

DYEING OF GLASS FIBRES BY THE SOL GEL METHOD

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Abstract:

This study focused on the dyeing of glass fibres by colour layers created by the sol gel method. Glass fibres are used as a typical example of fibres with non-ideal dyeing properties. Glass and similar dyes are rigid, the internal fibre structure is non-porous and the glass transition temperature is very high. The sol gel method is used for the fixation of selected dyes on the fibre surface. In this study, we compared basic, disperse and metal complex dyes. The properties of coloured textiles were tested by standard and modified fastness tests. The stability to temperature, washing and light was different according the basic properties of the used dyes. The results of the tests are discussed in this paper. The process of dyeing fibres with sol simultaneously results in reasonable dye fastnesses to the fibres; at the same time, bright and dark shades can also be obtained. The sol used is based on the blending of 3-trimethoxysilyl propyl methacrylate in isopropanol with supporting chemicals (water, HCl, benzoyl peroxide).

Key words:

Sol gel method, dyeing, glass microfibres, fastness.

Introduction

The dyeing technology of standard textile fibres is already developed to a high level of standards. It is easy to use dyes on cotton, wool and similar fibre substrates with many dyeing technologies. In all cases, we typically obtain selected shades with good fastness and low price. These positive results for standard textile dyeing technologies are connected with the special properties of common textile fibres: the polymer in the fibre body is temporally changed during the dyeing process. The porosity of the fibre is high and these pores are used for the transport of dyestuff to the inside of the fibre. Porosity is connected with water-based swelling in the case of cellulose fibres, or is based on the rotation of polymer segments above the glass transition temperature in the case of polyester, polyamide and acrylic fibres.

At this is time, we can observe an intensive increase in the production of technical textiles. In these applications we can find not only the standard textile fibres such as cotton or polyester, but many other fibres with special physical and chemical properties. These special fibres with high mechanical properties are extremely rigid, with low porosity, low swelling and low influence of temperature. These properties are connected directly with low dyeability with standard dyeing technology.

The dying of special fibres is vital because, in many applications, we need not only high level mechanical properties, but also colour and other visual properties in our fibre-based products.

Special fibres normally have a high glass transition temperature which makes it impossible for the dye molecule to penetrate into the fibres, especially when using water (H₂O) as a solvent. In some cases, it is possible to use other solvents or other fibre-swelling compounds to reduce the glass transition temperature of fibres. Due to these problems, the dyeing of these fibres has added to production costs because special solvents and techniques are used to obtain reasonable fastness properties with limited colour shades.

In this group of fibres with high mechanical stability and low dyeability we can add, for example, the following fibres: aramides, glass, mineral fibres, carbides, metal fibres and aromatics. In this study, we used glass fibres as a typical example of these fibres with low dyeability.

If the fibres are too rigid and too closed to absorbing dyes, then we should use non-standard methods for their colouration. One of them is the "sol gel" method, which is applicable for all solid substrates.

Sol gel method

Under the abbreviation "sol gel method" is the proposed application of sol to fibre surfaces where the sol will be changed into a gel. This solid gel keeps our dyes on textiles.

The principle of the sol-gel method is the preparation of the homogeneous solution from its starting components, which is transferred into sol by controlled hydrolysis and polycondensation [1]. This sol is deposited on the surface of materials, transferred into a gel and finally into a layer of oxide by heat treatment. The oxide layer is nonporous and glassy, or crystalline, at higher temperatures of heat treatment. However, at lower temperatures of heat treatment, it stays amorphous and porous. In production and for research purposes, SiO₂ and TiO₂ layers are deposited most often. Also, layers of many other constitutions containing Al₂O₃, B₂O₃, ZrO₂, PbO and another oxides are often prepared. Next to the clearly inorganic layers, hybrid inorganic-organic layers have also been developed (production terms ORMOCER, ORMOSIL and NANOMER), which contain both chemical bonding of organic substances and functional groups next to silicon, titanium, zirconium and oxygen.

In the surface treatment of polymer structures, it is necessary to use hybrid layers based on a mixture of inorganic and organic polymer compounds, which are connected at the end of the process to a single macromolecular network. The inorganic part is linked with chemical, mechanical and thermal stability. The organic part works as a networking agent and increases

the stability of layers against selected chemicals. In some hybrid polymers, metal complex bonds are used to increase stability. These hybrid layers are able to stabilise at relatively low temperatures, about 100°C. Preparing very thin layers (10 up to 500 nm thick) of composite nanomaterials is a further possibility in this method [1]. Layers prepared by the sol gel method are used industrially, for example in reflex and antireflex layers in optics, protective, catalytic, modified and functional layers in material engineering and functional layers in microelectronics and biotechnology [1].

It is possible to change the properties of surface materials with deposition functional or inorganic top-coat using the sol gel method. One of the advantages of this method is the possibility of preparing thin layers on various materials. Up to now, mainly inorganic substrates (glass, ceramics, metals, etc.) were used, however thin layers can also be deposited on organic materials, especially on polymers. Using this method, it is possible to prepare TiO₂ layers with photocatalytic properties or dye substrates.

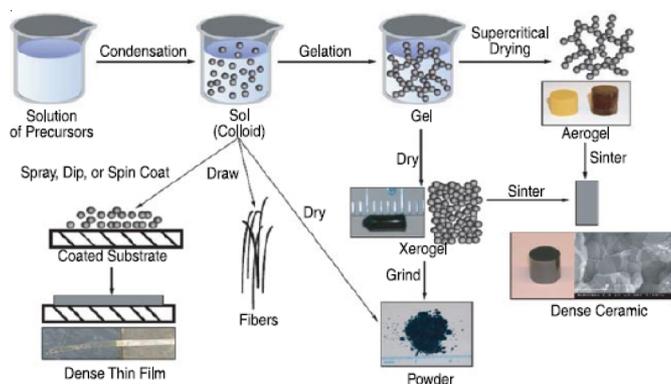


Figure 1. Steps of the sol gel process of materials and examples of the microstructure of final products. Bold-lined rectangles show possible final products of the sol gel method [2].

Using sol gel layers on fibre substrates is the optimal method for dyeing special fibres. Sol gel layers can cover all fibres with enough high adhesion, and in general we can dye not only pure glass fibres, but a mixture of fibres as well (for example, a mixture of glass fibres with polyester fibres).

The use of these surface coatings for dyeing is a good method of obtaining stable shades on different substrates. If we have fibres of different fineness, then we can obtain different results from classic dyeing process, because the rate of dyestuff absorption is connected with the fibre diameter and the optical properties of the fibre structure are connected with fibre fineness (diameter). In the case of surface coating by thin layers, the achieved colour theoretically depends on fibre fineness. This idea is proposed by the model in which there are stable thicknesses of layers on the fibre surfaces.

This complicated optical problem will be made clearer following Figures 2 and 3. In Figure 2, we can see the flow of light rays through the fibre structure. The fibres are shown in the cross-section view as circles. Figure 2A focuses on coarse fibres with larger diameter, while Figure 2B is a similar focus on fine fibres with smaller diameter. All fibres presented in Figure 2 have the same concentration of dyestuff in them. Therefore, the light reflected from the textile after going through four fibres is more reduced in the case of Figure 2B, because according to the well known Lambert-Beer equation, light absorption is equal to the length of the light trajectory in a medium containing the dyestuff (in fibres).

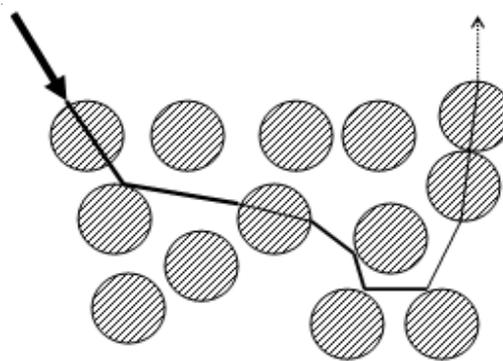


Figure 2A. Light flow through textile structure from coarse fibres.

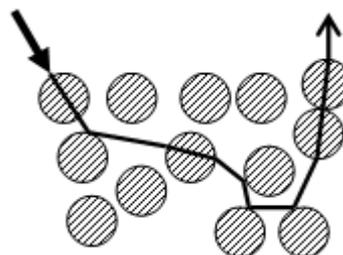


Figure 2B. Light flow through textile structure from fine fibres.

In the case of thin layers on fibres, the colour situation is relatively different. The trajectory of light rays in the fibre structure is similar to the situation presented in Figure 2, but the absorption of these light rays are dependent on the diameter of the fibres. The light absorption of textile and colour of textile depends only on the colourants used, its quantity of layers and the thickness of the colour layers on the fibre surface. This theory is supported by Figure 3. Figure 3A focuses on the situation of thick fibres, and in Figure 3B focuses on thin fibres. According to the Lambert-Beer equation, the light absorption is constant in both cases (Figure 3A and 3B), because the length of the trajectory in the fibres is approximately independent on fibre thickness.

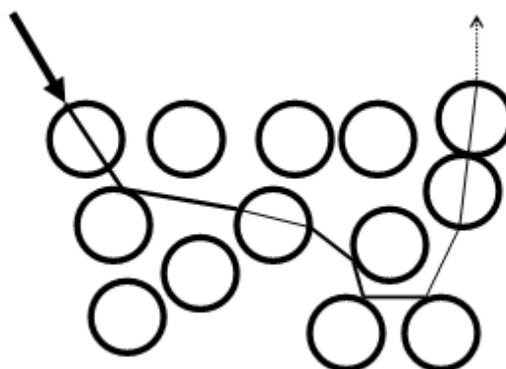


Figure 3A. Light flow through textile structure from surface dyed thick fibres.

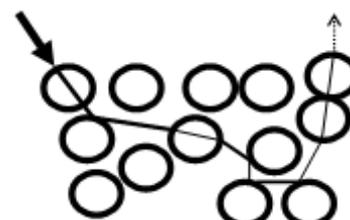


Figure 3B. Light flow through textile structure from surface dyed fine fibres.

Methods and materials

Textile structure glass microfibre

The substrate used (Spepat-F, Czech Republic) was the laboratory filter material Z75, which was made from 100% glass microfibrils. The areal density of the material used was 75 g/m². The average diameter of the fibres was about 1 µm.

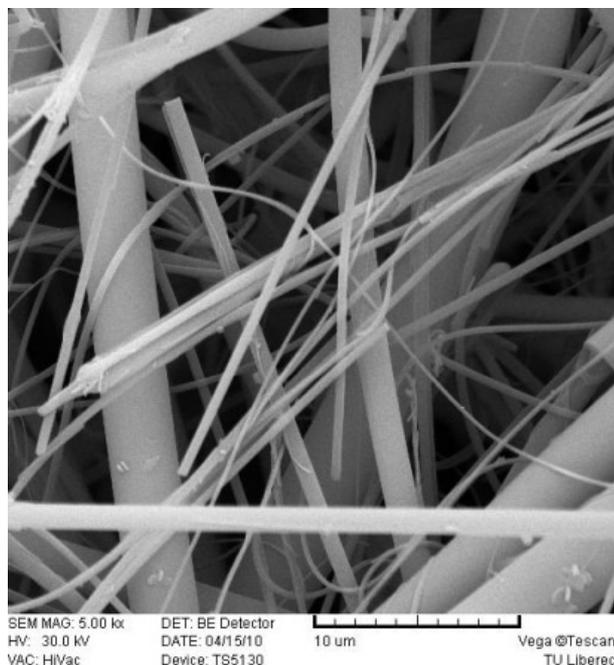


Figure 4. Glass fibres Z75.

Dyes

The first experiments were for testing the solubility of the dyes. In this study, three dye classes (cationic dyes, disperse dyes, metal complex dyes) were selected and all the available dyes of these classes were tested for solubility. The first step was to use the normal visual test, whereby a small amount of dyestuff was added to the test tube followed by addition of a solvent. In our case, isopropyl alcohol was used as the solvent for testing the solubility of dyes. The different dyes were selected for their different chemical structures.

Dyes bond to textile materials with Van der Waals forces, ionic, covalent bonding and polar interactions, etc., depending on the types of dyes and substrates for dyeing using exhausting processes. In the case of sol gel processing, dyes can be embedded into sol gel coatings and deposited onto textile materials. The sol gel technique allows different dyes to be embedded in modified silica matrices.

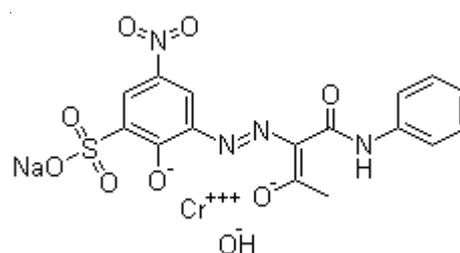
Basic dyes are water-soluble and contain cationic groups. The positive charge on the dyes may be localised on a quaternary ammonium group or delocalised over the entire aromatic structure (such as in triarylmethanes, methines, xanthenes and other heterocyclic systems). These dyes are applied primarily to acrylics and occasionally to polyester and polyamide fibres. Although basic dyes produced brilliant colours on wool, silk, and cellulosic fibres, they had poor fastness properties on these same fibres.[3]

Disperse dyes are non-ionic, have very limited solubility in water and have substantivity for one or more hydrophobic fibres

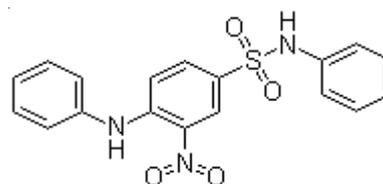
(polyester and nylon) They are applied from a fine aqueous dispersion containing some dissolved dye.

The general structure of disperse dyes is small, planar and non-ionic, with attached polar functional groups like -NO₂ and -CN. Their small size means that disperse dyes are quite volatile, and tend to sublime out of the polymer at sufficiently high temperatures [5].

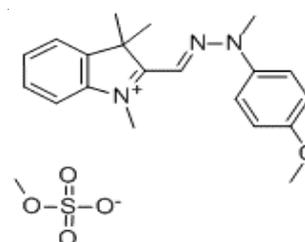
Acid dyes are water-soluble dyes for polyamide fibres, wool and silk. The chromophore is often based on anthraquinone or one to several azo groups which vary in molecular size. Characteristic to all acid dyes are one or more sulphonic acid or carboxylic acid groups, attached to the chromophore, which not only provide water solubility, but also form ionic bonds with amino groups of the fibre polymer under acidic conditions [6].



C.I. Acid Yellow 99



C.I. Disperse Yellow 42



C.I. Basic Yellow 28

Figure 5. Examples of different chemical structures of selected dyes.

Table 1. Dyes soluble in isopropanol used in the study.

| Samples coloured by |
|-------------------------|
| C.I. Acid Red 179 |
| C.I. Acid Yellow 99 |
| C.I. Acid Blue 158 |
| C.I. Acid Black 52 |
| C.I. Disperse Red 60 |
| C.I. Disperse Yellow 42 |
| C.I. Disperse Yellow 23 |
| C.I. Disperse Blue 81 |
| C.I. Basic Yellow 28 |
| C.I. Basic Red 46 |
| C.I. Basic Red 18 |
| C.I. Basic Blue 41 |

Sol description

The principle preparation of sol is based on 3-trimethoxysilyl propyl methacrylate disbandment in the first half of the needed volume of isopropanol and other components (water, HCl, BPO) disbandment in the second half of the needed volume of isopropanol. Then, both solutions were blended with intensive mixing. The produced sol was warmed to boiling under a backward cooler for 30 minutes. After 30 minutes, the sol was cooled. Part of the sol was diluted with IPA in a proportion of 1:4. Sol was labeled as AC4.

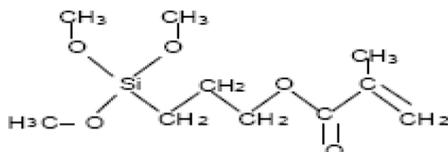


Figure 6. Chemical formula for 3-trimethoxysilyl propyl methacrylate sol gel solvent.

This solution is used as a solvent for dyeing high thermal fibres. It has to be controlled carefully because of its quick evaporation property, and failing to do so results in the dyes becoming less soluble in solution, and there is a possibility of the dye being removed from the surface of the substrate due to this evaporation. When not in use, it should be kept tightly sealed, and it only remains stable for a few days.

Dyeing

The samples were covered with a solution of AC4 + a dye. The sample was dunked into the solution for 1 minute. Next, it was dried for 30 minutes at laboratory temperature. After 30 minutes, it was dried in the laboratory dryer, Venticell (Brninská medicínská technika, Czech Republic) for 3 hours at 90 °C [7].

Wash Fastness

One sample was used for testing wash fastness. The sample was placed inside the test tube and 10 ml of water was added followed by heat treatment on the stove at 60 °C for 60 minutes.

Temperature Fastness

Twelve samples were used at a temperature of 200 °C for testing dye fastness at high temperatures. The heating box, which can reach high temperature parameters, was used for conducting this experiment. Samples were tested at the selected temperature for 5 minutes each.

Light Fastness

Two samples from each coloured substrate were used for testing fastness in light usage, utilizing UV light at a distance of 23.5 cm. The first samples were exposed to UV light for 20 minutes and the second samples were exposed for 120 minutes. The results were evaluated using the blue scale.

Results and discussion

Wash Fastness

One sample from each dyestuff was tested for wash fastness properties by using water at 60 °C for 1 hour. The following results were obtained from the grey scale.

Tables 2. All dyestuffs tested for wash fastness properties using the grey scale.

| Samples coloured by | Fastness/ grey scale |
|-------------------------|----------------------|
| C.I. Acid Red 179 | 2 |
| C.I. Acid Yellow 99 | 2 |
| C.I. Acid Blue 158 | 1-2 |
| C.I. Acid Black 52 | 2 |
| C.I. Disperse Red 60 | 4-5 |
| C.I. Disperse Yellow 42 | 4 |
| C.I. Disperse Yellow 23 | 4 |
| C.I. Disperse Blue 81 | 4 |
| C.I. Basic Yellow 28 | 2-3 |
| C.I. Basic Red 46 | 3 |
| C.I. Basic Red 18 | 3 |
| C.I. Basic Blue 41 | 3 |

Disperse dyestuffs had the highest wash fastness, because these dyestuffs are insoluble in water.

Temperature fastness

Six samples were used for the evaluation of stability at a temperature of 200 °C for testing dye fastness at high temperatures. Six samples from the selected dyes were tested at a temperature of 200 °C for 5 minutes. The results were evaluated by a colour measurement spectrometer and visual observation in comparison to the original untreated sample.

Table 3. K/S values.

| Samples coloured by | K/S ₀ | K/S _{200°C} | (K/S _{200°C})/(K/S ₀) |
|-------------------------|------------------|----------------------|---|
| C.I. Acid Red 179 | 0.83 | 0.22 | 0.27 |
| C.I. Acid Yellow 99 | 1.46 | 1.28 | 0.87 |
| C.I. Acid Blue 158 | 1.82 | 1.16 | 0.63 |
| C.I. Acid Black 52 | 2.19 | 1.90 | 0.87 |
| C.I. Disperse Red 60 | 0.81 | 0.60 | 0.74 |
| C.I. Disperse Yellow 42 | 2.91 | 2.39 | 0.82 |
| C.I. Disperse Yellow 23 | 3.16 | 2.62 | 0.83 |
| C.I. Disperse Blue 81 | 0.66 | 0.42 | 0.64 |
| C.I. Basic Yellow 28 | 3.19 | 1.35 | 0.42 |
| C.I. Basic Red 46 | 1.49 | 0.28 | 0.19 |
| C.I. Basic Red 18 | 3.52 | 2.85 | 0.81 |
| C.I. Basic Blue 41 | 0.24 | 0.14 | 0.60 |

An alternation of the remission curves is visible in the graph for the selected dyes. The sol gel layer could not protect the dyes sufficiently from the high temperature.

Light fastness

Two samples were used for testing fastness in UV light at a distance of 23.5 cm. The first samples were exposed to UV light for 20 minutes and the second samples were exposed for 120 minutes. The results were evaluated using the grey scale.

Light fastness was relatively high for all selected dyestuffs. The dyes had low variance compared to samples not exposed to light. The best results were obtained with the metal complex

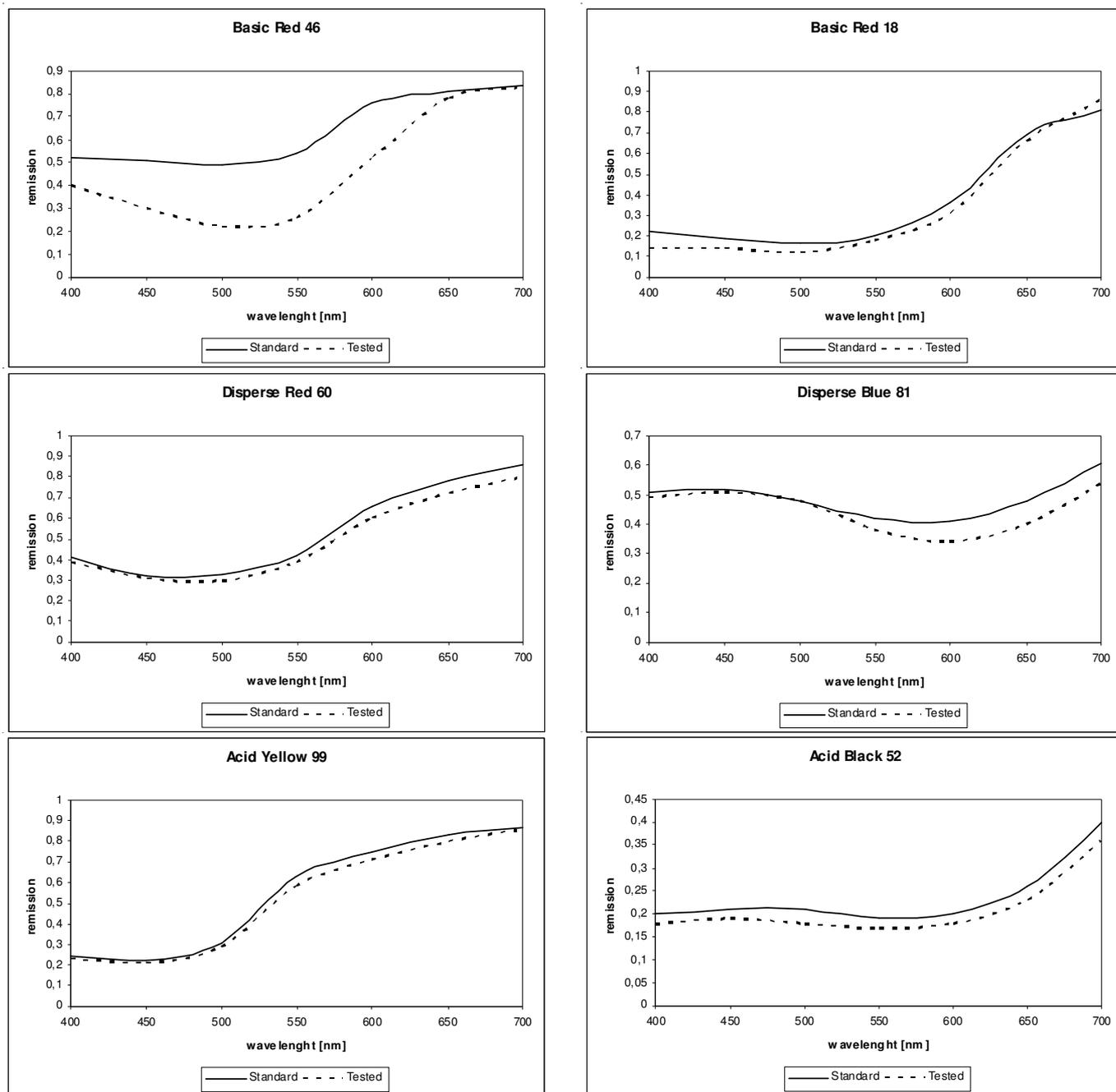


Figure 7. Alterations to the remission curves by the selected dyes.

Table 3. Light fastness of samples using the grey scale.

| Samples coloured by | 1st samples at 20 min | 2nd samples at 120 min |
|-------------------------|-----------------------|------------------------|
| C.I. Acid Red 179 | 4 | 4 |
| C.I. Acid Yellow 99 | 5 | 4 |
| C.I. Acid Blue 158 | 5 | 4-5 |
| C.I. Acid Black 52 | 4 | 4 |
| C.I. Disperse Red 60 | 4-5 | 3-4 |
| C.I. Disperse Yellow 42 | 3 | 3 |
| C.I. Disperse Yellow 23 | 3 | 2-3 |
| C.I. Disperse Blue 81 | 4 | 3-4 |
| C.I. Basic Yellow 28 | 4-5 | 4 |
| C.I. Basic Red 46 | 3-4 | 3 |
| C.I. Basic Red 18 | 5 | 5 |
| C.I. Basic Blue 41 | 3-4 | 3 |

dyestuffs, which are commonly not very sensitive to light degradation. On the contrary, cationic dyes had low light fastness, but the sol gel layer slightly improved their fastness.

Conclusion

This is a very simple method for the colourization of glass fibres using 3-trimethoxysilyl propyl methacrylate solvent as a medium for transporting dye molecules to the non-wettable surface of the fibre, while at the same time, the dyes are able to be bonded to the fibre. The 3-trimethoxysilyl propyl methacrylate solvent forms a film on the fibre surface by means of bond creation using the hydrogen from the CH₃ methyl groups which are bonded to the oxides of the solvent structure. Since the structure of the glass fibre is composed of SiO₄, bonds can be formed, and thus a film is created on the fibre surface which can be coloured by any acid (-SO₃Na, -COONa), disperse (-OH, -NH₂, -SO₂NH₂) or cationic dye (-N+R₃Cl-) with

suitable end groups which can react with the 3-trimethoxysilyl propyl methacrylate and therefore result in bond formation. There were changes in the hardness of the glass filter paper (it was stiffer) which could be explained by the solvent forming a film on the surface of fibres. Overall, the dye-fibre properties were moderate; bright and dark shades can be obtained using this solvent along with a good selection of dye. Additionally, the glass fibres were not damaged.

Acknowledgements

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