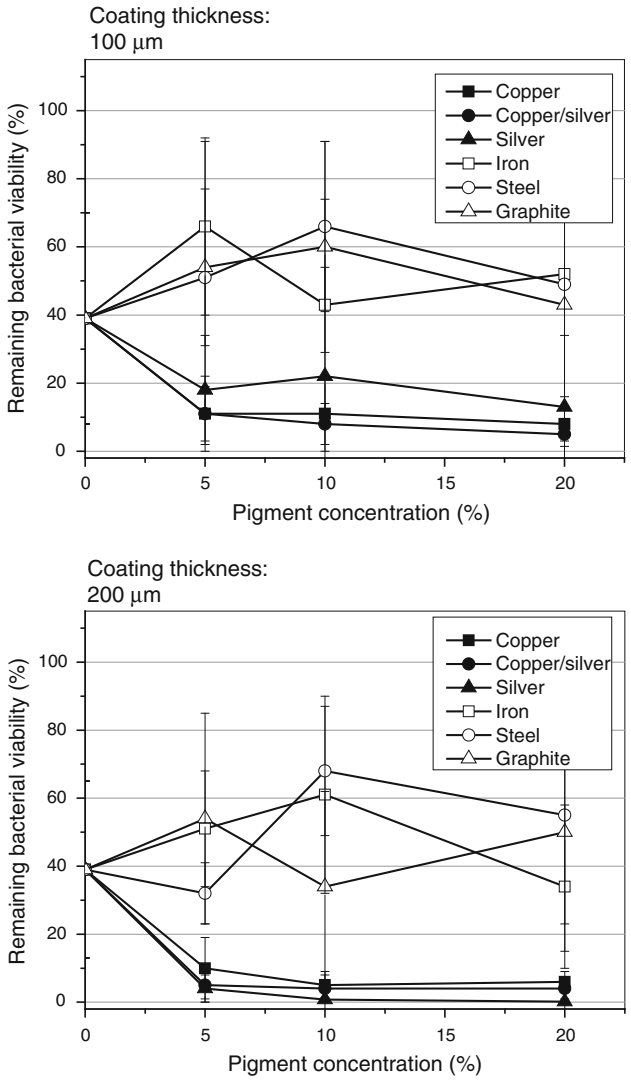


Fig. 9: Remaining bacterial viability of *S. aureus* bacteria after contact with the acrylate/polyaniline-coated textiles. The data are shown as a function of the concentration of pigments added to the coating. Comparison of effects resulting from different coating thickness (above, 100 μm; below, coatings with 200 μm). Values are reported for all six investigated types of pigments

increasing pigment concentration and coating thickness can be clearly stated for copper- and silver-containing pigments added. Against *S. aureus*, analogous antibacterial activities were observed for the different pigments added, as compared to the tests with *E. coli*. It is remarkable that, with the acrylate/polyaniline systems, the copper pigments seem to have a slightly better effectiveness compared to the pure silver pigments (Fig. 9).

Electrical properties

The electrical properties of the coated fabrics were investigated as a function of the concentration of added pigments. The electrical properties were determined as values of electrical surface resistance. As presented in Fig. 10, the surface resistance in acrylate-based coatings was mainly related to the type and concentration of the pigments added to the coating. However, the thickness of the applied coating had less influence on the surface resistance. Values of <1000 Ω which are related to conductive surfaces are only reached by addition of silver-coated copper pigments and graphite pigments added in pigment concentrations of >10 wt%. By use of iron pigments, no resistance values below 10^9 Ω were realized. Through addition of the other pigments, intermediate values of around 10^6 Ω were gained. These observations cannot

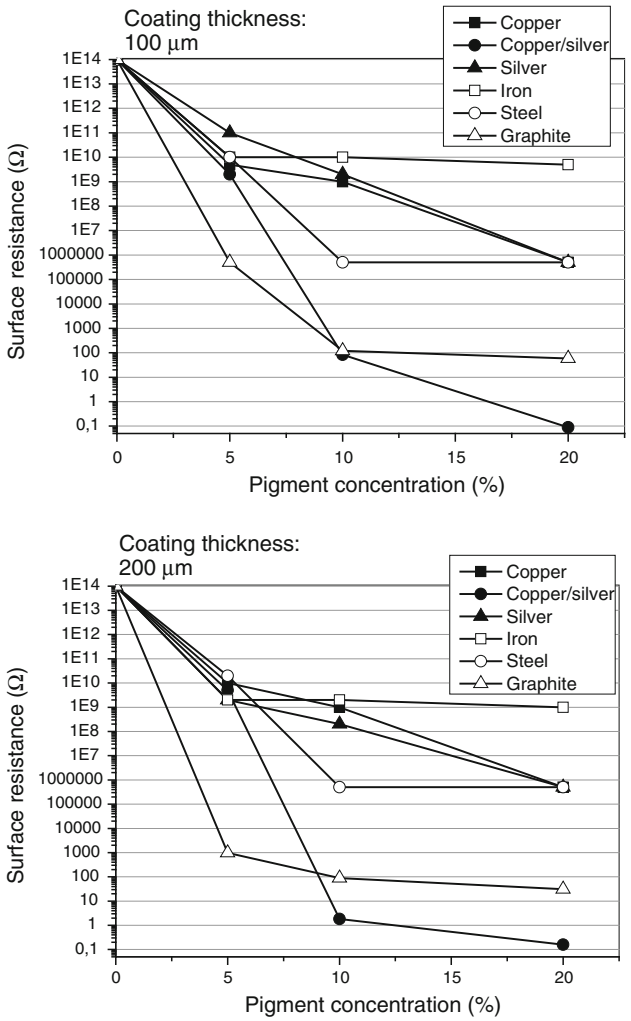
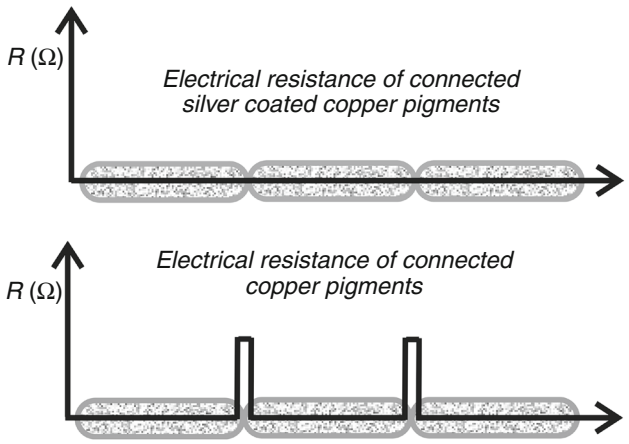


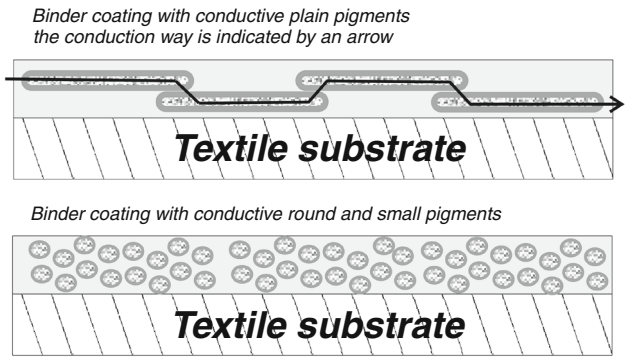
Fig. 10: Surface resistance of acrylate-coated samples as a function of added pigment concentration. The coating is prepared from acrylate composition with the thickness of 100 µm (pictured above) or 200 µm (pictured below). Values are reported for all six investigated types of pigments

be explained by the conductivity of the pigment material alone, because in the present coating, the use of silver pigment led nearly to the same conductivity as steel pigments, even if the element silver itself contained the highest intrinsic electrical conductivity. For this, it should be expected that the particle size, particle shape, and particle surface contain strong influences on the electrical resistance of the prepared coating. Iron and copper pigments are supposed to be coated by a nonreactive material, to prevent a corrosion of the pigment surface by oxidation with air.[65] A hint on this statement is the silicon content in the iron-containing coating as determined by the EDS method (Table 2). For copper pigment, the typical usage of polymer layers is reported to prevent the corrosion of the copper pigments by oxidation under air.[65] This coating on the pigments acts as a kind of insulation layer, if two conductive pigments are in contact with



Scheme 2: Schematic drawing of the electrical resistance *R* through interconnected copper pigments and the pigment/pigment interface; the drawing above is for silver-coated copper pigments; the drawing below is for copper pigments

each other in the coating (illustrated in Scheme 2). In the case of the silver-coated copper pigments, the corrosion inhibition is indicated by the highly conductive silver coating instead of an insulating layer. By transferring from one to the next pigment, no isolation barrier with high resistance between the pigments has to be passed by the current (Scheme 2). Therefore, for this pigment system, the best electrical conductivity for the prepared coatings is determined. The only remaining question is why the investigated pure silver pigments led to less performance compared to the better conductive silver-coated copper pigments. The surface properties of both pigment types can be supposed to be roughly similar, because both pigment types contain a silver surface. The main difference is the larger size and the anisotropic shape of the silver-coated copper pigments (Table 1; Fig. 3). Larger pigments require less content to generate a conductive way compared to smaller pigments (illustration in Scheme 3). Also, the number of pigment/pigment interfaces necessary for building up a sufficient pathway for the current is lower for larger and anisotropic pigments, when compared to the smaller silver pigments. For this, larger pigments should be more effective for preparation of conductive coatings compared to coatings with smaller pigments. In comparison to the acrylate-based coating, the coating based on acrylate/polyaniline without addition of further pigments itself contained a surface resistance of around 10^9 Ω (Fig. 11). Such coated surfaces can be stated to have antistatic properties and the reason for this is probably the intrinsic conductivity of the polyaniline embedded into the acrylate coating. For most of the investigated pigments, the addition of pigments changed the conductivity of the coating in the same manner even if the coating was based on acrylate or on acrylate and polyaniline. The only pigment leading to significant lower surface resistance in the case of using the



Scheme 3: Schematic drawing of pigment containing binder coating on a textile substrate; the drawing above is for anisotropic plain pigments; the drawing below is for small and round pigments

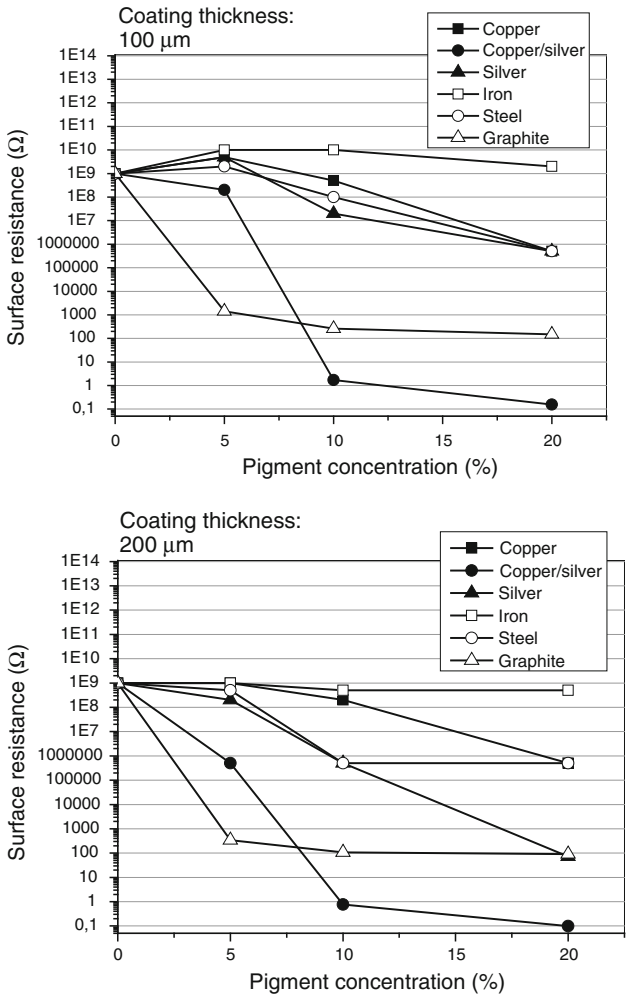


Fig. 11: Surface resistance of acrylate/polyaniline-coated samples as a function of added pigment concentration. The coating is prepared from an acrylate/polyaniline composition with the thickness of 100 µm (pictured above) or 200 µm (pictured below). Values are reported for all six investigated types of pigments

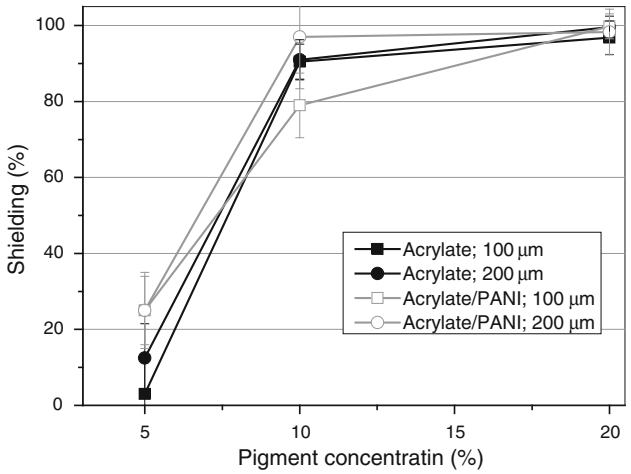


Fig. 12: Shielding properties of coated polyester against radiation with the frequency of 868 MHz as a function of concentration of silver-coated copper (econduct) embedded in the coating. The values are given for four different coating systems of acrylate and acrylate/polyaniline composition applied with two different coating thicknesses of 100 and 200 µm

acrylate/polyaniline system is the silver pigment. In this case, a better conductive connection of the silver pigments by the polyaniline-containing coating could be expected.

Shielding properties

The shielding properties against electromagnetic radiation with a frequency of 868 MHz were tested for all prepared samples. However, from all tested samples, only a few samples exhibited a significant shielding effectiveness of >90%. In acrylate coatings, only coatings with silver-coated copper pigments in a content of 10% or 20% showed such a shielding of >90% (Fig. 12). In the case of using the acrylate/polyaniline coating composition, in addition to the silver-coated copper pigments, coatings with the silver pigments also led to shielding of more than >90%. While the silver-coated copper pigments were also effective in the insulating acrylate coating, the silver pigments led only to sufficient shielding properties if they were embedded in a coating containing the conductive polymer polyaniline. The results from shielding properties were in certain agreement with the microscopic results and the surface resistance values reported in earlier sub-chapters. By microscopic images, it was clearly shown that a full coverage of the textile surface was not reached at the lowest investigated pigment concentration of 5%. For this reason, it can be explained why a pigment concentration of at least 10% is necessary to yield a certain shielding effect (Fig. 12). It can also be stated that good shielding effects are only reached by use of metal pigments as

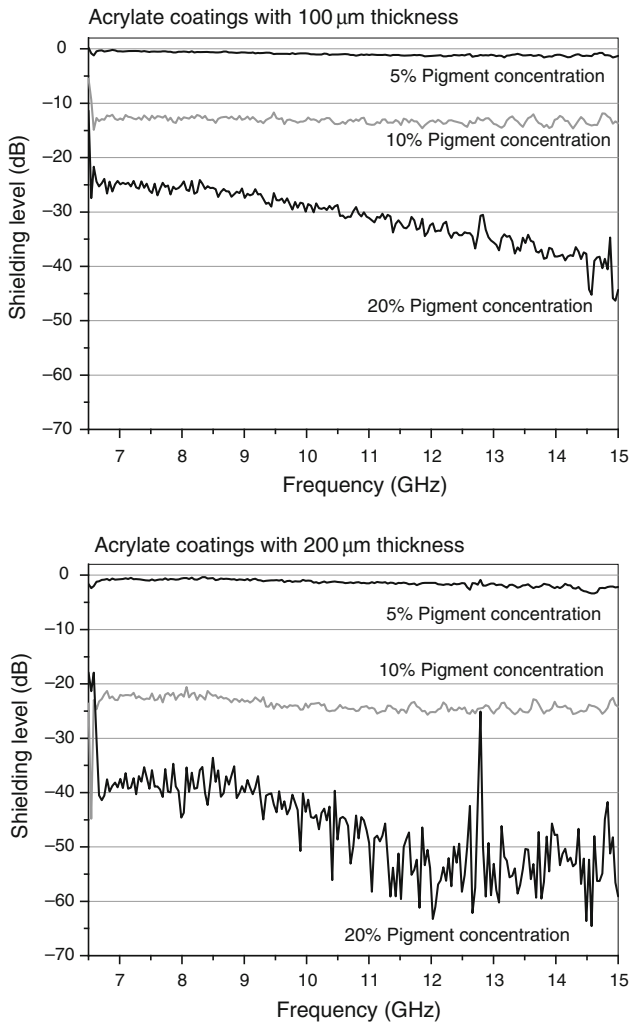


Fig. 13: Shielding properties of coated samples against radiation in the frequency range from 6 to 15 GHz. The properties are reported for coatings containing the pigment econduct with increasing concentrations. The picture above reports on acrylate coatings with 100 μm thickness and the picture below reports on coatings with the same composition but 200 μm thickness

additives which enable coating with a low surface resistance. However, it is remarkable that the relation of measured electrical resistance and shielding properties is not valid for the investigated graphite-containing coatings. By the addition of the graphite pigments to the coating systems, coatings with low resistance values of smaller <1000 Ω can also be realized. However, for these coating systems, no significant shielding effect was determined. Due to the fact that the best results for shielding against 868 MHz were gained with the silver-coated copper pigments, these coatings were also investigated according to their shielding properties against electromagnetic radiation in the range of frequencies 6.5–15 GHz (Fig. 13). Also for this range of frequencies, with a pigment concentration of only 5%, no shielding effect was gained, which was in accordance with the measurements at 868 MHz. For the other investigated samples prepared with silver-coated copper pigment, the shielding effect increased with increasing pigment concentration and coating thickness. The shielding properties were caused by this type of pigment and the amount of this pigment which was present on the coated textile was related to the measured shielding effect.

Conclusions

Metallic effect pigments are versatile additives for coatings to achieve textiles with a broad range of useful functional properties. These properties are far beyond the enhanced optical properties which were the original purpose for those effect pigments. Effective antibacterial properties as well as electric conductive-coated textile materials can be reached by copper- and silver-containing pigments. Especially effective for attaining these properties is a silver-coated copper pigment, which can be also used to prepare textile materials for shielding of radio waves and microwaves.

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