Inorganic Effect Pigment-binger System: Pigment Pickup% of Sol-gel Processed Cotton Textile

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ABSTRACT
Cotton plain-weaved woven fabric has been treated with inorganic effect pigment-binder system in water following the sol-gel process. Thickener and dispersing agent have been added to the solution. The fabric was then coated with the prepared solution using the sol-gel process. The pigment-coating was carried on Hochschule Niederrhein, Mönchengladbach, Germany Laboratory Padder by the help of squeezing roller. After coating, pigment pickup% was measured and compared with each other. In this work, the pickup% of effect pigment coated cotton textile will be measured and compared with each other.

Key Words: Sol-gel Coating, Pigment Pickup %, Textile Coating

Source of Support: None, No Conflict of Interest: Declared

INTRODUCTION
Sol-gel process
According to the definition of Royal Society of Chemistry, the process of the settling of nanometer-sized particles from a colloidal suspension onto a surface is called sol-gel (Royal Society of Chemistry). In case of inorganic effect pigment, the desired metal-oxide is suspended in a liquid and forms the 'sol' which is deposited on a substrate. The particles in the sol form the 'gel' are then heated at high temperature to give the final solid product on surface. The sol-gel method is one of the well-established synthetic approaches to prepare novel metal oxide as well as mixed oxide composites. This method has potential control over the textural and surface properties of the materials (Rao et al., 2017).

Inorganic effect pigments
Effect pigments have been used for a long time to achieve an optical effect such as reflection, interference and color travel by parallel alignment on the surface. Effect pigments generate their attractiveness in the application system because of the ability of parallel orientation of a multitude of platelet-like particles (Maile et al., 2005). Effect pigments are two types: metal effect pigment and pearlescent effect pigment. Most pearlescent pigments now consist of at least three
layers of two materials with different refractive indices. Thin flakes such as mica, silica, alumina, glass, having a low refractive index are coated with metal oxide such as Fe$_2$O$_3$, TiO$_2$ etc., having a highly refractive metal oxide (Pfaff et al., 2009). The most important effect pigments without a layer structure are by far the metal effect pigments. Metal effect pigments consist of small metal platelets which act like little mirrors and almost reflect all the incident light.

**Binder system**

iSys MTX is a new organic-inorganic binder system based on a nanotechnological sol-gel process. It is a reactive organic-inorganic sol to functionalize textile surfaces by padding, iSys MTX is stable to hard water and weak acids in the industrial concentrations. iSys MTX is combined without problems with the products applied in finishing. iSys Ag (CHT, Germany) in combination with a silane binder – iSys MTX (CHT, Germany) was used for antimicrobial functionalization of modal fibers (Hribernik et al., 2012) and protection against Fungi and Bacteria (Tomšič et al., 2008; Tomšič et al., 2009; Klemenčič et al. 2012; Manda et al. 2015). iSys MTX (CHT GmbH, Germany) can be used as a reactive organic–inorganic binder (RB) with Kollasol CDO (antifoaming agent) (Klemenčič et al., 2013; Bras et al., 2017). Chitosan dissolved in a diluted 5 % CH$_3$COOH solution was used in combination with iSys MTX (Demir et al., 2010). The use of iSys MTX leads to an increase in the hydrophobic character compared to the untreated sample (Pivec et al., 2012). Using the sol-gel process, effect pigments are applied on the textile surface. It causes a metal oxide layer on the textile surface. That has significant influence on pigment pickup%.

**MATERIALS AND METHODS**

**Reference cotton**

Plain-weave 100% cotton woven fabric was used in the experiments. Cotton is the most important natural and cellulosic textile fiber. The whole cotton fiber contains 88 to 96.5% of cellulose, and after scouring and bleaching, it becomes 99% cellulosic (Wakelyn et al., 2006). Cellulose is made up of a long chain of glucose molecules linked by C-1 to C-4 oxygen bridges by beta position. Two adjacent cellulose molecules combine with the hydroxyl group on the cellulosic unit. The abundant hydroxyl groups and the chain conformation causes the highly fibrillary and crystalline structure, and the extensive intermolecular and intramolecular hydrogen-bonding (Hsieh, 2007).

**Binder system**

iSys MTX supplied by CHT R. Beitlich GmbH was used as binder system. iSys MTX is miscible with water at every ratio. Alkaline industrial water has to be adjusted on pH 5.0 - 5.5 with acetic acid before iSys MTX is added to guarantee good bath stability. This has been used in a ratio of 1:1 with water. Longer storing times should be avoided (CHT Germany GmbH, Germany).

**Thickener**

Aerosil COK 84 supplied by Evonik Resource Efficiency GmbH was used as a thickener to give the required viscosity to the coating paste. AEROSIL® COK 84 is a mixture of AEROSIL® 200 and aluminum oxide in the ratio of 5:1. It provides strong thickening effects in aqueous media and is used in coatings pastes. For protective coating, it can be used with polyacrylate-based composites (Sadej, & Andrzejewska, 2016). It controls rheology in aqueous, highly polar liquids and binder systems. This Aerosil COK 84 has two types of metal content. Al$_2$O$_3$ content is 14-18% and SiO$_2$ based on ignited material is 82-86% (CHT Germany GmbH, Germany).
Pigments

Supplied by Eckart GmbH/Eckart Effect Pigments, Germany.

The Symic C001 is an inorganic effect pigment based on artificial mica. Compared with natural mica, synthetically produced pearlescent pigments show considerably higher color purities and ideal processing qualities. Having interference silver in color, Symic C001 is the smallest pigments for transparent shimmering effects on preferably smooth substrates. The base is pearlescent and the pigment contains titanium dioxide =20-30%, tin oxide <=1%, fluorphlogopite (Mg3K[AlF2O(SiO3)3]) =69-80% and the particle size distribution 10 – 40 µm [18]. The ratio of synthetic fluorphlogopite and TiO2 is 80:20 (Powell et al., 2015).

The Luxan D393 is an inorganic pigment. This sparkling pearlescent pigment is based on synthetically borosilicate glass. Like a polished diamond, they show an exceptional, three-dimensional light reflection and brightness. Golden reflection color is because of glass flakes coated with titanium dioxide, iron oxides, silica and tin oxide. The particle size distribution of Luxan D393 is 20-100 (Eckart GmbH, Germany). eConduct 421000 is lamellar copper powder, fine, based on copper, 99.9 % purity coated with silver (inside copper).

The eProduct contains electrically conductive pigments which can be used as a cost-effective alternative to real silver in various application. Specific applications of these granular pigments can be found in adhesives and sealants, plastics, printed electronics or coatings for electromagnetic shielding. These products generally consist of a metal or non-metal based material core and have a pure silver coating. Optionally the pigments can also be surface modified. This product can be used in water based, solvent based, UV curing systems. Ag content = 9.0 - 11.0 % and particle size distribution is 13-71 (Eckart GmbH, Germany).

Texmet 5000 is Eco Passport (Ökotex) certified silver effect pigment for aqueous varnishes. The pigments create different sparkle effects. The pigment content / non-volatile content is 63,0 - 67,0 % and solvent content is 33,0 - 37,0 % (Eckart GmbH, Germany).

Dispersing Agent

Laponite RD supplied by Rockwood Clay Additives GmbH has been used as dispersing agent. The dispersion process involves the breakdown of associated particles into smaller particles and form a colloidal suspension. In a colloidal suspension, particles do not settle under their gravitational forces (Pal et al., 2006). As the dispersing agent, a layered silicate manufactured from naturally occurring inorganic mineral sources. Laponite has been used to disperse the pigment-binder system in the solution. It can be used with water either having very high or very low pH. Significant dissolution of this laponite material occurs in aqueous solutions of pH < 9 with solution concentrations of magnesium exceeding 10-3 tool dm-3 at pH ~< 7 (Thompson & Butterworth, 1992). Viscosity begins to rise when the sol premix is added to a water-based system containing other solids without hampering another used chemical (Rockwood Clay Additives GmbH, Germany).

It has very high sol stability grade which is very important in our experiment as we failed a lot while preparing coating solutions because of instability of liquor due to precipitation of sol-gel-binder mixture. In aqueous coating systems, thickeners are used to control flow as well as to provide adequate stability in storage and suitable rheology for application. Combination with other thickeners, Laponite RD can be used to improve the properties and performance of surface coatings.
Sample planning
The samples of fabric for 5%, 10% and 20% concentrations of the same pigment have been taken. Binder and water ratio was 1:1. Thickener had been added 10 mg for each. For pigment 2, 3 and 4, dispersing agent had been added for the better solvent. For example, 50g Symic C001 has been treated with 50g iSys MTX, 10g Aerosil COK 84 in 5%, 10% and 20% pigment concentrations. Thus, three coated samples were prepared for one pigment i.e., 12 samples for 4 pigments.

Table 1: Sol-gel coated sample preparation

|       | Sample 1 | Sample 2 | Sample 3 |
|-------|----------|----------|----------|
| water | 25       | 25       | 25       |
| iSys MTX | 25     | 25       | 25       |
| Aerosil | 5       | 5        | 5        |
| SYMIC C001 | 2,5   | 5        | 10       |

|       | Sample 4 | Sample 5 | Sample 6 |
|-------|----------|----------|----------|
| water | 25       | 25       | 25       |
| iSys MTX | 25     | 25       | 25       |
| Aerosil | 5       | 5        | 5        |
| LUXAN D393 | 2,5   | 5        | 10       |
| Laponite RD | 2,5  | 2,5      | 2,5      |

|       | Sample 7 | Sample 8 | Sample 9 |
|-------|----------|----------|----------|
| water | 25       | 25       | 25       |
| iSys MTX | 25     | 25       | 25       |
| Aerosil | 5       | 5        | 5        |
| eConduct 421000 | 2,5   | 5        | 10       |
| Laponite RD | 2,5  | 2,5      | 2,5      |

|       | Sample 10 | Sample 11 | Sample 12 |
|-------|------------|------------|-----------|
| water | 25         | 25         | 25        |
| iSys MTX | 25     | 25         | 25        |
| Aerosil | 5       | 5          | 5         |
| Texmet 5000 | 2,5 | 5         | 10        |
| Laponite RD | 2,5  | 2,5       | 2,5       |

Process description
The coating of sol-gel binder system on a fabric (either cotton or polyester) can be done by using different methods; from the conventional padding to frequently used spray technique. In some cases, it is the same as a conventional printing method. The solvent uptake of the fabric is extremely higher compared with the polymer film padding.

This process is divided into two steps-1. Formation of nano-sols (by hydrolysis of precursor material and subsequent condensation reactions) and 2. Coating process
The sol–gel process can be described as the creation of a metal oxide network by condensation reactions of molecular precursors in a liquid medium. The coating process was done using the padding method. In this process, according to Mahltig (2008), there are two advantages like uniform distribution of coating material to the fabric as well as liquor absorbed by the fabric can be reduced drastically. In this process, complete penetration is not necessary. Liquor concentration is relatively higher as mentioned above. The process has been done as following.

**Sol preparation**: During sol-gel thin film formation via dipping, inorganic or metal organic sols are deposited on the substrate surface. Higher sol concentration may lead to lower uniform coating on textile, since a higher concentration of sol-gel binder system has more preceptor.

**Coating**: During sol-gel thin film formation via dipping, inorganic or metal organic sols are deposited on the substrate surface. This is a complex steady-state process combining gravitational draining, solvent evaporation, and continued condensation reactions (Brinker et al., 1990). The important microstructural properties of the deposited film (% porosity, surface area, and pore size) depend on the size and structure of the inorganic species, the relative rates of condensation and evaporation during deposition, the magnitude of the capillary pressure, and the accompanying shear stress. The processes are done as following:

- Firstly, the weight of dried samples has been taken
- Sample specimens were laid on the table which are already ironed to get the perfect result to absorb the stuffs
- Samples were set on strand to be hold up
- solutions are poured on the fabric
- Rollers confirm uniform distribution of sol to the fabric to being penetrated.
- Squeezing roller helps the fabric to be coated. (the thickness of the coating can be controlled either by sol concentration or by squeezing rollers)
- The weight of wet samples has been taken
- Pigment pickup % were calculated using the following formula.

\[
\text{Pickup \%} = \left( \frac{W_2 - W_1}{W_1} \right) \times 100
\]

Mathematically,

\[
\text{Pickup \%} = \left[ \frac{(W_2 - W_1)}{W_1} \right] \times 100
\]

Where,

- \( W_2 \) = weight of fabric after padding
- \( W_1 \) = weight of fabric before padding
Figure 2: Different Inorganic effect pigment-binder system coated textile

The four images show different effect pigment coated cotton textiles. Figure 2.1 and 2.2 show coated cotton textile by pearlescent effect pigments, respectively Symic C001 and Luxan D393. Metal effect pigment - eConduct 421000 and Texmed5000 coated textile are shown respectively in figure 2.3 and figure 2.4.

RESULTS AND DISCUSSION

During the sol-gel coating process, an extra layer of the solution is added on the textile surface. The additional layer includes chemical such as pigment, binder, thickener, dispersing agent and definitely water. These components increase the fabric weight which leads different pickup % for the different pigment-binder system. For all the specimens used in experiments, the textile surface was the same cotton. So, the pickup % varies according to the pigments to be absorbed. It is shown that if the pigment pickup % increases, the
reflection% is increased and by the textile. Symic C001 showed highest 137% pickup %. The average picks up % for Symic C001, Luxan D393, eConduct 421000 and Texmet 5000 are respectively about 118%, 101%, 88% and 88%.

Figure 3: Pickup % of different inorganic effect pigment-binder system coated textile

Two pearlescent effect pigments—Symic C001 and Luxan D393 shows higher pickup percentages [figure 3(a) and 3(b)] as they absorb more chemical stuff during the coating process. On the other hand, in figure 3(c) and 3(d), metal effect pigment —eConduct 421000 and Texmet 5000 show relatively lower pickup percentages. The results differ as construction and the internal properties of pigments differ from each other.
CONCLUSION

Effect pigments are small insoluble particles which have almost no affinity for fibers and for this reason they are applied with the help of a binder system with the inclusion of other chemicals. As the effect pigments consist of either metal platelets or pearl luster particles, they show 68-137% pickup which is significantly higher compared to conventional one.

ACKNOWLEDGMENTS

We would like to thank Thomas Heistermann, Hochschule Niederrhein, for supplying the chemicals as well as technical help.

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