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LIGHT STABILISATION OF PHOTOCHROMIC PRINTS

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Abstract

Light stabilisation of photochromic dyes is seen as the most challenging part in the development of photochromic dyes. The aim of this research is to compare stabilisation methods and their effect on the lifetime of a photochromic print on textile. The vision is to create a textile UV-sensor that detects current UV-light exposure in the surroundings and alarms the wearer by showing colour.

The developed inks have been formulated for ink-jet printing as a novel production method with resource saving properties. UV-LED light curable ink formulations were prepared for two dye classes; a non-commercial spirooxazine, a commercial spirooxazine (Oxford Blue) and a commercial naphthopyran (Ruby Red). Two different stabilisation methods were applied; chemically by incorporation of hindered amine light stabilisers and physically by polyurethane coating. Fatigue tests were performed to evaluate and compare the stabilisation methods. The tests included were household washing, multiple activations and intensive sun-lamp exposure.

As a result it was found that Oxford Blue and spirooxazine had an initial better resistance to photodegradation than Ruby Red. The coating reduced the ability of colour development in higher extend for Oxford Blue and spirooxazine compared to Ruby Red. Moreover, the photocolouration increased with the number of activations for Oxford Blue and spirooxazine in particular. In general, the physically stabilised samples showed a better or similar fatigue resistance compared to chemically stabilised samples. On the other hand the results are weak in significance. It is concluded that the developed coating method in combination with further optimising has potential.

Key words: Photochromic dye, textile sensor, flexible sensor, lightweight material, light stabilisation, HALS, ink-jet printing, protective coating, spirooxazine, naphthopyran

Popular abstract

Today, we are more than ever aware of the harmful UV-radiation and its effects on human health. UV-light detectable sensor could be a useful tool to warn the wearer of current UV-light intensity in the surroundings by colours. Thanks to photochromic compounds, this is possible. Photochromic compounds show a reversible colour change trigged by external stimuli as UV-light. The higher photoelectric energy induced by irradiation changes the molecular arrangement, the absorption spectra and therewith shows a colour that is visible to the human eye. A smart flexible textile UV-sensor can be worn as an everyday application and alarm on cloudy days where harmful UV-radiation is not an obvious threat.

This research gives light on photochromic dyes on textile substrate in a sensor application. The challenge is to improve their photostability to extend the lifetime of the dye and its function. Ways of stabilisation of the photochromic inks have been done chemically and physically and then evaluated by fastness tests. The testing has been tailored for textile applications and includes household washing, multiple and intensive activation of the prints.

As a result, stabilisation was found for both methods. In the physically stabilised samples a lower degradation was found in comparison to chemically stabilised samples. Although, the trends are not significant for a real conclusion to be made, it is concluded that the developed coating method in combination with further optimising has potential.

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List of abbreviations

CFC – chlorofluorocarbon

UV – ultraviolet radiation with wavelength 10 – 400 nm

UVA – ultraviolet A with wavelengths 315 – 400 nm

UVB – ultraviolet B with wavelengths 280–315 nm

ΔE – colour difference

HALS – hindered amine light stabilisers

LED – light emitting diode

IR – infrared radiation

PP – polypropylene

PA – polyamide

PET – poly(ethylene terephthalate)

PMMA – poly(methyl methacrylate)

EC – ethylene cellulose

CMC – Colour Measurement Committee

SCI – specular component included

PLA – polylactic acid

MIT – Massachusetts Institute of Technology

ABS – acrylonitrile butadiene styrene

PU – polyurethane

FTIR – fourier transform infrared spectroscopy

DPGDA – dipropylene glycol diacrylate

NMP – n-methyl-2-pyrrolidone

ANOVA – analysis of variance

1 Introduction

Sunburn, skin cancer, premature aging and negative impact on the immune system are some of the harmful effects of acute and cumulative exposure to ultraviolet (UV)-radiation. Most people are aware of the ozone depletion of the earth's atmosphere as a global environmental threat. The ozone protects the earth and its living organisms from harmful UV-radiation. If it would not exist neither life on earth would be possible. Since the 1960's this layer is constantly being destroyed by emissions caused by the human being and exclusivity by the industrialised countries. The gases are nitrogen oxides and chlorine- and bromine containing gases, especially chlorofluorocarbons (CFC's) that catalyse the degradation of ozone in the atmosphere. CFC's are artificial compounds that are very persistent and even if they are international banned since 1996, there are large quantities of ozone destroying substances spread around the world. A decrease of 1% in ozone would lead to increases in the radiation at the earth's surface and may eventually lead to a 2.3% increase in skin cancer (NationalGeographic 2016; Viková & Vik 2006).

Photochromism is a reversible and repeatable transformation induced by absorption of short-wave electromagnetic radiation between two forms on molecular level. These have different absorption spectra and give a visible colour change of the photochromic material. The inactive form is usually colourless and gets coloured when irradiated by UV-light or exposed to sunlight that includes UV-radiation. This property creates potential for enhancing the functionality of products. A typical example of this is opthalmic lenses that have photochromic compounds incorporated in polymer matrices or glass. The matrices also protect the photochromic dyes against photooxidation by oxygen in the atmosphere (Nechwatal & Nicolai 2015).

In sensor technology based on textiles, the combination of photochromism and textiles provides a lightweight, flexible and highly incorporated function for wearable applications. The main aspect in the UV-sensor development is the sensitivity to the level of UV radiation, to selected parts of UV-light respectively. Only then a sensor can alarm environmental circumstances and danger (Viková & Vik 2006).

Integration of photochromic dye in textile structures has been proven successful by fibre integration, exhaust dying and screen-printing in previous studies. Incorporation of photochromic dyes into a polymer matrix by adding stabilisers or apply a solid physically shield, provide a barrier to oxygen and chemicals. Application on textiles will extend the photochromic material to a functional textile material providing large surfaces and flexible benefits to the photochromic material.

1.1 Problem description

Previous studies on photochromic prints show that it is possible to apply photochromic materials on textile substrate by varies methods and also that the activation by UV-light can work as an indicator for UV-radiation. However, the real photochromic reaction is accompanied by undesirable side effects. These processes continuously decrease the colour change due to poor light stability caused by photooxidation of the photochromic dye and fast fading of the developed colour effect. To extend the lifetime of the dynamic colour performance and enable use as UV-sensor, fastness properties have to be improved as well as the indicated response to UV-light, for a more accurate textile based sensor technology. However, studies on light stabilised photochromic material have been successful but are limited. Textile substrate does not give enough protection against the atmosphere as photochromic dyes that are not locked into a well protective matrix (glass or plastic).

The aim of this thesis is to investigate alternative possibilities of light stabilisation of photochromic dyes applied on textile substrate for a sensor application. Additionally, the photochromic material will be adapted for ink-jet printing technology and applied by a UV-light curable matrix.

1.2 Research questions

- How do different concentrations of light stabilisers in the photochromic formulation affect the lifetime of a textile UV-sensor?

- How does a protective coating layer on the photochromic print affect the lifetime of a textile UV-sensor?

Hypothesis
A transparent protective layer gives similar/better results in light fastness performance as light stabilised printing pastes using HALS

1.3 Research objective

The ultraviolet part of the solar radiation is important in several processes in the biosphere thus UV-radiation has several beneficial effects. However, when the level of exposure to UV-light exceeds the normal it may have very harmful consequences. The self-protection ability may be eliminated by the UV-radiation and biological species may suffer from the consequences of exposure. Therefore, there is a need to reach out to the public with simple information about UV-radiation and its possible detrimental effects. This reason has motivated research for an indicator of UV-radiation exposure (Viková et al. 2014).

The aim of this thesis is to increase the knowledge of the photochromic behaviour on textile substrate printed by ink-jet printing technology, cured by UV-LED light and answer the question if it possible to create a physical shield protection against photooxidation. Novel application method may display improved functionality and stability properties. 3D-printing technology and coating by polyurethane are used for the creation of the physical shield. The technologies are chosen for their opportunity to fast development in the field and capability to play a more important role for the industry in the future.

The scope of this research includes a literature review and practical work on the organic photochromic compounds with focus on naphthopyran and spirooxazine, the ink-jet printing method, chemical light stabilisation and stabilisation by protective physical shield. To complete the study on fatigue resistance, measurement on colour development and simulation of usage i.e. fastness properties are investigated for a development for use in practise.

2 Literature review

2.1 Chromism

Chromism is an effect that describes an induced reversible colour change of substances and is a well-known phenomenon. The effect is activated by an external stimuli and inactivated when the stimuli is removed. This is due to physical and chemical changes in the dye molecule as change of the electron density of substances or change in the arrangement of the structure of the supramolecule assemble (Rijavec & Bračko 2015; Viková & Vik 2006).

Chromic dyes or pigments can change their colour in the presence of acids (acidchromism), polarity (solvatochromism) or temperature changes (thermochromism) or when exposed to water (hygrochromism), mechanical loading (mechanochromism), electric power (electrochromism), pressure (piezochromism) etc. The changes are temporary or permanent. In this paper the focus will be on the colour change induced by light, photochromism on textile substrate for smart textile application (Bouas-Laurent & Dürr 2001; Rijavec & Bračko 2015).

Additionally, thermochromic dyes are more stable and more used in textile applications than photochromic dyes. There are very few examples of mechanochromic dyes on textiles whereas electrochromic dyes on textiles is in progress. Besides the interest in fashion and decorative applications for photochromic dyes, many smart textiles with functions as thermoregulation, camouflage, product labelling and security etc. attracts interest. These applications of smart dyes in textiles are increasing (Rijavec & Bračko 2015).

The list below contains factors that are used to measure and evaluate the quality of chromism and its function (Rijavec & Bračko 2015).

- Intensity of colour change, ΔE
- Colour shift
- Conditions of transitions
- Speed of shift
- Interval of shift
- Reversibility
- Fatigue resistance
- Cycles before degradation
- Resistance to atmospheric conditions
- Simplicity of use
- Body reactions: allergy, toxicity

Up to now, numerous of both natural and synthetic smart dyes have been discovered and investigated in different ways, but very few of these smart dyes are suitable for dyeing textile materials due to low fatigue resistance i.e. an ability to develop colour after several reversible molecular transformations. Moreover a low resistance to external impacts such as washing cycles and its detergents, exposure to sunlight and higher ironing temperatures, are necessary for use in practice (Rijavec & Bračko 2015).

The focus in this thesis paper will be on the quality factors; fatigue resistance, cycles before degradation and resistance to atmospheric conditions and theirs improvability of photochromism in textile sensors.

2.2 Photochromism

Photochromism is a light induced transformation between two molecular states, A and B. It is a rearrangement process where the photochromic organic compound undertakes a reversible colour change, typically from non-coloured to coloured form when exposed to a specific range in the electromagnetic radiation field, usually UV-light. Photochromism is therefore simply defined as a light induced reversible colour change. Basically, the molecular change between two states has different absorption spectra, which the observer perceives as different colours or non-colours. State A of a photochromic material does not absorb any visible light and perceives as typically colourless for the observer. However, it will be activated by high-energy photons ($h\nu_1$) from the near UV-radiation (200-400 nm) of the electromagnetic spectrum. The photonic reaction is due to changes in the electron density, resulting photochromic material in state B that is capable of absorbing low energy photons ($h\nu_2$) from the visible light spectrum (400-700nm). The same material but in different forms has different appearance. The reverse reaction, decolouration, takes place when the excited molecule in state B absorbs light ($h\nu_2$) with the frequency close to the absorption maximum and returns to the non-excited state A i.e. colourless. Alternatively in T-type photochromic material a reverse reaction can be induced by heat absorption. Generally, reaction A → B goes faster than the reverse reaction B → A. In outdoor conditions these reaction is going on simultaneous.

$$A\ (\text{colourless}) + h\nu_1 \rightarrow B\ (\text{coloured})$$

$$B\ (\text{coloured}) + h\nu_2 \rightarrow A\ (\text{colourless})$$

As mention, there are two categories defining the reverse reaction, P-type where the reverse reaction is photo induced i.e. when the light source is altering or removed the reversible colour change from coloured to colourless form. The other category is thermally reversible, T-type photochromic material. Moreover, positive photochromism describes the transformation from colourless to coloured form when irradiated and negative photochromism describes the colour change that goes from coloured to colourless under influence of light but is much less common (Bouas-Laurent & Dürr 2001; Viková & Vik 2006).

Historically, Fritzsche reported the first scientific research on photochromic effect 1867 on a solution of tetracene. The solution undergoes a bleaching in daylight but returns to its initial orange-coloured state in the dark. Later, ter Meer found a colour change in solid potassium salt of dinitroethane that goes form yellow to red when exposed to sunlight. The term photochromism was coined in 1950 by Hirschberg to describe the phenomenon of compounds that changes colour due to light as external stimuli. However, photochromism is not limited to visible coloured compounds, it also applies to systems absorbing from the far UV- to IR-radiation, and from very slow to very rapid reactions (Bouas-Laurent & Dürr 2001; Zmija & Malachowski 2010).

At present, many inorganic and organic photochromic substances are well known. However, most of the inorganic compounds, such as various metal oxides, alkaline earth metal sulphides, titanates, copper compounds, mercury compounds, certain minerals among others, are not suitable for dyeing textiles. Organic compounds,

photochromic dyes have been seen effective for dyeing textiles and are also more environmental friendly substances. Furthermore, due to the photodegradation of these organic photochromes, their potential for application is limited. This fact stimulated many researches in the 1980's in development of fatigue resistant spirooxazine and chromene derivatives (Rijavec & Bračko 2015; Zmija & Malachowski 2010).

2.2.1 Photochromic dyes

The most important photochromic families known are spiropyrans, spirooxazines, naphthopyrans, fulgides, fulgimides and diarylethenes. Spiropyrans, spirooxazines and naphthopyrans are sensitive to thermal effects and return to the colourless state under heat (T-type) or/and visible light (P-type). Fulgides and diarylethenes are thermally stable and decolourise by light absorption (P-type).

In this research naphthopyran, also known as chromene (Fig. 2) and spirooxazine (Fig. 3) are used as photochromic material.

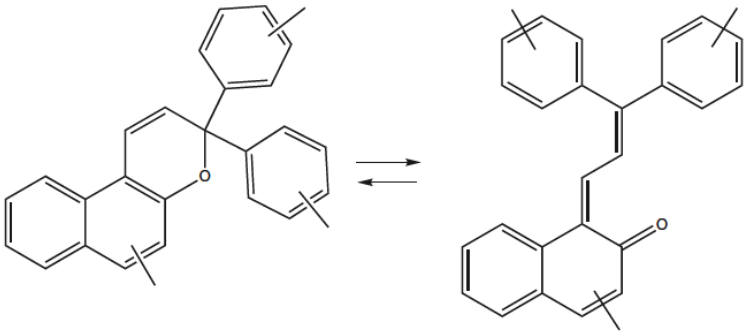

Fig. 2 The general naphthopyran/chromene molecule (Little & Christie 2010a)

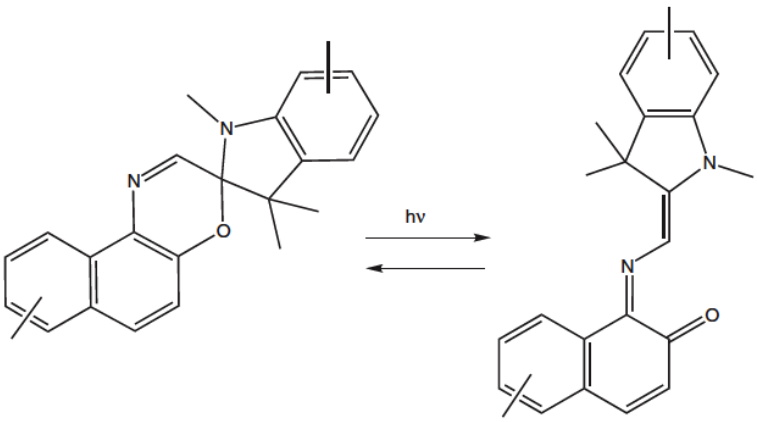

Fig. 3 The general form of spirooxazine (Little & Christie 2010a)

The photochromic mechanism for naphthopyrans is similar to spiro-compounds that will be described below. The photochromic mechanism for spiro-compounds is the most researched in the area of photochromic substances.

Spiro-compounds consist of a pyran ring linked to another heterocyclic ring via a spiro-group. The colourless molecule of spiropyrans or spirooxazines has a non-planar molecular structure (Fig. 4) that blocks delocalization of electrons and colouration of the substance. UV-radiation induces a heterolytic cleavage of a C-O bond within the pyran ring. UV-light absorption enables the formation of a planar ring-opened molecular structure with enlarged conjugated system and delocalization of electrons and colouration followed by this change in structure. This excited state is the zwitterionic (both positive and negative charged ion) *merocyanine*, a cis-isomer, which transforms to a trans-isomer (Fig. 4). The reverse open-to-close process takes place under the influence of visible light and/or heat. Spirooxazines are compounds containing nitrogen with similar structure to spiropyrans (Rijavec & Bračko 2015). Furthermore, spirooxazines have been interesting for researchers since they have better fatigue resistant compared to spiropyrans (Feczkó et al. 2012a).

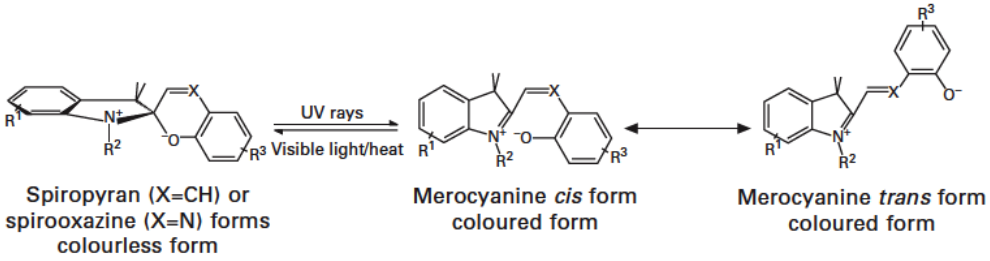

Fig. 4 Photochromism in a compound is a consequence of reversible rearrangement of the molecule (Rijavec & Bračko 2015)

The loss of performance over time due to chemical degradation of a photochromic material, fatigue, is a side reaction that is a quality issue in photochromism. Today, spirooxazines have been improved and show a good resistance to photodegradation, yet they are sensitive to high temperatures. However, naphthopyrans show good stability to high temperatures but have moderate fatigue resistance (Bouas-Laurent & Dürr 2001; Rijavec & Bračko 2015). Moreover, the development of fatigue resistance sprirooxazine and naphthopyran derivate triggered the commercialization of photochromic lenses in the 80's (Bouas-Laurent & Dürr 2001).

Moreover, photochromic compounds are temperature dependent. The reversion of photochromic compounds from coloured to colourless form is stimulated during UV irradiation due to accelerating thermal back reaction. Spirooxazine are more sensitive in comparison to naphthopyran compounds. Increased temperatures decrease the developed colour, especially in solid states i.e. cured ink. The rate of photocolouration decreases as a function of temperature and at 100°C the reverse and forward reactions are equal and resulting in no colour change when irradiated to UV light (Little & Christie 2010a; Ramachandran & Urban 2011; Viková, Christie & Vik 2014).

2.3 Effect of matrices

Protecting dyes within inorganic matrices increases their stability. The concept is inspired by nature, for instance in the incorporation of fragile colorants such as carotenoids and melanins in seashells. Developments in sol-gel technology have enabled incorporation of organic photochromes, into inorganic matrices i.e. formation of inorganic-organic hybrids containing dyes. These hybrids can be used to produce transparent films with excellent optical quality (Bamfield & Hutchings 2010)

Photochromic dyes can react to their surrounding microenvironment and to the structure of the substrate but also to the presence of degradation products or influences from the outside. As a consequence it has not been possible to achieve same light- and colour- fastness as common textile dyes. The coloured and colourless states of photochromic dyes vary in structure and polarity of the molecule. That leads to the fact that the microenvironment of the dye is important for the photochromic behaviour. The steric demand of the shift in the molecular structure of the dye requires space. Moreover, in for example a polymeric matrix, amorphous plastic materials are better than materials with larger crystalline regions as other plastics and fibres. Internal charge distribution changes between the coloured and colourless forms of the photochromic dyes also when incorporated in a matrix. Because of this, non-polar polymers e.g. PP stabilise the non-polar state of the dye that is usually the colourless form and polar polymers e.g. PA and PET stabilise the polar state of the dye that is usually the coloured form for incorporated dye (Nechwatal & Nicolai 2015). Usually, photochromic materials are used in the form of films, sheets, plates, fibres and beads and the photochromic dye is incorporated into a polymer matrix or doped in a polymer solid. However, the factors, which effect photochromic response, such as rigidity, free volume and polarity, directly around the dye molecule could be controlled by the choice of the polymer. Poly(methyl methacrylate) (PMMA) and ethyl cellulose (EC) are polymeric material used in as polymer support in photochromic materials. PMMA has an outstanding water clear colour, stability even under severe conditions, high surface resistivity, and resistance to weathering and moisture. EC is used for its good optical properties (Feczkó, Kovács & Voncina 2012a).

A study by Nechwatal & Nicolai shows that the intermediates generated under thermal exposure of photochromic dyes i.e. long term thermally aged samples of the material have a decreasing effect on the photochromic function. It leads to a significant accelerated photochromic fatigue caused by followed UV-irradiation (Nechwatal & Nicolai 2015).

Little and Christie did an investigation on wash fastness of photochromic print. The test showed that the colouration of the spirooxazine photochromic print on a textile increased after the initial wash. A potential explanation is that the binder matrix loosens around the dye molecules with initial washing, facilitating transformation between colourless and coloured forms of the spirooxazines, which are more rigid in structure than the more flexible naphthopyrans (Little & Christie 2011).

In a study by Feczkó *et al.* the photostability of spirooxazines was investigated. With the aim to improve its photostability spirooxazine was incorporated into thin solid films instead of doped into polymers. These photochromic films were prepared by polymerizing the dyes by encapsulation with different polymers. And as a result they prolong the fatigue resistance significant (Feczkó et al. 2011).

2.5 Photodegradation

In one cycle, state A is transformed into state B that returns again to state A. The terms “switch on” and “switch off” are often used. Ideally, the yields of the two reactions are quantitative, but biproducts are formed and locked in transition state for every cycle (Fig. 5) (Bouas-Laurent & Dürr 2001).

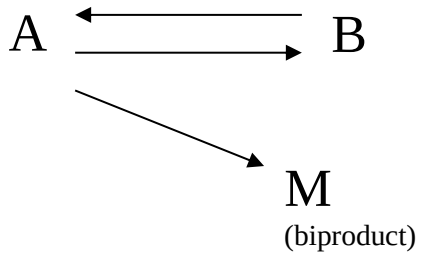

Fig. 5 Schematic figure of reaction processes in photo induced transformation

UV-radiation trigged photooxidation causes fatigue of the material due to chemical degradation and loss of photochromic performance. Light and heat are both responsible for the photodecomposition of organic photochromic compounds. Further, the photochromic reactions do also involve side reactions that are not able to revert back to its original photochromic species. Improvements of photostability i.e. a decrease of photodegradation can be gain by additives in the formula, stabilisers of different kinds (Feczkó, Kovács & Voncina 2012a).

In a research by Ballet on degradation processes of organic photochromes incorporated in polymers, showed clearly that degradation was mainly caused by oxidation. The conclusion was based on experiments where an oxygen barrier was applied above a photochromic polymer coating. The additional coating was water-soluble carboxymethylcellulose, known for its barrier properties. It was found that this coating increased the photostability and the slowed down the degradation time for naphthopyran and naphthooxazine up to two times (Ballet 1997).

The degradation of photochromic dye will decrease the function of the smart dye. This specific sensitivity to degradation due to oxidation significantly limits their potential for application on textile materials, where they are exposed to repeated washing and various environmental conditions, that is essential for wearable textile applications (Rijavec & Bračko 2015).

Not only photochromic dye molecules are sensitive to light on a molecular level. When a coloured textile material is exposed to light, the temperature will increase on the surface and chemical reactions will start. Degradation by fibre- and dye modifications will appear. On traditional dyed textiles a fading of the colour is more or less visible (Little & Christie 2011).

Furthermore, textiles are fibrous materials build up by the smaller units called fibres, which are characterized by having a high ratio of length to thickness. Fibres are interlaced to form threads that get twisted to form a yarn. Yarn is converted into fabrics by different techniques such as weaving and knitting. This structure does also allow oxygen to pass through and interact with the textile surface.

Due to the problem of the photostability of the photochromic material applied on textile substrates, studies on stabilisation of such dyes has been done. These

investigations have included different types of dyes, additives and coatings. Parhizkar *et al.* have investigated three methods for photostabilisation of photochromic material on textile substrate. Firstly by incorporating an UV-light stabiliser in an organosilica coating layer, a second method by hydrophobic treatment of the porous surface and a third method included a protective layer on the coating layer by an additional silica layer. All treatments improved photostability to different extents. Additionally, the other photochromic properties did not affect significantly. The best result gave the incorporation of a quencher UV-light stabiliser, second best effective treatment was the additional extra silica (APS sol-gel) layer (Parhizkar et al. 2014).

2.6 Applications

Traditional textile dyes, are not able to develop reversible colour change and do not provide significant colour effects in conditions of different light intensity. The intensity of colours, colour type and pattern remain the same regardless of the sunlight intensity.

The capacity of photochromic dyes to reversibly change their colour due to light provides potential for new creative design effects applications. Since the first report on photo induced colour change, its fascinating property has been interesting for both science and industry. The typical example, which is a widely commercial product is the photochromic lenses, opthalmic glasses that darken in the sunlight when it exposed to intensive UV-radiation in the sunlight and reverse to transparent in low UV-light intensity on a cloudy day or indoors. In opthalmic glasses the photochromic compounds are incorporated in a polymeric matrix. This support material protects the photochromic material from oxygen and further photodegradation. Other non-textile examples are jewelleries, nail polish, toys and furnishings. Furthermore, photochromic dyes are also used for the protection from forgery of money, cheques, documents and brand names by security printing. Moreover, the photochromic dyes sensitivity to UV-irradiation allows the development of sensors to indicate UV-radiation based on photochromic material. (Feczkó et al. 2012b; Parhizkar et al. 2014; Rijavec & Bračko 2015; Transitions 2016).

The development of photochromic textiles for camouflage purpose has been studied since the 1960's when American Cynamid Co. first developed photochromic spiropyrans. The process of photochromic dye application on textiles was patented 1998. This process showed a result of a camouflage effect at various levels of light intensity. The effect is based on additive mixing of the colour of photochromic material and conventional dye that produce various colours of the camouflage pattern in different outdoors conditions and sunlight exposure to mimic the surrounding environment (Rijavec & Bračko 2015). Swedish Interactive Institute use photochromic compounds in UV-light sensitive curtains where various parts of the curtain are dynamically illuminated by a computer controlled UV-light source. This generating a dynamic textile pattern, controlled by a computer digitised pattern (Chowdhury et al. 2014).

The photochromic function has been used in fashion design for special effects and creative designs. In indoor environment the print design is invisible but appears in the present of external stimuli, UV-radiation in the sunlight in outdoor conditions. The most central limitation for industrial applications of photochromic material is their fatigue.

2.7 Textile sensor

A textile based sensor senses environmental changes by reacting on it. In the case of photochromic prints this reaction occurs as a colour change that is visible for the human eye.

Textile sensors are soft-type sensors and have properties that are difficult to reach by other materials. The structure makes it flexible and easy to maintain. It has low specific weight and good strength, tensibility and elasticity. It has a large specific surface area that makes it suitable as indicator on environmental conditions. The wearability of a textile based sensor make it possible to integrate into systems of protective clothes or every day clothes as an active smart textile (Viková & Vik 2006).

A textile UV-sensors based on photochromic dyes integrated in clothing could be able to inform the wearer of current UV-light intensity exposure. Linked to the information about the sun protection factor, it would enable safer movement of the wearer outdoors. A research by Viková showed that it was a relation between intensity of light and depth of colour observed. Further, this finding is a property essential for sensors. Under the influence of UV-radiation, the reflectance curve shape changes in the visible part of the spectrum and colouration takes place. At reversion to the original state in the absence of UV-radiation, the shapes of the reflectance curves exhibit the changed time dependence and hysteresis occurs. A good selectivity of amount of UV-light could be seen for a photochromic dye type of spironaphooxazines (Viková 2003; Viková & Vik 2006).

Furthermore, to create a commercial textile sensor or functional photochromic material on textiles at all, some main criteria's are to be fulfilled. A fast colouration as well as a decolouration over a large temperature range, appropriate colourability and fatigue resistance (Little & Christie 2010a) (Feczkó et al. 2012b).

2.8 Colour difference ΔE

The description of colours for assessment of performance is difficult, for the reason it is very subjective (Bamfield & Hutchings 2010). For the experiments has ΔE been used to define the colour differences between inactivated and activated dye. In 1984, the CMC, Colour Measurement Committee of the Society of Dyes and Colourists of Great Britain developed and adopted an equation to calculate colour difference based on light, chroma and hue. These elements are used to describe a colour. First, the hue distinguish red from orange, blue and green etc. Then the chroma describes the vividness or dullness of a colour i.e. saturation. The third element, lightness describes the luminous intensity of a colour (Mokrzycki & Tatol 2011).

ΔE is used for comparison between a sample and a known reference. The formula is based on the colorimetric principles of the CIE 1976 system. CMC is developed for the textile industry and *l:c* allow the setting of lightness (*l*) and chroma (*c*) factors. In practice the default ratio for *l:c* is 2:1 allowing 2 times higher difference in lightness than chroma as the eye is more sensitive to chroma differences. If $0 < \Delta E < 1$, the difference is unnoticeable for the observer. Moreover CMC is not a colour space but rather a tolerance system that provides better agreement between visual assessment and measured colour difference (Kuehni 2005; Mokrzycki & Tatol 2011).

The geometrical representation of ΔE_{CMC} is an ellipsoid, where the size and orientation are different depending on the location in space. Assuming a particular value for tolerance of ΔE_{CMC}, the colours acceptable for a given value can be placed inside an ellipsoid (Fig. 6), whose centre is the value. On its basis the coefficient *cf* is obtained, which is tolerance limit for each sample's evaluated colour (Mokrzycki & Tatol 2011).

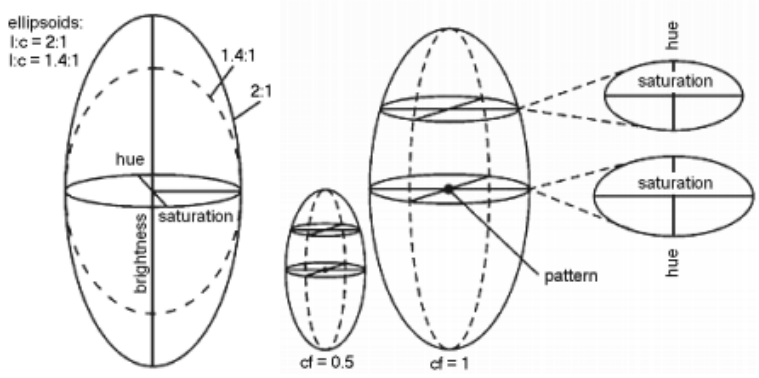

Fig. 6 Ellipsoids defining the unnoticeable colour area difference and tolerance (*cf*) in the CMC (*l:c*) formula (Mokrzycki & Tatol 2011)

The most common instrument to measure colour are spectrophotometers. Spectro technology measures reflected or transmitted light at many points on the visual spectrum, which results in a reflectance curve. The curve is unique for each colour. A spectrophotometer is used to identify, specify and match colours where a ΔE can be obtained (unknown 2007).

The dynamic colour changing properties of photochromic compounds is challenging for assessment by traditional colour measurement instruments. For the measurement of colour yield in photochromic material it is necessary to carefully control temperature and time interval between UV-irradiation and measurement. However, a prototype of a measurement system for photochromic material was developed at the Laboratory of Colour and Appearance Measurement in the Faculty of Textile Engineering, the Technical University of Liberec Prototype. This measurement system (LCAM Photochrom system) allows measurement of a textured surface coloured by photochromic compounds. This is made by a hemispherical illumination and eliminates the problem of the texture of the textile samples. This is stated as one step closer to a standardized measurement system for photochromic material (Chowdhury et al. 2014) (Viková, Christie & Vik 2014).

2.9 Radiation curing

For ink-jet printing, the dye formulation is polymerised by radiation curing. Curing by UV-LED light is a fast and energy saving method developed for inline production.

The benefits of ink cured by UV-light are that it does not evaporate and it means less ink used. Basically, a chemical reaction induced by the exposure of UV-light makes the ink cure (Fig. 7). UV-light curable ink systems are leading the future of industrial inkjet printing. UV-light cured ink is preferred in inkjet printing system thus it does not clog the nozzle caused by the ink dry up in the printing head, which is the case in many solvent inks. Further, UV-light curable inks can be printed at higher speeds in both narrow and wide format sizes. These properties give the ink high flexibility.

Normally four components, a photoinitiator, monomer, oligomer and colorant comprise the UV-light cured ink. The photoinitiators start and complete the UV-LED curing process and are the prime components in the varnish. When absorbing the UV-light the material get reactive and a chemical reaction called polymerisation occur and convert the liquid ink into a solid film. Monomer is small, single molecule that may chemically bond to other monomers to form at polymer. The monomer provide flow by reduce viscosity, that is important for the inks functionality in the inkjet formulation. After curing the monomer becomes a part of the polymer matrix. Oligomer forms the chemical spine of a UV-light curable ink formulation. It has high molecule weight and induces the final properties of the cured ink as elasticity and chemical resistance. The colorant is dye- or pigment based. Moreover, additives as stabilisers can be added in the formulation. Stabilisers are used to improve the ink's tolerance to heat that is important for high jetting temperatures in ink-jet printing. They also neutralise or absorb reactive molecules in the ink during storage and prevent polymerisation.

UV-light excites the photoinitiator and passing energy along to the other components in the formulation. The excited components are called free radicals and keep the reaction going. This simulates a bonding between the molecules and a resin cross-linking is formed. When all of the components are used up, the material is cured. Cured ink is known as a polymer.

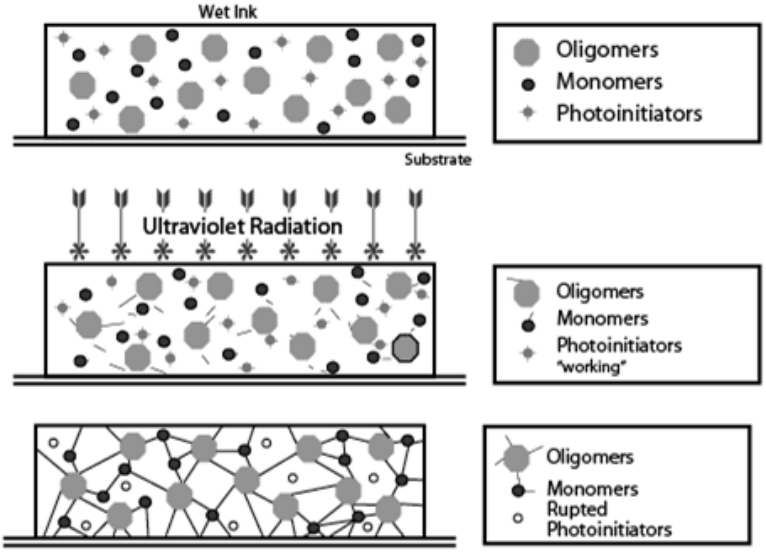

Fig. 7 Schematic description of the UV light curing process (Burton 2008)

The UV-light curing was made using a modular ink-jet printer, a belt with included UV-LED curing system. The UV-LED lamp has its wavelength maximum at 385 nm. It is a smaller version of an industry machine which makes it comparable to mass production i.e. inline production (Fig. 8).

As the UV light curable resin does not contain any volatile components, it does not contaminate the work environment. This adhesive is cured within seconds. Its excellence in mass production significantly helps reduce the production processes and costs.

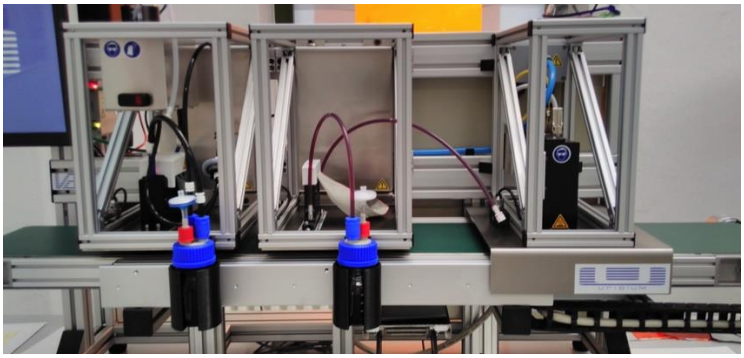

Fig 8 Continuous modular ink-jet printer with UV-LED curing

2.10 Chemical light stabilisation

Photodegradation is not an easy defined mechanism but depends on different factors. All organic polymers are sensitive to photooxidation to some extend trigged by UV-irradiation, from commonly the sunlight. Photochromism is itself a non-destructive process. However, side reactions generate products that are unable to revert back to original photochromic form. This leads to loss of performance of the photochromic function over time, fatigue of dye due to chemical degradation. Light or heat or a combination of these is responsible for the photodecomposition of organic photochromic compounds. Light stabilisers that are commercially available have been developed to slow down the rate of photooxidation of polymers and photochromic dyes. These additives can be incorporated in a polymer matrix at the processing stage or applied before, during or after the dyeing process (Feczkó, Kovács & Voncina 2012a).

Light stabilisers have an ability to protect the photochromic material against undesirable mechanical, physical and chemical degradation. By block UV-radiation and/or catch high-energy intermediates and slow down or inhibit fatigue behaviour triggered by high temperatures, oxygen, light and humidity (Nechwatal & Nicolai 2015). The most investigated light stabiliser classes in the area are hindered amine light stabilisers (HALS) and UV-radiation absorbers. The later converts absorbed radiation into thermal energy through tautomerism, where protons and electrons change position in the compound while the carbon skeleton remains. UV-radiation absorbers are efficient UV-light blockers and slow down photooxidation and double the time to reach half time degradation (50% of original value). However they are not suitable for photochromic applications due to inhibit of the photocolouration since they create a screening effect by absorbing UV-radiation in same region as the photochromic use. HALS are photoantioxidants i.e. free radical scavengers incorporated for improved photostability of dyes. They have an ability to participate in energy transfer or peroxide decomposition and do not usually absorb UV-radiation which is benefit for photochromic systems where it is essential for the UV-light to reach to the photochromic dye (Feczkó, Kovács & Voncina 2012a; Little & Christie 2010b; Little & Christie 2011).

Other classes of light stabilisers for dyes are antioxidants, thermal stabilisers and quenchers. Antioxidants and thermal stabilisers are free radical scavengers and hydrogen donating components that also take part in metal inactivation and peroxide decomposition. Additionally, thermal stabilisers work most effective at higher temperatures >100°C. Quenchers transfer energy from excited chromophores, it converts light into thermal energy or other forms of emission. Since conventional phenolic antioxidants usually have low photostability, antioxidants are only suitable for thermal stabilisation and are not effective in

photochemical systems. Moreover, most of the quenchers are salts or chelates of nickel or zinc that can cause compatibility but also environmental problems and are less common (Feczkó, Kovács & Voncina 2012a).

2.10.1 Hindered Amine Light Stabilisers

HALS compounds are probably the most studied compounds in the field of polymer stabilisation. However, data on the influence of HALS on photochromic dyes is more rare. Existing studies on HALS incorporated in the print has shown a significant improvement of the photostability (Little & Christie 2011).

During sunlight exposure and under normal environmental conditions, tetramethylpiperidine moiety, a basic element in HALS, is initially oxidized to produce a nitroxyl radical, which acts as a scavenger with an ability of multiple regenerations. This mechanism of HALS is described in "Denisov cycle" (Fig. 9). Regeneration of the nitroxyl radicals limits the consumption of HALS during degradation allowing the use of these additives in low concentration. The common application level of HALS is generally 1–1.5% in polymer stabilisation (Feczkó, Kovács & Voncina 2012a; Schaller 2010).

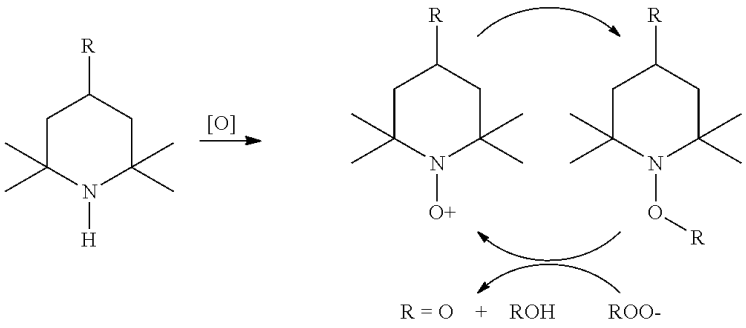

Fig. 9 Denisov cycle describes the mechanism of HALS, HALS compound converts into the corresponding nitroxyl functional group that traps a free radical with formation of an aminoether function (*Patent Images* n.d.)

2.11 Physical light stabilisation

Uses of an oxygen barrier layer above the photochromic print will protect the active photochromic substance from degradation. This degradation of the photochromic dye is not only chemical but also mechanical caused and a shield could provide reinforced properties. To achieve a durable sensor, an extra layer of light stable material may give physical protection and improve the material to endure washing, abrasion etc.

Poly(methyl methacrylate), PMMA, has outstanding transparency, good stability, high surface resistivity, and resistance to weathering and moisture. Due to these superior properties, PMMA has been used as host material in photochromic polymeric systems but also as for example additive, coating and binder, sealer, optical fibre, insulator, and outdoor electrical applications. Ethyl cellulose, EC, is a natural polymer frequently used as a hydrophobic polymeric coating material for drug release applications and controlled herbicide release. It has also been used as encapsulating material of fragrances. Both PMMA and EC have been found to be appropriate due to their transparent character as polymers for encapsulating photochromic dye (Feczkó et al. 2011).

Results from studies have indicated that hybrid silica containing photochromic dye is a promising coating material to develop photochromic fabric with fast optical response. Photochromic silica coating prepared from a silane precursor bearing a long alkyl chain shows very fast photochromic responses, reasonable abrasion fastness, and minimal effect on the fabric handle (Cheng et al. 2008).

2.11.1 3D-printing

In 1993, Michael Cima and Emanuel Sachs of MIT invented a special apparatus known as 3D-printer. This machine is capable of printing plastic, metal, and ceramic parts (Olivera et al. 2016). The most common 3D-printing plastics are PLA (polylactic acid) and ABS (acrylonitrile butadiene styrene) thermoplastics. PLA is based on renewable resources such as corn starch or sugar cane and is biodegradable. However, the material is not available in transparent form. ABS is an oil-based thermoplastic made by polymerizing styrene and acrylonitrile in the presence of polybutadiene (Fig. 10). ABS polymers have high toughness, good thermal stability and high resistance to chemical attack. It has a higher melting point than PLA. The ease of moulding allows the fabrication of dimensionally stable ABS with good surface quality. When exposed to heat, light, and weathering conditions, yellowing of the surface and also decrease of toughness is seen as a result of degradation. Oxidation also causes reduction of toughness. Yet, the polymer chain decomposes at temperatures above 300°C. In 3D-printing, filament is available in transparent form. However, ABS can experience deforming if cooled while printing, a heated building plate is required (Hesse 2015; Olivera et al. 2016).

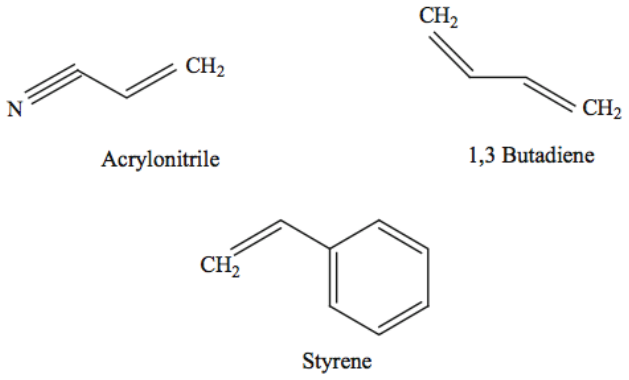

Fig 10 Monomers for a polymerisation of ABS. Different ratios can optimise the polymer for its purpose (Olivera et al. 2016)

A less common used thermoplastic in 3D-printing is PMMA, Poly(methyl methacrylate). PMMA is a transparent thermoplastic widely used as a substitute for inorganic glass. It is a lightweight and durable polymer. PMMA has outstanding properties in thermal stability and weather resistance thus it can hardly decompose at a temperature below 200°C considering both thermal and thermally oxidative decompositions of PMMA (Ali et al. 2015). However a PMMA based material has been investigated on its mechanical and surface characteristics after 3D-printing process. These characteristics do decrease in 3D-printing process. However, by infiltration with wax, surface roughness can be reduced and with epoxy, mechanical properties can be improved (Polzin et al. 2013).

2.11.2 Polyurethane coating

Polyurethane is a polymer obtained by step-growth polymerization and used in various applications as for example; foams, elastomeric, thermoplastic, or thermoset solid products, adhesives, fibres, synthetic leathers, isolated or conducting materials and coatings. Aliphatic (polyisocyanate) polyether polyurethane is a kind of polyurethane that has excellent weathering properties i.e. highly UV-light stable and is non-yellowing upon exposure to sunlight. It also offers superb optical clarity and in film form used as glass laminations, as an adhesive interlayer for textile lamination. A coating can be formulated for a good abrasion resistance, hydrolytic stability and resistance to a variety of solvents and chemicals (Best & Squiller 2008).

Two-component polyurethane is used as coating with excellent adhesion to various substrates and resistance to chemicals and water. Co-reactants represent one of the two parts of a two-component polyurethane coating. To obtain polymerisation, either the co-reactant or the polyisocyanate must have more than two reactive sites and a crosslinked thermoset polymer can be formed. Further crosslinking results in a harder and more chemically resistant polymer. Co-reactants are generally characterized by their backbone chemistries and could be polyether but can also polyester or polyacrylate (*Aliphatic Polyether, The premium choice for optical interlayer films* 2016; Best & Squiller 2008; Janik et al. 2014).

Curing of polyurethane coatings can take place physically by evaporation of the solvent at temperatures of 0°C or rely on the cross-linking process at a temperature up to 200°C. (Janik, Sienkiewicz & Kucinska-Lipka 2014).

3 Materials and methods

The photodegradation behaviour has been investigated on three different photochromic inks developed to be applicable in ink-jet printing. The photodegradation was accelerated by two fatigue test methods; colour fastness by household washing and multiple activations over 10 days. The aim was to simulate natural solar exposure and usage of a wearable textile sensor.

Printing is a preferable application method for photochromic inks where the material stays close to the surface where the light has access and a good photochromic effect is possible (Little & Christie 2010b). The many possibilities and benefits that digital ink-jet printing brings is the background to why ink-jet printing technology is involved in this study. Moreover, it could be preferable for future design of a textile UV sensor (El-Molla 2007).

Advantages for use of ink-jet printing include,

- Reduced ecological footprint
- Minimized consumption of water, energy and chemicals
- Functional chemistry applied locally
- Artwork processed by a computer that can give complex detail print
- Thinner layer of print
- Time saving
- UV-light curing that is minimizing energy consumption and emissions and eliminates water consumption.

3.1 Materials

3.1.1 Fabric

Polyester fabric was used as textile substrate, selected as the most important synthetic fibre. The chosen polyester material is an off-white staple fibre in plain weave produced by Almedahls. The fabric is scoured and heat-set with a weight of 159g/m^2 and thread count 125 threads per inch.

3.1.2 Dyes

For the experimental part three dyes were investigated. Spirooxazine was chosen for its good results in previous studies on photochromic materials. Two types of spirooxazine were examined and compared, 1,3-Dihydro-1,3,3-trimethylspiro[2Hindole-2,3'-[2,1-b][1,4]oxazine] and the commercial dye Reversacol Oxford Blue from Vivimed Labs Ltd.

For dispersion of the powder formed dye, Chromasolve® Plus, a 99.9% ethyl acetate was used.

The third dye in this research was ready-made naphthopyran ink formulation, prepared for UV light curing. In the formulation the commercial dye Reversacol Ruby Red from Vivimed Labs Ltd was used.

3.1.3 UV-light curable varnish

The components included in the varnish are monomer DPGDA from Allnex with a density of 1.06 g/cm^3 and the oligomer Ebecryl® 81 from Allnex with a density of

1.06 g/cm3. Additionally the photoinitiator used was Genocure TPO-L from Rahn AG, an Ethyl phenyl(2,4,6-trimethylbenzoyl)phosphinate, with a density of 1.13 g/cm^3.

3.1.4 Hindered Amine Light Stabiliser

The commercial Hindered Amine Light Stabiliser, HALS Tinuvin® 292 (Fig. 11), produced by BASF is a liquid hindered amine light stabiliser. This multi-purpose HALS has an excellent long-term stability and solubility in formulations. The formulation contains two active substances that keep the product liquid and binds to the UV-light curable system in the varnish. For clear appearance, the recommendation is to combine Tinuvin® 292 with an UV-light absorber, e.g. Tinuvin® 400. Recommend concentration for a clear result is 0.5 wt% (*Tinuvin® light stabilizers & UV absorbers* 2011).

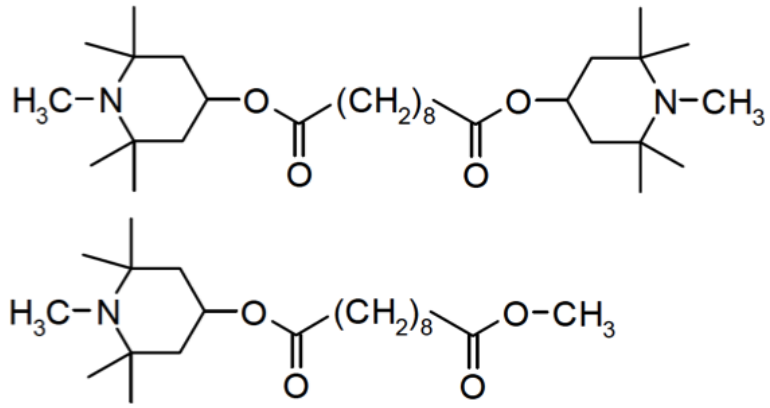

Fig 11 The chemical nature of multi-purpose Tinuvin 292

3.1.5 3D-printing filament

ABS (acrylonitrile butadiene styrene) filament is purchased at Creative Tools, fabricated by ECO, 1.75 mm in diameter and has a transparent (natural) colour. PMMA (poly(methyl methacrylate)) filament is purchased at Rigid Ink, 1.75 mm in diameter and has a transparent (natural) colour .

The software Rhinoceros was used to create the model of the 3D-printed plate and the printer used was Duplicator D4S manufactured by WANHAO©.

3.1.6 Polyurethane coating

®RUCO-COAT PU 1110, is an aqueous aliphatic polyether polyurethane dispersion for coating purchased at Rudolph Group. The coating is stable to hydrolysis which makes it suitable for outdoor applications and it is free from NMP(n-methyl-2-pyrrolidone). The coating formula was prepared with 0.6 wt% hydrophobically modified ethoxylated polyurethane thickener, Borchi® Gel L75N (BGL75N) in the paste for an appropriate viscosity 0.2271 Pa·s to enable easy application (Table 10, Appendix I). The coating formulation results in a soft, transparent protective layer, resistant to yellowing, washing and dry cleaning (®*RUCO-COAT PU 1110 by Rudolf GmbH* 2016).

In an additionally experiment was ®RUCO-COAT PU 8551, a hard polycarbonate-based polyurethane purchased at Rudolph Group used. The polyurethane was

mixed with 0.6 wt% thickener BGL75L. The viscosity was 0.2781 Pa·s for the formulation (Table 11, Appendix I).

3.2 Methods

Preparation of ink and chemical stabilisation by incorporation of light stabilisers was followed by applying the ink on the textile substrate. Although the difficulty to simulate an ink-jet printers resolution by hand, the photochromic ink was applied by single drops of 1.0 µl substance on the textile substrate. This is 1 000 000 times more than one single drop printed through one nozzle of the ink-jet print head. The ink-jet printer has a resolution of 300 dpi (dots per inch) ink on the substrate and applies 10 pl (picolitre) for each drop. Moreover, a pre-experiment was made for the selection of textile. The ink was applied on different substrates; polyamide and polyester, filament and staple fibre fabrics. Evaluation was made by the visible dispersion on the substrate. Best result, most even and with a fast spreading was seen on woven polyester staple fibre fabric and was the selected textile substrate for further experiments.

After curing and alternatively stabilisation by coating the samples was ready for testing. The dependent variable in the experiments is the performance in photocolouration of the activated ink, represented by colour difference ΔE. The value depends on the independent variables i.e. the type of stabilisation, chemical or physical, and its concentration or thickness. The colourability describes the ability of a colourless or slightly coloured chromic material to develop colour (Fig. 12-14). Fatigue is the fading of the efficiency of chromic compounds caused by e.g. washing or multiple activation cycles due to degradation of the dye. Under influence of UV-radiation, the reflectance curve shape for these colours changes in the visible part of the spectrum and colouration takes place, the reflectance curve changes by photodegradation (Rijavec & Bračko 2015).

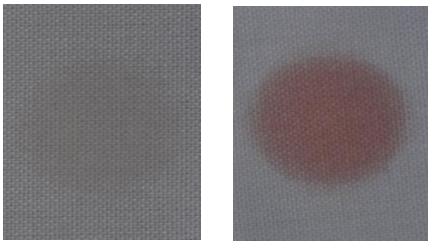

Fig. 12 Ruby Red ink printed on textile before and after activation and goes from slightly yellow to deep red.

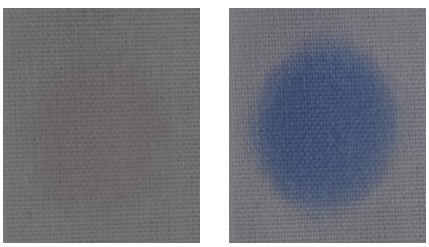

Fig. 13 Oxford Blue ink printed on textile before and after activation and goes from light pink to deep blue

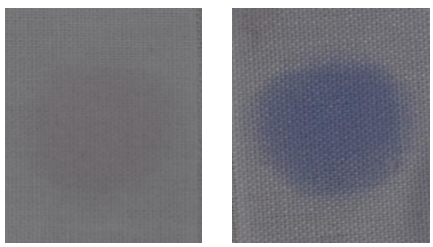

Fig. 14 Spirooxazine ink printed on textile before and after activation and goes from light pink to blue

3.2.1 Preparation of photochromic ink

The development of the ink formulations for the three dyes was based on a recipe formulated for ink-jet printing purpose. The varnish is UV-light curable and cures the ink formulation on the textile substrate by UV-LED light. The components included in the curing varnish are oligomer, monomer and photoinitiator (Table 1).

Table 1: Varnish recipe for UV light curing, Total 23 parts in the varnish formulation of 15 ml i.e. 1 part is equal to 0.652 ml

Part(s)	Component	Density [g/ cm^3]	Recipe [ml]
1	Ebecryl 81 (oligomer)	1.06	0.652
21	DPGDA (monomer)	1.06	13.692
1	TPO-L (photoinitiator)	1.13	0.652 (i.e 0.737 g)

18.7 parts dye in solvent was prepared for 15 ml of ink formulation for each dye. The concentration of dye powder was 2.5 mg/ml. A UV filter film, purchased from ASMETEC GmbH, filters all UV-rays below 520 nm and was used during the procedure to avoid degradation of the dye. Further, the dye was dissolved in 12.19 ml ethylene acetate and stirred at 300 rmp for 2 hours.

In the preparation of spirooxazine and Oxford Blue ink, curing varnish was prepared for both dyes in the same batch and then distributed between the two dissolved dyes. The photoinitiator was weighted because of its high viscosity and a UV-light filter film protected the procedure to avoid initial curing. The components in the varnish were stirred at 300 rpm for 2 hours. The dye solution and varnish were blended together at 300 rpm for 2 more hours and then put in vacuum for 16 hours where the solvent, ethyl acetate, was evaporated from the ink formulation (Fig. 15).

The commercial naphthopyran ink formulation, Ruby Red, was a ready-made and prepared for UV-light curing.

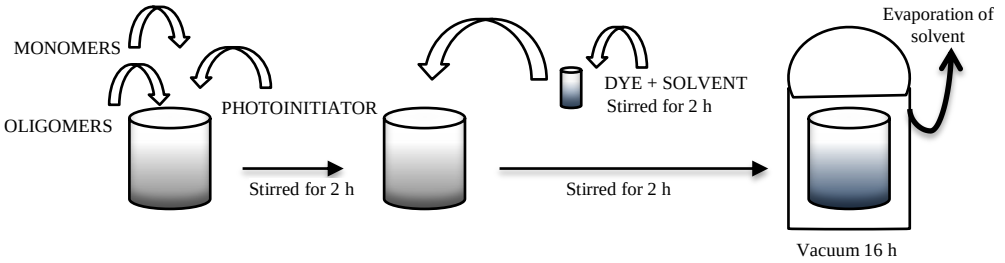

Fig. 15 Scheme of the preparation process of the photochromic ink

3.2.2 Preparation of light stabilised ink

Three concentrations of HALS stabilised ink were prepared; 0.05, 0.5 and 1.0 weight percentage (wt%). The HALS used is designed for radiation-curable systems which is required for the ink formulation and the chosen curing method. The weight of HALS was calculated for the formulation and concentration and then measured on a scale (Precisa 205 A SCS) protected by a UV-light filter film. The HALS stabilised ink was stirred at 300 rpm for 2 hours. Further, four more concentrations were prepared after the first test sequence for all inks and an extended washing fatigue test was made for 1.5, 2.0, 2.5 and 3.0 wt% of HALS.

3.2.3 Ink characterisation

The formulated ink was characterised according to its jetting properties; viscosity and surface tension to confirm that they would be appropriate for the printing head of the ink-jet printer. The tests were repeated for the 0.05 wt% HALS stabilised inks.

Viscosity
The viscosity was measured using the Physica MCR 500 from Anton Paar (Fig. 17). The ink should have a viscosity between 8-20 mPa·s to be appropriate for the ink-jet printer. The ink was poured in the double gap sample holder. The viscosity was measured in 9 intervals with increasing steady and decreasing shear rate up to 10 000 1/s at 20 °C (Appendix II). Also, the viscosity in relation to rising temperature from 15-40 °C, during 9 intervals (Appendix II) was measured.

Surface tension
Surface tension was measured by Attension Theta Tensiometer, Biolin Scientific (Fig. 16). The ink should have a surface tension, ϒ, between 25-35 mN/m to be appropriate for the ink-jet printer. A 10 µl droplet was pushed carefully through a pipette for measurement and read by a camera. Up to 121 data points was collected for each test (Appendix II). Three tests per ink formula were made.

Fig. 17 Physica MCR from Anton Paar for measurements on viscosity

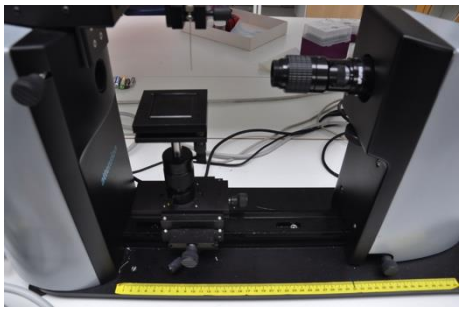

Fig. 16 Attension Theta Tensiometer from Biolin Scientific for measurements on surface tension

3.2.4 Preparation of samples

A pipette was used for the application of 1.0 µl ink on the textile substrate. The sample was then cured by UV-LED light (Fig. 18).

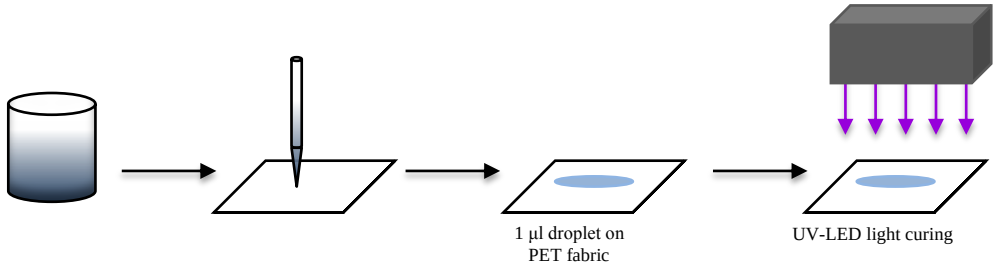

Fig. 18 Scheme of the sample production

3.2.6 UV-light curing

The UV-light curing settings were selected by a pre-experiment where samples with different curing settings were evaluated by photocolouration before and after household washing according standard (ISO 105-C06:2010, Colour fastness to domestic and commercial laundering). Three different UV-LED light intensities (15, 20 and 25%) and two curing speeds (100 and 150 mm/s) were chosen and correspond to a desirable intensity and speed for industrial manufacturing. The result did not show significant differences between the chosen settings. However, the best colour development and lowest decrease after washing for all inks was selected for further experiments, UV-LED light power of 15% and speed of 150 mm/s. Further investigation of the curing level was made by FTIR (Fourier Transform Infrared Spectroscopy). However, the small amount photochromic material in relation to the textile content and the instrument's sensitivity gave no reliable results.

3.2.7 Preparation of 3D printed protective layer

Important factors in the choice of coating are light stability and transparency of the material. Transparency is essential to be able to activate the photochromic material. A square layer, 30×30 mm ABS was printed at extruder temperature 240°C (recommended 230-250°C) and at the printing speed 3600 mm/min. The layers was printed directly on the chosen PET fabric placed on a heated building surface, heated to its maximum, 100°C. The number of layers was optimised for the purpose of a dense and transparent plate. It was seen that holes were created between the thin extruded filaments in 1-3 layers, applied 45° and -45° (Fig. 19). A PMMA filament was also tested in same setting as for ABS but at higher extruder temperature, 270°C, as recommended by supplier.

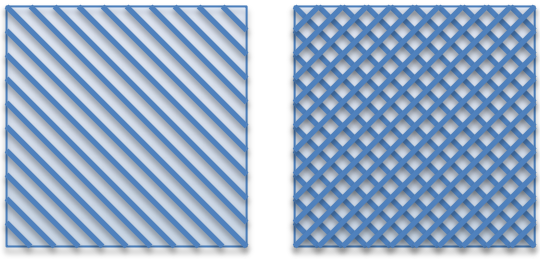

Fig. 19 Illustration of the printing angles, 1st (and 3rd) layer 45° and 2nd layer -45°

3.2.8 Preparation of knife coated protective layer

The polyurethane coating was prepared with a thickener in a concentration of 0.6 wt%. The formulation was stirred at 500 rpm for 15 min.

The polyurethane coating was applied on the textile by with a universal applicator from Zehntner testing instrument (Fig. 20) at three thicknesses, 50, 150 and 250 µm for PU 1110. The samples were cured in an oven at 85°C for 15 min. The curing temperature was set slightly lower than recommended (90-120°C) to minimise the risk of ink degradation and to keep an elastic handle of the coating.

In a second test sequence of coating with PU 8551, three thicknesses were added; 25, 100 and 350 µm and the curing process was repeated.

Fig. 20 Application of knife coating a universal applicator from Zehntner

3.2.9 Fastness tests

Testing is made to simulate the use of a textile UV-sensor and evaluate its fatigue behaviour after one washing cycle and by use over time including several activation cycles.

Washing test
Testing of colour fastness by household washing was made according to the standard, Colour fastness to domestic and commercial laundering (ISO 105-C06:2010). The unwashed samples' photocolouration performance was measured before and after 1 min UV-light activation followed by the washing procedure. Then the samples were flat dried under protection of an UV-light filter film, placed in dark storage over night and new measurements before and after 1 min of UV-light activation were made of the washed samples. The washing test was applied for the HALS stabilised samples with concentrations of 0.05, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 wt% and the coated samples with thickness of 50, 150 and 250 μm.

Multiple activations test
The fatigue was also examined by multiple activations of the photochromic dyes. One measuring cycle starts with a colour performance measurement before and after 1 min of UV-light exposure. After that, the sample was stored for 23 hours, allowing the ink to reverse back to its background colour before next measurement. The measurements were taken 5 days in a row and then stored in a dark, dry place for 10 days (240 hours). Then the measurements were repeated for 5 more days. In total the samples were activated 10 times in 10 days with 10 days of storage in between. The multiple activations test was applied for the HALS stabilised samples with concentrations of 0.05, 0.5 and 1.0 wt% and the coated samples with thickness of 50, 150 and 250 μm.

Sun-lamp exposure
Further, to simulate longer exposure to sunlight, selected multi activated samples were exposed to artificial sunlight by SUNTECH HI1200 for 1 hour and then measured again after 23 hours. The samples were placed 10 cm from the protective glass on the bottom of the lamp. The selected samples for this test were 1.0 wt% HALS stabilised and 250 μm coated and their references.

Activation test for coated samples
The PU 8551 coated samples were activated by UV-LED light for 1 min for three days in a row for colour difference (ΔE) measurement. The test was applied for samples with the coating thicknesses; 25, 50, 100, 150, 250 and 350 μm.

3.2.10 Colour performance

The colour performance before and after fatigue tests is evaluated using a spectrophotometer Datacolor CHECK$^{PRO™}$, a valuation instrument to communicate colours by numbers. In the experiments the data ΔE has been used to assess the colour differences and estimate the fatigue behaviour for the photochromic prints. For commercial purpose, ΔE-value can be set as a tolerance for reproduction of a colour. The used CMC colour system is standard for the textile industry.

ΔE was measured for the colour difference between the activated and inactivated print by UV-light, 1 min exposure of 365 nm (UVA), which is sufficient to develop the full colour (Fig. 21). To minimize time delay between illumination and measurement, measuring was made on site i.e. at the same place where the sample was irradiated by UV-light. The sample was placed 13 cm from the UV-light source and exposed in an angle of 45°. To avoid decolouration by thermal decay, the temperature was controlled at 0°C. Based on a previous study on colour development of photochromic dyes in various solutions a lower temperature increases the visible colour change for spirooxazine (Appendix III). The measuring aperture of the spectrophotometer was placed directly onto the printed sample. The prints faded back completely to their original/inactivated colour or state in room temperature and storage in the dark over night.

The absorbance of the photochromic systems was recorded by the spectrophotometer. The measurement settings were D65/10° standard observer view by illuminate and observer angle. Specular component included (SCI) that measure the total appearance, diffuse and specular reflectance. CMC l:c ratio was set to 2:1 as the standard in textile industry.

The fatigue (%) of the ink was calculated as follows (Equation 1):

$$\text{Fatigue (\%)} = \left(\frac{\Delta E_t}{\Delta E_0}\right) \times 100\,, \qquad (1)$$

where ΔE_0 is the difference between the activated sample at initial activation and the background colour i.e. inactivated sample. ΔE is the colour difference between activated sample after fatigue test and the background colour. The higher number the better fatigue resistance does the photochromic print perform (Feczkó, Kovács & Voncina 2012a).

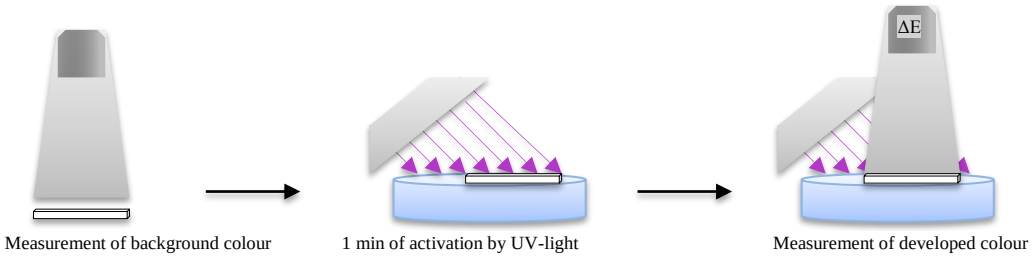

Fig. 21 Scheme of the colour performance measurement

3.2.11 Statistical analysis

For calculation of the distribution of data within the sample set and between before and after test, population standard deviation is used (Equation 2).

$$\text{STDAV.P} = \sqrt{\frac{\sum(x-\bar{x})^2}{n}} \quad (2)$$

Complete data on standard deviations are gathered in Appendix VII.

Statistical analysis by T-test has been made. Calculations on the significance between two sets of data have been used to validate the qualitative findings. A confidence interval of 95% has been used for a two-tailed distribution in two-sample unequal variance sets of data (Equation 3 and 4) (Fig. 22). This leads to a probability where p-value below 0.05 is accepted for a significant result taking variations within the groups into account. Complete data on p-values are gathered in Appendix IX.

$$t = \frac{\bar{X}_1 - \bar{X}_2}{s_{\bar{X}_1 - \bar{X}_2}} \quad (3)$$

where,

$$s_{\bar{X}_1 - \bar{X}_2} = \sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}} \quad (4)$$

Additional, an analysis of variance (ANOVA) is calculated in Minitab software. The calculation includes a larger amount of data, the whole batch before and after test. Probability values for HALS/coating and washing/activations influence on the ΔE value are recognised and gathered in Appendix X.

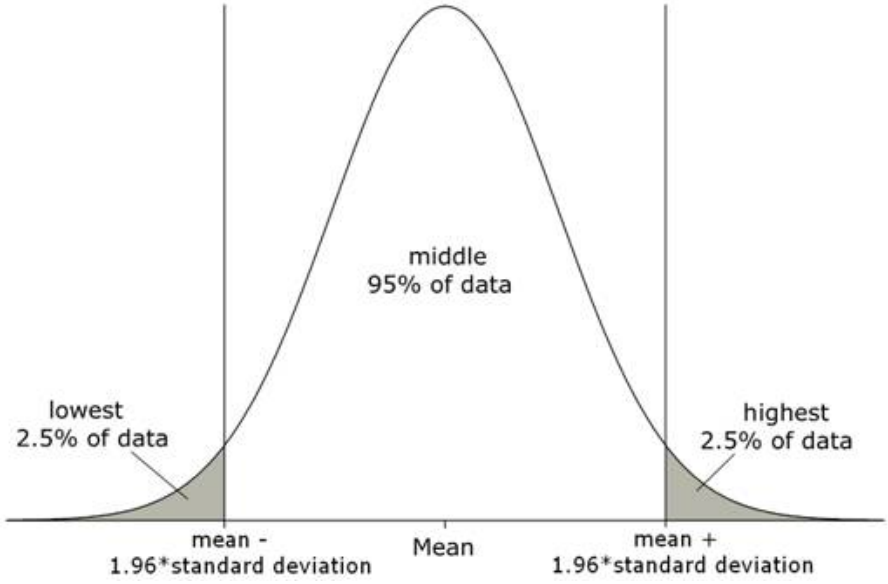

Fig. 22 Confidence interval for normal distribution in calculations of probability value (p)

4 Result

The results are presented in diagrams and tables for assessment of the ink characteristics and the colour performance of the ink by its stabilisation method; chemical and physical. Moreover the results of the protection layer methods' are presented.

4.1 Ink characterisation

4.1.1 Viscosity

The second cycle of the shear rise and temperature rise i.e. interval 6 is plotted in the diagrams below (Fig. 23 and 24). The viscosity is approx. 3.0 mPa·s and 1.0 mPa·s lower for Ruby Red than for spirooxazine and Oxford Blue in terms of viscosity as a function of shear rate respectively the change of viscosity as a function of temperature.

The graph in Fig. 23 starts at shear rate 100 1/s and ends at 10 000 1/s with 100 measuring points plotted (Appendix II). A shear thinning rheology behaviour is observed.

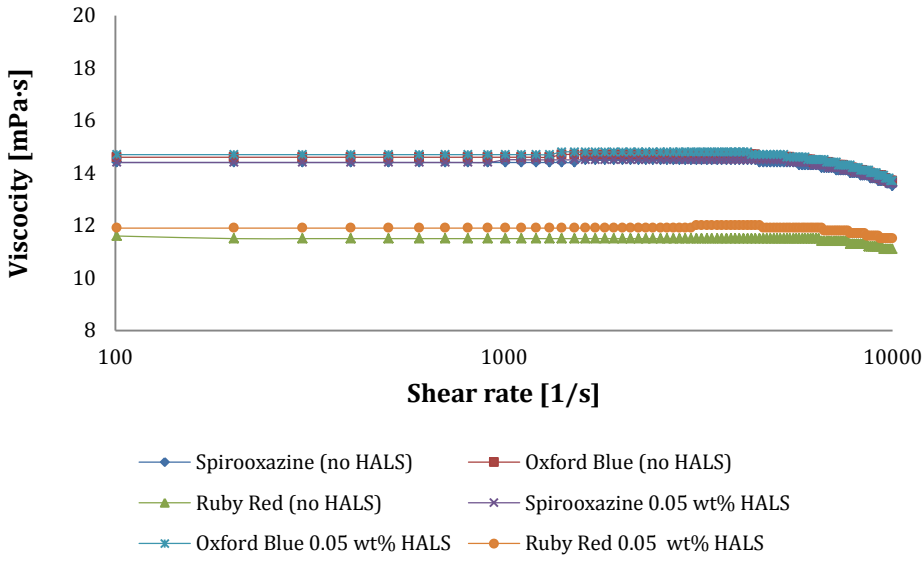

Fig. 23 The change in viscosity as a function of shear rate

The measured start point is at 20 °C and ends at 40°C. However, 40 °C is not reached by Ruby Red within time (Fig. 24). 20 measuring points are plotted (Appendix II). A shear tinning rheology behaviour is observed.

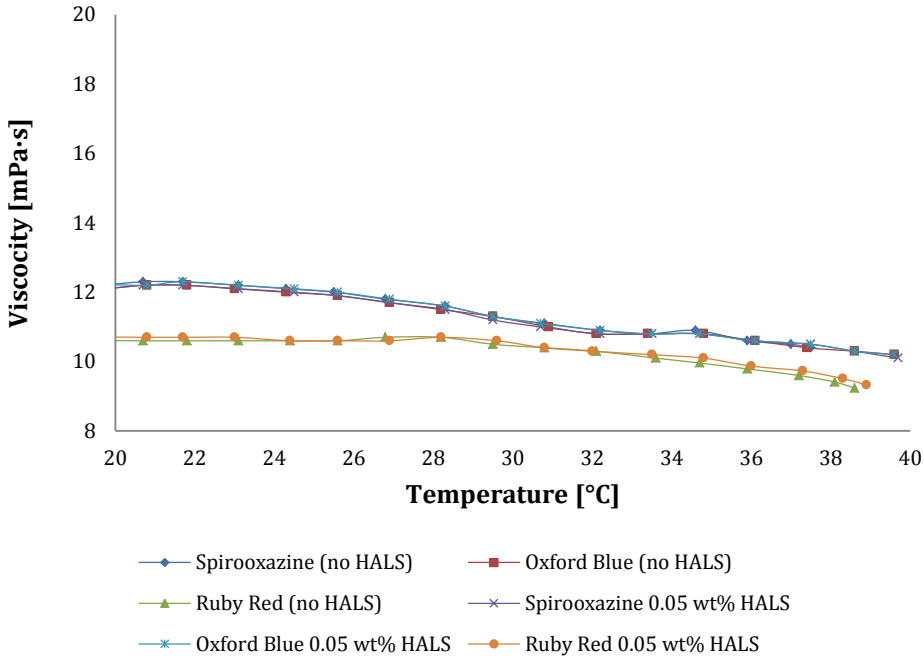

Fig. 24 The change in viscosity as a function of temperature

4.1.2 Surface tension

Three repetitions for each ink formulation were done. The surface tension was measured for a single 10 µl droplet with up to 120 measuring points (Appendix II). No significant differences are seen in the plotted data (Fig. 25). Table 2 displays the mean values for the tests for the inks respectively. Mean values between 29.78 and 31.11 mN/m are observed for the inks.

Table 2: Mean values of surface tension test of inks, non-stabilised and stabilised

Sample name	Formulation	Mean value [mN/m]
SO	Spirooxazine, pure	30.80
SO + HALS	Spirooxazine, 0.05 wt% HALS	30.77
OB	Oxford Blue, pure	31.02
OB + HALS	Oxford Blue, 0.05 wt% HALS	31.11
RR	Ruby Red, pure	29.78
RR + HALS	Ruby Red, 0.05 wt% HALS	31.04

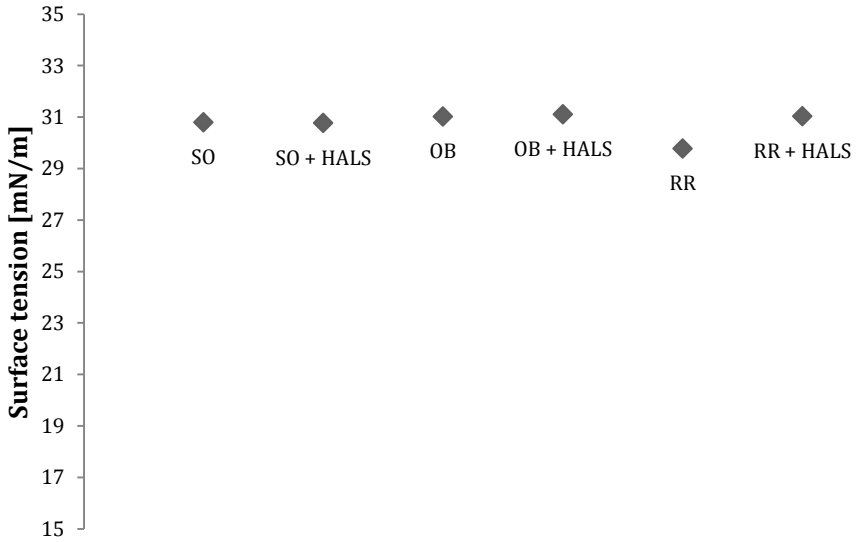

Fig. 25 Mean values of surface tension test of inks, non-stabilised and stabilised

4.2 Physical protection layer

3D-printed ABS showed a higher transparency than PMMA, however, visible holes were created between the extruded filaments in 2 layers ABS (Fig. 26). In 3 layers ABS (Fig. 27) the construction appears like separate layers and not a dense single layer. Layers of PMMA resulted in a denser material but show an opaque appearance and has a more brittle handle than ABS (Fig. 28 and 29).

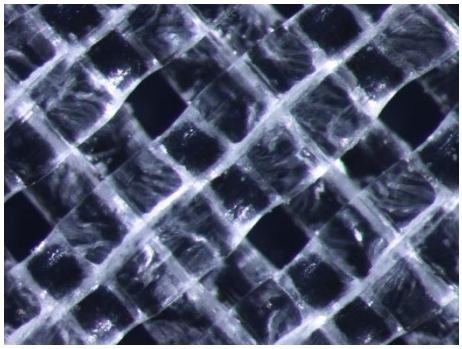

Fig. 26 ABS 2 layers

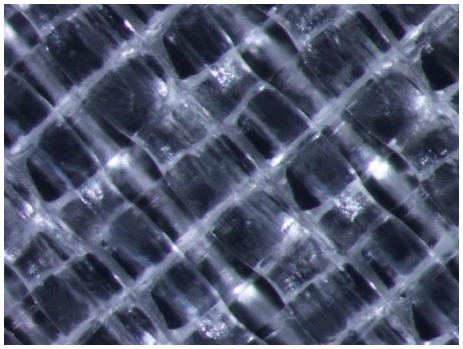

Fig. 27 ABS 3 layers

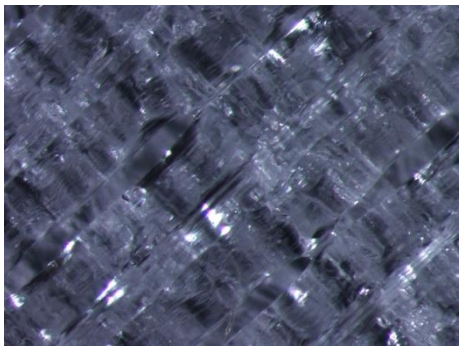

Fig. 28 PMMA 2 layers

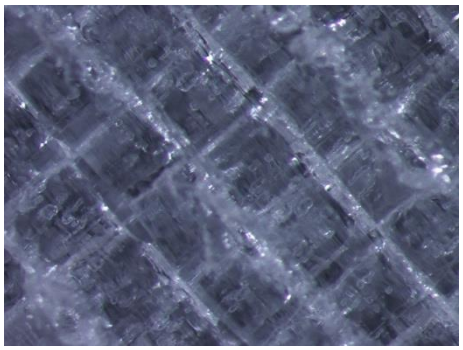

Fig. 29 PMMA 3 layers

The polyurethane coating ®RUCO-COAT PU 1110 gave a soft transparent coating. ®RUCO-COAT PU 8551 was harder but no difference in transparency was perceived compared to PU 1110. The reflection caused by the coating was measured for both coatings. It is found that PU 1110 reflected slightly more yellow than PU 8551 (Appendix VI). The thickness also affected the reflected light, 250 µm had a slightly more yellow reflection than 50 µm compare to the blank fabric (Appendix VI).

4.3 Colour performance

The colour performance is evaluated by ΔE value, the colour difference between the ink in inactivated versus activated state. The colour change goes from an undefined inherent print background to a specific colour tone. The visible difference between the two spirooxazines is that commercial Oxford Blue shows a more saturated colour development compared to pure spirooxazine ink, which is indicated by the ΔE value (Fig. 31-32). Ruby Red shows similar colour intensity as Oxford Blue according to the ΔE value (Fig. 30).

Fig. 30 Photocolouration of non-stabilised Ruby Red at first activation ΔE = 21.03

Fig. 31 Photocolouration of non-stabilised Oxford Blue at first activation ΔE = 20.87

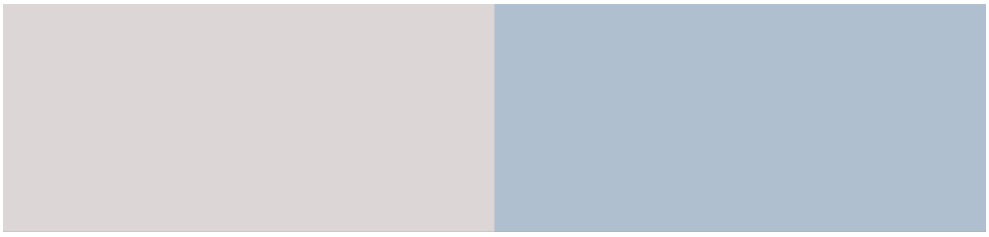

Fig. 32 Photocolouration of non-stabilised spirooxazine at first activation ΔE = 16.56

4.3.1 Performance of colour development in washing test

The value ΔE between background and developed colour after 1 min of UV light exposure was measured before and after washing. ΔE data is plotted in the diagrams for the different configurations. Trendlines are plotted for analysing.

The trendlines follow the average value of unwashed vs. washed samples. All three samples for each formulation/stabilisation, the sample set, are presented in the scatter graphs (Fig. 33-38). The fatigue behaviour representing the colour performance before and after washing is presented in Table 3 and 4.

A slight increase of photocolouration with concentration of HALS incorporated is seen (Fig. 33). A decrease in photocolouration performance after washing test for all formulations is observed. The decrease is constant and approx. 6 units in ΔE for all concentrations (Table 24, Appendix IV).

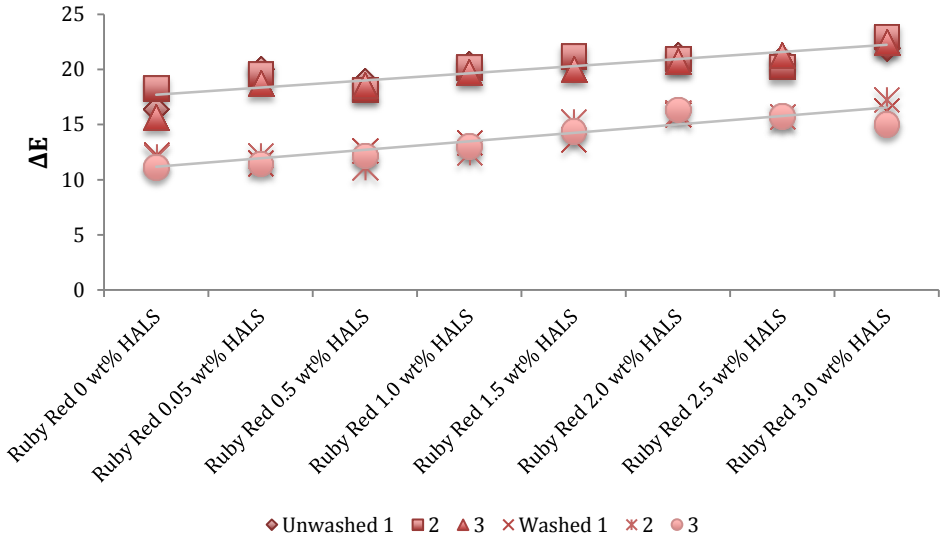

Fig. 33 The effect of washing on the degree of photocolouration of light stabilised Ruby Red

The effect of washing on chemically stabilised Oxford Blue (Fig. 34) shows a constant decrease of photocolouration performance by approx. 4 units in ΔE (Table 24, Appendix IV). The trendlines shows a slightly increase of photocolouration performance with concentration HALS.

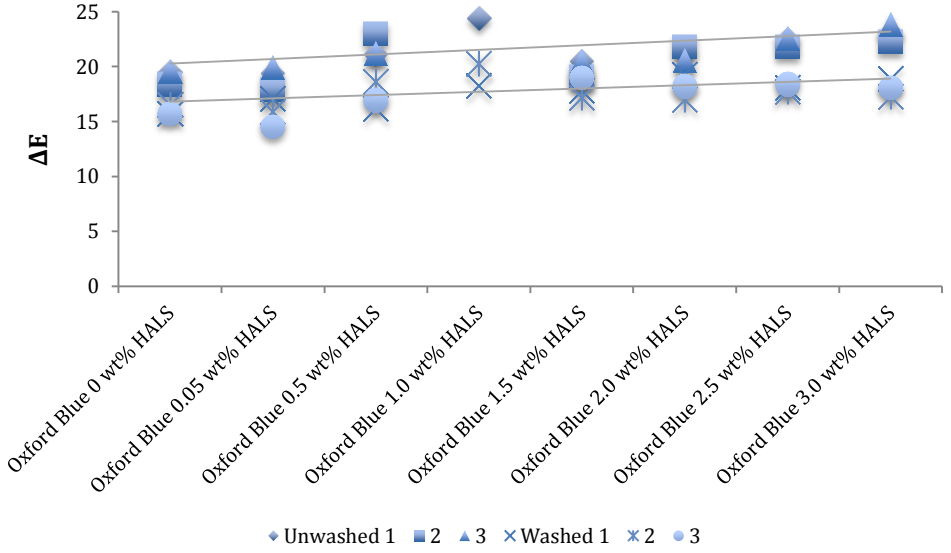

Fig. 34 The effect of washing on the degree of photocolouration of light stabilised Oxford Blue

The effect of washing on chemically stabilised spirooxazine (Fig. 35) shows a constant decrease of photocolouration performance by approx. 4 units in ΔE. This decrease slightly reduces with concentration of HALS to approx. 2 units for (Table 24, Appendix IV).

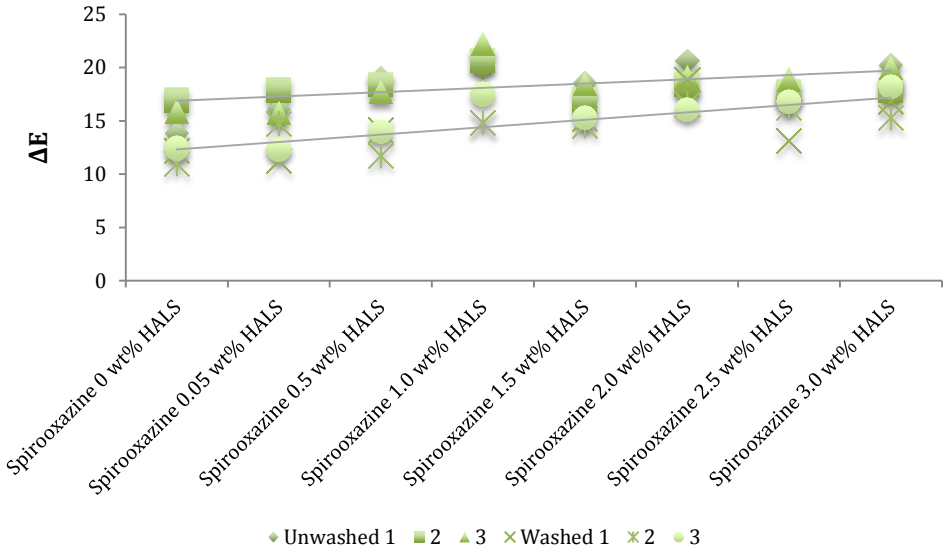

Fig. 35 The effect of washing on the degree of photocolouration of light stabilised spirooxazine

The fatigue behaviour is presented as a percentage of initial value (Table 3). Minimum and maximum values of fatigue are 60.31% (0.05 wt%) and 76.70% (2.0 wt%) for Ruby Red, 78.34% (3.0 wt%) and 89.94% (1.5 wt%) for Oxford Blue and 72.39% (0.5 wt%) and 88.63% (2.0 wt%) for spirooxazine. HALS concentrations; 1.5 and 2.0 wt% show best fatigue resistance. However, the lowest value is not represented by the non-stabilised sample in any of the inks.

Table 3: Fatigue behaviour of ink formulations based on average ΔE before and after one wash

Ink formulation [wt%] HALS	Fatigue [%]
Ruby Red 0	70,34
Ruby Red 0.05	**60,31**
Ruby Red 0.5	64,61
Ruby Red 1.0	64,42
Ruby Red 1.5	70,25
Ruby Red 2.0	**76,70**
Ruby Red 2.5	75,54
Ruby Red 3.0	71,90
Oxford Blue 0	81,57
Oxford Blue 0.05	83,10
Oxford Blue 0.5	79,21
Oxford Blue 1.0	79,21
Oxford Blue 1.5	**89,94**
Oxford Blue 2.0	85,51
Oxford Blue 2.5	81,02
Oxford Blue 3.0	**78,34**
Spirooxazine 0	76,38
Spirooxazine 0.05	76,89
Spirooxazine 0.5	**72,39**
Spirooxazine 1.0	74,93
Spirooxazine 1.5	83,25
Spirooxazine 2.0	**88,63**
Spirooxazine 2.5	85,43
Spirooxazine 3.0	86,64

In the coated samples a reduction of photocolouration development with coating thickness is observed for all samples.

The effect of washing on physically stabilised Ruby Red show a decrease in fatigue with the coating thickness (Fig. 36). ΔE before and after washing decreases with approx. 4 units for references and 1.5 units 250 µm coated samples (Table 25, Appendix IV).

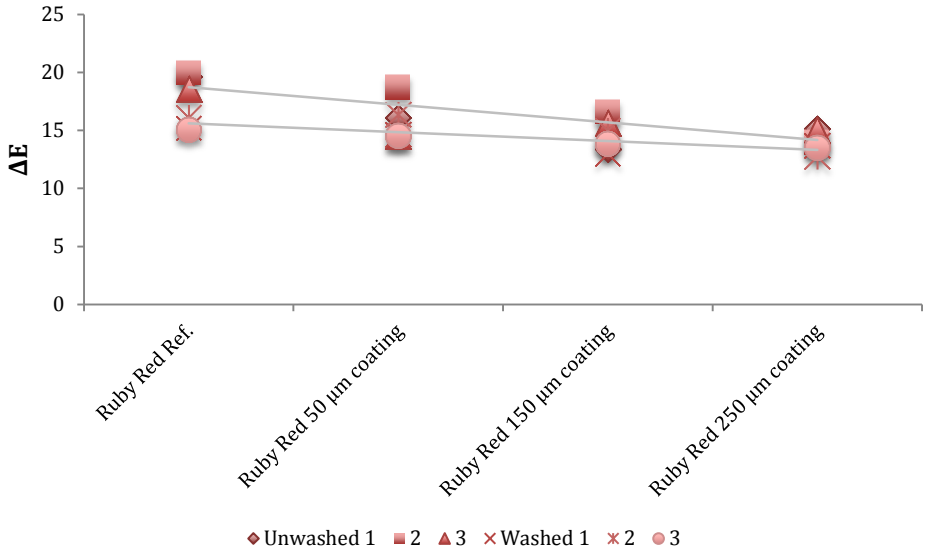

Fig. 36 The effect of washing on the degree of photocolouration of coated Ruby Red

The effect of washing on physically stabilised Oxford Blue show a small decrease in photocolouration performance for all samples, references included (Fig. 37). The photocolouration is seen to increase after washing for 50 µm coated samples. ΔE before and after washing decreases approx. 2 units for reference samples, increases approx. 1 unit for 50 µm coated samples and decrease approx. 1 unit for 150-250 µm coated samples (Table 25, Appendix IV).

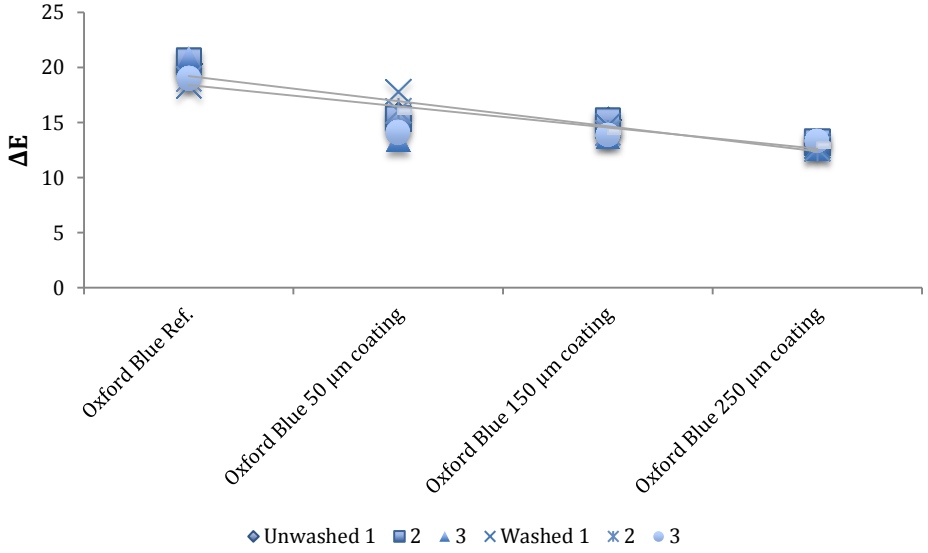

Fig. 37 The effect of washing on the degree of photocolouration of coated Oxford Blue

The effect of washing on physically stabilised spirooxazine show a small decrease in fatigue for all samples, references included (Fig. 38). The photocolouration performance is seen to increase for 150 µm coated samples after washing. ΔE before and after washing decreases approx. 1-2 units for references, 50 µm and 250 µm coated samples. An increase of approx. 0.5 units for 150 µm coated samples is observed (Table 25, Appendix IV).

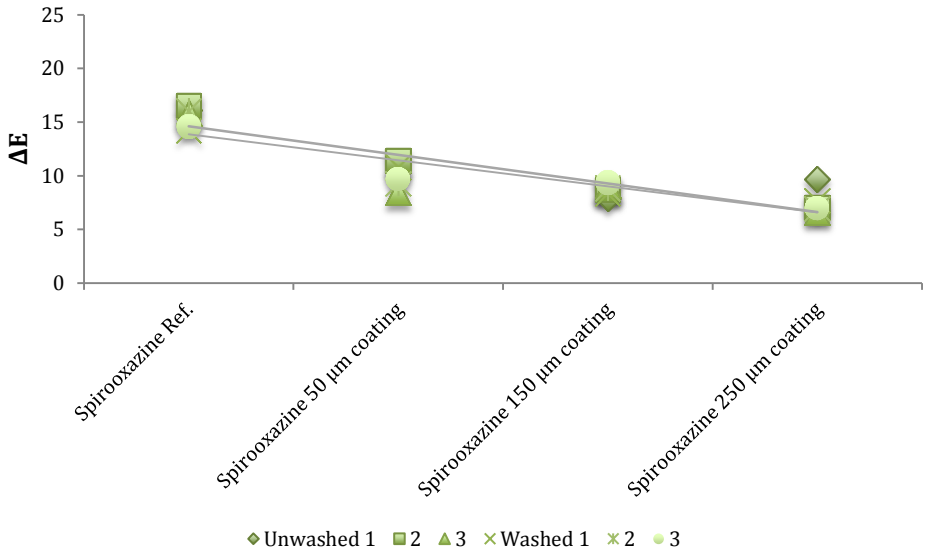

Fig. 38 The effect of washing on the degree of photocolouration of coated spirooxazine

The fatigue behaviour (Table 4) for the coated samples shows a slightly higher photocolouration after washing than before for Oxford Blue and spirooxazine. The lowest fatigue resistance is represented by the uncoated samples in all cases. Minimum and maximum values of fatigue are 79.67% (reference) and 92.32% (50 µm), 91.18% (reference) and 108.05% (50 µm) for Oxford Blue and 92.57% (reference) and 103.63% (150 µm) for spirooxazine.

Table 4: Fatigue behaviour coated inks based on average ΔE before and after one wash

Ink [µm] coating thickness	Fatigue [%]
Ruby Red Ref.	**79,67**
Ruby Red 50	**92,32**
Ruby Red 150	91,73
Ruby Red 250	90,34
Oxford Blue Ref.	**91,18**
Oxford Blue 50	**108,05**
Oxford Blue 150	96,49
Oxford Blue 250	99,49
Spirooxazine Ref.	**92,57**
Spirooxazine 50	98,94
Spirooxazine 150	**103,63**
Spirooxazine 250	93,03

4.3.3 Performance of colour development in multiple activations test

ΔE as a definition of colour difference was measured before and after 1 min of UV-light exposure every day for 5 days. The procedure was repeated 10 days after the last activation (cycle 5) for 5 more days, i.e. 10 activation cycles are obtained. Complete data of ΔE is found in Appendix IV. Fig. 39-41 are based on average ΔE value (Appendix V).

The effect of multiple activations on chemically stabilised Ruby Red shows a constant decrease in photocolouration with activations for all samples (Fig. 39). After 5th cycle a slightly stabilisation in decrease of ΔE is observed for stabilised samples (Table 26, Appendix IV). A drop for all samples is observed in the 8th activation.

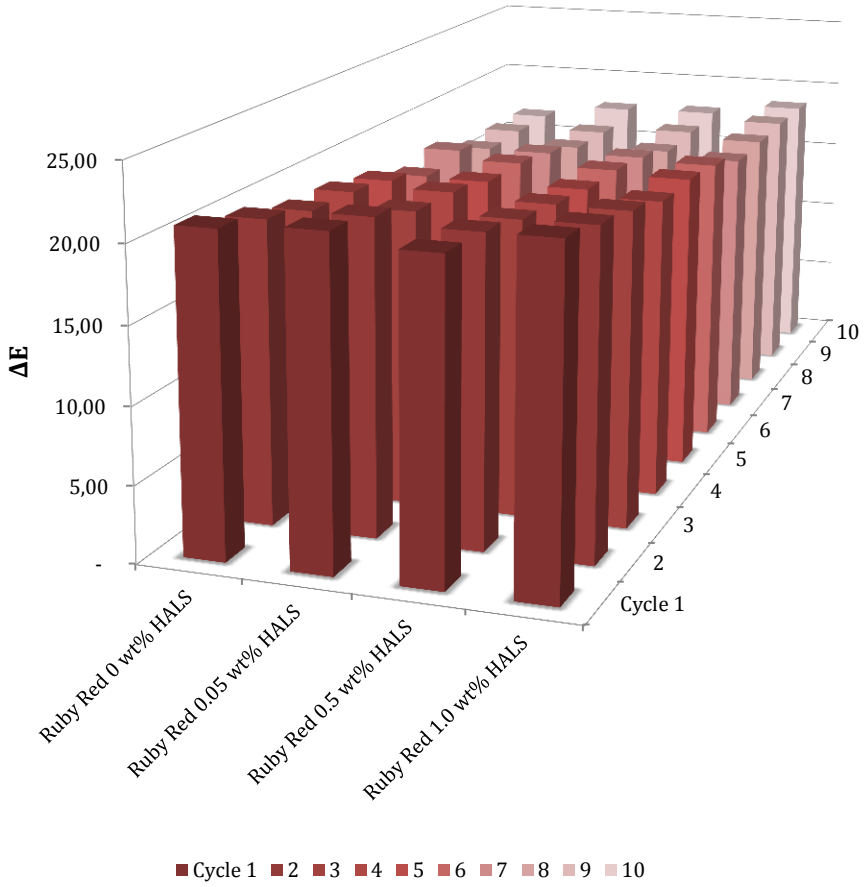

Fig. 39 The effect of multiple activations on the degree of photocolouration of chemically stabilised Ruby Red for 1 to 10 activations

The effect of multiple activations on chemically stabilised Oxford Blue shows a decrease followed by increase in photocolouration with activations for all samples (Fig. 40). However, the behaviour is more clear in HALS stabilised samples. A drop in photocolouration performance is observed in activation 3 and 8 for all samples.

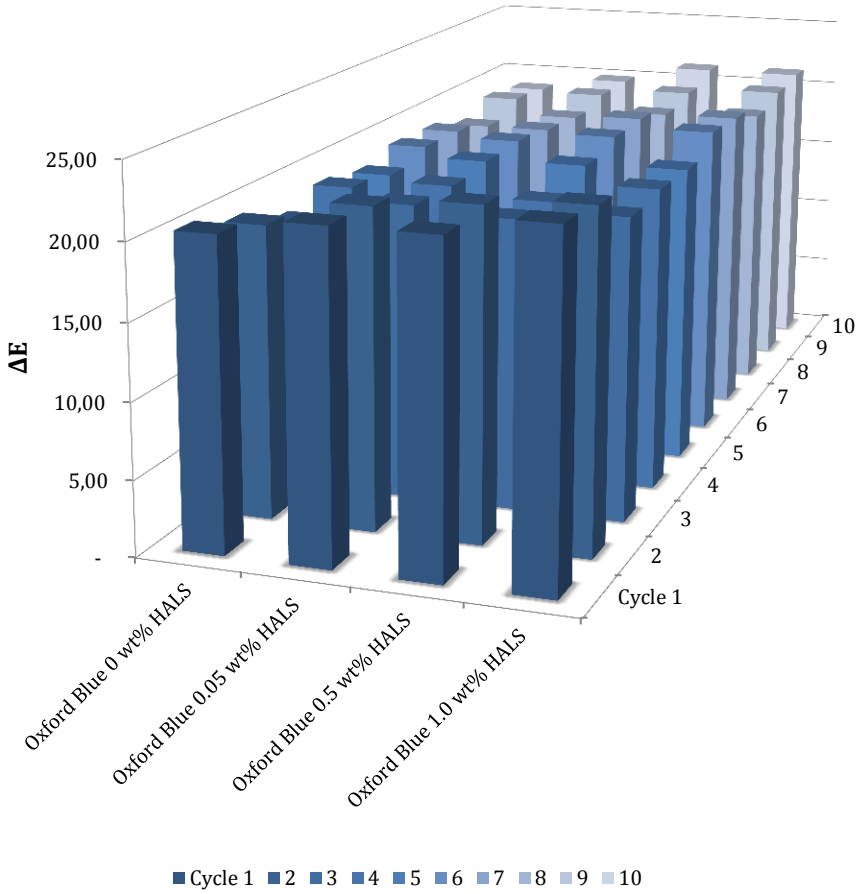

Fig. 40 The effect of multiple activations on the degree of photocolouration of chemically stabilised Oxford Blue

The effect of multiple activations on chemically stabilised spirooxazine shows a decrease followed by increase in photocolouration from 4th activation (Fig. 41). A drop in photocolouration performance is observed in the 8th activation for all samples.

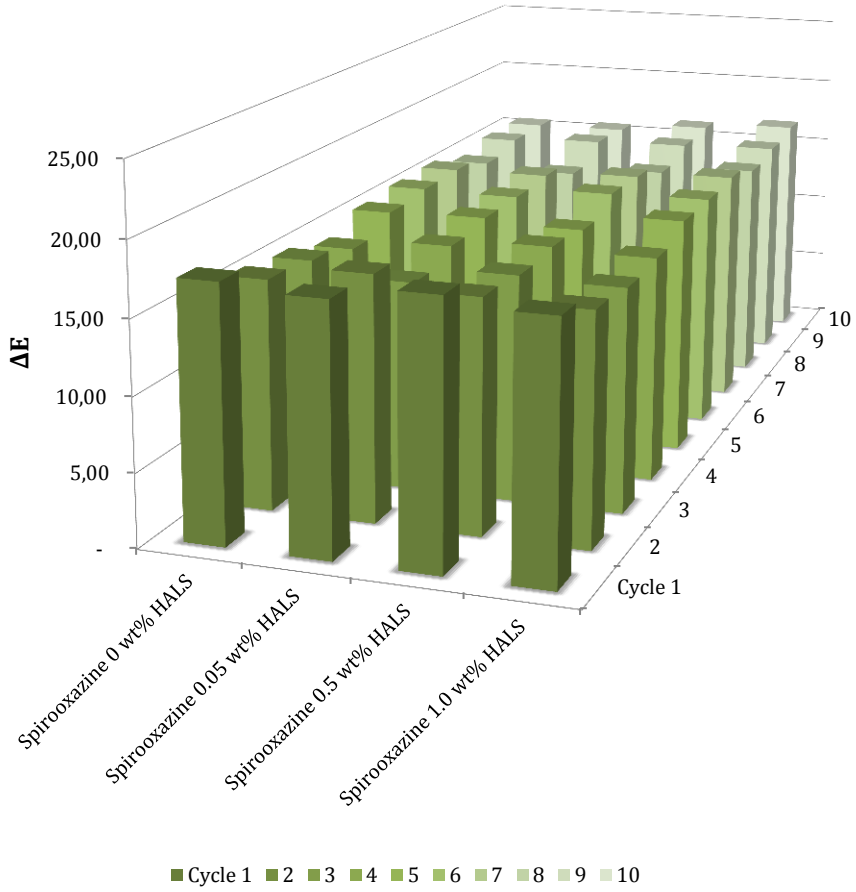

Fig. 41 The effect of multiple activations on the degree of photocolouration of chemically stabilised spirooxazine

The fatigue behaviour for the HALS stabilised samples in the multiple activations test shows that least resistance is represented by the non-stabilised samples (Table 5). Minimum and maximum fatigue values are 79.96% (reference) and 86.68% (0.5 wt%) for Ruby Red, 92.13% (reference) and 98.68% (0.5 wt%) for Oxford Blue and 89.71% (reference) and 97.34% for spirooxazine.

Table 5: Fatigue behaviour of ink formulations based on ΔE in first and last cycle activation

Ink formulation [wt%] HALS	Fatigue [%]
Ruby Red 0	**79,96**
Ruby Red 0.05	83,08
Ruby Red 0.5	**86,68**
Ruby Red 1.0	84,68
Oxford Blue 0	**92,13**
Oxford Blue 0.05	92,46
Oxford Blue 0.5	**98,68**
Oxford Blue 1.0	93,44
Spirooxazine 0	**89,71**
Spirooxazine 0.05	92,43
Spirooxazine 0.5	91,29
Spirooxazine 1.0	**97,34**

The effect on multiple activations on the degree in photocolouration of physically stabilised Ruby Red is insignificant (Fig 42). The 250 µm coated samples are almost constant throughout the 10 activations (Table 27, Appendix IV). A reduction in the ability of photocolouration due to coating is observed. 50 and 150 µm show same initial photocolouration ability approx. 2 units reduction compare to reference samples. However, the intensity in ΔE decreases by approx. 2 units between 150 and 250 µm coated samples (Table 27, Appendix IV).

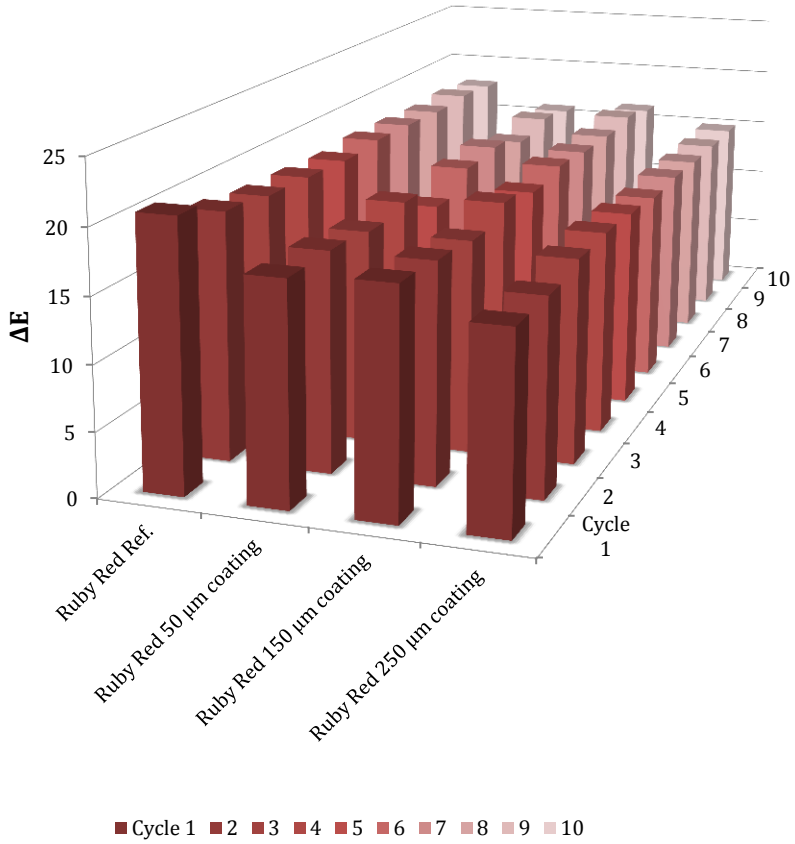

Fig. 42 The effect of multiple activations on the degree of photocolouration of coated Ruby Red for 1 to 10 activations

The ability of photocolouration reduces significant due to coating for physically stabilised Oxford Blue samples (Fig. 43). However, 50 and 150 µm show similar initial photocolouration ability approx. 7 units decrease of ΔE value from reference samples. A drop in the photocolouration ability is observed for 250 µm, the intensity in ΔE decreases by approx. 3 units compared to 150 µm coated samples (Table 27, Appendix IV). The effect of multiple activations on the degree of photocolouration of coated Oxford Blue slightly increases with number of activations. Reference samples show constant photocolouration throughout the activations.

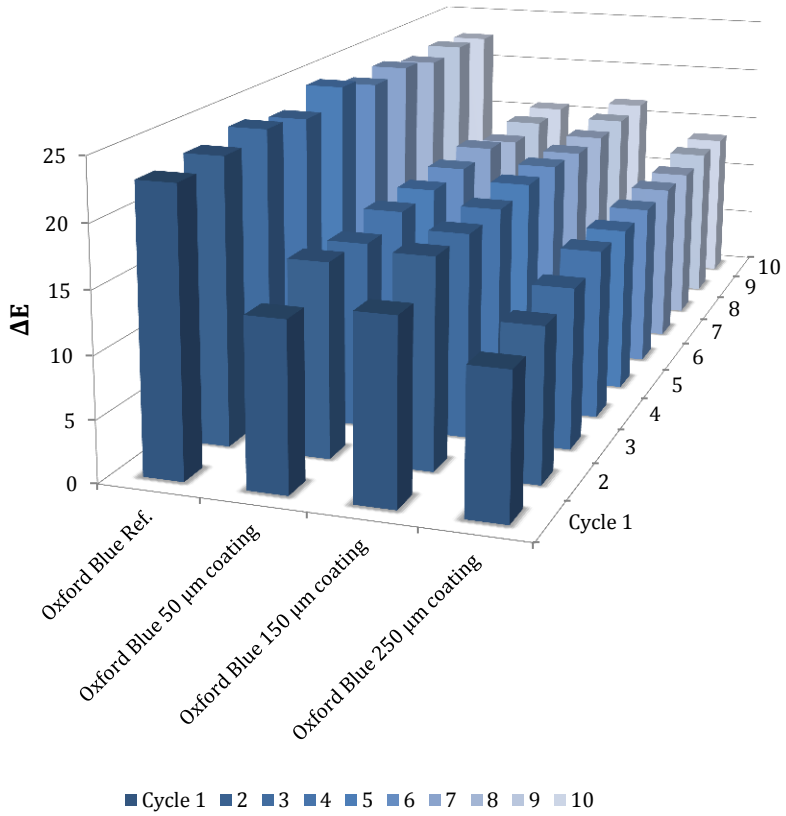

Fig. 43 The effect of multiple activations on the degree of photocolouration of coated Oxford Blue for 1 to 10 activations

The ability of photocolouration reduces significant due to coating for physically stabilised spirooxazine samples (Fig. 44). However, 50 and 150 µm show similar initial photocolouration ability approx. 5 units decrease of ΔE value from reference samples. A drop in the photocolouration ability is observed for 250 µm, the intensity in ΔE decreases by approx. 3 units compared to 150 µm coated samples (Table 27, Appendix IV). The effect of multiple activations on the degree of photocolouration of coated and non-coated spirooxazine slightly increases with number of activations.

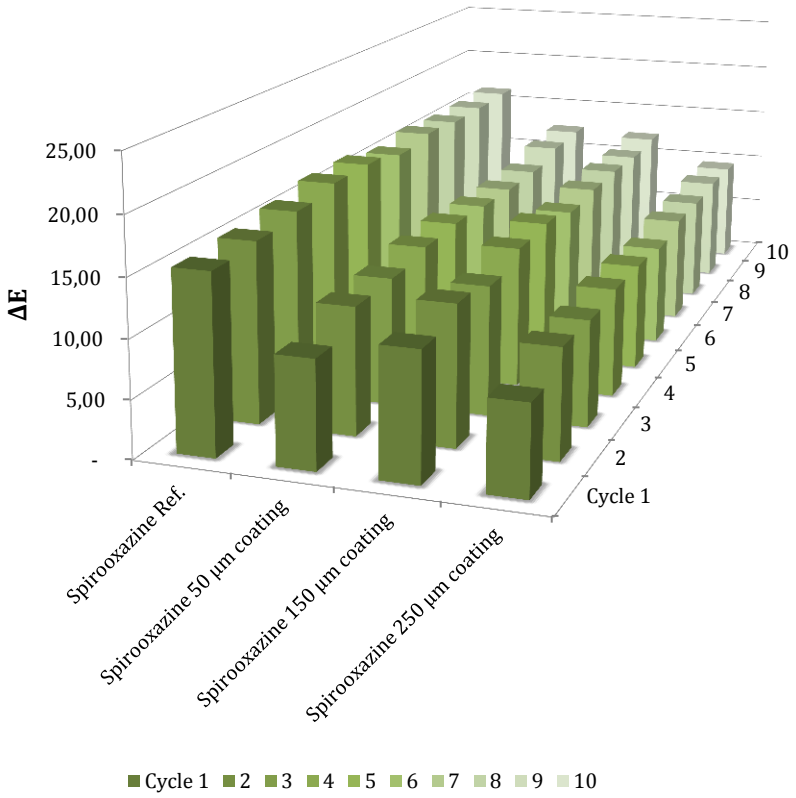

Fig. 44 The effect of multiple activations on the degree of photocolouration of coated spirooxazine for 1 to 10 activations

The fatigue behaviour for coated samples in the multiple activations test (Table 6) show lowest fatigue resistance for uncoated samples; 86.18% (Ruby Red), 98.68% (Oxford Blue) and 105.51% (spirooxazine). Highest resistances for all inks are represented by the 250 µm coated samples; 98.44% (Ruby Red), 116.27% (Oxford Blue) and 122.70% (spirooxazine). This results in an increase of photocolouration for all coated Oxford Blue and spirooxazine samples with time and activations by 11% or higher.

Table 6: Fatigue behaviour of all coated inks based on ΔE in first and last cycle activation

Ink [µm] coating thickness	Fatigue [%]
Ruby Red Ref.	**86,18**
Ruby Red 50	93,33
Ruby Red 150	94,34
Ruby Red 250	**98,44**
Oxford Blue Ref.	**98,68**
Oxford Blue 50	115,68
Oxford Blue 150	112,95
Oxford Blue 250	**116,27**
Spirooxazine Ref.	**105,51**
Spirooxazine 50	134,63
Spirooxazine 150	111,57
Spirooxazine 250	**122,70**

After an additional exposure for 1 hour in intensive artificial sunlight on the multiple activated samples, a significant reduction in colour development was seen. Samples without photochromic ink is presented in Fig. 45. Decrease of ΔE is <<1.0 for these samples and show very small or no influence on colouration of varnish or HALS compounds.

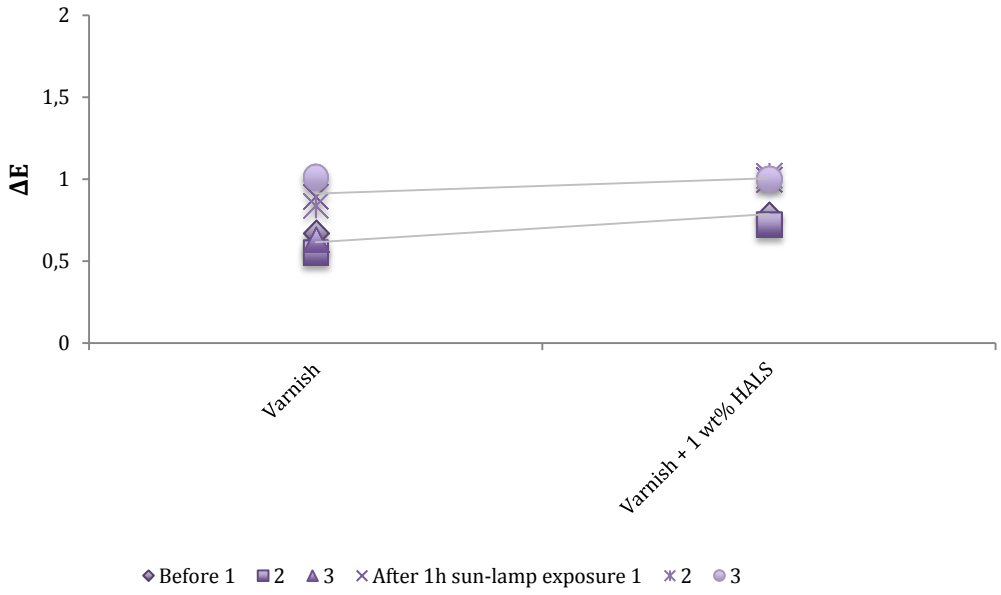

Fig. 45 Fatigue behaviour of blank samples with only varnish and varnish prepared with 1.0 wt% HALS (scale 0-2)

The decrease in photocolouration performance is significant for chemically stabilised Ruby Red (Fig. 46). HALS stabilised sample show a slightly higher initial degree of photocolouration compared to non-stabilised. However, the decrease of intensity represent by ΔE is approx. 13 units for non-stabilised and approx. 12 units for stabilised samples (Table 28, Appendix IV).

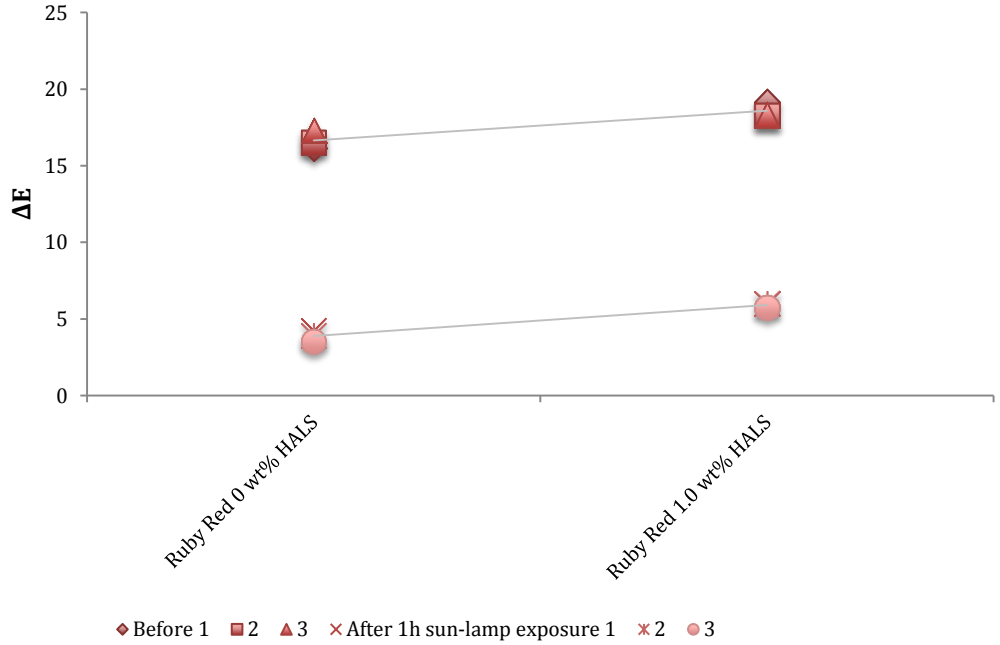

Fig. 46 Fatigue behaviour after 1-hour sun-lamp exposure of chemically stabilised Ruby Red

Fatigue behaviour after 1-hour sun-lamp exposure of chemically stabilised Oxford Blue shows a significant decrease in photocolouration (Fig. 47). The observed decreases in ΔE value are approx. 5 units for non-stabilised samples and 6 units for stabilised samples (Table 28, Appendix IV).

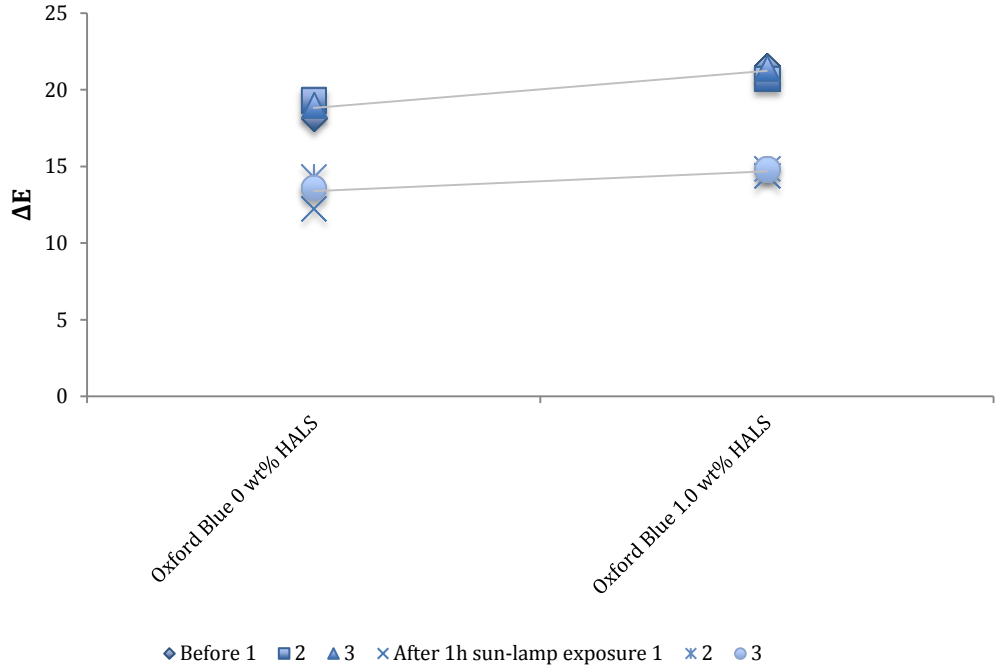

Fig. 47 Fatigue behaviour after 1-hour sun-lamp exposure of chemically stabilised Oxford Blue

Fatigue behaviour after 1-hour sun-lamp exposure of chemically stabilised spirooxazine shows a significant decrease in photocolouration (Fig. 48). The observed decreases in ΔE value are approx. 6 units both for non- stabilised and stabilised samples (Table 28, Appendix IV).

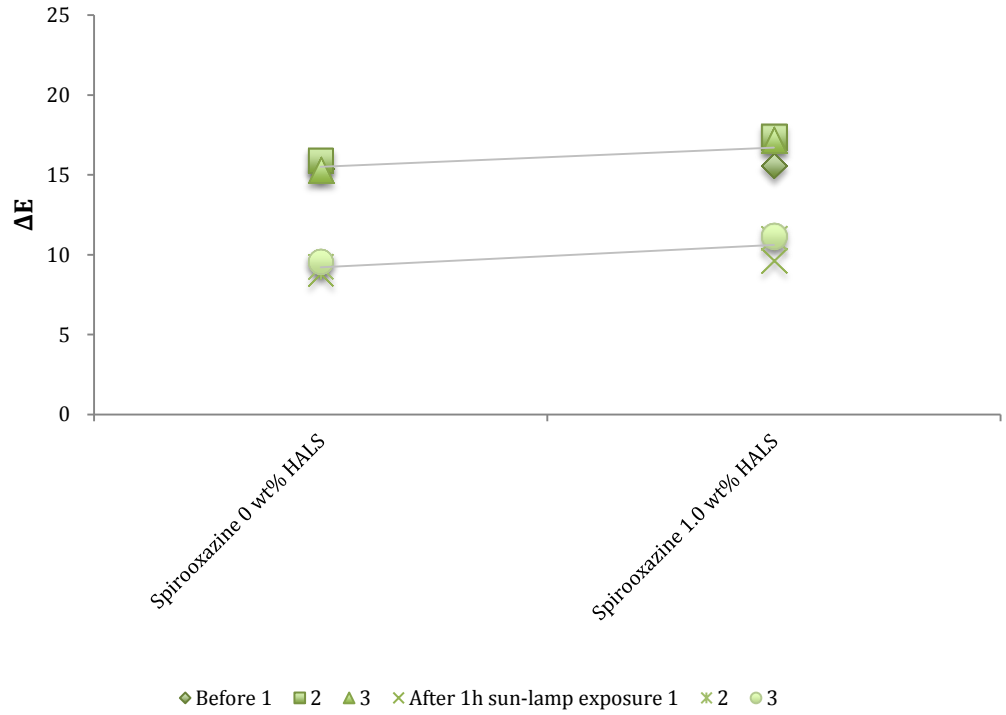

Fig. 48 Fatigue behaviour after 1-hour sun-lamp exposure of chemically stabilised spirooxazine

The fatigue is highest for Ruby Red (Table 7). The ability of photocolouration left is 23.34% and 31.85% for HALS stabilised and non-stabilised respectively. Oxford Blue and spirooxazine show a higher fatigue resistance and the ability of photocolouration left is approx. 70% for Oxford Blue and 61% for spirooxazine.

Table 7: Fatigue behaviour of ink formulations based on ΔE before and after exposure

Ink formulation [wt%] HALS	Fatigue [%]
Ruby Red 0	23,34
Ruby Red 1.0	31,85
Oxford Blue 0	71,16
Oxford Blue 1.0	69,11
Spirooxazine 0	59,36
Spirooxazine 1.0	63,55

The decrease in photocolouration performance is significant for physically stabilised Ruby Red after 1-hour sun-lamp exposure (Fig. 49). Coated samples show an initial lower degree of photocolouration compared to non-stabilised. The observed decrease of intensity represent by ΔE is approx. 12 units for non-stabilised and approx. 9 units for stabilised samples (Table 28, Appendix IV)

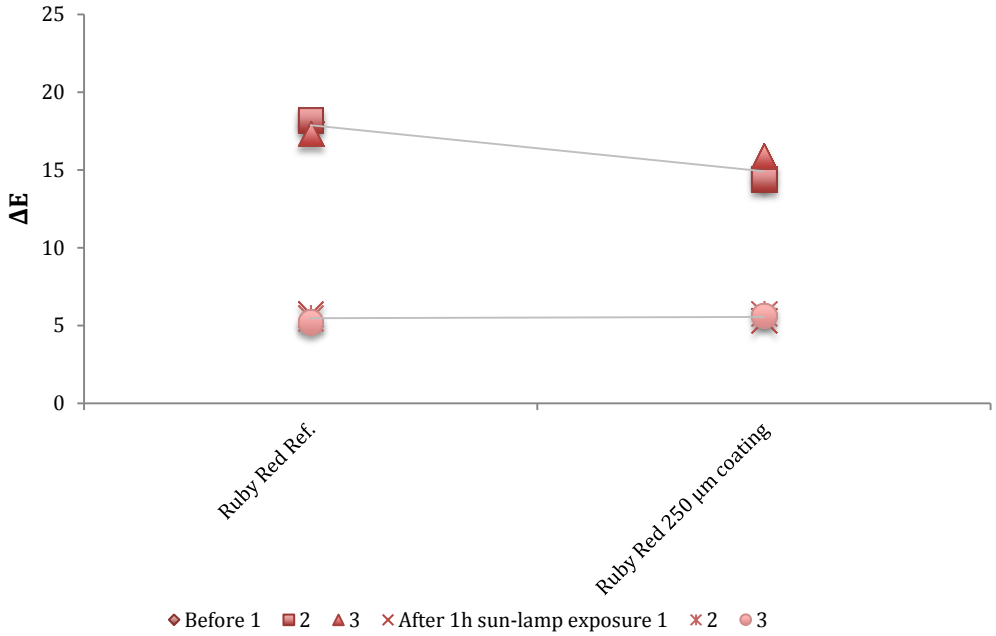

Fig. 49 Fatigue behaviour after 1-hour sun-lamp exposure of physically stabilised Ruby Red

A small decrease in photocolouration performance is seen for physically stabilised Oxford Blue after 1-hour sun-lamp exposure (Fig. 50). Coated samples show an initial lower degree of photocolouration compared to non-stabilised. The observed decrease of intensity represent by ΔE is approx. 5 units for non-stabilised and approx. 3 units for stabilised samples (Table 28, Appendix IV). Still, ΔE is lower for the coated samples both before and after sun-lamp exposure.

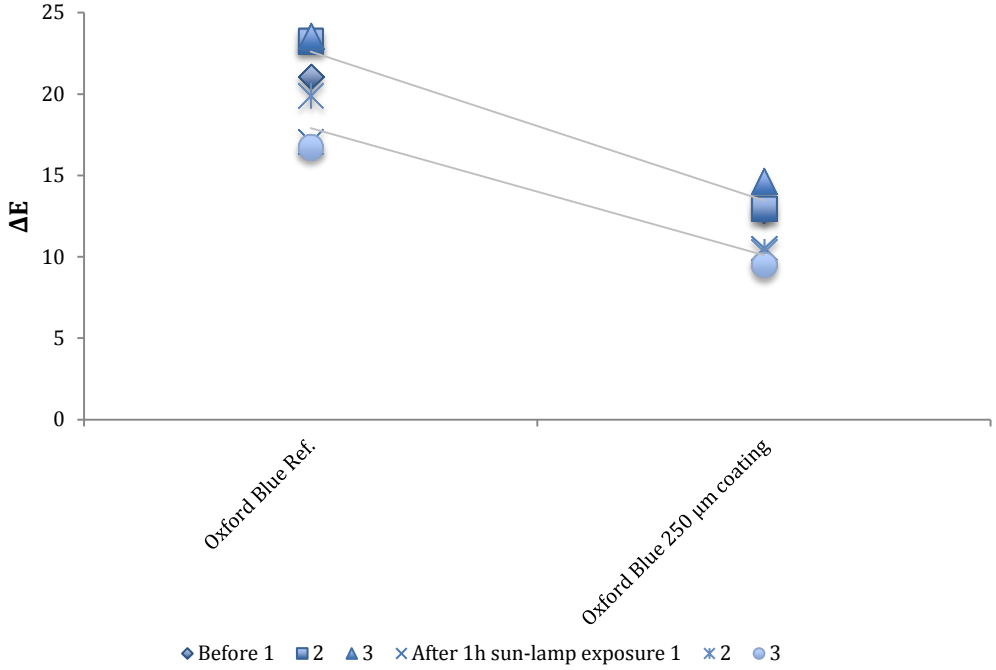

Fig. 50 Fatigue behaviour after 1-hour sun-lamp exposure of physically stabilised Oxford Blue

A small decrease in photocolouration performance is seen for physically stabilised spirooxazine after 1-hour sun-lamp exposure (Fig. 51). Coated samples show an initial lower degree of photocolouration compared to non-stabilised. The observed decrease of intensity represent by ΔE is approx. 4 units for non- stabilised and approx. 2 units for stabilised samples (Table 28, Appendix IV). Still, ΔE is lower for the coated samples both before and after sun-lamp exposure.

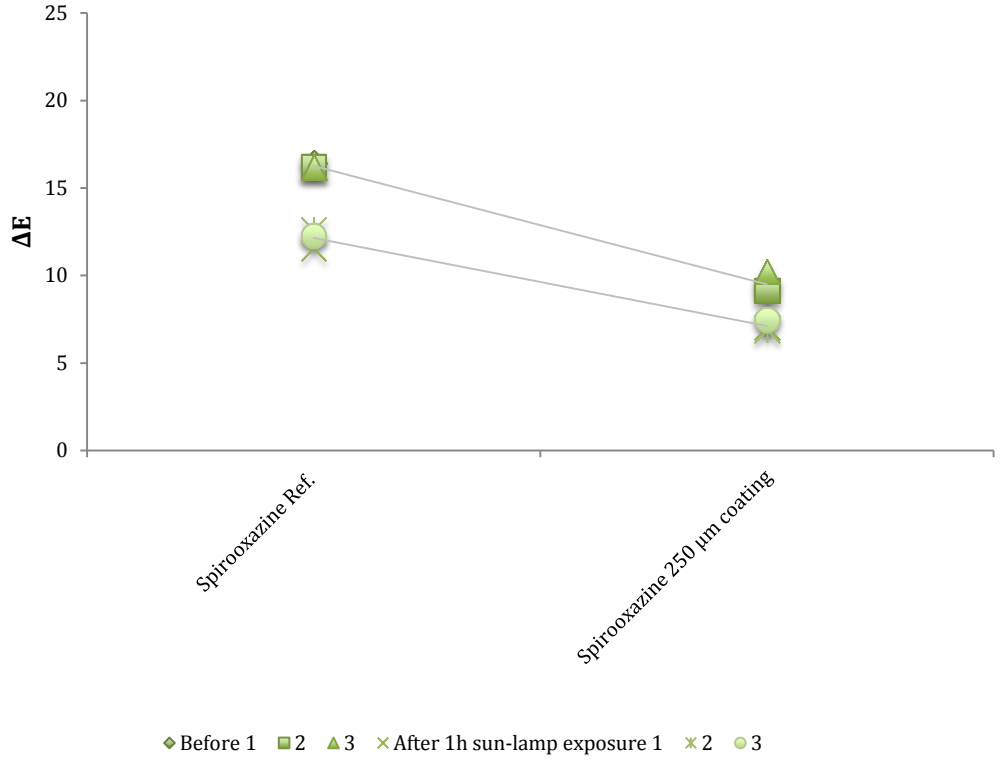

Fig. 51 Fatigue behaviour after 1-hour sun-lamp exposure of physically stabilised spirooxazine

The fatigue is highest for Ruby Red (Table 8). The ability of photocolouration left is 30.63% and 37.25% for coated and non-stabilised respectively. Oxford Blue and spirooxazine show a higher fatigue resistance. The ability of photocolouration left is 75.06% and 79.17% for coated and non-stabilised Oxford Blue respectively. The ability of photocolouration left is 74.83% and 74.67% for coated and non-stabilised spirooxazine respectively.

Table 8: Fatigue behaviour of coated inks based on ΔE before and after sun-lamp exposure

Ink [µm] coating thickness	Fatigue [%]
Ruby Red Ref.	30,63
Ruby Red 250	37,25
Oxford Blue Ref.	79,17
Oxford Blue 250	75,06
Spirooxazine Ref.	74,67
Spirooxazine 250	74,83

In an additional activation test, physically stabilised samples, coated by ®RUCO COAT PU 8551 in 6 variations of thickness between 25-350 µm (Fig. 52-55) were tested. Activations were repeated for 3 cycles.

A decrease in colour development is seen for coated Ruby Red samples (Fig. 52). The photocolouration reduces by approx. 1 unit in ΔE between coated and non-stabilised samples. A drop in photocolouration, approx. 1 unit, is observed for 150 and 250 µm coated samples followed by an increase for 350 µm coated samples for approx. 1 unit. However, the colour development is constant throughout the three cycles (Table 29, Appendix IV).

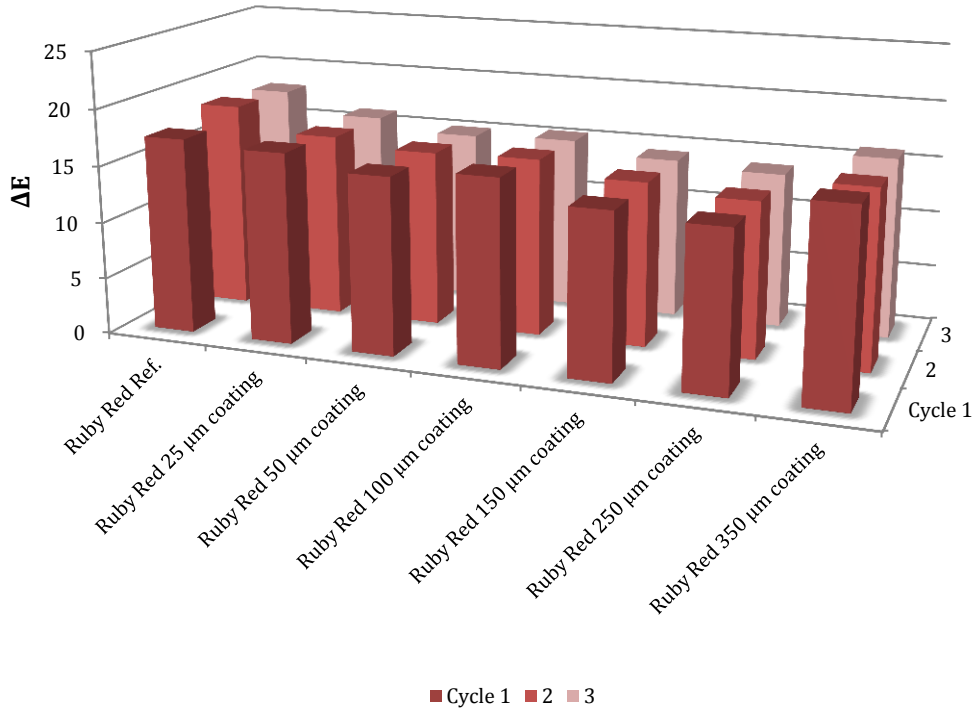

Fig. 52 The effect of activations on the degree of photocolouration of physically stabilised Ruby Red for 1 to 3 activations

A decrease in colour development is seen for coated Oxford Blue samples with increasing coating thickness (Fig. 53). The photocolouration reduces by approx. 4.5 units in ΔE between coated and non-stabilised samples. A drop in photocolouration, approx. 1 unit, is observed for 250 and 350 µm coated samples. However, the colour development is constant throughout the three cycles (Table 29, Appendix IV).

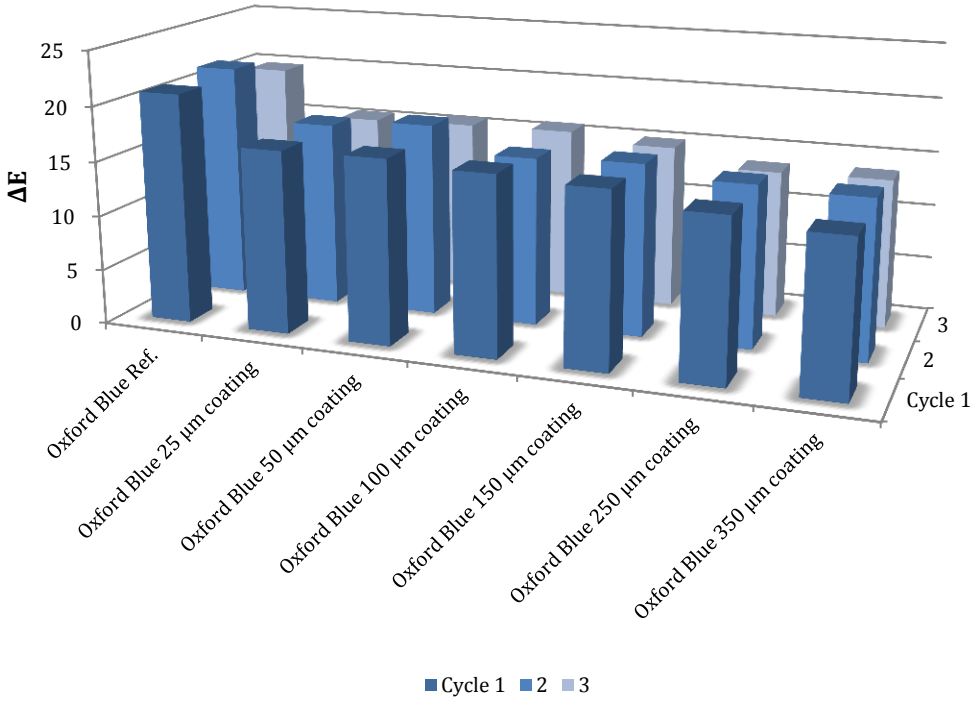

Fig. 53 The effect of activations on the degree of photocolouration of physically stabilised Oxford Blue for 1 to 3 activations

A decrease in colour development is seen for coated spirooxazine samples. However, no trend is observed between thickness and degree of photocolouration (Fig. 54). The photocolouration reduces by approx. 5 units in ΔE between coated and non-stabilised samples. The colour development is constant throughout the three cycles (Table 29, Appendix IV).

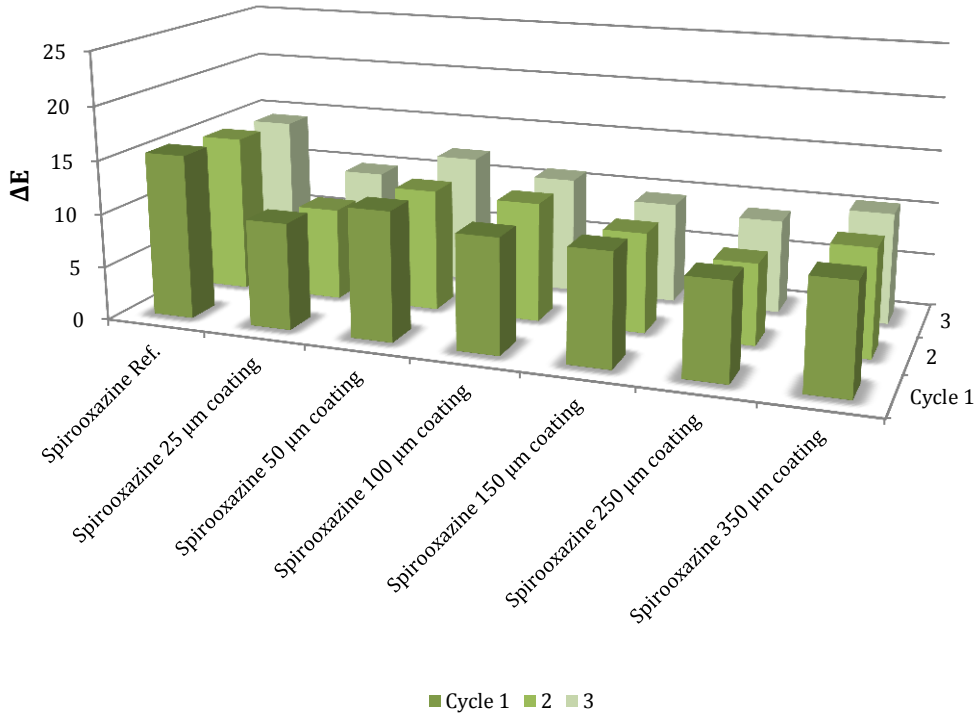

Fig. 54 The effect of activations on the degree of photocolouration of physically stabilised spirooxazine for 1 to 3 activations

The fatigue behaviour for the additional coated samples in the activation test shows a similar percentage of fatigue for all samples (Table 9). Minimum and maximum values in fatigue is 94.01% (100 µm) and 103.99% (reference) for Ruby Red, 92.54% (250 µm) and 98.65% (350 µm) for Oxford Blue and 90.04% (150 µm) and 103.10% (350 µm) for spirooxazine.

Table 9: Fatigue behaviour of coated inks based on ΔE between first and last activation

Ink [µm] coating thickness	Fatigue [%]
Ruby Red Ref.	**103.99**
Ruby Red 25	95.67
Ruby Red 50	96.78
Ruby Red 100	**94.01**
Ruby Red 150	98.71
Ruby Red 250	98.55
Ruby Red 350	95.69
Oxford Blue Ref.	94.26
Oxford Blue 25	92.93
Oxford Blue 50	93.53
Oxford Blue 100	96.97
Oxford Blue 150	94.65
Oxford Blue 250	**92.54**
Oxford Blue 350	**98.65**
Spirooxazine Ref.	93.23
Spirooxazine 25	99.13
Spirooxazine 50	101.44
Spirooxazine 100	102.66
Spirooxazine 150	**90.04**
Spirooxazine 250	97.41
Spirooxazine 350	**103.10**

4.3.4 Statistical analysis

Most significant standard deviation (above 2.0 units) is observed in the washing test for chemically stabilised samples with up to 3.86 units for Ruby Red 0.05 wt% HALS. These values are supported by a significant t-test between washed and unwashed for all samples for Ruby Red (Table 35, Appendix VII)(Table 43, Appendix IX). However, this fatigue is not significant according ANOVA (Appendix X). In the multiple activations test, a standard deviation of 2.09 units for Ruby Red 0 wt% HALS is seen. The data for HALS stabilised Ruby Red in multiple test are significant fatigue. No significant fatigue can be observed for Oxford Blue and Spirooxazine including reference samples (Table 38, Appendix VII)(Table 45, Appendix IX)(Appendix X). In the sun-lamp exposed samples significant fatigues are observed for all samples (Table 7-8) and a standard deviation up to 6.39 units for Ruby Red 0 wt% HALS. Analysis supported by results in t-test and ANOVA(Table 46, Appendix IX)(Appendix X).

5 Discussion

5.1 Ink characterisation

A stiff handle of the textile material due to the photochromic print can be decreased by the use of ink-jet printing technology, where the amount of material is minimised among other positive environmental aspects. In this research the ink-jet printing was not applied but the inks were developed and characterised tested for this purpose.

The ink characterisation was made to confirm the inks to be in the range of what is required by the print head in an inkjet printer in terms of viscosity and surface tension. Particle size is not necessary to be measured as the dyes dissolve on molecular level. Both non-stabilised and stabilised, 0.05 wt% HALS inks were tested. It is found that the viscosity as a function of shear rate respectively temperature are in the required interval; 8-20 mPa·s for all inks, including the stabilised ink. The viscosity shows a shear thinning behaviour, which is desirable in ink developed for ink-jet printers. A difference in viscosity is observed between Ruby Red and the other inks. This is probably due to calculations in volume percentage and weight percentage respectively. The varnish for Oxford Blue and spirooxazine is made out of same batch.

The mean values of surface tension did not differ significantly between non-stabilised and stabilised ink. The values are in the range required, 25-35 mN/m and are sufficient for ink-jet printing.

5.2 Physical protection layer

Two 3D printable thermoplastics were examined as physical shield on the photochromic print. The adhesion to the textile was not optimal for none of them and made it hard to guarantee 100% dense and physical protection of the print. The technology was chosen for its potential and the increasing interest in development of the technology for new applications in industry.

The achieved resulting structure of ABS was not dense enough and did not create a single layer but several individual layers in a net structure. In the result of PMMA the layers show a milky appearance due to an uneven inner structure. Both these problems might be avoided by higher temperatures on the building plate to slow down the solidifying process of the extruded filaments. Thickness, stiffness, opaque appearance and lack of adhesion to the fabric were unavoidable drawbacks.

The polyurethane coating had an excellent adhesion to the textile with good transparent property. It added a soft but slightly sticky handle to the fabric. However, the effect on the ink reduced the ability of photocolouration for Oxford Blue and spirooxazine in particular.

5.3 Colour performance

This part is based on tables and figures for comparison and evaluation of stabilisation methods due to the performance in colour development and fatigue resistance of the photochromic prints.

5.3.1 Effect of washing

In the washing test for the chemically stabilised samples, it is found that the photocolouration decreases linearly for all concentrations after performed test. It is seen that the higher HALS concentration the higher colour development by UV-light activation for the inks before and after washing. In spirooxazine prints (Fig. 35) the trends show a slightly reduction of fatigue for the higher concentrations e.g. the gap between the colour performances before and after washing becomes smaller while the same lines are more parallel for Oxford Blue and Ruby Red. Generally, this gap is more distinct for Ruby Red over the whole range. This behaviour confirms that Ruby Red is more sensitive and exhibits lower degradation resistance than Oxford Blue and spirooxazine to photodegradation as found in the previous research (Rijavec & Bračko 2015). In table 3 the fatigue behaviour gives an indication about the impact of the washing on the photocolouration performance for comparisons. The fatigue resistance is around 80% for Oxford Blue and spirooxazine and 70% for Ruby Red in all samples including the non-stabilised. This information makes it clear that it is uncertain if the fatigue resistance really does follow a trend to increase by concentration of HALS since it also applies the non-stabilised samples. However, in a more detailed reflection, it is found that 1.5 and 2.0 wt% HALS gave best results in added fatigue resistance by chemical stabilisation and distinguish in ΔE (Table 24, Appendix IV).

For the physically stabilised samples, as seen in Fig. 36-38, the colour development decreases with thickness of coating layer. Possible reasons are based on two mechanisms of the coating, reflections and transmission properties. The reflecting light could be perceived differently, affected by the coating and its thickness (Appendix VI). It is also possible that ΔE remains even if the hue or lightness changes since ΔE is based on the gap between two colours and not an offset. Additionally, the setting lets the default ratio allow higher difference in lightness than chroma. Another possible reason is a reduced ability of transmission due to the coating. By blockage of the UV-irradiation, light cannot reach the molecules for complete colour development.

As seen in Table 4, the colour development after washing is higher than before washing in two cases, both are coated samples in the dye group of spirooxazine (Oxford Blue and spirooxazine). Analysis of variance (ANOVA) (Appendix X) shows for these samples that there is no significant fatigue between before and after washing i.e. there is any fatigue identified. However, it could also be a variation within the sample sets making these values insignificant. More samples and several washing cycles could have been needed to see a significant test and decay of fatigue. The fatigue resistance for the coated samples show a low decrease of colour development, not lower than 91.73% and an average at 97.11% fatigue resistance i.e. how much the photocolouration performance remains. This shows a clear difference to HALS stabilised samples with an average at 77.51%.

5.3.2 Effect of multiple activations

The multiple activations test simulated UV-light activation and recovery in 10 cycles. Initially, chemically stabilised samples have slightly higher photocolouration with higher concentration of HALS, a significant observation (Appendix X). However, this trend is more clear for Oxford Blue and spirooxazine than Ruby Red. This finding could be that the mechanism of HALS works better with Oxford Blue and spirooxazine than Ruby Red. The consequence is that the colour development reduces with number of activations and time faster and more significant for Ruby Red (Fig. 39). It could also be based on the fact that Oxford Blue and spirooxazine are more stable from the beginning. According to previous research (Liu et al. 2010), spirooxazine compounds have demonstrated good resistance to photodegradation in short-term exposure to UV-irradiation. The conducted tests could have been too mild for the spirooxazine compounds and the reason for insignificant differences (Appendix IX and X). The fatigue behaviour (Table 5) shows that non-stabilised samples have lowest fatigue resistance and the higher concentrations 0.5 and 1.0 wt% represent the prints that perform best with a durability up to 98,68% (Oxford Blue 0.5 wt% HALS). Moreover, the reduction of colouration performance caused by coating is lower for Ruby Red in the multiple activations test. Also in the washing test, the trends are found to be more constant for Ruby Red. This indicates that the impact on photocolouration intensity caused by the coating is lower for Ruby Red.

Variations of ΔE-value in the multiple activations tests are found to not only decrease but also increase with number of activations in both chemically and physically stabilised samples. Possible reason could be that the ink is not fully cured in the ink-curing process and continues to cure by UV-light in the activation process and increases the colour development performance in later activations.

The coated samples show no significant decrease of photocolouration by number of activations and time (Appendix IX). For Oxford Blue and spirooxazine in particular, samples in cycle 10 have higher ΔE compare to cycle 1. For HALS stabilised samples an irregularity of photocolouration with number of activations is seen for Oxford Blue and spirooxazine. In the ink characterising, (Fig. 23-24) a higher viscosity is observed for Oxford Blue and spirooxazine compared to Ruby Red, probably due to differences in calculations or/and the human factor. If this is true, an excess of photoinitiator in Oxford Blue and spirooxazine formulations can be assumed. This makes them more likely to continue to cure in the activation process than Ruby Red. However, these variations are similar in number of units to the standard deviation within the sample set (Appendix VII) and might be random. Moreover, a variation of ΔE lower than 1 unit is not visible for the human eye and could depend on undefined errors (Mokrzycki & Tatol 2011).

As identified, the coated samples of Oxford Blue and spirooxazine show all a higher photocolouration in tenth than first activation. However, this is also the case for uncoated spirooxazine (Table 32-33, Appendix V). The possible reason could be as mention that the ink is not fully cured and continue to cure during the activations and is not limited to the coated samples. However, a possible explanation for the higher fatigue resistance in coated samples could be that the coating layer protects the ink better from degradation and it does not cancel out the assumed continued curing. A neutralisation between degradation and continuing curing could be the reason for non-stabilised and HALS stabilised samples to be more constant. The degradation behaviour of Ruby Red does not show the same tendency but the fatigue resistance is increasing by thickness (Table 6). The possible reason could be that higher protection is needed as in double-sided coating

or no such continuous curing occurs for Ruby Red. The opposite way is also a motive, that the curing process by UV-LED light could have started degradation already in the preparation of the samples and are more significant for Ruby Red.

5.3.3 Effect of stabilisation

For all samples a reduction in visible photocolouration by increasing thickness of coating is observed. But as mentioned, this reduction is lower for Ruby Red (Fig 42) and could be explained by a difference in required space for the rearrangement of spirooxazine (Oxford Blue) and naphthopyran (Ruby Red) upon activation. A significant decrease between 150 µm and 250 µm coating thickness is found for all prints. This was the reason for further investigation by a second sequence of coating with additional thicknesses (Fig. 52-54). For this sequence, another PU coating was the only available (PU 8551). The result was found to be close to the initial coating (PU1110) with a fatigue resistance not lower than 90%. In the fatigue calculations for those, the variation between first and last activation is very small or not existing regardless to thickness. However, only three cycles were repeated in this sequence because of the time limit. The possible explanation for this finding could be that the coating thickness does not affect the transmission but could also be that the coating influence on ΔE itself. In a detailed reflection a small drop in colouration is found for thickness 250 µm and then an increase for 350 µm. This increase is found to be more significant for Ruby Red and spirooxazine, these prints have in common to be the more sensitive ones, Ruby Red because of its dye group belonging and spirooxazine because of the pure formulation.

In previous studies it has been found that the support material has an impact on the light stability (Bamfield & Hutchings 2010; Feczkó et al. 2011; Nechwatal & Nicolai 2015). Stabilisation due to incorporation of the dye within a polymeric matrix as in ophthalmic lenses or sol-gel coating protects the dye from the atmosphere. The polarity, amorphous and crystalline regions do affect the photocolouration performance. In this experiment a UV-light curable matrix was used, its impact on the dyes could not only have an affect on the photocolouration but also the fatigue behaviour by lack of bonds to the substrate. Further, not fully cured ink could give the dye more space for steric molecular changes but also no maximum protection is reached.

The 1-hour artificial sun exposure test was examined as a tougher testing method. There is a significant difference of the fatigue behaviour between Ruby Red and the others. In Ruby Red prints, photocolouration stops at a ΔE value around 5 after the intensive exposure for both non-stabilised and stabilised samples. A very small or no influence on colouration is observed by varnish or varnish with HALS (Fig. 45). Based on that, it is possible to say that the fatigue and ΔE value changes only depend on the ink photodegradation. Moreover, the unexposed or exposed coating did not result in any colour differences by significant yellowing (Appendix VI). In a comparison between chemically and physically stabilised methods the degradation is less pronounced in the coated samples after the 1-hour exposure and spirooxazine. Non-stabilised Oxford Blue showed better result after the 1-hour exposure than the stabilised. Continuously curing could have been slowing the degradation down since small or non-existing degradation differences are found between non-stabilised and stabilised for Oxford Blue and spirooxazine (Table 7-8). Better fatigue resistance has already been observed in the previous multiple activations test for the samples in the batch for Oxford Blue and spirooxazine. In this test the most interesting result is found in the fatigue behaviour of Ruby Red. The fatigue clearly exists and the stabilisation is shown to have an effect. However,

a difference between the stabilisation methods cannot be distinguished (Fig. 46 and 49, Table 7-8).

To summarise the comparison between chemically and physically stabilised samples, the fatigue resistance tends to be higher for all inks in the coated samples for the main tests. The chemical stabilisation shows a weak trend in increased fatigue resistance with concentration of HALS. The coated samples reach best fatigue performance by 250 μm coating thickness. However, the final 1-hour exposure test shows no differences in performance between the stabilisation methods. Moreover, Ruby Red shows a better performance stabilised by HALS, opposite to previous testing. This analysis and on the basis of standard deviations, t-tests and analysis of variances no logic trend of significant fatigue for the non-stabilised samples in correlation to insignificant fatigue for stabilised samples is seen.

5.3.4 Statistical analysis

The statistical analysis does support the discussion by standard deviations (Appendix VII), t-test (Appendix IX) and ANOVA (Appendix X). The analysis is made by calculation of standard deviation within the sample sets and compared with the variation between stabilised groups in the sample batch and between batches. Standard deviation within the sample set has been found to be less than 2.0, more likely less than 1.0 with a few exceptions (Appendix VII). By this information a variation between two configurations and fatigue resistance are considered clear if their standard deviation is 2.0 or higher.

The standard deviation is evaluated between unwashed and washed samples and the first and last activation in the multiple activations test. It was found that the variations are within the same frame of standard deviation units as sample sets' standard deviation. The cases where the standard deviation is higher there is no logic trend of fatigue resistance increase by stabilisation degree or relationship between test methods. For example, the chemically stabilised Ruby Red samples show a standard deviation >2.0 after washing test (Table 35, Appendix VII). The explanation is fatigue of the Ruby Red print (Table 3). But the finding is not supported by standard deviations in the multiple activations test (Table 38, Appendix VII) nor the ANOVA calculation (Appendix X).

T-test and ANOVA are made to validate findings and support the qualitative analysing made (Appendix IX and X). When t-test is not supported by ANOVA it depends on the larger amount of data and distribution ANOVA takes into account. Moreover, the analysing should be significant to be able to compare the performance of the stabilisation methods and not consider a variation that could be seen within the sample sets.

Significant fatigue can be seen and validated by t-test (Appendix IX) and ANOVA (Appendix X) for all sun-lamp exposed samples. None of the stabilisation methods' were seen to have a greater impact on stabilisation. Ruby Red showed a difference in fatigue between non-stabilised and stabilised (Table 7-8) for both methods. However, no difference in fatigue behaviour is seen between the stabilisation methods.

5.3.5 Errors

Error in the calculation procedure has been discussed to have an influence on the results by preventing the degradation and instead continue curing of the ink by activations. An excess of photoinitiator in the varnish could have affected this for Oxford Blue and spirooxazine.

Possible errors by the measuring instrument cannot be excluded. Measuring small amounts of components for the ink formulations require high precision of the instruments. Larger batches could lead to higher accuracy.

The human error has a major role in preparation and measuring processes involving the sensitive photochromic compounds. In the colour measurements a manual procedure with several steps was performed. Timing, measuring spot and triggering for measurement of the spectrophotometer could differ regardless to caution taken.

The climate in the lab could differ from day to day and has an impact on the colour development performance for the multiple activations test in particular. Especially spirooxazine compounds are temperature sensitive (Little & Christie 2010a; Ramachandran & Urban 2011; Viková, Christie & Vik 2014). A cooling system was used to minimise this risk.

Moreover, other steps in the testing methods could have influenced. The amount of detergent and/or the cleanness of the machine in the washing test could have an impact. These errors could be possible reasons why the references in the chemical stabilised samples have lower fatigue resistance and ΔE data than the references in the physically stabilised samples (Table 3-4) (Appendix IV).

6 Conclusion

The aim of this research was to investigate how the stabilisation influenced the lifetime of photochromic prints in a UV-sensor application. Two ways of stabilisation have been applied and examined for three ink formulations. The results show a weak increase of degradation resistance by the stabilised samples. From the results of fatigue behaviour it could be concluded that a better stabilisation is found for the physical stabilised samples. However, more testing must be done to eliminate the variations within sample set as a reason of the measured variations considers fatigue. Highlights in the discussion concluded;

- Chemically stabilised samples did not show a clear increase in fatigue resistance by higher concentrations of HALS
- Physically stabilised samples did show similar or slightly better performance in light fastness than stabilisation using HALS in the formulation
- Samples followed a trend that confirmed Oxford Blue and spirooxazine having a better resistance to photodegradation
- The degree of degradation cannot be proven because of the possible reason that the fatigue and decrease in ΔE is compensated by continuously curing under UV-light activation (Oxford Blue and spirooxazine)

The assumptions are based on fatigue behaviour. In the discussion it was stated that errors have to be eliminated, curing method optimised and long-term testing applied.

The trends found in the results are not believed to be completely random even if further investigations have to be done for a conclusion. Generally, the inks show a better resistance in fatigue behaviour by physical coating in the washing and multiple activations tests. In a comparison of the fatigue resistance between stabilisation methods for Ruby Red it is found that physical stabilisation has a better performance in the washing test. In contrast the chemical stabilisation was similar in the 1-hour exposure test for same formulation. However, the variations in performance of the reference samples in the batches are too high to make a conclusion.

In the end, neither a conclusion can be made nor is the hypothesis proven false. This is due to variations within the sample sets. More testing and larger sample sets have to be examined. If the reference performance would have distinguished more from the stabilised samples, the fatigue resistance behaviour found could be proven. But as long as the collection of references does not show a higher and more significant degradation, the stabilisation methods cannot be recognised to have an effect on the resistance. In this conclusion, I would like to highlight that a new stabilisation method with an additional protective layer was developed and investigated. Although the method cannot be concluded to have worked in a completely successful way, it did have an effect on the print in the right direction and is a good starting point for future research.

7 Future research

In future research, 3D-printing technology could be an option for development of protective layer and an optimisation of the process should be done. Printer settings and material testing are examples of interesting start. Acrylic based PMMA printed on an acrylic fabric could have potential for better adhesion and protection of photochromic print.

Physical stabilisation by PU coating should be investigated more in long-term testing that induces a more significant result. Alternative methods for measuring degradation behaviour could be done for a more accurate result within small variations. The curing method has to be optimised and complete curing of the ink has to be guaranteed. However, the developed inks in this project are suitable for ink-jet printing, by this method the print requires less material and it should be more likely to cure in the curing process.

8 References

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Appendix I

Viscosity data gathered for ®RUCO COAT PU110 and PU8551 in a formulation with thickener BGL75L.

Table 10: Data on coating formulation PU1110 + BGL75L

Coating formulation, 29 measuring points, shear rate rise 0-2000 1/s								
1st test			**2nd test**			**3rd test**		
Shear Rate [1/s]	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Shear Rate [1/s]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Shear Rate [1/s]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**
0,608	33,1	54,5	0,564	34,6	61,4	0,6	33,5	55,8
1,21	50	41,2	1,2	53,6	44,8	1,21	50,6	41,7
1,66	60	36,2	1,65	64,5	39,1	1,66	60,7	36,6
2,19	70,9	32,3	2,19	76,1	34,8	2,2	71,4	32,5
2,9	83,7	28,9	2,89	89,4	30,9	2,9	83,9	28,9
3,82	98,9	25,9	3,81	105	27,7	3,83	98,1	25,6
5,03	117	23,3	5,02	124	24,7	5,06	114	22,5
6,62	138	20,9	6,61	146	22,1	6,66	131	19,7
8,71	163	18,7	8,71	172	19,7	8,77	150	17,1
11,5	192	16,7	11,4	201	17,6	11,5	170	14,7
15,1	223	14,8	15,1	234	15,5	15,1	191	12,6
19,8	255	12,8	19,8	269	13,6	19,8	217	10,9
26	283	10,9	26	304	11,7	26	247	9,49
34,1	314	9,2	34,1	330	9,67	34	284	8,35
44,7	347	7,77	44,7	364	8,13	44,7	322	7,19
58,7	379	6,46	58,7	397	6,76	58,7	357	6,09
76,9	409	5,32	77	426	5,54	77	390	5,07
101	436	4,32	101	451	4,47	101	418	4,14
132	457	3,45	132	472	3,56	132	442	3,34
174	474	2,72	174	489	2,81	174	460	2,65
228	484	2,12	228	502	2,2	228	474	2,08
299	488	1,63	299	510	1,71	299	482	1,61
393	478	1,22	392	515	1,31	392	473	1,21
515	477	0,927	515	518	1,01	515	473	0,92
675	477	0,707	676	508	0,752	675	476	0,705
886	482	0,544	886	505	0,57	886	477	0,538
1 160	488	0,42	1 160	524	0,451	1 160	485	0,417
1 520	500	0,328	1 520	536	0,352	1 530	402	0,264
2 000	515	0,258	2 000	552	0,276	2 000	298	0,149
Coating formulation, 70 measuring points, shear rate decrease 2000 to 0 1/s								
1st test			**2nd test**			**3rd test**		
Shear Rate [1/s]	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Shear Rate [1/s]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Shear Rate [1/s]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**
2 000	515	0,257	2 000	544	0,272	2 000	301	0,151

1 970	514	0,261	1 970	524	0,266	1 970	289	0,147
1 940	513	0,264	1 940	535	0,275	1 940	284	0,146
1 910	512	0,268	1 910	540	0,282	1 910	281	0,147
1 880	512	0,272	1 880	543	0,288	1 880	283	0,15
1 860	511	0,276	1 860	546	0,294	1 860	280	0,151
1 830	510	0,279	1 830	548	0,3	1 830	281	0,154
1 800	508	0,283	1 800	551	0,306	1 800	279	0,155
1 770	508	0,287	1 770	544	0,307	1 770	278	0,157
1 740	507	0,292	1 740	523	0,301	1 740	276	0,159
1 710	507	0,296	1 710	525	0,307	1 710	276	0,162
1 680	506	0,301	1 680	530	0,315	1 680	277	0,165
1 650	506	0,306	1 650	533	0,322	1 650	281	0,17
1 620	505	0,311	1 620	535	0,33	1 620	283	0,174
1 590	505	0,317	1 590	538	0,337	1 590	283	0,178
1 570	504	0,322	1 570	540	0,345	1 570	283	0,181
1 540	504	0,328	1 540	541	0,352	1 540	283	0,184
1 510	503	0,334	1 510	541	0,359	1 510	284	0,188
1 480	503	0,34	1 480	538	0,364	1 480	283	0,192
1 450	502	0,347	1 450	522	0,36	1 450	283	0,196
1 420	502	0,353	1 420	467	0,328	1 420	283	0,199
1 390	502	0,361	1 390	358	0,257	1 390	282	0,203
1 360	500	0,367	1 360	295	0,217	1 360	281	0,207
1 330	498	0,373	1 330	243	0,182	1 330	281	0,211
1 300	498	0,382	1 310	213	0,163	1 300	281	0,215
1 280	497	0,39	1 280	203	0,159	1 280	281	0,22
1 250	496	0,398	1 250	186	0,149	1 250	282	0,226
1 220	495	0,407	1 220	186	0,153	1 220	282	0,232
1 190	495	0,416	1 190	201	0,169	1 190	283	0,238
1 160	492	0,424	1 160	277	0,24	1 160	283	0,244
1 130	495	0,438	1 130	265	0,235	1 130	284	0,251
1 100	494	0,448	1 100	270	0,245	1 100	285	0,259
1 070	491	0,458	1 070	272	0,253	1 070	284	0,265
1 040	492	0,471	1 040	284	0,272	1 040	284	0,272
1 010	493	0,486	1 010	292	0,288	1 010	285	0,281
985	491	0,498	986	299	0,303	985	285	0,289
957	491	0,513	957	299	0,313	957	285	0,298
928	490	0,529	927	303	0,326	927	286	0,309
899	488	0,543	899	304	0,338	899	286	0,319
870	488	0,561	870	304	0,35	870	287	0,33
841	487	0,58	840	311	0,37	841	285	0,338
812	485	0,598	812	308	0,379	811	282	0,347
782	485	0,62	782	315	0,403	782	288	0,369
754	486	0,645	753	321	0,426	754	288	0,383
725	486	0,67	725	322	0,444	725	288	0,397
696	482	0,693	696	325	0,467	696	287	0,413

667	481	0,721	667	329	0,493	667	288	0,431
638	484	0,759	638	361	0,566	638	288	0,452
609	488	0,802	609	331	0,543	609	289	0,475
580	487	0,84	580	340	0,586	580	290	0,501
551	486	0,883	551	342	0,621	551	292	0,53
522	486	0,932	522	343	0,657	522	294	0,564
493	487	0,988	493	345	0,7	493	296	0,601
464	489	1,05	464	344	0,741	464	297	0,641
435	490	1,13	435	344	0,791	435	298	0,685
406	490	1,21	406	343	0,846	406	301	0,741
377	489	1,3	376	350	0,929	377	304	0,807
348	487	1,4	348	345	0,991	348	306	0,88
319	486	1,52	319	345	1,08	319	307	0,962
290	484	1,67	290	344	1,19	290	306	1,06
261	481	1,84	261	343	1,32	261	304	1,17
232	477	2,06	232	352	1,52	232	302	1,3
203	472	2,33	203	361	1,78	203	299	1,47
174	465	2,67	174	363	2,09	174	294	1,69
145	455	3,14	145	358	2,47	145	286	1,98
116	440	3,79	116	346	2,98	116	275	2,37
87	415	4,77	87	325	3,74	87	256	2,95
58	368	6,34	58	286	4,94	58	221	3,82
29	272	9,36	29	210	7,25	29	154	5,31
1,02	49,3	48,4	0,737	34,3	46,5	0,38	19,6	51,6

Table 11: Data on coating formulation PU8551 + BGL75L

Coating formulation, 29 measuring points, shear rate from 0 to 2000 1/s								
1st test			**2nd test**			**3rd test**		
Shear Rate [1/s]	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Shear Rate [1/s]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Shear Rate [1/s]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**
0,9673	12,51	12,94	0,9097	17,47	19,21	0,8844	19,27	21,79
1,309	15,37	11,74	1,301	22,34	17,17	1,297	24,96	19,24
1,718	18,6	10,83	1,71	27,09	15,84	1,705	30,14	17,68
2,255	22,52	9,988	2,246	32,82	14,62	2,242	36,41	16,24
2,96	27,23	9,198	2,951	39,74	13,47	2,946	43,92	14,91
3,884	32,84	8,454	3,876	47,96	12,37	3,871	52,85	13,65
5,099	39,43	7,734	5,088	57,72	11,34	5,084	63,45	12,48
6,691	47,09	7,037	6,681	69,18	10,36	6,676	75,8	11,35
8,78	55,93	6,37	8,766	82,53	9,415	8,765	90,12	10,28
11,52	65,81	5,712	11,5	97,93	8,516	11,5	106,4	9,248
15,1	77,18	5,112	15,1	115,2	7,63	15,1	124,6	8,25
19,78	91,2	4,61	19,81	133,8	6,752	19,82	144,1	7,271
25,94	108,5	4,185	25,99	153,7	5,914	25,98	165,6	6,377
34,02	128,7	3,784	34,09	175,6	5,151	34,1	188,6	5,532
44,65	151,2	3,386	44,73	197,1	4,406	44,71	212,1	4,745
58,59	170,7	2,912	58,7	219,4	3,738	58,67	235,9	4,021
76,85	193,8	2,521	76,99	240,8	3,128	76,98	259,5	3,371
100,9	219,6	2,176	101	261,5	2,59	101	282,3	2,796
132,4	241,1	1,821	132,5	282,1	2,13	132,5	304,2	2,297
173,7	262,9	1,513	173,8	302,3	1,739	173,8	326,5	1,879
228	284,8	1,249	228	321,2	1,409	228	348,7	1,529
299	305,9	1,023	299,1	340,5	1,139	299,1	369,4	1,235
392,3	326,1	0,8313	392,3	360,1	0,9179	392,4	392,3	0,9998
514,7	347,5	0,6752	514,7	381	0,7403	514,7	416,4	0,8089
675,2	370,8	0,5492	675,2	404,7	0,5994	675,3	442,4	0,6552
885,8	397,3	0,4485	885,8	432,2	0,4879	885,8	473,7	0,5348
1 162	428,2	0,3685	1 162	465,4	0,4005	1 162	510,4	0,4392
1 524	465,7	0,3055	1 524	506,2	0,3321	1 525	552,5	0,3624
2 000	512	0,256	2 000	556,7	0,2783	2 000	601,9	0,301
Coating formulation, 70 measuring points, shear rate from 2000 to 0 1/s								
1st test			**2nd test**			**3rd test**		
Shear Rate [1/s]	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Shear Rate [1/s]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Shear Rate [1/s]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**
2 000	511,9	0,2559	2 000	555,6	0,2778	2 000	599,9	0,2999
1 971	509,2	0,2584	1 971	552	0,2801	1 971	597,3	0,3031
1 942	506,7	0,2609	1 942	548,7	0,2825	1 942	595,3	0,3065
1 913	504,3	0,2636	1 913	545,7	0,2852	1 913	592,3	0,3096
1 884	501,9	0,2664	1 884	542,3	0,2878	1 884	589,8	0,3131
1 855	499,4	0,2692	1 855	539,1	0,2906	1 855	586,4	0,3161

1 826	496,9	0,2721	1 826	536,4	0,2937	1 826	583,8	0,3197
1 797	494,5	0,2752	1 797	533	0,2966	1 797	580,8	0,3232
1 768	492	0,2783	1 768	529,7	0,2996	1 768	577,7	0,3267
1 739	489,5	0,2815	1 739	526,9	0,3029	1 739	574,6	0,3304
1 710	487,1	0,2848	1 710	523,8	0,3063	1 710	571,5	0,3342
1 681	484,6	0,2883	1 681	521,1	0,3099	1 681	568,4	0,3381
1 652	482,2	0,2919	1 652	518,4	0,3138	1 652	565,3	0,3421
1 623	479,7	0,2955	1 623	515,8	0,3178	1 623	562,2	0,3463
1 594	477,2	0,2993	1 594	513	0,3218	1 594	559,2	0,3507
1 565	474,7	0,3033	1 565	510,2	0,326	1 565	556,1	0,3553
1 536	472,1	0,3073	1 536	507,4	0,3303	1 536	553	0,36
1 507	469,6	0,3115	1 507	504,6	0,3348	1 507	550	0,3649
1 478	467	0,3159	1 478	501,8	0,3394	1 478	546,8	0,3699
1 449	464,5	0,3205	1 449	499	0,3443	1 449	543,7	0,3752
1 420	461,8	0,3252	1 420	496,1	0,3493	1 420	540,5	0,3806
1 391	459,2	0,3301	1 391	493,3	0,3545	1 391	537,5	0,3863
1 362	456,6	0,3352	1 362	490,5	0,36	1 362	534,3	0,3922
1 333	454	0,3405	1 333	487,7	0,3657	1 333	531,1	0,3983
1 304	451,2	0,3459	1 304	484,8	0,3717	1 304	527,7	0,4046
1 275	448,6	0,3517	1 275	482	0,3779	1 275	524,5	0,4113
1 246	445,9	0,3578	1 246	479,1	0,3844	1 246	521,4	0,4183
1 217	443,2	0,3641	1 217	476,2	0,3912	1 217	517,9	0,4255
1 188	440,4	0,3706	1 188	473,3	0,3983	1 188	514,8	0,4332
1 159	437,7	0,3775	1 159	470,4	0,4057	1 159	511,3	0,441
1 130	434,9	0,3847	1 130	467,4	0,4135	1 130	508,1	0,4494
1 101	432,1	0,3923	1 101	464,4	0,4216	1 101	504,5	0,458
1 072	429,2	0,4002	1 072	461,4	0,4302	1 073	501,2	0,4673
1 043	426,3	0,4086	1 043	458,3	0,4392	1 043	497,7	0,4769
1 015	423,4	0,4174	1 014	455,3	0,4488	1 014	494,3	0,4873
985,5	420,5	0,4267	985,5	452,1	0,4588	985,5	490,7	0,4979
956,5	417,5	0,4365	956,5	449	0,4694	956,5	487,2	0,5094
927,5	414,5	0,4469	927,6	445,8	0,4807	927,5	483,6	0,5214
898,6	411,4	0,4579	898,6	442,6	0,4926	898,6	479,8	0,534
869,6	408,3	0,4696	869,6	439,4	0,5053	869,6	476,2	0,5476
840,6	405,2	0,482	840,6	436,1	0,5188	840,6	472,4	0,5619
811,6	402	0,4953	811,6	432,7	0,5331	811,6	468,5	0,5772
782,6	398,8	0,5095	782,6	429,3	0,5485	782,6	464,5	0,5936
753,6	395,5	0,5247	753,6	425,8	0,565	753,6	460,6	0,6112
724,7	392,1	0,5411	724,6	422,2	0,5827	724,7	456,6	0,6301
695,7	388,6	0,5587	695,7	418,6	0,6018	695,7	452,4	0,6503
666,7	385,1	0,5777	666,7	414,9	0,6223	666,6	448,3	0,6725
637,7	381,5	0,5983	637,7	411,1	0,6447	637,7	444	0,6962
608,7	377,8	0,6207	608,7	407,2	0,669	608,7	439,4	0,7219
579,7	374	0,6452	579,7	403,1	0,6954	579,7	434,9	0,7502
550,7	370,1	0,6721	550,7	399	0,7245	550,7	430,3	0,7813

521,7	366,1	0,7017	521,7	394,8	0,7567	521,8	425,5	0,8154
492,8	361,9	0,7344	492,7	390,2	0,7919	492,8	420,3	0,853
463,8	357,6	0,771	463,8	385,5	0,8312	463,8	415,3	0,8954
434,8	353	0,8118	434,8	380,7	0,8757	434,8	409,7	0,9424
405,8	348,1	0,8579	405,8	375,7	0,9258	405,8	403,9	0,9954
376,8	343,1	0,9104	376,8	370,1	0,9823	376,8	397,8	1,056
347,8	337,6	0,9706	347,8	364,2	1,047	347,8	391,3	1,125
318,8	331,7	1,04	318,8	357,8	1,122	318,8	384,4	1,206
289,9	325,4	1,122	289,8	351	1,211	289,9	376,6	1,299
260,9	318,3	1,22	260,9	343,5	1,317	260,9	368,1	1,411
231,9	310,4	1,339	231,9	334,9	1,444	231,9	358,8	1,547
202,9	301,3	1,485	202,9	325,2	1,602	202,9	347,9	1,715
173,9	290,6	1,671	173,9	313,8	1,804	173,9	335,5	1,929
144,9	277,8	1,917	144,9	299,8	2,068	144,9	320,3	2,21
115,9	261,7	2,257	115,9	282,1	2,433	115,9	301,3	2,599
86,96	240,1	2,761	86,95	258,6	2,974	86,93	276,4	3,18
57,97	208,6	3,598	57,97	224,8	3,877	57,94	240,3	4,147
28,97	154,1	5,318	28,98	167,3	5,775	28,99	178,9	6,17
0,3431	7,953	23,18	0,4188	10,65	25,43	0,4855	13,19	27,17

Appendix II

Data on viscosity and surface tension in ink characterisation.

Table 12: Viscosity as a function of shear rate for non-stabilised and chemically stabilised Ruby Red

Ruby Red 100 measuring points, share rate from 0.1 to 10 000 1/s			**Ruby Red 0.05 wt% HALS 100 measuring points, shear rate from 0.1 to 10 000 1/s**		
Shear Rate [1/s]	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Shear Rate [1/s]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**
0,1	0,0106	0,106	0,1	0,0101	0,101
101	1,17	0,0116	101	1,21	0,0119
202	2,33	0,0115	202	2,41	0,0119
303	3,49	0,0115	303	3,61	0,0119
404	4,66	0,0115	404	4,81	0,0119
505	5,81	0,0115	505	6,01	0,0119
606	6,97	0,0115	606	7,21	0,0119
707	8,13	0,0115	707	8,41	0,0119
808	9,3	0,0115	808	9,62	0,0119
909	10,5	0,0115	909	10,8	0,0119
1 010	11,6	0,0115	1 010	12	0,0119
1 110	12,8	0,0115	1 110	13,2	0,0119
1 210	14	0,0115	1 210	14,4	0,0119
1 310	15,1	0,0115	1 310	15,7	0,0119
1 410	16,3	0,0115	1 410	16,9	0,0119
1 520	17,5	0,0115	1 520	18,1	0,0119
1 620	18,6	0,0115	1 620	19,3	0,0119
1 720	19,8	0,0115	1 720	20,5	0,0119
1 820	20,9	0,0115	1 820	21,7	0,0119
1 920	22,1	0,0115	1 920	22,9	0,0119
2 020	23,3	0,0115	2 020	24,1	0,0119
2 120	24,4	0,0115	2 120	25,3	0,0119
2 220	25,6	0,0115	2 220	26,5	0,0119
2 320	26,8	0,0115	2 320	27,7	0,0119
2 420	27,9	0,0115	2 420	28,9	0,0119
2 530	29,1	0,0115	2 530	30,1	0,0119
2 630	30,3	0,0115	2 630	31,4	0,0119
2 730	31,5	0,0115	2 730	32,6	0,0119
2 830	32,6	0,0115	2 830	33,8	0,0119
2 930	33,8	0,0115	2 930	35	0,0119
3 030	35	0,0115	3 030	36,2	0,0119
3 130	36,1	0,0115	3 130	37,4	0,012
3 230	37,3	0,0115	3 230	38,6	0,012
3 330	38,5	0,0115	3 330	39,9	0,012
3 430	39,7	0,0115	3 430	41,1	0,012
3 540	40,8	0,0115	3 540	42,3	0,012
3 640	42	0,0115	3 640	43,5	0,012

3 740	43,2	0,0115	3 740	44,7	0,012
3 840	44,3	0,0115	3 840	45,9	0,012
3 940	45,5	0,0115	3 940	47,1	0,012
4 040	46,7	0,0115	4 040	48,3	0,012
4 140	47,8	0,0115	4 140	49,5	0,012
4 240	49	0,0115	4 240	50,7	0,012
4 340	50,1	0,0115	4 340	51,9	0,012
4 440	51,3	0,0115	4 440	53,1	0,012
4 550	52,4	0,0115	4 550	54,3	0,012
4 650	53,6	0,0115	4 650	55,5	0,0119
4 750	54,7	0,0115	4 750	56,7	0,0119
4 850	55,9	0,0115	4 850	57,9	0,0119
4 950	57	0,0115	4 950	59,1	0,0119
5 050	58,2	0,0115	5 050	60,3	0,0119
5 150	59,3	0,0115	5 150	61,5	0,0119
5 250	60,5	0,0115	5 250	62,7	0,0119
5 350	61,6	0,0115	5 350	63,8	0,0119
5 450	62,7	0,0115	5 450	65	0,0119
5 560	63,9	0,0115	5 560	66,2	0,0119
5 660	65	0,0115	5 660	67,4	0,0119
5 760	66,1	0,0115	5 760	68,5	0,0119
5 860	67,3	0,0115	5 860	69,7	0,0119
5 960	68,4	0,0115	5 960	70,9	0,0119
6 060	69,5	0,0115	6 060	72	0,0119
6 160	70,7	0,0115	6 160	73,2	0,0119
6 260	71,8	0,0115	6 260	74,4	0,0119
6 360	72,9	0,0115	6 360	75,5	0,0119
6 460	74	0,0115	6 460	76,7	0,0119
6 570	75,1	0,0114	6 570	77,8	0,0119
6 670	76,2	0,0114	6 670	79	0,0118
6 770	77,4	0,0114	6 770	80,1	0,0118
6 870	78,5	0,0114	6 870	81,2	0,0118
6 970	79,6	0,0114	6 970	82,4	0,0118
7 070	80,7	0,0114	7 070	83,5	0,0118
7 170	81,8	0,0114	7 170	84,6	0,0118
7 270	82,9	0,0114	7 270	85,8	0,0118
7 370	83,9	0,0114	7 370	86,9	0,0118
7 470	85	0,0114	7 470	88	0,0118
7 580	86,1	0,0114	7 580	89,1	0,0118
7 680	87,2	0,0114	7 680	90,2	0,0118
7 780	88,3	0,0113	7 780	91,3	0,0117
7 880	89,3	0,0113	7 880	92,4	0,0117
7 980	90,4	0,0113	7 980	93,5	0,0117
8 080	91,4	0,0113	8 080	94,6	0,0117
8 180	92,5	0,0113	8 180	95,7	0,0117

8 280	93,5	0,0113	8 280	96,8	0,0117
8 380	94,6	0,0113	8 380	97,9	0,0117
8 480	95,6	0,0113	8 480	98,9	0,0117
8 590	96,7	0,0113	8 590	100	0,0116
8 690	97,7	0,0112	8 690	101	0,0116
8 790	98,7	0,0112	8 790	102	0,0116
8 890	99,7	0,0112	8 890	103	0,0116
8 990	101	0,0112	8 990	104	0,0116
9 090	102	0,0112	9 090	105	0,0116
9 190	103	0,0112	9 190	106	0,0116
9 290	104	0,0112	9 290	107	0,0115
9 390	105	0,0112	9 390	108	0,0115
9 490	106	0,0111	9 490	109	0,0115
9 600	107	0,0111	9 600	110	0,0115
9 700	108	0,0111	9 700	111	0,0115
9 800	109	0,0111	9 800	112	0,0115
9 900	110	0,0111	9 900	113	0,0115
10 000	111	0,0111	10 000	115	0,0115

Table 13: Viscosity as a function of temperature for non-stabilised and chemically stabilised Ruby Red

Ruby Red 20 measuring points, temperature from 17.3 to 38.6 °C			**Ruby Red 0.05 wt% HALS 20 measuring points, temperature from 17.4 to 38.9 °C**		
Temperature [°C]	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Temperature [°C]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**
17,3	104	0,0104	17,4	104	0,0104
17	105	0,0105	17,1	105	0,0105
18	105	0,0105	18	106	0,0106
19,5	106	0,0106	19,6	107	0,0107
20,7	106	0,0106	20,8	107	0,0107
21,8	106	0,0106	21,7	107	0,0107
23,1	106	0,0106	23	107	0,0107
24,4	106	0,0106	24,4	106	0,0106
25,6	106	0,0106	25,6	106	0,0106
26,8	107	0,0107	26,9	106	0,0106
28,2	107	0,0107	28,2	107	0,0107
29,5	105	0,0105	29,6	106	0,0106
30,8	104	0,0104	30,8	104	0,0104
32,1	103	0,0103	32	103	0,0103
33,6	101	0,0101	33,5	102	0,0102
34,7	99,6	0,00996	34,8	101	0,0101
35,9	97,9	0,00979	36	98,7	0,00987
37,2	96	0,0096	37,3	97,3	0,00973
38,1	94,1	0,00941	38,3	95,1	0,00951

38,6	92,4	0,00924	38,9	93,3	0,00933

Table 14: Viscosity as a function of shear rate for non-stabilised and chemically stabilised Oxford Blue

Oxford Blue 100 measuring points, share rate from 0.1 to 10 000 1/s			**Oxford Blue 0.05 wt% HALS 100 measuring points, shear rate from 0.1 to 10 000 1/s**		
Shear Rate [1/s]	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Shear Rate [1/s]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**
0,1	0,0115	0,115	0,1	0,0101	0,101
101	1,47	0,0146	101	1,48	0,0147
202	2,95	0,0146	202	2,96	0,0147
303	4,42	0,0146	303	4,45	0,0147
404	5,9	0,0146	404	5,93	0,0147
505	7,37	0,0146	505	7,42	0,0147
606	8,85	0,0146	606	8,91	0,0147
707	10,3	0,0146	707	10,4	0,0147
808	11,8	0,0146	808	11,9	0,0147
909	13,3	0,0146	909	13,4	0,0147
1 010	14,8	0,0146	1 010	14,9	0,0147
1 110	16,2	0,0146	1 110	16,4	0,0147
1 210	17,7	0,0146	1 210	17,9	0,0147
1 310	19,2	0,0146	1 310	19,4	0,0147
1 410	20,7	0,0147	1 410	20,9	0,0148
1 520	22,2	0,0147	1 520	22,4	0,0148
1 620	23,7	0,0147	1 620	23,9	0,0148
1 720	25,2	0,0147	1 720	25,4	0,0148
1 820	26,7	0,0147	1 820	26,9	0,0148
1 920	28,1	0,0147	1 920	28,4	0,0148
2 020	29,6	0,0147	2 020	29,9	0,0148
2 120	31,1	0,0147	2 120	31,4	0,0148
2 220	32,7	0,0147	2 220	32,9	0,0148
2 320	34,2	0,0147	2 320	34,4	0,0148
2 420	35,7	0,0147	2 420	35,9	0,0148
2 530	37,1	0,0147	2 530	37,3	0,0148
2 630	38,6	0,0147	2 630	38,8	0,0148
2 730	40,1	0,0147	2 730	40,3	0,0148
2 830	41,6	0,0147	2 830	41,8	0,0148
2 930	43,1	0,0147	2 930	43,3	0,0148
3 030	44,6	0,0147	3 030	44,8	0,0148
3 130	46,1	0,0147	3 130	46,3	0,0148
3 230	47,6	0,0147	3 230	47,8	0,0148
3 330	49,1	0,0147	3 330	49,3	0,0148
3 430	50,5	0,0147	3 430	50,8	0,0148
3 540	52	0,0147	3 540	52,3	0,0148
3 640	53,5	0,0147	3 640	53,8	0,0148

3 740	54,9	0,0147	3 740	55,3	0,0148
3 840	56,4	0,0147	3 840	56,7	0,0148
3 940	57,8	0,0147	3 940	58,2	0,0148
4 040	59,3	0,0147	4 040	59,7	0,0148
4 140	60,8	0,0147	4 140	61,1	0,0148
4 240	62,2	0,0147	4 240	62,6	0,0148
4 340	63,7	0,0147	4 340	64	0,0147
4 440	65,1	0,0147	4 440	65,5	0,0147
4 550	66,5	0,0146	4 550	66,9	0,0147
4 650	68	0,0146	4 650	68,4	0,0147
4 750	69,4	0,0146	4 750	69,9	0,0147
4 850	70,9	0,0146	4 850	71,3	0,0147
4 950	72,3	0,0146	4 950	72,7	0,0147
5 050	73,7	0,0146	5 050	74,1	0,0147
5 150	75,1	0,0146	5 150	75,6	0,0147
5 250	76,5	0,0146	5 250	77	0,0147
5 350	77,9	0,0146	5 350	78,4	0,0146
5 450	79,4	0,0146	5 450	79,8	0,0146
5 560	80,8	0,0145	5 560	81,2	0,0146
5 660	82,2	0,0145	5 660	82,6	0,0146
5 760	83,6	0,0145	5 760	84	0,0146
5 860	84,9	0,0145	5 860	85,4	0,0146
5 960	86,3	0,0145	5 960	86,8	0,0146
6 060	87,7	0,0145	6 060	88,2	0,0145
6 160	89,1	0,0145	6 160	89,6	0,0145
6 260	90,5	0,0144	6 260	91	0,0145
6 360	91,8	0,0144	6 360	92,3	0,0145
6 460	93,2	0,0144	6 460	93,7	0,0145
6 570	94,6	0,0144	6 570	95	0,0145
6 670	95,9	0,0144	6 670	96,4	0,0145
6 770	97,3	0,0144	6 770	97,7	0,0144
6 870	98,6	0,0144	6 870	99,1	0,0144
6 970	100	0,0143	6 970	100	0,0144
7 070	101	0,0143	7 070	102	0,0144
7 170	103	0,0143	7 170	103	0,0144
7 270	104	0,0143	7 270	104	0,0143
7 370	105	0,0143	7 370	106	0,0143
7 470	107	0,0143	7 470	107	0,0143
7 580	108	0,0142	7 580	108	0,0143
7 680	109	0,0142	7 680	110	0,0143
7 780	110	0,0142	7 780	111	0,0143
7 880	112	0,0142	7 880	112	0,0142
7 980	113	0,0141	7 980	113	0,0142
8 080	114	0,0141	8 080	115	0,0142
8 180	115	0,0141	8 180	116	0,0142

8 280	117	0,0141	8 280	117	0,0141
8 380	118	0,0141	8 380	118	0,0141
8 480	119	0,014	8 480	120	0,0141
8 590	120	0,014	8 590	121	0,0141
8 690	121	0,014	8 690	122	0,0141
8 790	123	0,014	8 790	123	0,014
8 890	124	0,0139	8 890	124	0,014
8 990	125	0,0139	8 990	126	0,014
9 090	126	0,0139	9 090	127	0,014
9 190	127	0,0139	9 190	128	0,0139
9 290	129	0,0138	9 290	129	0,0139
9 390	130	0,0139	9 390	130	0,0139
9 490	131	0,0138	9 490	132	0,0139
9 600	132	0,0138	9 600	133	0,0138
9 700	133	0,0137	9 700	134	0,0138
9 800	134	0,0137	9 800	135	0,0138
9 900	136	0,0137	9 900	136	0,0137
10 000	137	0,0137	10 000	137	0,0137

Table 15: Viscosity as a function of temperature for non-stabilised and chemically stabilised Oxford Blue

Oxford Blue 20 measuring points, temperature from 17.3 to 39.6°C			**Oxford Blue 0.05 wt% HALS 20 measuring points, temperature from 17.4 to 49.6°C**		
Temperature [°C]	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Temperature [°C]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**
17,3	115	0,0115	17,4	115	0,0115
17,1	117	0,0117	17,1	118	0,0118
18,1	120	0,012	18,1	120	0,012
19,7	121	0,0121	19,7	122	0,0122
20,8	122	0,0122	20,8	122	0,0122
21,8	122	0,0122	21,7	123	0,0123
23,0	121	0,0121	23,1	122	0,0122
24,3	120	0,012	24,5	121	0,0121
25,6	119	0,0119	25,6	120	0,012
26,9	117	0,0117	26,9	118	0,0118
28,2	115	0,0115	28,3	116	0,0116
29,5	113	0,0113	29,5	113	0,0113
30,9	110	0,011	30,7	111	0,0111
32,1	108	0,0108	32,2	109	0,0109
33,4	108	0,0108	33,5	108	0,0108
34,8	108	0,0108	34,7	108	0,0108
36,1	106	0,0106	36,1	106	0,0106
37,4	104	0,0104	37,5	105	0,0105
38,6	103	0,0103	38,6	103	0,0103

39,6	102	0,0102	39,6	102	0,0102

Table 16: Viscosity as a function of shear rate for non-stabilised and chemically stabilised spirooxazine

Spirooxazine 100 measuring points, share rate from 0.1 to 10 000 1/s			**Spirooxazine 0.05 wt% HALS 100 measuring points, shear rate from 0.1 to 10 000 1/s**		
Shear Rate [1/s]	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Shear Rate [1/s]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**
0,1	-0,00869	-0,0869	0,1	0,0105	0,105
101	1,46	0,0144	101	1,45	0,0144
202	2,91	0,0144	202	2,91	0,0144
303	4,36	0,0144	303	4,37	0,0144
404	5,81	0,0144	404	5,83	0,0144
505	7,27	0,0144	505	7,28	0,0144
606	8,73	0,0144	606	8,74	0,0144
707	10,2	0,0144	707	10,2	0,0144
808	11,6	0,0144	808	11,7	0,0144
909	13,1	0,0144	909	13,1	0,0144
1 010	14,6	0,0144	1 010	14,6	0,0145
1 110	16	0,0144	1 110	16,1	0,0145
1 210	17,5	0,0144	1 210	17,5	0,0145
1 310	19	0,0144	1 310	19	0,0145
1 410	20,4	0,0144	1 410	20,5	0,0145
1 520	21,9	0,0144	1 520	21,9	0,0145
1 620	23,4	0,0145	1 620	23,4	0,0145
1 720	24,8	0,0145	1 720	24,9	0,0145
1 820	26,3	0,0145	1 820	26,4	0,0145
1 920	27,8	0,0145	1 920	27,8	0,0145
2 020	29,2	0,0145	2 020	29,3	0,0145
2 120	30,7	0,0145	2 120	30,8	0,0145
2 220	32,2	0,0145	2 220	32,2	0,0145
2 320	33,6	0,0145	2 320	33,7	0,0145
2 420	35,1	0,0145	2 420	35,2	0,0145
2 530	36,6	0,0145	2 530	36,6	0,0145
2 630	38	0,0145	2 630	38,1	0,0145
2 730	39,5	0,0145	2 730	39,6	0,0145
2 830	40,9	0,0145	2 830	41,1	0,0145
2 930	42,4	0,0145	2 930	42,5	0,0145
3 030	43,9	0,0145	3 030	44	0,0145
3 130	45,3	0,0145	3 130	45,5	0,0145
3 230	46,8	0,0145	3 230	46,9	0,0145
3 330	48,3	0,0145	3 330	48,4	0,0145
3 430	49,7	0,0145	3 430	49,9	0,0145
3 540	51,2	0,0145	3 540	51,4	0,0145
3 640	52,6	0,0145	3 640	52,9	0,0145

3 740	54,1	0,0145	3 740	54,3	0,0145
3 840	55,6	0,0145	3 840	55,8	0,0145
3 940	57	0,0145	3 940	57,3	0,0145
4 040	58,5	0,0145	4 040	58,7	0,0145
4 140	59,9	0,0145	4 140	60,2	0,0145
4 240	61,4	0,0145	4 240	61,6	0,0145
4 340	62,8	0,0145	4 340	63,1	0,0145
4 440	64,2	0,0145	4 440	64,5	0,0145
4 550	65,7	0,0144	4 550	66	0,0145
4 650	67,1	0,0144	4 650	67,4	0,0145
4 750	68,5	0,0144	4 750	68,8	0,0145
4 850	69,9	0,0144	4 850	70,3	0,0145
4 950	71,4	0,0144	4 950	71,7	0,0145
5 050	72,8	0,0144	5 050	73,1	0,0145
5 150	74,2	0,0144	5 150	74,5	0,0145
5 250	75,6	0,0144	5 250	76	0,0145
5 350	77	0,0144	5 350	77,4	0,0145
5 450	78,4	0,0144	5 450	78,8	0,0144
5 560	79,8	0,0144	5 560	80,2	0,0144
5 660	81,2	0,0144	5 660	81,6	0,0144
5 760	82,6	0,0143	5 760	83	0,0144
5 860	83,9	0,0143	5 860	84,3	0,0144
5 960	85,3	0,0143	5 960	85,7	0,0144
6 060	86,7	0,0143	6 060	87,1	0,0144
6 160	88	0,0143	6 160	88,4	0,0144
6 260	89,4	0,0143	6 260	89,8	0,0143
6 360	90,8	0,0143	6 360	91,1	0,0143
6 460	92,1	0,0143	6 460	92,5	0,0143
6 570	93,5	0,0142	6 570	93,8	0,0143
6 670	94,8	0,0142	6 670	95,2	0,0143
6 770	96,1	0,0142	6 770	96,5	0,0143
6 870	97,5	0,0142	6 870	97,9	0,0142
6 970	98,8	0,0142	6 970	99,2	0,0142
7 070	100	0,0142	7 070	100	0,0142
7 170	101	0,0141	7 170	102	0,0142
7 270	103	0,0141	7 270	103	0,0142
7 370	104	0,0141	7 370	104	0,0142
7 470	105	0,0141	7 470	106	0,0141
7 580	107	0,0141	7 580	107	0,0141
7 680	108	0,0141	7 680	108	0,0141
7 780	109	0,014	7 780	110	0,0141
7 880	110	0,014	7 880	111	0,0141
7 980	112	0,014	7 980	112	0,014
8 080	113	0,014	8 080	113	0,014
8 180	114	0,014	8 180	115	0,014

8 280	115	0,0139	8 280	116	0,014
8 380	117	0,0139	8 380	117	0,014
8 480	118	0,0139	8 480	118	0,0139
8 590	119	0,0139	8 590	120	0,0139
8 690	120	0,0139	8 690	121	0,0139
8 790	122	0,0138	8 790	122	0,0139
8 890	123	0,0138	8 890	123	0,0139
8 990	124	0,0138	8 990	124	0,0138
9 090	125	0,0138	9 090	126	0,0138
9 190	126	0,0137	9 190	127	0,0138
9 290	128	0,0137	9 290	128	0,0138
9 390	129	0,0137	9 390	129	0,0137
9 490	130	0,0137	9 490	130	0,0137
9 600	131	0,0137	9 600	131	0,0137
9 700	132	0,0136	9 700	133	0,0137
9 800	133	0,0136	9 800	134	0,0136
9 900	134	0,0136	9 900	135	0,0136
10 000	135	0,0135	10 000	136	0,0136

Table 17: Viscosity as a function of temperature for non-stabilised and chemically stabilised spirooxazine

Spirooxazine 20 measuring points, temperature from 17.2 to 35.7 °C			**Spirooxazine 0.05 wt% HALS 20 measuring points, temperature from 17.3 to 39.7 °C**		
Temperature [°C]	**Shear Stress [Pa]**	**Viscosity [Pa·s]**	**Temperature [°C]**	**Shear Stress [Pa]**	**Viscosity [Pa·s]**
17,2	116	0,0116	17,3	115	0,0115
17,0	118	0,0118	17,1	117	0,0117
18,0	121	0,0121	18,1	120	0,012
19,6	122	0,0122	19,7	121	0,0121
20,7	123	0,0123	20,7	122	0,0122
21,7	123	0,0123	21,7	122	0,0122
23,1	122	0,0122	23,1	121	0,0121
24,3	121	0,0121	24,5	120	0,012
25,5	120	0,012	25,6	119	0,0119
26,8	118	0,0118	26,9	117	0,0117
28,3	116	0,0116	28,3	115	0,0115
29,5	113	0,0113	29,5	112	0,0112
30,8	111	0,0111	30,7	110	0,011
32,2	109	0,0109	32,2	108	0,0108
33,5	108	0,0108	33,5	108	0,0108
34,6	109	0,0109	34,7	108	0,0108
35,9	106	0,0106	36,1	106	0,0106
37,0	105	0,0105	37,5	105	0,0105
37,5	104	0,0104	38,6	103	0,0103

35,7	102	0,0102	39,7	101	0,0101

Table 18: Surface tension data for non-stabilised Ruby Red, 3 repetitions of test

Ruby Red, time 0-10 s						
Time [s]	**1st test**		**2nd test**		**3rd test**	
	ST [mN/m]	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**
0	30,08	6,2	29,76	5,5	29,83	5,46
0,08	30,41	5,86	29,51	5,48	29,93	5,46
0,17	29,79	5,81	29,72	5,47	29,57	5,46
0,25	30,03	5,8	29,78	5,48	29,85	5,43
0,33	29,91	5,81	29,79	5,47	29,7	5,46
0,42	30,01	5,83	29,8	5,5	29,76	5,43
0,5	29,82	5,82	29,65	5,47	29,6	5,46
0,58	29,86	5,83	29,6	5,49	29,79	5,45
0,67	30,17	5,82	29,79	5,5	29,4	5,46
0,75	30,26	5,81	29,84	5,48	29,96	5,43
0,83	30,08	5,8	29,93	5,47	29,77	5,45
0,92	30,16	5,8	29,95	5,47	29,69	5,46
1	29,82	5,8	29,83	5,5	29,6	5,46
1,08	29,93	5,74	29,93	5,47	29,61	5,43
1,17	29,55	5,61	29,69	5,5	29,67	5,43
1,25	30,12	5,56	29,84	5,5	29,66	5,43
1,33	29,86	5,55	29,71	5,47	29,76	5,46
1,42	29,83	5,55	29,89	5,47	29,9	5,46
1,5	29,78	5,55	29,85	5,47	29,6	5,43
1,58	29,63	5,55	29,61	5,47	29,62	5,46
1,67	29,84	5,55	29,74	5,5	29,54	5,46
1,75	29,92	5,54	29,82	5,49	29,74	5,44
1,83	29,93	5,55	29,73	5,49	29,63	5,44
1,92	29,97	5,55	29,87	5,49	29,75	5,44
2	29,76	5,55	29,88	5,47	29,81	5,41
2,08	30,04	5,55	29,88	5,47	29,85	5,46
2,16	29,86	5,55	29,89	5,47	29,73	5,43
2,25	29,91	5,56	29,92	5,5	29,97	5,43
2,33	29,95	5,56	29,81	5,47	29,63	5,46
2,41	29,79	5,56	29,68	5,47	29,93	5,43
2,5	29,78	5,56	29,91	5,47	29,71	5,43
2,58	30,11	5,55	29,72	5,5	29,54	5,43
2,66	29,74	5,56	29,84	5,5	29,7	5,43
2,75	29,97	5,56	29,86	5,47	29,71	5,43
2,83	29,67	5,56	29,82	5,47	29,8	5,43
2,91	29,68	5,56	29,69	5,47	29,77	5,43
3	30,13	5,55	29,9	5,47	29,72	5,46
3,08	29,68	5,56	30,02	5,47	29,6	5,43
3,16	29,95	5,56	29,8	5,47	29,74	5,43

3,25	29,79	5,56	29,81	5,47	29,46	5,43
3,33	29,85	5,56	29,7	5,47	29,67	5,43
3,41	29,73	5,57	29,78	5,47	29,66	5,46
3,5	29,95	5,56	29,8	5,47	29,79	5,44
3,58	29,8	5,57	29,82	5,49	29,81	5,46
3,66	29,95	5,57	29,86	5,46	29,71	5,46
3,75	29,89	5,57	29,82	5,49	29,66	5,43
3,83	29,75	5,57	29,8	5,44	29,69	5,45
3,91	29,88	5,57	29,94	5,47	29,58	5,43
4	29,69	5,57	29,71	5,49	29,69	5,43
4,08	29,92	5,57	29,82	5,47	29,57	5,46
4,16	29,82	5,57	29,88	5,49	29,64	5,45
4,25	29,67	5,57	29,74	5,49	29,9	5,43
4,33	29,81	5,57	29,66	5,46	29,57	5,43
4,41	29,76	5,57	29,61	5,49	29,69	5,43
4,5	29,78	5,57	29,81	5,47	29,73	5,43
4,58	29,85	5,57	29,74	5,46	29,56	5,45
4,66	29,75	5,57	29,89	5,49	29,66	5,43
4,75	29,82	5,57	29,84	5,49	29,88	5,43
4,83	29,68	5,57	29,77	5,49	29,75	5,43
4,91	29,92	5,57	29,92	5,49	29,71	5,43
5	29,67	5,57	29,62	5,46	29,73	5,43
5,08	29,94	5,57	29,72	5,46	29,64	5,45
5,16	29,93	5,58	29,69	5,46	29,72	5,45
5,25	29,88	5,57	29,95	5,47	29,76	5,43
5,33	29,95	5,57	29,96	5,49	29,57	5,43
5,41	29,77	5,57	29,81	5,46	29,64	5,45
5,5	30,11	5,57	29,78	5,46	29,64	5,43
5,58	29,87	5,57	29,85	5,46	29,68	5,43
5,66	30,1	5,57	29,85	5,48	29,65	5,45
5,75	29,73	5,57	30,02	5,48	29,81	5,46
5,83	30,05	5,57	29,66	5,46	29,7	5,45
5,91	29,75	5,57	29,87	5,46	29,64	5,45
6	29,79	5,57	29,69	5,46	29,9	5,43
6,08	29,91	5,57	29,72	5,46	29,83	5,45
6,16	29,79	5,57	29,88	5,48	29,71	5,45
6,25	29,89	5,57	29,58	5,46	29,81	5,42
6,33	29,9	5,57	29,81	5,45	29,69	5,45
6,41	29,75	5,57	29,91	5,49	29,9	5,45
6,5	29,83	5,57	29,75	5,48	29,59	5,43
6,58	29,75	5,57	29,92	5,46	29,74	5,43
6,66	29,86	5,57	29,69	5,48	29,74	5,45
6,75	29,67	5,57	30,04	5,45	29,57	5,42
6,83	29,79	5,57	29,72	5,46	29,85	5,42
6,91	29,74	5,57	29,87	5,45	29,62	5,45

7	29,75	5,57	29,65	5,48	29,92	5,42
7,08	29,87	5,57	29,88	5,48	29,71	5,44
7,16	29,83	5,57	29,88	5,45	29,78	5,42
7,25	29,75	5,57	29,9	5,47	29,79	5,45
7,33	29,83	5,57	29,76	5,47	29,52	5,42
7,41	29,75	5,57	29,58	5,45	29,85	5,45
7,5	29,75	5,57	29,96	5,45	29,65	5,42
7,58	29,78	5,57	29,74	5,47	29,69	5,44
7,66	29,89	5,57	29,83	5,45	29,57	5,45
7,75	29,72	5,57	29,79	5,45	29,65	5,45
7,83	29,77	5,58	29,95	5,45	29,64	5,42
7,91	29,69	5,57	29,78	5,42	29,7	5,45
8	29,77	5,57	29,77	5,45	29,71	5,42
8,08	29,81	5,58	29,74	5,47	29,6	5,45
8,16	29,91	5,57	29,79	5,47	29,59	5,42
8,25	29,78	5,57	29,64	5,47	29,8	5,44
8,33	29,86	5,57	29,7	5,44	29,76	5,42
8,41	29,92	5,57	29,78	5,47	29,82	5,45
8,5	29,75	5,58	29,51	5,44	29,85	5,42
8,58	29,96	5,57	29,68	5,44	29,58	5,45
8,66	29,79	5,57	29,84	5,44	29,48	5,42
8,75	29,86	5,57	29,81	5,47	29,72	5,42
8,83	29,9	5,57	29,77	5,47	29,49	5,45
8,91	29,78	5,57	29,79	5,46	29,67	5,47
9	29,86	5,57	29,64	5,44	29,77	5,44
9,08	29,82	5,57	29,7	5,44	29,61	5,42
9,16	29,84	5,57	29,8	5,44	29,8	5,42
9,25	29,69	5,57	29,86	5,46	29,78	5,42
9,33	29,87	5,57	29,65	5,44	29,59	5,44
9,41	29,54	5,58	29,68	5,43	29,77	5,42
9,5	29,82	5,57	29,89	5,46	29,8	5,42
9,58	29,71	5,57	30,09	5,46	29,74	5,44
9,66	29,76	5,57	30,04	5,46	29,85	5,44
9,75	29,76	5,57	29,79	5,46	29,93	5,44
9,83	29,86	5,57	29,9	5,43	29,79	5,44
9,91	29,71	5,57	29,69	5,43	29,7	5,41
10	29,85	5,57	29,62	5,43	29,98	5,42

Table 19: Surface tension data for chemically stabilised Ruby Red, 3 repetitions of test

Ruby Red 0.05 wt% HALS, time 0-10 s						
Time [s]	**1st test**		**2nd test**		**3rd test**	
	ST [mN/m]	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**
0	30,9	1,97	31,08	5,01	30,9	5,46
0,08	31,01	2,04	31,03	5,03	30,96	5,47
0,17	30,81	2,15	31,2	5,03	31,11	5,46

0,25	31,19	2,21	30,98	5,04	31,18	5,46
0,33	31,01	2,22	31,01	5,04	31,08	5,46
0,42	31,02	2,22	30,97	5,04	31,02	5,47
0,5	31,11	2,24	31,11	5,04	31,12	5,47
0,58	30,99	2,32	31,13	5,04	31,17	5,47
0,67	30,78	2,41	31,08	5,04	31,18	5,46
0,75	30,97	2,45	30,99	5,04	31,13	5,46
0,83	31,07	2,51	31,05	5,03	31,08	5,47
0,92	30,54	2,59	31,04	5,04	31,1	5,46
1	31,06	2,66	31,05	5,04	31,22	5,46
1,08	30,78	2,75	31,01	5,04	31,21	5,46
1,17	30,9	2,85	31,1	5,05	30,88	5,47
1,25	30,79	2,93	31,08	5,11	31,02	5,47
1,33	30,76	2,96	31,02	5,14	31,03	5,56
1,42	31,02	3	31,11	5,15	31	5,63
1,5	30,75	3,08	31,09	5,15	31,18	5,65
1,58	30,95	3,13	30,81	5,17	31,2	5,66
1,67	30,99	3,17	31,02	5,16	30,93	5,66
1,75	31,15	3,18	31,16	5,17	31,08	5,66
1,83	31,12	3,19	30,9	5,17	30,99	5,67
1,92	31,11	3,21	30,92	5,17	31,07	5,67
2	31,12	3,27	31,08	5,17	31,05	5,66
2,08	31,16	3,31	31,16	5,16	31,15	5,66
2,17	30,84	3,37	31,14	5,17	31,03	5,66
2,25	31,02	3,4	31,13	5,17	30,88	5,66
2,33	30,98	3,42	30,89	5,17	31,12	5,66
2,42	30,92	3,44	30,99	5,16	30,81	5,66
2,5	30,97	3,47	31,12	5,16	31,18	5,66
2,58	31,01	3,49	31,13	5,17	30,9	5,65
2,67	31,03	3,56	31,1	5,17	31,15	5,66
2,75	31,15	3,62	30,89	5,17	31,03	5,65
2,83	31,06	3,69	31,01	5,17	31,11	5,65
2,92	31,02	3,76	31,07	5,17	30,95	5,65
3	31,06	3,8	31,16	5,17	31,05	5,65
3,08	31,1	3,84	31,09	5,17	30,99	5,65
3,17	30,86	3,88	31,21	5,16	31,05	5,65
3,25	31,01	3,91	31,03	5,17	30,95	5,65
3,33	31	3,93	31,19	5,17	31,11	5,65
3,42	30,92	3,95	31,04	5,17	31,11	5,65
3,5	30,94	3,99	30,95	5,17	31,25	5,65
3,58	30,93	4,02	31,15	5,16	30,99	5,65
3,67	31,2	4,03	31,12	5,16	31,1	5,65
3,75	31,07	4,04	31,06	5,16	30,96	5,65
3,83	31,02	4,03	31	5,16	31,08	5,65
3,92	30,87	4,03	31,06	5,16	31,03	5,65

4	30,89	4,03	31,06	5,16	31,05	5,65
4,08	31,11	4,01	31,21	5,16	31,19	5,64
4,17	30,98	4,03	31,17	5,16	31,34	5,64
4,25	31,15	4,07	30,96	5,16	31,09	5,65
4,33	31,12	4,14	30,85	5,16	31,02	5,64
4,42	30,87	4,16	31,19	5,16	31,12	5,64
4,5	31,02	4,18	30,9	5,21	31,27	5,64
4,58	31,12	4,17	31,08	5,27	31,05	5,64
4,67	30,83	4,21	31,19	5,28	31,16	5,64
4,75	31,06	4,23	31,18	5,29	31,1	5,64
4,83	30,87	4,25	30,98	5,3	31,06	5,64
4,92	30,83	4,27	31,06	5,3	31,25	5,64
5	30,99	4,29	31,06	5,31	31,09	5,64
5,08	30,97	4,3	31,15	5,31	31,12	5,64
5,17	30,84	4,33	31,16	5,31	30,99	5,64
5,25	31,06	4,35	31,1	5,31	31,13	5,64
5,33	31,04	4,37	31,01	5,31	30,92	5,64
5,42	30,96	4,38	31,1	5,31	30,94	5,64
5,5	31,18	4,37	31,08	5,31	30,94	5,64
5,58	30,98	4,39	31,14	5,31	31,12	5,64
5,67	30,98	4,4	30,95	5,31	31,21	5,64
5,75	31,01	4,4	31,03	5,31	31,09	5,64
5,83	30,86	4,4	30,94	5,31	31,18	5,64
5,92	30,97	4,4	31,03	5,31	30,96	5,65
6	30,93	4,4	31,23	5,3	31,12	5,64
6,08	30,96	4,4	31,04	5,31	30,95	5,64
6,17	31,01	4,41	30,99	5,3	31,17	5,64
6,25	30,97	4,41	31,13	5,3	31,03	5,64
6,33	30,86	4,44	30,94	5,3	31,2	5,64
6,41	31	4,45	31,21	5,3	31,17	5,65
6,5	31,07	4,45	31,1	5,3	31,26	5,64
6,58	30,92	4,47	31,2	5,3	31,06	5,65
6,66	30,95	4,49	30,92	5,3	30,96	5,7
6,75	31	4,53	30,95	5,3	31,08	5,76
6,83	30,91	4,57	31,21	5,3	31,03	5,78
6,91	30,86	4,59	31,23	5,3	30,93	5,81
7	30,87	4,61	30,99	5,31	31,17	5,82
7,08	30,95	4,63	31,23	5,31	30,96	5,84
7,16	30,9	4,65	31,31	5,32	31,1	5,85
7,25	30,84	4,66	31,1	5,37	31,07	5,85
7,33	30,79	4,66	31,04	5,42	30,98	5,85
7,41	31,02	4,66	31,05	5,45	30,95	5,85
7,5	30,95	4,66	31,09	5,46	30,98	5,86
7,58	31,02	4,66	30,93	5,47	31,14	5,86
7,66	31	4,66	31,06	5,48	31,08	5,86

7,75	31,05	4,66	31,02	5,48	31,16	5,86
7,83	31,04	4,66	30,91	5,48	31,03	5,86
7,91	31,06	4,66	30,92	5,48	30,86	5,87
8	31,09	4,67	30,89	5,49	31,15	5,86
8,08	30,9	4,7	31	5,49	31,13	5,86
8,16	30,86	4,73	30,87	5,48	31,01	5,87
8,25	31	4,77	31,06	5,48	30,98	5,86
8,33	30,97	4,8	30,89	5,48	31,08	5,87
8,41	30,97	4,83	30,84	5,48	31,01	5,86
8,5	30,89	4,85	31,15	5,48	31,09	5,87
8,58	30,8	4,87	30,94	5,48	30,91	5,87
8,66	30,93	4,86	31,09	5,47	30,86	5,87
8,75	30,89	4,87	31,15	5,47	31,13	5,86
8,83	31	4,86	31,11	5,47	31,06	5,86
8,91	30,9	4,87	31,01	5,48	31,25	5,86
9	30,98	4,86	31,09	5,47	31,26	5,87
9,08	30,96	4,87	31,03	5,48	31,14	5,87
9,16	31,04	4,87	31,02	5,48	31,03	5,87
9,25	30,91	4,88	31,09	5,48	31,39	5,86
9,33	31,07	4,89	31,13	5,47	31,07	5,87
9,41	31,03	4,92	31,07	5,47	31,16	5,87
9,5	30,92	4,93	31,23	5,47	31,2	5,87
9,58	30,91	4,95	30,97	5,47	31,06	5,87
9,66	30,85	4,96	31,2	5,47	31,09	5,87
9,75	31	4,97	31,15	5,47	31,14	5,87
9,83	30,92	4,97	31,17	5,47	31,14	5,87
9,91	30,96	4,98	31,06	5,47	31,19	5,87
10	31,03	4,98	30,93	5,47	31,13	5,87

Table 20: Surface tension data for non-stabilised Oxford Blue, 3 repetitions of test

Oxford Blue, time 0-10 s						
Time [s]	**1st test**		**2nd test**		**3rd test**	
	ST [mN/m]	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**
0	31,06	6,09	30,86	5,74	31,1	5,09
0,08	31,02	6,15	31,18	5,73	30,96	5,09
0,17	31,08	6,18	31,11	5,74	30,94	5,1
0,25	31,22	6,18	31,01	5,74	30,98	5,09
0,33	31	6,2	31,1	5,75	30,99	5,09
0,42	31,04	6,2	30,97	5,75	31	5,09
0,5	30,94	6,21	31,06	5,75	31,15	5,09
0,58	31,09	6,22	30,96	5,75	31,1	5,09
0,67	31	6,23	31,01	5,75	31,09	5,09
0,75	30,98	6,25	31,11	5,76	30,94	5,09
0,83	30,98	6,25	31,02	5,76	31,22	5,08
0,92	31,04	6,26	30,9	5,76	31,14	5,08

1	31,07	6,26	30,98	5,76	30,91	5,09
1,08	31,06	6,25	30,88	5,76	30,97	5,09
1,17	31,27	6,15	30,96	5,76	31,14	5,08
1,25	31,1	6,06	30,97	5,77	31,02	5,08
1,33	31,08	6,04	31	5,78	30,78	5,09
1,42	31,01	6,03	30,91	5,79	31,03	5,08
1,5	31,03	6,04	30,94	5,79	31,15	5,08
1,58	31,02	6,05	31,02	5,79	31,07	5,09
1,67	30,97	6,05	31,17	5,79	31,15	5,09
1,75	30,9	6,04	31,07	5,79	30,89	5,09
1,83	30,95	6,04	31	5,79	30,95	5,09
1,92	31,04	6,03	31,16	5,77	31,09	5,09
2	31,08	6,04	31,06	5,19	31,08	5,09
2,08	30,94	6,07	30,85	4,76	31,13	5,09
2,17	30,95	6,09	30,9	4,67	31,06	5,09
2,25	31,07	6,1	30,92	4,66	31,11	5,09
2,33	31,07	6,11	31	4,66	31,01	5,09
2,42	30,99	6,12	30,91	4,71	30,82	5,11
2,5	31,03	6,14	30,96	4,76	31,13	5,13
2,58	30,94	6,16	30,93	4,82	31,2	5,14
2,67	31,08	6,17	31,04	4,93	31,03	5,15
2,75	31,14	6,17	31,11	4,95	30,96	5,15
2,83	31,03	6,17	31,1	4,97	30,99	5,15
2,92	30,99	6,19	31,04	4,97	31,01	5,15
3	31,11	6,19	31,02	4,97	30,96	5,15
3,08	31,01	6,19	30,99	4,97	30,98	5,15
3,17	30,96	6,19	31,15	4,97	31,15	5,14
3,25	30,98	6,19	31,2	4,97	31,2	5,15
3,33	30,94	6,19	31,12	4,98	31,02	5,15
3,42	31,05	6,19	31,09	4,98	30,94	5,15
3,5	31,11	6,19	31,11	4,98	31,1	5,15
3,58	30,9	6,2	31,15	4,98	31,13	5,15
3,67	31,05	6,2	31,06	4,98	31,16	5,14
3,75	31,08	6,2	30,94	4,98	31,01	5,14
3,83	30,96	6,2	31,05	4,98	30,94	5,15
3,92	30,99	6,2	31,05	4,99	31,11	5,15
4	30,89	6,2	31,03	4,99	31,22	5,14
4,08	30,96	6,2	30,94	4,99	31,13	5,15
4,17	31,11	6,2	30,94	4,99	30,93	5,15
4,25	30,99	6,2	31,02	4,99	31,01	5,14
4,33	31,08	6,2	30,92	4,99	31,13	5,14
4,42	31	6,2	30,93	4,99	31,16	5,15
4,5	30,92	6,2	31,03	4,99	31	5,15
4,58	31,03	6,15	31,05	4,99	30,76	5,15
4,67	31,24	5,97	31,03	4,99	30,87	5,15

4,75	31,07	5,91	31,02	4,99	31,07	5,15
4,83	30,92	5,91	31,06	4,98	30,96	5,15
4,92	30,91	5,91	31,07	4,98	30,95	5,15
5	31,04	5,91	30,97	4,98	31,15	5,15
5,08	30,95	5,91	30,95	4,98	31,1	5,15
5,17	30,98	5,91	31,03	4,98	31,01	5,15
5,25	30,93	5,91	30,87	4,98	31,12	5,15
5,33	30,97	5,91	30,99	4,98	30,99	5,15
5,42	30,92	5,91	31,04	4,98	30,85	5,15
5,5	30,89	5,91	31,02	4,98	31,02	5,15
5,58	31,01	5,91	31,03	4,98	31,1	5,15
5,67	31,1	5,91	31,12	4,98	30,99	5,15
5,75	30,87	5,91	31,02	4,99	31,05	5,15
5,83	30,91	5,91	30,94	4,99	31,15	5,14
5,91	30,96	5,91	30,84	4,97	31	5,15
6	30,94	5,91	30,88	4,98	30,95	5,15
6,08	30,92	5,91	31,04	4,98	30,88	5,15
6,16	30,93	5,91	31,11	4,98	31	5,15
6,25	30,9	5,92	31,07	4,98	31,24	5,15
6,33	30,91	5,92	30,96	4,99	31	5,15
6,41	30,95	5,91	31,08	4,98	31,07	5,14
6,5	30,96	5,91	31,07	4,99	31,31	5,14
6,58	31	5,91	31,17	4,98	31,14	5,14
6,66	30,95	5,92	31,13	4,98	30,89	5,15
6,75	30,9	5,92	31,07	4,98	30,88	5,15
6,83	31,02	5,91	30,97	4,98	30,94	5,15
6,91	30,98	5,91	30,96	4,98	31,15	5,15
7	30,98	5,92	30,98	4,98	31,12	5,14
7,08	30,99	5,91	31,02	4,98	30,94	5,15
7,16	30,97	5,91	31	4,98	30,75	5,16
7,25	30,93	5,97	31,06	4,98	30,98	5,15
7,33	30,87	6	31,04	4,98	31,1	5,15
7,41	30,94	6,01	30,96	5,05	31,04	5,15
7,5	30,84	6,01	31,08	5,07	31	5,16
7,58	30,91	6,02	31,03	5,08	31,06	5,16
7,66	30,98	6,01	31,1	5,08	31,26	5,15
7,75	30,97	6,01	30,98	5,08	31,07	5,16
7,83	30,83	6,01	30,94	5,08	31,15	5,15
7,91	30,89	6,01	30,95	5,08	30,92	5,16
8	30,91	6,01	31,13	5,08	30,92	5,15
8,08	30,99	6,01	31,13	5,08	31,14	5,15
8,16	30,89	6,02	31,13	5,08	31,41	5,15
8,25	30,92	6,02	31,1	5,08	31,15	5,14
8,33	31,09	6,01	31,14	5,08	30,9	5,15
8,41	31,11	6,01	31,13	5,08	30,9	5,15

8,5	31,01	6,01	31,02	5,08	31,1	5,15
8,58	31,03	6,01	31,08	5,08	31,16	5,14
8,66	31	6,01	31,05	5,08	30,97	5,15
8,75	30,95	6,01	31,08	5,08	31,01	5,15
8,83	30,95	6,01	31,05	5,08	31,14	5,14
8,91	30,9	6,01	30,94	5,08	31,08	5,14
9	30,97	6,01	30,98	5,08	31,02	5,15
9,08	30,95	6,01	31,1	5,08	31,03	5,15
9,16	31,04	6,01	30,98	5,08	31,07	5,14
9,25	30,96	6,01	31,05	5,08	31,08	5,15
9,33	30,95	6,01	30,95	5,08	31,01	5,15
9,41	30,84	6,01	31,09	5,08	31,01	5,14
9,5	31	6,01	31,08	5,09	30,93	5,15
9,58	31,06	6	31,16	5,08	31,01	5,14
9,66	30,97	6,01	31,06	5,09	31,08	5,15
9,75	30,98	6,01	31,12	5,09	31,22	5,14
9,83	30,87	6,01	31,16	5,09	31,14	5,15
9,91	30,91	6,01	31,19	5,09	30,99	5,14
10	30,97	6,01	30,86	5,09	31,06	5,14

Table 21: Surface tension data for chemically stabilised Oxford Blue, 3 repetitions of test

Oxford Blue 0.05 wt% HALS, time 0-10 s						
Time [s]	**1st test**		**2nd test**		**3rd test**	
	ST [mN/m]	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**
0	31,14	5,7	31,24	5,69	31,05	5,66
0,08	31,17	5,7	31,24	5,69	31,02	5,66
0,17	31,2	5,69	30,98	5,69	31,14	5,66
0,25	31,18	5,69	31,14	5,69	30,98	5,66
0,33	31,22	5,7	30,96	5,69	30,85	5,66
0,42	31,04	5,7	31,15	5,68	30,75	5,67
0,5	31,21	5,7	31,16	5,69	31,18	5,66
0,58	31,14	5,7	31,06	5,69	30,93	5,66
0,67	31,16	5,7	30,97	5,69	31,17	5,66
0,75	30,89	5,7	30,97	5,69	31,12	5,66
0,83	31,05	5,7	31,21	5,69	31	5,66
0,92	31,05	5,7	31,19	5,69	31,08	5,67
1	31,39	5,7	31,1	5,69	30,96	5,66
1,08	31,08	5,69	31,13	5,7	31,13	5,66
1,17	31,17	5,7	31,02	5,69	31,17	5,66
1,25	31,18	5,7	31,02	5,69	31,11	5,66
1,33	30,97	5,7	31,01	5,69	31,11	5,66
1,42	31,1	5,69	31,18	5,69	31,06	5,67
1,5	31,26	5,69	31,07	5,69	31,09	5,66
1,58	31,17	5,69	31,12	5,69	31,1	5,67
1,67	31,1	5,69	31,07	5,69	31,05	5,67

1,75	31,37	5,69	31,01	5,7	30,99	5,67
1,83	31,26	5,69	31,14	5,69	31,09	5,66
1,92	31,16	5,69	31,12	5,69	31,06	5,66
2	31,03	5,69	31,22	5,69	31,27	5,66
2,08	31	5,69	31,16	5,69	31,01	5,67
2,17	30,92	5,69	31,17	5,69	31,06	5,67
2,25	31,14	5,69	31,04	5,69	31,04	5,67
2,33	31,05	5,69	30,94	5,69	31,13	5,67
2,42	31,22	5,69	31,18	5,69	31,16	5,67
2,5	31,11	5,69	31,19	5,69	31,03	5,67
2,58	31,2	5,68	31,17	5,69	31,08	5,67
2,67	31,12	5,68	31,21	5,69	31,05	5,67
2,75	31,02	5,68	31,04	5,69	31,14	5,67
2,83	31	5,69	31,17	5,69	30,89	5,67
2,92	31,15	5,69	31,12	5,69	31,14	5,67
3	31	5,69	31,17	5,69	31,05	5,67
3,08	31,19	5,68	31,07	5,69	31,22	5,67
3,17	31,12	5,68	31,03	5,69	31	5,67
3,25	31,1	5,68	31,17	5,69	31,13	5,67
3,33	31,2	5,68	31,29	5,68	31,35	5,67
3,42	30,92	5,69	31,28	5,68	31,25	5,67
3,5	31,13	5,68	31,17	5,69	31,09	5,67
3,58	31,09	5,68	31,2	5,69	31,15	5,67
3,67	31,11	5,68	30,95	5,68	31,03	5,67
3,75	31,11	5,68	31,05	5,68	31,13	5,67
3,83	31,08	5,68	31,11	5,68	31,25	5,67
3,92	30,92	5,68	31,08	5,68	31,15	5,67
4	31,14	5,68	31,12	5,68	31,16	5,67
4,08	31,24	5,68	30,95	5,68	30,92	5,67
4,17	31,22	5,69	30,98	5,68	31,24	5,67
4,25	31,19	5,69	31,05	5,68	31,18	5,67
4,33	31,04	5,69	31,09	5,68	31,22	5,67
4,42	31,09	5,69	31,13	5,68	31,18	5,66
4,5	31,06	5,69	31,29	5,68	31,04	5,66
4,58	31,21	5,68	31,22	5,68	30,94	5,67
4,67	31,15	5,68	31,12	5,68	30,97	5,67
4,75	31,05	5,68	31,01	5,68	31,11	5,67
4,83	30,94	5,69	31,1	5,68	30,97	5,67
4,92	30,96	5,69	31,3	5,67	31,19	5,67
5	31,25	5,68	31,25	5,68	31,11	5,67
5,08	31,25	5,68	31,13	5,67	31,22	5,67
5,17	31,11	5,68	31,02	5,68	31,31	5,66
5,25	31,33	5,68	31,06	5,67	31,1	5,67
5,33	31,12	5,68	31,1	5,67	31,18	5,66
5,42	31,26	5,68	31,16	5,67	31,21	5,66

5,5	31,03	5,68	30,96	5,67	31,11	5,66
5,58	31,13	5,68	31,1	5,67	30,98	5,67
5,67	31,11	5,68	31,16	5,67	31,15	5,66
5,75	31,15	5,68	31,02	5,67	31,13	5,66
5,83	31,18	5,68	31,04	5,66	31,02	5,66
5,91	31,25	5,69	31,14	5,66	31,3	5,66
6	31,24	5,69	31,08	5,66	31,09	5,66
6,08	31,15	5,69	31,04	5,66	31,18	5,66
6,16	31,18	5,69	31,03	5,66	31,23	5,66
6,25	31,17	5,69	31,21	5,66	31,03	5,66
6,33	31,05	5,7	31,12	5,66	31,08	5,66
6,41	31,05	5,7	31,17	5,65	31,09	5,66
6,5	31,04	5,69	31,03	5,66	31,2	5,67
6,58	31,33	5,69	31,12	5,65	31,16	5,66
6,66	30,91	5,69	31,09	5,66	31,01	5,66
6,75	31,18	5,69	31,13	5,66	30,99	5,67
6,83	31,12	5,69	31,21	5,65	31,15	5,67
6,91	31,11	5,69	31,11	5,66	31,04	5,67
7	31,07	5,69	31,15	5,65	31,23	5,67
7,08	30,97	5,69	31,2	5,66	31,08	5,67
7,16	31,15	5,69	31,17	5,66	31,06	5,68
7,25	31	5,69	31,07	5,66	31,08	5,68
7,33	31,21	5,69	31,22	5,66	31,16	5,67
7,41	31,3	5,69	30,89	5,66	31,01	5,67
7,5	30,99	5,7	31,21	5,66	31,18	5,67
7,58	30,97	5,69	31,11	5,65	31,2	5,67
7,66	30,97	5,69	31,25	5,65	31,27	5,67
7,75	31,05	5,69	30,88	5,66	31,02	5,67
7,83	31,06	5,69	30,87	5,66	30,97	5,67
7,91	31,37	5,69	30,9	5,66	30,94	5,67
8	31,13	5,69	31,11	5,66	31,06	5,67
8,08	31,35	5,69	31,27	5,65	31,09	5,67
8,16	31,04	5,69	31,22	5,65	31,17	5,67
8,25	31,31	5,69	31,02	5,65	31,26	5,67
8,33	31,04	5,69	31,03	5,66	31,04	5,67
8,41	31,19	5,69	31,16	5,66	31,15	5,67
8,5	30,98	5,7	31,17	5,65	30,93	5,67
8,58	31,14	5,69	31,09	5,66	31,14	5,67
8,66	31,13	5,69	31,22	5,65	30,99	5,67
8,75	31,12	5,69	31,2	5,65	31,21	5,67
8,83	31,11	5,69	31,08	5,66	31,12	5,68
8,91	31,08	5,69	31,07	5,66	31,01	5,67
9	31,13	5,7	31,11	5,66	30,94	5,68
9,08	31,53	5,68	31,15	5,66	30,94	5,68
9,16	30,92	5,69	30,9	5,66	31,01	5,67

9,25	31,37	5,68	31,05	5,66	31,05	5,68
9,33	31,17	5,69	31,04	5,66	31,16	5,68
9,41	31	5,69	31,22	5,66	31,03	5,68
9,5	31,09	5,69	31,08	5,66	30,98	5,68
9,58	31,13	5,69	31,05	5,66	30,95	5,68
9,66	31,06	5,69	31	5,66	30,91	5,68
9,75	30,94	5,69	31,09	5,65	31,18	5,68
9,83	31,01	5,69	31,12	5,66	31,05	5,67
9,91	31,17	5,69	31,09	5,66	31,15	5,67
10	31,21	5,69	30,99	5,67	31,2	5,67

Table 22: Surface tension data for non-stabilised spirooxazine, 3 repetitions of test

Spirooxazine, time 0-10 s						
Time [s]	**1st test**		**2nd test**		**3rd test**	
	ST [mN/m]	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**
0	31,22	6,41	32,01	4,49	30,74	4,6
0,08	31,48	6,39	31,52	5,11	30,58	4,59
0,17	29,56	6,21	31,23	5,87	30,62	4,59
0,25	29,2	6,2	31,1	6,57	30,67	4,59
0,33	31,6	6,39	30,8	6,41	30,8	4,57
0,42	31,46	6,41	30,83	5,78	30,98	4,59
0,5	31,26	6,41	30,74	5,25	30,92	4,57
0,58	28,37	6,14	30,9	5,06	30,73	4,59
0,67	28,96	6,22	30,89	5,02	30,78	4,59
0,75	29,56	6,18	30,83	5,03	30,71	4,59
0,83	31,37	6,41	30,64	5,04	30,76	4,65
0,92	31,56	6,41	30,56	5,06	31,02	4,59
1	31,35	6,41	30,78	5,06	30,89	4,58
1,08	31,36	6,39	30,89	5,07	30,8	4,57
1,17	31,4	6,38	31,08	5,06	30,6	4,66
1,25	31,42	6,38	30,7	5,07	30,7	4,58
1,33	31,35	6,39	30,7	5,07	30,64	4,57
1,42	31,28	6,41	30,82	5,06	30,79	4,58
1,5	31,64	6,4	30,95	5,05	30,71	4,58
1,58	31,22	6,4	30,89	5,06	30,65	4,56
1,67	28,96	6,16	30,89	5,06	30,67	4,57
1,75	28,98	6,18	30,72	5,05	30,82	4,57
1,83	31,31	6,39	30,75	5,05	30,91	4,64
1,92	31,2	6,4	30,94	5,05	30,84	4,57
2	31,58	6,39	30,86	5,05	30,81	4,57
2,08	31,32	6,4	30,78	5,06	30,95	4,58
2,17	31,52	6,4	30,68	5,06	30,7	4,57
2,25	31,42	6,4	30,82	5,06	30,79	4,56
2,33	31,48	6,39	30,91	5,06	30,87	4,56
2,42	29,14	6,18	30,91	5,06	30,83	4,64

2,5	29,3	6,16	30,88	5,06	30,8	4,57
2,58	29,11	6,14	30,63	5,06	30,6	4,57
2,67	29,23	6,15	30,73	5,06	30,68	4,64
2,75	30,06	6,24	30,95	5,06	30,7	4,57
2,83	29,62	6,23	30,88	5,06	30,65	4,64
2,92	29,67	6,18	30,9	5,06	30,73	4,58
3	29,51	6,25	30,78	5,06	30,88	4,56
3,08	29,51	6,22	30,67	5,06	30,9	4,48
3,17	31,74	6,38	30,87	5,06	30,67	4,56
3,25	31,4	6,39	30,92	5,06	30,77	4,56
3,33	31,42	6,4	30,76	5,06	30,6	4,55
3,42	31,33	6,4	30,76	5,06	30,77	4,57
3,5	29,19	6,15	30,83	5,06	30,95	4,63
3,58	29,62	6,21	30,66	5,06	30,97	4,55
3,67	29,42	6,18	30,75	5,06	30,74	4,56
3,75	31,46	6,39	30,92	5,06	30,63	4,63
3,83	31,59	6,39	30,92	5,07	30,66	4,56
3,92	31,49	6,4	30,77	5,07	30,75	4,56
4	31,47	6,4	30,79	5,07	30,82	4,56
4,08	31,37	6,39	30,77	5,07	30,73	4,56
4,17	28,99	6,17	30,9	5,07	30,64	4,63
4,25	29,5	6,17	30,86	5,07	30,65	4,55
4,33	29,5	6,15	30,92	5,07	30,77	4,55
4,42	29,52	6,16	30,78	5,07	30,74	4,56
4,5	31,37	6,39	30,7	5,07	30,78	4,55
4,58	31,45	6,4	30,76	5,06	30,77	4,56
4,67	31,4	6,39	30,86	5,06	30,71	4,55
4,75	31,71	6,38	30,88	5,06	30,65	4,55
4,83	31,43	6,39	30,8	5,07	30,65	4,56
4,92	31,45	6,38	30,83	5,06	30,57	4,56
5	31,56	6,38	30,74	5,07	30,81	4,55
5,08	31,67	6,38	30,77	5,07	30,9	4,47
5,17	31,39	6,4	30,82	5,07	30,95	4,55
5,25	31,52	6,39	30,81	5,06	30,7	4,54
5,33	29,24	6,14	30,86	5,06	30,67	4,63
5,42	29,75	6,23	30,77	5,06	30,85	4,55
5,5	29,87	6,24	30,85	5,06	31,03	4,54
5,58	31,25	6,41	30,79	5,06	30,83	4,55
5,67	31,25	6,42	30,67	5,06	30,74	4,55
5,75	31,5	6,41	30,73	5,06	30,79	4,53
5,83	31,17	6,06	30,85	5,06	30,93	4,54
5,91	30,23	5,92	30,95	5,07	30,9	4,54
6	31,65	5,9	30,97	5,06	30,93	4,53
6,08	31,26	5,91	30,78	5,06	30,8	4,54
6,16	30,66	5,91	30,76	5,06	30,72	4,54

6,25	31,16	5,91	30,92	5,06	30,75	4,54
6,33	31,07	5,92	30,85	5,06	30,66	4,55
6,41	30,91	5,93	30,9	5,05	30,59	4,54
6,5	31,03	5,94	30,85	5,06	30,64	4,54
6,58	30,95	5,94	30,75	5,05	30,82	4,53
6,66	30,84	5,94	30,78	5,06	30,75	4,46
6,75	31,26	5,94	30,79	5,06	30,63	4,55
6,83	31,11	5,94	30,81	5,05	30,62	4,54
6,91	31	5,94	30,87	5,05	30,82	4,54
7	31,01	5,94	30,92	5,05	30,81	4,55
7,08	31,23	5,94	30,79	5,05	30,74	4,54
7,16	31,08	5,94	30,78	5,06	30,75	4,53
7,25	30,93	5,94	30,82	5,06	30,63	4,61
7,33	30,94	5,94	30,76	5,06	30,74	4,54
7,41	31,14	5,93	30,69	5,06	30,72	4,55
7,5	31,01	5,94	30,78	5,05	30,88	4,61
7,58	30,86	5,93	30,85	5,05	30,86	4,54
7,66	31,09	5,82	30,79	5,05	30,87	4,52
7,75	31,06	5,59	30,84	5,04	30,69	4,54
7,83	31,1	5,52	30,93	5,05	30,74	4,61
7,91	30,74	5,5	30,7	5,05	30,74	4,61
8	31,06	5,49	30,78	5,05	30,85	4,54
8,08	30,96	5,49	30,8	5,04	30,73	4,61
8,16	30,71	5,49	30,73	5,05	30,68	4,52
8,25	31,04	5,49	30,72	5,05	30,81	4,54
8,33	31,04	5,49	30,74	5,05	30,83	4,53
8,41	31,05	5,48	30,89	5,04	30,81	4,53
8,5	30,78	5,43	30,74	5,04	30,78	4,6
8,58	30,86	5,28	30,82	5,04	30,82	4,53
8,66	31,06	5,22	30,87	5,04	30,71	4,53
8,75	30,75	5,2	30,77	5,04	30,71	4,53
8,83	30,74	5,2	30,76	5,04	30,78	4,53
8,91	30,97	5,2	30,92	5,04	30,8	4,54
9	31,09	5,2	30,82	5,04	30,85	4,52
9,08	30,85	5,2	30,75	5,03	30,79	4,54
9,16	30,81	5,2	30,74	5,03	30,7	4,53
9,25	30,72	5,2	30,57	5,04	30,68	4,54
9,33	30,77	5,2	30,78	5,03	30,83	4,53
9,41	30,9	5,2	30,82	5,03	30,92	4,53
9,5	31,1	5,2	30,75	5,03	30,9	4,53
9,58	30,82	5,2	30,69	5,03	30,93	4,6
9,66	30,61	5,2	30,75	5,03	30,79	4,53
9,75	30,83	5,2	30,84	5,03	30,78	4,53
9,83	30,98	5,2	30,71	5,02	30,81	4,52
9,91	30,92	5,2	30,72	5,03	30,68	4,53

10	30,89	5,2	30,73	5,02	30,77	4,52

Table 23: Surface tension data for chemically stabilised spirooxazine, 3 repetitions of test

Spirooxazine 0.05 wt% HALS, time 0-10 s						
Time [s]	**1st test**		**2nd test**		**3rd test**	
	ST [mN/m]	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**	**ST [mN/m]**	**Volume [µl]**
0	30,77	5,61	30,67	5,4	30,92	5,41
0,08	30,72	5,61	30,89	5,4	30,75	5,41
0,17	30,84	5,61	30,87	5,4	30,76	5,41
0,25	30,84	5,61	30,78	5,4	31,1	5,41
0,33	30,82	5,61	30,81	5,4	30,93	5,41
0,42	30,84	5,61	30,78	5,4	30,82	5,42
0,5	30,67	5,61	30,84	5,4	30,84	5,42
0,58	30,85	5,61	30,7	5,4	30,78	5,42
0,67	30,86	5,61	30,86	5,4	30,77	5,42
0,75	30,96	5,61	30,74	5,4	30,9	5,42
0,83	30,76	5,61	30,75	5,41	30,92	5,41
0,92	30,75	5,61	30,73	5,41	30,87	5,41
1	30,76	5,61	30,74	5,41	30,67	5,41
1,08	30,8	5,61	30,8	5,41	30,85	5,41
1,17	30,79	5,61	30,81	5,41	30,86	5,41
1,25	30,75	5,61	30,89	5,4	30,84	5,41
1,33	30,56	5,61	30,72	5,4	30,88	5,41
1,42	30,84	5,61	30,73	5,4	30,71	5,41
1,5	30,76	5,61	30,76	5,4	30,82	5,41
1,58	30,84	5,61	30,87	5,4	30,79	5,41
1,67	30,85	5,61	30,66	5,4	30,78	5,41
1,75	30,98	5,61	30,82	5,4	30,82	5,41
1,83	30,75	5,61	30,96	5,4	30,73	5,41
1,92	30,89	5,61	30,75	5,39	30,74	5,41
2	30,75	5,61	30,84	5,39	30,66	5,4
2,08	30,73	5,6	30,75	5,39	30,78	5,4
2,17	30,83	5,6	30,93	5,36	30,69	5,39
2,25	30,9	5,6	30,69	5,32	30,78	5,39
2,33	30,71	5,6	30,7	5,32	30,91	5,39
2,42	30,87	5,6	30,79	5,31	30,68	5,4
2,5	30,78	5,6	30,98	5,31	30,65	5,4
2,58	30,77	5,6	30,72	5,32	30,69	5,4
2,67	30,74	5,6	30,64	5,32	30,8	5,4
2,75	30,91	5,6	30,77	5,31	30,65	5,4
2,83	30,77	5,6	30,69	5,32	30,81	5,4
2,92	31,05	5,6	30,92	5,31	30,8	5,39
3	30,72	5,6	30,57	5,32	30,78	5,4
3,08	30,75	5,6	30,74	5,31	30,59	5,4
3,17	30,74	5,6	30,85	5,31	31	5,4

3,25	31,1	5,6	30,58	5,31	30,73	5,4
3,33	30,96	5,59	30,84	5,31	30,63	5,4
3,42	30,76	5,52	30,84	5,31	30,78	5,4
3,5	30,89	5,47	30,68	5,31	30,94	5,4
3,58	30,95	5,45	30,59	5,31	30,89	5,4
3,67	30,86	5,44	30,71	5,31	30,71	5,4
3,75	30,8	5,44	30,83	5,31	30,62	5,4
3,83	30,85	5,44	30,76	5,32	30,75	5,4
3,92	30,77	5,44	30,69	5,32	30,74	5,4
4	30,8	5,43	30,92	5,31	30,94	5,4
4,08	30,66	5,44	30,92	5,31	30,65	5,4
4,17	30,74	5,43	30,77	5,31	30,77	5,4
4,25	31,01	5,43	30,83	5,31	30,72	5,4
4,33	30,73	5,43	30,6	5,31	30,74	5,4
4,42	30,73	5,43	30,79	5,31	30,94	5,4
4,5	30,9	5,43	30,74	5,31	30,69	5,4
4,58	30,78	5,43	30,84	5,3	30,82	5,4
4,67	30,86	5,42	30,93	5,3	31,05	5,33
4,75	30,69	5,43	30,71	5,3	30,64	5,22
4,83	30,73	5,43	30,68	5,31	30,58	5,19
4,92	30,81	5,43	30,82	5,3	30,79	5,12
5	30,67	5,43	30,9	5,3	30,88	5,08
5,08	30,82	5,43	30,93	5,3	30,76	5,07
5,17	30,81	5,43	30,77	5,3	30,81	5,07
5,25	30,87	5,43	30,73	5,31	30,76	5,07
5,33	30,81	5,43	30,89	5,3	30,71	5,07
5,42	30,88	5,42	30,88	5,3	30,59	5,07
5,5	30,77	5,43	30,83	5,3	30,66	5,07
5,58	30,73	5,43	30,87	5,3	30,75	5,07
5,67	30,76	5,43	30,69	5,31	30,84	5,07
5,75	30,72	5,43	30,74	5,31	30,7	5,04
5,83	30,8	5,43	30,89	5,31	30,53	4,95
5,91	30,8	5,43	30,82	5,3	30,68	4,82
6	30,73	5,43	30,62	5,31	30,65	4,75
6,08	30,83	5,43	30,7	5,31	30,65	4,64
6,16	30,78	5,44	30,95	5,31	30,63	4,54
6,25	30,84	5,44	30,63	5,31	30,62	4,49
6,33	30,79	5,43	30,85	5,31	30,71	4,45
6,41	30,88	5,43	30,75	5,31	30,54	4,39
6,5	30,75	5,44	30,75	5,31	30,54	4,34
6,58	30,62	5,44	30,81	5,31	30,49	4,32
6,66	30,88	5,43	30,84	5,31	30,49	4,31
6,75	30,88	5,43	30,76	5,31	30,47	4,31
6,83	30,95	5,43	30,87	5,31	30,49	4,31
6,91	30,99	5,43	30,8	5,31	30,47	4,31

7	30,66	5,43	30,6	5,31	30,47	4,31
7,08	30,75	5,43	30,83	5,31	30,46	4,31
7,16	30,83	5,43	30,81	5,31	30,64	4,31
7,25	30,95	5,43	30,83	5,3	30,55	4,27
7,33	30,75	5,43	30,82	5,31	30,65	4,22
7,41	30,8	5,42	30,73	5,31	30,59	4,15
7,5	30,73	5,43	30,76	5,3	30,58	4,13
7,58	30,78	5,43	30,82	5,31	30,61	4,13
7,66	30,79	5,42	30,82	5,31	30,59	4,13
7,75	30,94	5,42	30,8	5,31	30,62	4,13
7,83	30,78	5,42	30,76	5,31	30,61	4,13
7,91	30,84	5,42	30,77	5,3	30,53	4,13
8	30,75	5,42	30,8	5,3	30,55	4,13
8,08	30,77	5,42	30,87	5,3	30,69	4,13
8,16	30,82	5,42	30,84	5,3	30,72	4,06
8,25	30,85	5,42	30,77	5,31	30,58	4,01
8,33	30,87	5,42	30,73	5,31	30,66	4
8,41	30,76	5,42	30,81	5,31	30,54	4
8,5	30,83	5,42	30,84	5,31	30,64	4
8,58	30,73	5,43	30,81	5,31	30,59	4
8,66	30,76	5,42	30,78	5,31	30,85	4
8,75	30,8	5,42	30,77	5,31	33,17	4
8,83	30,69	5,43	30,67	5,31	30,8	4
8,91	30,99	5,43	30,82	5,31	30,78	4
9	30,65	5,43	30,75	5,31	30,66	4
9,08	30,74	5,43	30,85	5,31	30,82	4
9,16	30,76	5,43	30,67	5,31	30,58	4,01
9,25	30,7	5,43	30,73	5,31	30,74	4,01
9,33	30,89	5,42	30,75	5,31	30,76	4,03
9,41	30,79	5,42	30,76	5,31	30,57	4,17
9,5	30,84	5,43	30,76	5,32	30,73	4,23
9,58	30,7	5,43	30,74	5,32	30,74	4,32
9,66	30,78	5,42	30,78	5,31	30,66	4,42
9,75	30,74	5,42	30,7	5,31	30,73	4,46
9,83	30,75	5,43	30,85	5,31	30,87	4,46
9,91	30,86	5,42	30,66	5,31	30,74	4,47
10	30,72	5,43	30,73	5,31	30,77	4,48

Appendix III

Dye solutions absorbance as a function of temperature.

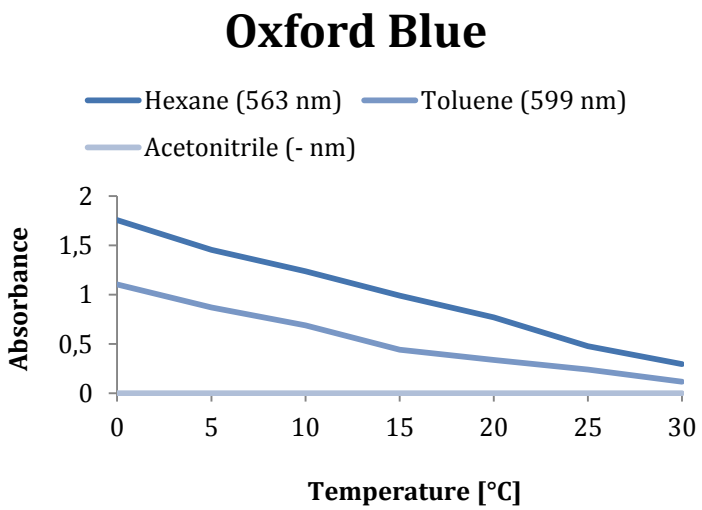

Fig. 55 Absorbance for Oxford Blue as a function of temperature

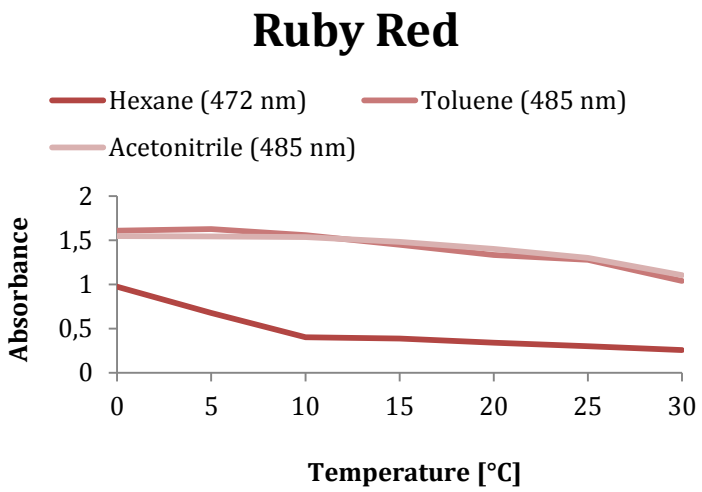

Fig. 56 Absorbance for Ruby Red as a function of temperature

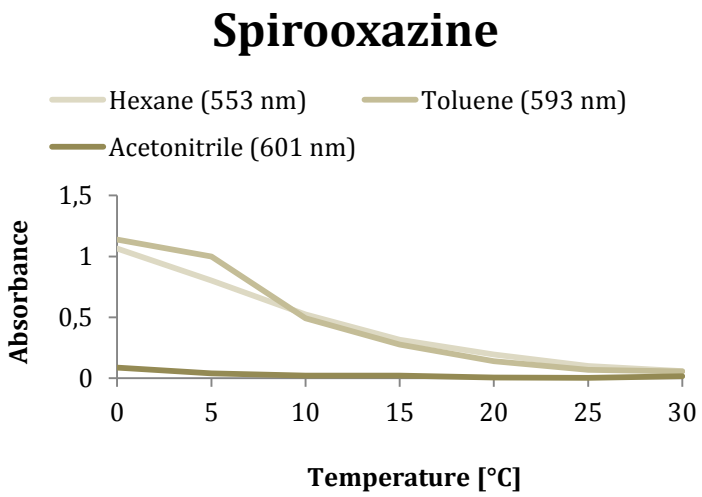

Fig. 57 Absorbance for spirooxazine as a function of temperature

Appendix IV

Complete data of ΔE colour difference for the samples in inactivated and activated state in measurements done in connection with test method.

Table 24: ΔE data on chemically stabilised samples in washing test

Ink formulation [wt%] HALS	ΔE unwashed samples			ΔE washed samples		
Ruby Red 0	16,38	18,28	15,68	12,23	12,06	11,12
Ruby Red 0.05	20,00	19,58	18,75	11,52	12,21	11,45
Ruby Red 0.5	18,93	18,16	18,55	12,63	11,14	12,18
Ruby Red 1.0	20,45	20,19	19,78	13,38	12,48	13,06
Ruby Red 1.5	20,47	21,18	20,00	13,67	15,24	14,40
Ruby Red 2.0	21,25	20,95	20,75	15,89	16,07	16,32
Ruby Red 2.5	20,99	20,22	21,27	15,72	15,72	15,76
Ruby Red 3.0	21,96	22,96	22,52	16,23	17,23	15,03
Oxford Blue 0	19,52	18,38	19,61	15,71	16,55	15,73
Oxford Blue 0.05	19,41	17,86	19,94	17,10	15,88	14,56
Oxford Blue 0.5	21,12	23,00	21,24	16,20	18,64	16,93
Oxford Blue 1.0	24,43	26,63	30,35	18,24	20,27	25,56
Oxford Blue 1.5	20,48	19,09	20,46	15,71	16,55	15,73
Oxford Blue 2.0	21,38	21,83	20,57	17,10	15,88	14,56
Oxford Blue 2.5	22,54	21,79	22,58	16,20	18,64	16,93
Oxford Blue 3.0	23,15	22,28	23,91	18,24	20,27	25,56
Spirooxazine 0	13,82	16,93	15,91	12,18	11,00	12,46
Spirooxazine 0.05	16,10	17,89	15,77	11,24	14,72	12,30
Spirooxazine 0.5	18,99	18,36	17,74	14,12	11,76	14,00
Spirooxazine 1.0	20,00	20,66	22,25	14,08	14,83	17,51
Spirooxazine 1.5	18,59	17,03	18,48	15,18	14,58	15,28
Spirooxazine 2.0	20,66	18,37	19,08	18,88	16,56	16,06
Spirooxazine 2.5	17,38	17,71	18,93	13,17	16,2	16,78
Spirooxazine 3.0	20,22	17,9	19,98	16,84	15,28	18,22

Table 25: ΔE data on physically stabilised samples in washing test

Ink formulation and coating [µm]	ΔE unwashed samples			ΔE washed samples		
Ruby Red Ref.	19,64	19,95	18,56	15,20	16,09	15,04
Ruby Red 50	16,12	18,74	14,48	14,66	16,36	14,53
Ruby Red 150	13,43	16,60	15,65	13,01	15,01	13,88
Ruby Red 250	15,17	13,99	15,04	13,69	12,75	13,49
Oxford Blue Ref.	20,36	20,56	20,90	18,39	18,96	19,02
Oxford Blue 50	15,67	15,35	13,43	17,80	16,11	14,12
Oxford Blue 150	15,28	15,12	13,79	14,69	14,08	13,87
Oxford Blue 250	13,26	13,22	12,65	12,96	12,61	13,36
Spirooxazine Ref.	16,10	16,52	15,83	14,22	16,03	14,60
Spirooxazine 50	10,31	11,34	8,43	10,81	9,27	9,68
Spirooxazine 150	7,92	8,66	9,06	8,36	8,84	9,37
Spirooxazine 250	9,64	7,01	6,60	7,71	6,90	7,02

Table 26: ΔE data on chemically stabilised samples in multiple activations test

Ink formulation/HALS[wt%]		**ΔE**		
Ruby Red 0		20,49	21,00	21,03
Ruby Red 0.05		21,17	21,24	21,35
Ruby Red 0.5		20,08	20,52	20,95
Ruby Red 1.0		22,24	21,61	22,01
Oxford Blue 0		20,30	20,07	20,87
Oxford Blue 0.05	**1st cycle**	20,73	21,63	22,12
Oxford Blue 0.5		21,39	20,99	22,17
Oxford Blue 1.0		22,38	22,36	23,43
Spirooxazine 0		16,67	18,66	16,56
Spirooxazine 0.05		15,70	18,27	16,60
Spirooxazine 0.5		17,26	18,29	17,74
Spirooxazine 1.0		16,06	17,12	18,31
Ruby Red 0		19,73	19,78	20,17
Ruby Red 0.05		20,39	20,47	20,90
Ruby Red 0.5		20,11	20,36	20,17
Ruby Red 1.0		22,25	21,03	20,29
Oxford Blue 0		17,66	20,62	19,97
Oxford Blue 0.05	**2nd cycle**	20,69	21,72	21,12
Oxford Blue 0.5		22,45	20,50	22,46
Oxford Blue 1.0		22,83	21,59	22,54
Spirooxazine 0		16,06	15,63	15,35
Spirooxazine 0.05		16,91	17,15	15,99
Spirooxazine 0.5		15,70	15,46	16,36
Spirooxazine 1.0		15,44	14,90	16,71
Ruby Red 0		18,98	19,39	18,45
Ruby Red 0.05		19,07	19,27	20,00
Ruby Red 0.5		20,00	19,10	19,30
Ruby Red 1.0		21,33	20,44	19,89
Oxford Blue 0		16,03	19,88	18,18
Oxford Blue 0.05	**3rd cycle**	19,55	20,83	18,88
Oxford Blue 0.5		20,53	17,22	20,35
Oxford Blue 1.0		20,48	19,97	19,77
Spirooxazine 0		15,83	15,82	14,11
Spirooxazine 0.05		15,32	13,49	14,29
Spirooxazine 0.5		15,56	14,46	16,45
Spirooxazine 1.0		14,93	15,94	15,04
Ruby Red 0		18,81	18,63	18,83
Ruby Red 0.05		19,21	19,03	19,53
Ruby Red 0.5		19,22	18,99	18,72
Ruby Red 1.0	**4th cycle**	19,75	19,71	19,60
Oxford Blue 0		17,59	19,91	19,34
Oxford Blue 0.05		19,91	19,82	19,00
Oxford Blue 0.5		19,61	17,18	20,25

Oxford Blue 1.0		19,88	20,88	20,43
Spirooxazine 0		14,84	13,36	15,00
Spirooxazine 0.05		15,43	15,87	14,32
Spirooxazine 0.5		15,12	15,74	16,39
Spirooxazine 1.0		14,55	15,96	16,18
Ruby Red 0	**5th cycle**	18,00	18,16	18,26
Ruby Red 0.05		18,66	18,03	19,03
Ruby Red 0.5		18,45	18,81	18,38
Ruby Red 1.0		20,47	19,52	19,21
Oxford Blue 0		18,47	18,93	17,84
Oxford Blue 0.05		19,54	20,45	19,71
Oxford Blue 0.5		20,15	19,21	20,92
Oxford Blue 1.0		20,55	21,21	19,11
Spirooxazine 0		15,29	16,01	15,12
Spirooxazine 0.05		15,90	15,67	15,33
Spirooxazine 0.5		14,75	15,20	16,03
Spirooxazine 1.0		15,22	17,29	17,09
Ruby Red 0	**6th cycle**	16,09	17,42	17,74
Ruby Red 0.05		18,55	18,37	18,64
Ruby Red 0.5		18,72	18,67	18,15
Ruby Red 1.0		20,47	19,23	18,31
Oxford Blue 0		18,22	19,96	19,20
Oxford Blue 0.05		20,28	19,75	20,03
Oxford Blue 0.5		20,70	20,49	21,19
Oxford Blue 1.0		21,68	21,37	21,70
Spirooxazine 0		15,12	15,99	16,12
Spirooxazine 0.05		15,50	15,85	15,66
Spirooxazine 0.5		15,75	16,32	17,24
Spirooxazine 1.0		16,04	17,34	16,29
Ruby Red 0	**7th cycle**	17,44	17,85	17,72
Ruby Red 0.05		18,42	17,16	18,25
Ruby Red 0.5		18,45	18,16	17,68
Ruby Red 1.0		20,05	16,58	18,32
Oxford Blue 0		18,22	19,59	19,22
Oxford Blue 0.05		19,66	19,86	19,23
Oxford Blue 0.5		21,04	20,42	21,15
Oxford Blue 1.0		20,86	21,75	21,44
Spirooxazine 0		15,96	15,72	15,72
Spirooxazine 0.05		15,94	16,68	14,97
Spirooxazine 0.5		16,00	16,08	16,79
Spirooxazine 1.0		15,09	17,29	17,84
Ruby Red 0	**8th cycle**	15,77	17,14	16,61
Ruby Red 0.05		17,62	16,05	17,56
Ruby Red 0.5		17,58	17,18	16,98
Ruby Red 1.0		19,03	18,23	18,03

Oxford Blue 0		17,08	18,65	18,75
Oxford Blue 0.05		19,23	19,55	19,07
Oxford Blue 0.5		20,04	19,21	20,66
Oxford Blue 1.0		20,53	19,68	20,64
Spirooxazine 0		14,20	16,10	14,47
Spirooxazine 0.05		14,47	15,03	14,29
Spirooxazine 0.5		14,35	15,01	16,24
Spirooxazine 1.0		14,46	16,69	16,37
Ruby Red 0	**9th cycle**	16,35	16,82	16,78
Ruby Red 0.05		17,45	16,02	17,54
Ruby Red 0.5		17,45	17,72	17,25
Ruby Red 1.0		19,35	18,47	17,96
Oxford Blue 0		18,25	20,19	19,03
Oxford Blue 0.05		19,58	20,29	19,82
Oxford Blue 0.5		21,21	19,75	20,46
Oxford Blue 1.0		20,47	21,35	20,98
Spirooxazine 0		15,34	15,95	15,26
Spirooxazine 0.05		15,71	16,08	15,75
Spirooxazine 0.5		15,20	16,27	16,62
Spirooxazine 1.0		15,54	16,65	16,54
Ruby Red 0	**10th cycle**	16,16	16,51	17,32
Ruby Red 0.05		17,93	17,03	18,01
Ruby Red 0.5		18,03	18,02	17,30
Ruby Red 1.0		19,16	18,30	18,31
Oxford Blue 0		18,14	19,31	18,97
Oxford Blue 0.05		19,94	19,98	19,70
Oxford Blue 0.5		21,00	21,11	21,59
Oxford Blue 1.0		21,57	20,72	21,41
Spirooxazine 0		15,39	15,87	15,29
Spirooxazine 0.05		16,18	15,74	14,82
Spirooxazine 0.5		14,83	16,61	17,21
Spirooxazine 1.0		15,57	17,36	17,19

Table 27: ΔE data on physically stabilised samples in multiple activations test

Ink formulation and coating thickness [µm]	**ΔE**			
Ruby Red Ref.	**1st cycle**	20,30	22,57	19,34
Ruby Red 50		16,93	16,56	17,47
Ruby Red 150		17,10	17,48	17,57
Ruby Red 250		14,34	14,05	17,10
Oxford Blue Ref.		22,20	23,80	22,76
Oxford Blue 50		14,43	13,03	13,16
Oxford Blue 150		14,81	14,23	14,97
Oxford Blue 250		11,52	11,47	11,74
Spirooxazine Ref.		14,10	16,30	15,85
Spirooxazine 50		8,69	9,14	9,92

Spirooxazine 150		11,29	11,16	10,40
Spirooxazine 250		7,11	7,75	8,36
Ruby Red Ref.	**2nd cycle**	18,66	19,87	19,18
Ruby Red 50		17,24	16,32	17,45
Ruby Red 150		16,54	17,86	16,57
Ruby Red 250		15,13	14,22	16,21
Oxford Blue Ref.		21,58	24,14	24,03
Oxford Blue 50		16,69	15,11	15,31
Oxford Blue 150		16,70	15,99	18,01
Oxford Blue 250		12,77	12,49	11,93
Spirooxazine Ref.		17,11	16,32	13,76
Spirooxazine 50		10,37	10,90	11,85
Spirooxazine 150		12,42	12,62	11,45
Spirooxazine 250		9,24	9,46	9,80
Ruby Red Ref.	**3rd cycle**	17,71	19,52	18,75
Ruby Red 50		16,61	16,90	16,09
Ruby Red 150		16,08	16,82	16,66
Ruby Red 250		16,90	13,86	16,78
Oxford Blue Ref.		23,57	24,18	23,54
Oxford Blue 50		15,93	14,08	15,41
Oxford Blue 150		16,49	16,23	17,24
Oxford Blue 250		13,34	13,19	12,67
Spirooxazine Ref.		16,23	16,02	16,52
Spirooxazine 50		10,49	11,43	11,52
Spirooxazine 150		11,97	10,42	11,50
Spirooxazine 250		8,62	9,29	9,82
Ruby Red Ref.	**4th cycle**	18,06	18,41	18,92
Ruby Red 50		17,25	16,95	16,96
Ruby Red 150		17,64	17,76	17,56
Ruby Red 250		15,76	14,34	17,70
Oxford Blue Ref.		23,06	24,36	21,79
Oxford Blue 50		16,92	13,57	17,08
Oxford Blue 150		16,49	16,63	17,11
Oxford Blue 250		14,43	13,24	14,14
Spirooxazine Ref.		17,16	16,12	17,38
Spirooxazine 50		11,39	11,63	12,32
Spirooxazine 150		12,07	12,65	12,50
Spirooxazine 250		9,64	8,02	11,04
Ruby Red Ref.	**5th cycle**	18,57	17,84	17, 37
Ruby Red 50		16,17	14,54	14,09
Ruby Red 150		15,83	17,75	16,69
Ruby Red 250		14,73	15,05	17,07
Oxford Blue Ref.		23,98	25,00	24,14
Oxford Blue 50		17,23	14,85	15,66
Oxford Blue 150		17,25	16,45	17,36

Oxford Blue 250		13,74	12,87	14,46
Spirooxazine Ref.		17,65	16,93	15,95
Spirooxazine 50		11,58	11,81	12,35
Spirooxazine 150		13,00	12,82	12,05
Spirooxazine 250		9,42	8,22	10,66
Ruby Red Ref.	**6th cycle**	18,63	18,64	18,07
Ruby Red 50		16,61	16,32	16,67
Ruby Red 150		16,89	17,80	17,21
Ruby Red 250		14,90	14,09	16,57
Oxford Blue Ref.		21,94	23,07	24,60
Oxford Blue 50		16,71	15,18	16,33
Oxford Blue 150		17,10	16,21	17,30
Oxford Blue 250		14,22	13,40	13,32
Spirooxazine Ref.		15,66	16,25	16,21
Spirooxazine 50		11,02	11,37	12,51
Spirooxazine 150		11,48	11,51	12,22
Spirooxazine 250		7,33	9,19	10,34
Ruby Red Ref.	**7th cycle**	18,52	18,81	17,57
Ruby Red 50		16,89	16,88	16,68
Ruby Red 150		16,78	17,25	16,83
Ruby Red 250		15,29	14,47	16,10
Oxford Blue Ref.		23,33	23,18	23,78
Oxford Blue 50		17,25	15,64	16,07
Oxford Blue 150		16,74	16,19	16,42
Oxford Blue 250		13,13	13.08	14,12
Spirooxazine Ref.		16,30	16,65	16,60
Spirooxazine 50		11,14	11,00	12,17
Spirooxazine 150		11,58	11,86	12,80
Spirooxazine 250		8,11	9,10	11,60
Ruby Red Ref.	**8th cycle**	18,51	18,15	17,60
Ruby Red 50		15,05	16,61	15,69
Ruby Red 150		16,82	16,89	16,85
Ruby Red 250		14,62	13,68	16,80
Oxford Blue Ref.		22,04	23,10	22,85
Oxford Blue 50		16,25	14,57	15,20
Oxford Blue 150		16,02	15,84	17,13
Oxford Blue 250		14,15	12,10	13,72
Spirooxazine Ref.		16,13	15,98	16,36
Spirooxazine 50		11,97	9,85	12,56
Spirooxazine 150		12,10	11,96	12,37
Spirooxazine 250		8,38	9,81	10,28
Ruby Red Ref.	**9th cycle**	18,62	18,13	17,99
Ruby Red 50		16,28	16,68	16,52
Ruby Red 150		17,73	17,20	16,61
Ruby Red 250		15,09	13,69	16,10

Oxford Blue Ref.		21,38	23,15	24,33
Oxford Blue 50		15,83	15,33	15,89
Oxford Blue 150		16,50	15,85	17,01
Oxford Blue 250		13,20	12,77	14,80
Spirooxazine Ref.		16,25	15,70	16,49
Spirooxazine 50		12,28	12,12	12,46
Spirooxazine 150		11,97	12,25	11,55
Spirooxazine 250		8,12	10,09	10,89
Ruby Red Ref.	**10^{th} cycle**	18,10	18,17	17,34
Ruby Red 50		15,67	15,79	16,10
Ruby Red 150		16,11	16,54	16,55
Ruby Red 250		14,47	14,39	15,92
Oxford Blue Ref.		21,06	23,22	23,57
Oxford Blue 50		16,01	14,82	16,16
Oxford Blue 150		16,71	15,32	17,68
Oxford Blue 250		12,83	12,92	14,63
Spirooxazine Ref.		16,40	16,20	16,20
Spirooxazine 50		12,14	12,28	12,94
Spirooxazine 150		12,21	12,09	12,35
Spirooxazine 250		9,17	9,11	10,21

Table 28: ΔE data on sun-lamp exposed samples

Ink formulation and stabilisation	**ΔE before sun-lamp exposure**		
Varnish	0,67	0,55	0,63
Varnish + 1 wt% HALS	0,78	0,72	0,86
Ruby Red 0 wt% HALS	16,16	16,51	17,32
Ruby Red 1.0 wt% HALS	19,16	18,30	18,31
Oxford Blue 0 wt% HALS	18,14	19,31	18,97
Oxford Blue 1.0 wt% HALS	21,57	20,72	21,41
Spirooxazine 0 wt% HALS	15,39	15,87	15,29
Spirooxazine 1.0 wt% HALS	15,57	17,36	17,19
Ruby Red Ref.	18,10	18,17	17,34
Ruby Red 250 µm coating	14,47	14,39	15,92
Oxford Blue Ref.	21,06	23,22	23,57
Oxford Blue 250 µm coating	12,83	12,92	14,63
Spirooxazine Ref.	16,40	16,20	16,20
Spirooxazine 250 µm coating	9,17	9,11	10,21
	ΔE after 1 h sun-lamp exposure		
Varnish	0,89	0,84	1,01
Varnish + 1 wt% HALS	1,00	1,02	1,00
Ruby Red 0 wt% HALS	4,23	3,92	3,52
Ruby Red 1.0 wt% HALS	6,02	6,00	5,74
Oxford Blue 0 wt% HALS	12,27	14,29	13,59
Oxford Blue 1.0 wt% HALS	14,39	14,83	14,80
Spirooxazine 0 wt% HALS	8,81	9,25	9,57

Spirooxazine 1.0 wt% HALS	9,63	11,05	11,17
Ruby Red Ref.	5,72	5,49	5,21
Ruby Red 250 µm coating	5,30	5,75	5,63
Oxford Blue Ref.	17,10	19,90	16,72
Oxford Blue 250 µm coating	10,53	10,30	9,48
Spirooxazine Ref.	11,57	12,6	12,27
Spirooxazine 250 µm coating	7,02	6,85	7,45

Table 29: ΔE data on additional physically stabilised samples in multiple activations test

Ink formulation and coating thickness [µm]	**ΔE**			
Ruby Red Ref.	**1st cycle**	16,68	17,34	17,90
Ruby Red 25		15,72	17,54	17,30
Ruby Red 50		15,42	15,08	16,34
Ruby Red 100		16,63	17,68	14,78
Ruby Red 150		14,60	15,13	13,75
Ruby Red 250		14,09	14,85	13,10
Ruby Red 350		16,66	17,15	16,32
Oxford Blue Ref.		20,14	20,97	21,92
Oxford Blue 25		16,50	16,22	17,35
Oxford Blue 50		15,51	15,95	18,91
Oxford Blue 100		15,81	15,32	17,77
Oxford Blue 150		17,01	15,53	15,11
Oxford Blue 250		15,94	13,77	14,14
Oxford Blue 350		15,06	14,41	12,07
Spirooxazine Ref.		15,83	13,93	16,32
Spirooxazine 25		11,29	9,86	8,75
Spirooxazine 50		10,31	11,19	14,62
Spirooxazine 100		10,85	10,87	10,29
Spirooxazine 150		9,15	10,60	11,68
Spirooxazine 250		7,17	10,13	9,71
Spirooxazine 350		9,70	10,99	9,60
Ruby Red Ref.	**2nd cycle**	18,21	18,41	18,41
Ruby Red 25		15,28	17,01	16,48
Ruby Red 50		14,67	15,36	16,61
Ruby Red 100		15,58	16,60	15,00
Ruby Red 150		15,12	14,84	13,64
Ruby Red 250		14,68	14,11	12,49
Ruby Red 350		16,41	14,85	16,03
Oxford Blue Ref.		21,50	21,01	22,25
Oxford Blue 25		16,29	16,61	17,93
Oxford Blue 50		15,31	17,91	19,77
Oxford Blue 100		15,38	14,90	15,94
Oxford Blue 150		15,79	15,94	15,48
Oxford Blue 250		14,80	13,86	15,58
Oxford Blue 350		14,15	15,18	14,09

Spirooxazine Ref.		15,62	13,68	15,02
Spirooxazine 25		10,52	7,25	8,22
Spirooxazine 50		9,53	10,87	13,77
Spirooxazine 100		11,24	11,38	10,74
Spirooxazine 150		9,61	8,73	9,60
Spirooxazine 250		5,75	7,98	8,99
Spirooxazine 350		11,19	9,25	9,57
Ruby Red Ref.		17,61	17,99	18,39
Ruby Red 25		16,21	15,62	16,54
Ruby Red 50		14,32	14,41	16,60
Ruby Red 100		14,99	16,58	14,58
Ruby Red 150		14,75	14,39	13,78
Ruby Red 250		14,74	13,47	13,22
Ruby Red 350		15,87	15,97	16,13
Oxford Blue Ref.		19,77	20,50	19,14
Oxford Blue 25		14,19	15,19	17,15
Oxford Blue 50		14,55	14,11	18,45
Oxford Blue 100	**3rd cycle**	14,92	15,32	17,18
Oxford Blue 150		16,03	15,17	13,90
Oxford Blue 250		13,31	13,03	14,24
Oxford Blue 350		12,66	15,24	13,08
Spirooxazine Ref.		14,79	14,22	13,95
Spirooxazine 25		11,52	8,28	9,84
Spirooxazine 50		9,80	12,23	14,61
Spirooxazine 100		11,49	11,36	10,01
Spirooxazine 150		9,97	9,08	9,25
Spirooxazine 250		9,79	9,59	6,93
Spirooxazine 350		10,71	11,66	8,86

Appendix V

Table 30: Mean ΔE in multiple activations test (cycle 1-5) for chemically stabilised samples

Ink formulation [wt%] HALS	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Ruby Red 0	20,84	19,89	18,94	18,76	18,14
Ruby Red 0.05	21,25	20,59	19,45	19,26	18,57
Ruby Red 0.5	20,52	20,21	19,47	18,98	18,55
Ruby Red 1.0	21,95	21,19	20,55	19,69	19,73
Oxford Blue 0	20,41	19,42	18,03	18,95	18,41
Oxford Blue 0.05	21,49	21,18	19,75	19,58	19,90
Oxford Blue 0.5	21,52	21,80	19,37	19,01	20,09
Oxford Blue 1.0	22,72	22,32	20,07	20,40	20,29
Spirooxazine 0	17,30	15,68	15,25	14,40	15,47
Spirooxazine 0.05	16,86	16,68	14,37	15,21	15,63
Spirooxazine 0.5	17,76	15,84	15,49	15,75	15,33
Spirooxazine 1.0	17,16	15,68	15,30	15,56	16,53

Table 31: Mean ΔE in multiple activations test (cycle 6-10) for chemically stabilised samples

Ink formulation [wt%] HALS	Cycle 6	Cycle 7	Cycle 8	Cycle 9	Cycle 10
Ruby Red 0	17,08	17,67	16,51	16,65	16,66
Ruby Red 0.05	18,52	17,94	17,08	17,00	17,66
Ruby Red 0.5	18,51	18,10	17,25	17,47	17,78
Ruby Red 1.0	19,34	18,32	18,43	18,59	18,59
Oxford Blue 0	19,13	19,01	18,16	19,16	18,81
Oxford Blue 0.05	20,02	19,58	19,28	19,90	19,87
Oxford Blue 0.5	20,79	20,87	19,97	20,47	21,23
Oxford Blue 1.0	21,58	21,35	20,28	20,93	21,23
Spirooxazine 0	15,74	15,80	14,92	15,52	15,52
Spirooxazine 0.05	15,67	15,86	14,60	15,85	15,58
Spirooxazine 0.5	16,44	16,29	15,20	16,03	16,22
Spirooxazine 1.0	16,56	16,74	15,84	16,10	16,71

Table 32: Mean ΔE in multiple activations test (cycle 1-5) for physically stabilised samples

Ink [µm] coating thickness	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Ruby Red Ref.	20,74	19,24	18,66	18,46	18,21
Ruby Red 50	16,99	17,00	16,53	17,05	14,93
Ruby Red 150	17,38	16,99	16,52	17,65	16,76
Ruby Red 250	15,16	15,19	15,85	15,93	15,62
Oxford Blue Ref.	22,92	23,25	23,75	23,07	24,37
Oxford Blue 50	13,54	15,70	15,14	15,86	15,91
Oxford Blue 150	14,67	16,90	16,65	16,74	17,02
Oxford Blue 250	11,58	12,40	13,07	13,94	13,69
Spirooxazine Ref.	15,42	15,73	16,26	16,89	16,84
Spirooxazine 50	9,25	11,04	11,15	11,78	11,91
Spirooxazine 150	10,95	12,16	11,30	12,41	12,62
Spirooxazine 250	7,74	9,50	9,24	9,57	9,43

Table 33: Mean ΔE in multiple activations test (cycle 6-10) for physically stabilised samples

Ink [µm] coating thickness	Cycle 6	Cycle 7	Cycle 8	Cycle 9	Cycle 10
Ruby Red Ref.	18,45	18,30	18,09	18,25	17,87
Ruby Red 50	16,53	16,82	15,78	16,49	15,85
Ruby Red 150	17,30	16,95	16,85	17,18	16,40
Ruby Red 250	15,19	15,29	15,03	14,96	14,93
Oxford Blue Ref.	23,20	23,43	22,66	22,95	22,62
Oxford Blue 50	16,07	16,32	15,34	15,68	15,66
Oxford Blue 150	16,87	16,45	16,33	16,45	16,57
Oxford Blue 250	13,65	13,63	13,32	13,59	13,46
Spirooxazine Ref.	16,04	16,52	16,16	16,15	16,27
Spirooxazine 50	11,63	11,44	11,46	12,29	12,45
Spirooxazine 150	11,74	12,08	12,14	11,92	12,22
Spirooxazine 250	8,95	9,60	9,49	9,70	9,50

Table 34: Mean ΔE in multiple activations test (cycle 1-3) for additional physically stabilised samples

Ink [µm] coating thickness	Cycle 1	Cycle 2	Cycle 3
Ruby Red Ref.	17,31	18,34	18,00
Ruby Red 25	16,85	16,26	16,12
Ruby Red 50	15,61	15,55	15,11
Ruby Red 100	16,36	15,73	15,38
Ruby Red 150	14,49	14,53	14,31
Ruby Red 250	14,01	13,76	13,81
Ruby Red 350	16,71	15,76	15,99
Oxford Blue Ref.	21,01	21,59	19,80
Oxford Blue 25	16,69	16,94	15,51
Oxford Blue 50	16,79	17,66	15,70
Oxford Blue 100	16,30	15,41	15,81
Oxford Blue 150	15,88	15,74	15,03
Oxford Blue 250	14,62	14,75	13,53
Oxford Blue 350	13,85	14,47	13,66
Spirooxazine Ref.	15,36	14,77	14,32
Spirooxazine 25	9,97	8,66	9,88
Spirooxazine 50	12,04	11,39	12,21
Spirooxazine 100	10,67	11,12	10,95
Spirooxazine 150	10,48	9,31	9,43
Spirooxazine 250	9,00	7,57	8,77
Spirooxazine 350	10,10	10,00	10,41

Appendix VI

The graphs illustrate the visible colour absorbance in comparison to a blank sample (57-58). The two used coatings (PU1110 and PU8551) are included.

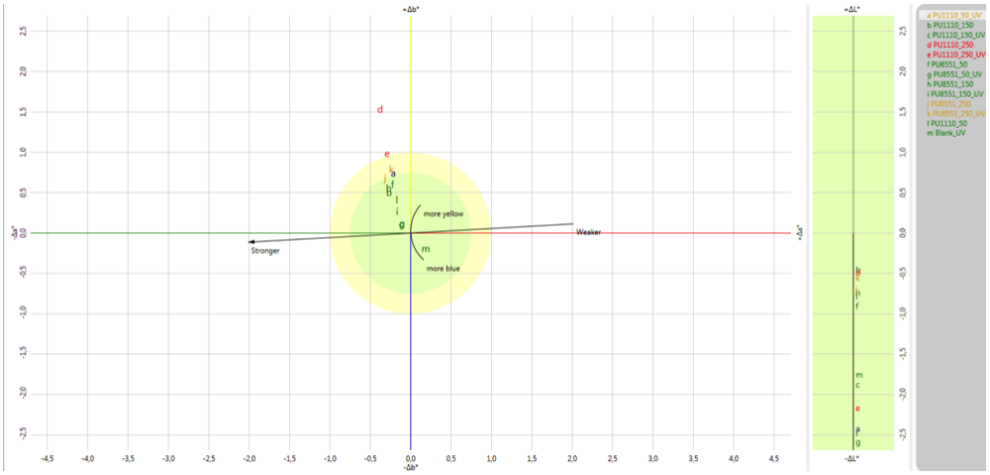

Fig. 58 K/S Absorbance vs. wavelength for coated samples

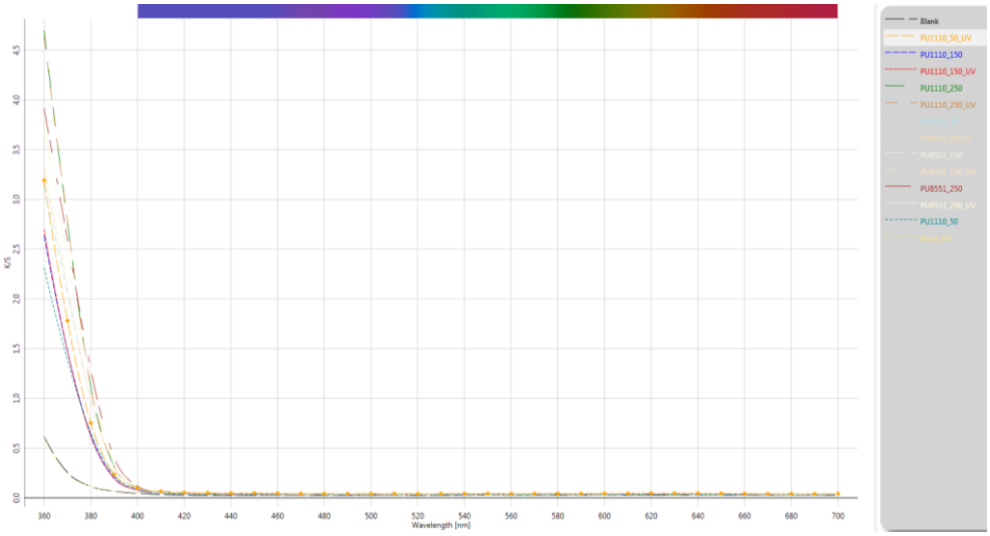

Fig. 59 Colour difference in Delta CMC for coated samples

Appendix VII

Complete data on standard deviations within sample sets. Last column presents the measured standard deviation of average values in before and after testing.

Table 35: Standard deviation within sample sets for chemically stabilised samples in washing test and before and after wash

Ink formulation [wt%] HALS	Standard deviation [σ]		
	Unwashed	Washed	Btw before and after wash
Ruby Red 0	1,10	0,49	2,49
Ruby Red 0.05	0,52	0,34	3,86
Ruby Red 0.5	0,31	0,62	3,28
Ruby Red 1.0	0,28	0,37	3,58
Ruby Red 1.5	0,49	0,64	3,06
Ruby Red 2.0	0,21	0,18	2,45
Ruby Red 2.5	0,44	0,02	2,55
Ruby Red 3.0	0,41	0,90	3,16
Oxford Blue 0	0,56	0,39	1,59
Oxford Blue 0.05	0,88	1,04	1,61
Oxford Blue 0.5	0,86	1,02	2,26
Oxford Blue 1.0	2,44	3,09	2,89
Oxford Blue 1.5	0,65	0,75	1,01
Oxford Blue 2.0	0,52	0,96	1,54
Oxford Blue 2.5	0,36	0,26	2,12
Oxford Blue 3.0	0,67	0,65	2,50
Spirooxazine 0	1,29	0,63	1,84
Spirooxazine 0.05	0,93	1,46	1,92
Spirooxazine 0.5	0,51	1,09	2,54
Spirooxazine 1.0	0,94	1,27	2,63
Spirooxazine 1.5	0,71	0,31	1,51
Spirooxazine 2.0	0,96	1,23	1,10
Spirooxazine 2.5	0,67	1,58	1,31
Spirooxazine 3.0	1,04	1,20	1,29

Table 36: Standard deviation within sample sets for physically stabilised samples in washing test and before and after wash

Ink formulation and coating thickness [µm]	Standard deviation [σ]		
	Unwashed	Washed	Btw before and after wash
Ruby Red Ref.	0,60	0,46	1,97
Ruby Red 50	1,75	0,83	0,63
Ruby Red 150	1,33	0,82	0,63
Ruby Red 250	0,53	0,40	0,71
Oxford Blue Ref.	0,22	0,28	0,91
Oxford Blue 50	0,99	1,50	0,60
Oxford Blue 150	0,67	0,35	0,26
Oxford Blue 250	0,28	0,31	0,03
Spirooxazine Ref.	0,28	0,78	0,60
Spirooxazine 50	1,20	0,65	0,05
Spirooxazine 150	0,47	0,41	0,16
Spirooxazine 250	1,35	0,36	0,27

Table 37: Standard deviation within sample sets for chemically stabilised samples in multiple activations test (1-5 cycles)

Ink formulation [wt%] HALS	Standard deviation [σ]				
	1st	2nd	3rd	4th	5th
Ruby Red 0	0,25	0,20	0,38	0,09	0,11
Ruby Red 0.05	0,07	0,22	0,40	0,21	0,41
Ruby Red 0.5	0,36	0,11	0,39	0,20	0,19
Ruby Red 1.0	0,26	0,81	0,59	0,06	0,54
Oxford Blue 0	0,34	1,27	1,58	0,99	0,45
Oxford Blue 0.05	0,58	0,42	0,81	0,41	0,40
Oxford Blue 0.5	0,49	0,92	1,52	1,32	0,70
Oxford Blue 1.0	0,50	0,53	0,30	0,41	0,88
Spirooxazine 0	0,97	0,29	0,81	0,74	0,39
Spirooxazine 0.05	1,06	0,50	0,75	0,65	0,23
Spirooxazine 0.5	0,42	0,38	0,81	0,52	0,53
Spirooxazine 1.0	0,92	0,76	0,45	0,72	0,93

Table 38: Standard deviation within the sample set for chemically stabilised samples in multiple activations test (cycle 6-10) and between first and last activation

Ink formulation [wt%] HALS	Standard deviation [σ]					
	6th	7th	8th	9th	10th	Btw 1st and 10th activation
Ruby Red 0	0,71	0,17	0,56	0,21	0,49	2,09
Ruby Red 0.05	0,11	0,56	0,73	0,70	0,44	1,80
Ruby Red 0.5	0,26	0,32	0,25	0,19	0,34	1,37
Ruby Red 1.0	0,89	1,42	0,43	0,57	0,40	1,68
Oxford Blue 0	0,71	0,58	0,76	0,80	0,49	0,80
Oxford Blue 0.05	0,22	0,26	0,20	0,29	0,12	0,81

Oxford Blue 0.5	0,29	0,32	0,59	0,60	0,26	0,14
Oxford Blue 1.0	0,15	0,37	0,43	0,36	0,37	0,74
Spirooxazine 0	0,44	0,11	0,84	0,31	0,25	0,89
Spirooxazine 0.05	0,14	0,70	0,32	0,17	0,57	0,64
Spirooxazine 0.5	0,61	0,36	0,78	0,60	1,01	0,77
Spirooxazine 1.0	0,56	1,19	0,98	0,50	0,81	0,23

Table 39: Standard deviation within sample set for physically stabilised samples in multiple activations test (1-5 cycles)

Ink formulation and coating thickness [µm]	**Standard deviation [σ]**				
	1st	**2nd**	**3rd**	**4th**	**5th**
Ruby Red Ref.	1,35	0,50	0,74	0,35	0,37
Ruby Red 50	0,37	0,49	0,34	0,14	0,89
Ruby Red 150	0,20	0,62	0,32	0,08	0,79
Ruby Red 250	1,37	0,81	1,41	1,38	1,04
Oxford Blue Ref.	0,66	1,18	0,29	1,05	0,45
Oxford Blue 50	0,63	0,70	0,78	1,62	0,99
Oxford Blue 150	0,32	0,84	0,43	0,27	0,41
Oxford Blue 250	0,12	0,35	0,29	0,51	0,65
Spirooxazine Ref.	0,95	1,43	0,20	0,55	0,70
Spirooxazine 50	0,51	0,61	0,47	0,39	0,32
Spirooxazine 150	0,39	0,51	0,65	0,25	0,41
Spirooxazine 250	0,51	0,23	0,49	1,23	1,00

Table 40: Standard deviation within the sample set for physically stabilised samples in multiple activations test (cycle 6-10) and between first and last activation

Ink formulation and coating thickness [µm]	**Standard deviation [σ]**					
	6th	**7th**	**8th**	**9th**	**10th**	**Btw 1st and 10th activation**
Ruby Red Ref.	0,27	0,53	0,37	0,27	0,38	1,43
Ruby Red 50	0,15	0,10	0,64	0,16	0,18	0,57
Ruby Red 150	0,38	0,21	0,03	0,46	0,21	0,49
Ruby Red 250	1,03	0,67	1,31	0,99	0,70	0,12
Oxford Blue Ref.	1,09	0,25	0,45	1,21	1,11	0,15
Oxford Blue 50	0,65	0,68	0,69	0,25	0,60	1,06
Oxford Blue 150	0,47	0,23	0,57	0,47	0,97	0,95
Oxford Blue 250	0,41	0,49	0,88	0,87	0,83	0,94
Spirooxazine Ref.	0,27	0,15	0,16	0,33	0,09	0,43
Spirooxazine 50	0,64	0,52	1,16	0,14	0,35	1,60
Spirooxazine 150	0,34	0,52	0,17	0,29	0,11	0,63
Spirooxazine 250	1,24	1,47	0,81	1,16	0,50	0,88

Table 41: Standard deviation within sample set before and after sun-lamp exposure and between before and after exposure

Ink formulation and stabilising	Standard deviation [σ]		
	Before sun-lamp exposure	After sun-lamp exposure	Btw before and after exposure
Varnish	0,05	0,07	0,15
Varnish + 1 wt% HALS	0,06	0,01	0,11
Ruby Red 0 wt% HALS	0,49	0,29	6,39
Ruby Red 1.0 wt% HALS	0,40	0,13	6,34
Oxford Blue 0 wt% HALS	0,49	0,84	2,71
Oxford Blue 1.0 wt% HALS	0,37	0,20	3,28
Spirooxazine 0 wt% HALS	0,25	0,31	3,15
Spirooxazine 1.0 wt% HALS	0,81	0,70	3,05
Ruby Red Ref.	0,38	0,21	6,20
Ruby Red 250 µm coating	0,70	0,19	4,68
Oxford Blue Ref.	1,11	1,42	2,36
Oxford Blue 250 µm coating	0,83	0,45	1,68
Spirooxazine Ref.	0,09	0,43	2,06
Spirooxazine 250 µm coating	0,50	0,25	1,20

Table 42: Standard deviation within sample set in additional physically stabilised samples

Ink formulation and coating thickness [µm]	Standard deviation [σ]			
	1st	2nd	3rd	Btw first and last activation
Ruby Red Ref.	0,50	0,09	0,32	0,35
Ruby Red 25	0,81	0,72	0,38	0,37
Ruby Red 50	0,53	0,80	1,05	0,25
Ruby Red	1,20	0,66	0,86	0,49
Ruby Red 150	0,57	0,64	0,40	0,09
Ruby Red 250	0,72	0,93	0,67	0,10
Ruby Red 350	0,34	0,66	0,11	0,36
Oxford Blue Ref.	0,73	0,51	0,56	0,60
Oxford Blue 25	0,48	0,71	1,23	0,59
Oxford Blue 50	1,51	1,83	1,95	0,54
Oxford Blue 100	1,06	0,42	0,98	0,25
Oxford Blue 150	0,81	0,19	0,87	0,43
Oxford Blue 250	0,95	0,70	0,52	0,55
Oxford Blue 350	1,28	0,50	1,13	0,09
Spirooxazine Ref.	1,03	0,81	0,35	0,52
Spirooxazine 25	1,04	1,37	1,32	0,04
Spirooxazine 50	1,86	1,77	1,96	0,09
Spirooxazine 100	0,27	0,27	0,67	0,14
Spirooxazine 150	1,04	0,41	0,39	0,52
Spirooxazine 250	1,31	1,35	1,30	0,12
Spirooxazine 350	0,63	0,85	1,16	0,16

Appendix VIII

Summarise of the fatigue behaviour for the inks and stabilisation methods.

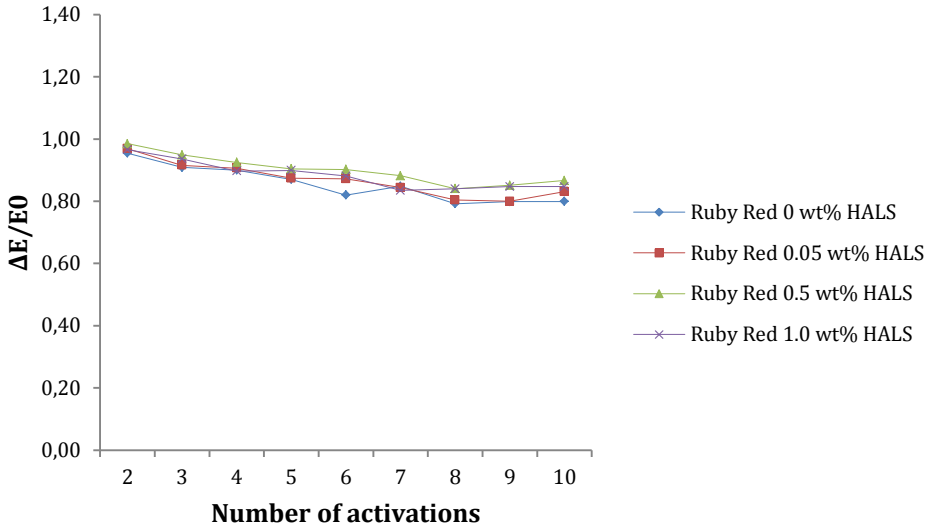

Fig. 60 Trend of photocolouration behaviour for chemically stabilised Ruby Red

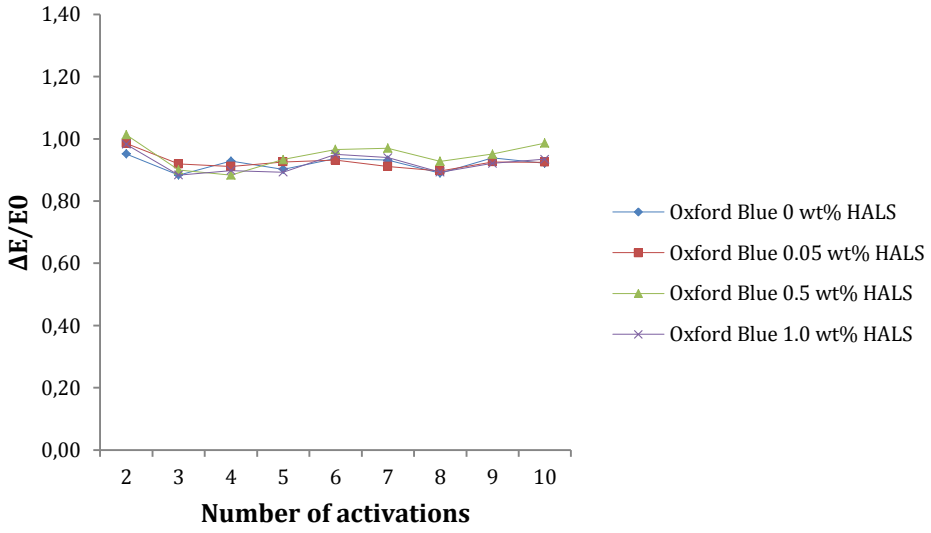

Fig. 61 Trend of photocolouration behaviour for chemically stabilised Oxford Blue

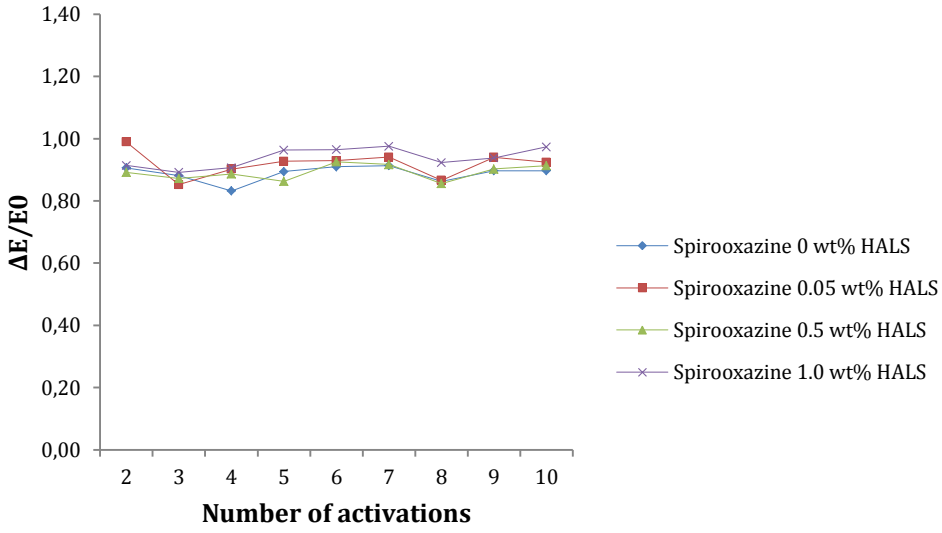

Fig. 62 Trend of photocolouration behaviour for chemically stabilised spirooxazine

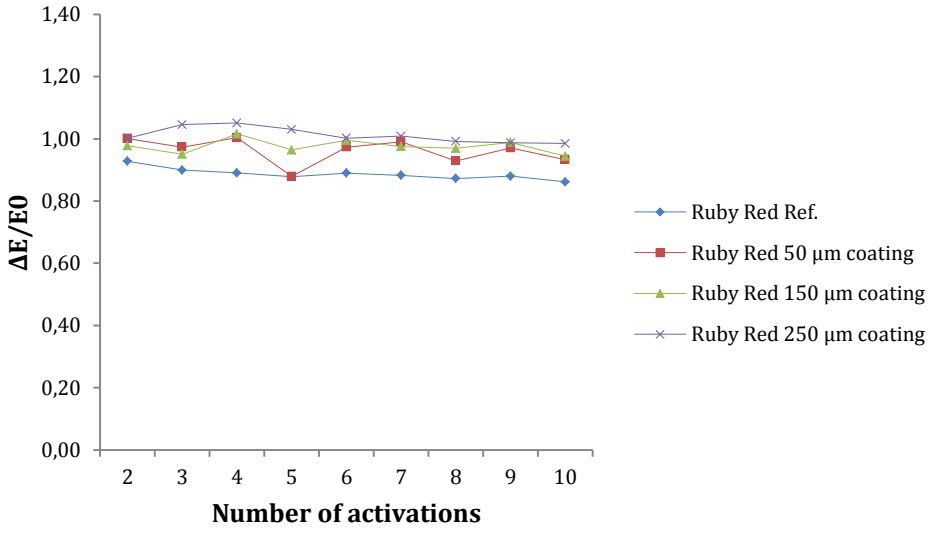

Fig. 63 Trend of photocolouration behaviour for physically stabilised Ruby Red

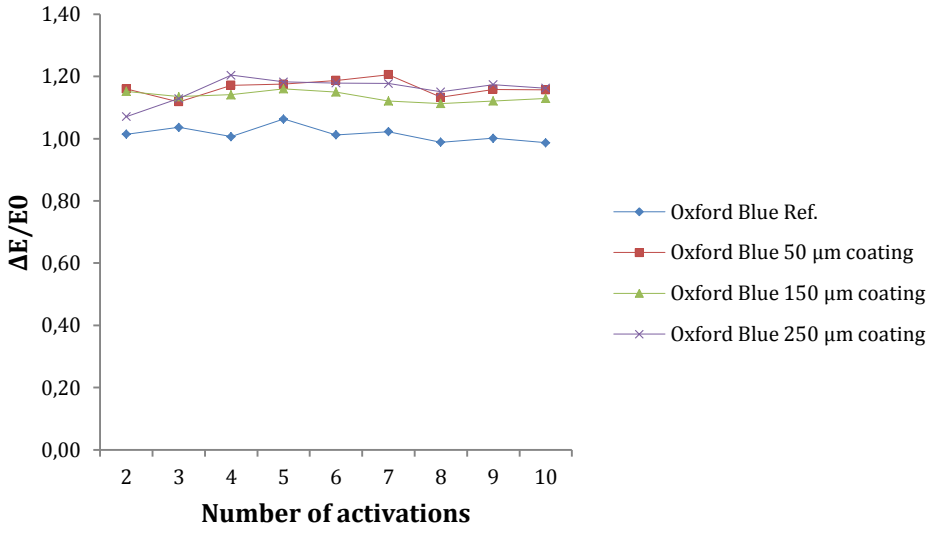

Fig. 64 Trend of photocolouration behaviour for physically stabilised Oxford Blue

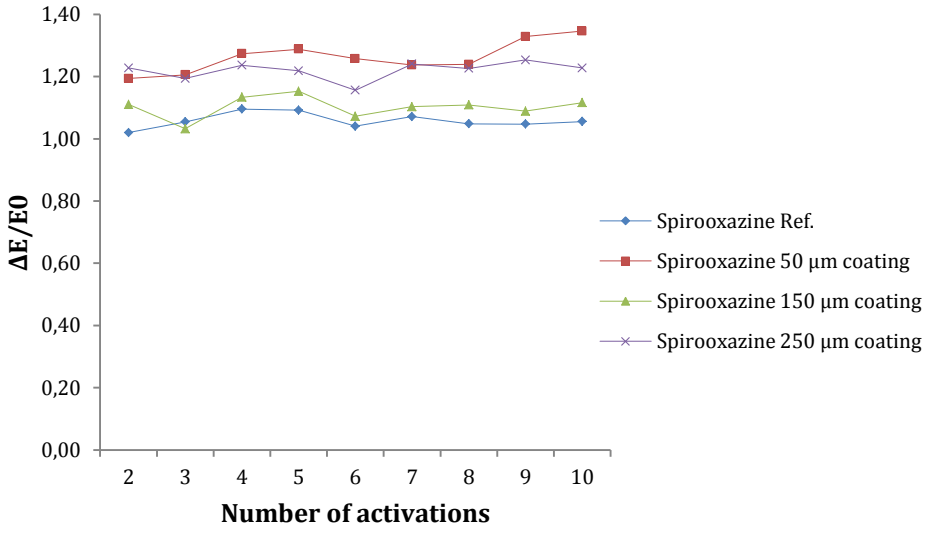

Fig. 65 Trend of photocolouration behaviour for physically stabilised spirooxazine

Appendix IX

Gathered data on probability value in a T-test for a normal distribution. P-value below 0.05 is accepted for a significant result taking variations within sample sets into account.

Table 43: P-values in a T-test between unwashed and washed chemically stabilised samples

Ink formulation [wt%] HALS	P-value
Ruby Red 0	0,012477593
Ruby Red 0.05	0,000165521
Ruby Red 0.5	0,000996953
Ruby Red 1.0	0,000048986
Ruby Red 1.5	0,000615014
Ruby Red 2.0	0,000016971
Ruby Red 2.5	0,003725996
Ruby Red 3.0	0,003769177
Oxford Blue 0	0,00406876
Oxford Blue 0.05	0,029765506
Oxford Blue 0.5	0,009323146
Oxford Blue 1.0	**0,110051870**
Oxford Blue 1.5	0,04655779
Oxford Blue 2.0	0,026431503
Oxford Blue 2.5	0,000320293
Oxford Blue 3.0	0,001586493
Spirooxazine 0	0,038612799
Spirooxazine 0.05	0,043687752
Spirooxazine 0.5	0,010892826
Spirooxazine 1.0	0,011307495
Spirooxazine 1.5	0,015014857
Spirooxazine 2.0	**0,120225725**
Spirooxazine 2.5	**0,129964797**
Spirooxazine 3.0	**0,084174021**

Table 44: P-values in a T-test between unwashed and washed physically stabilised samples

Ink formulation and coating thickness [µm]	P-value
Ruby Red Ref.	0,002254558
Ruby Red 50	**0,428527912**
Ruby Red 150	**0,328921361**
Ruby Red 250	0,042419046
Oxford Blue Ref.	0,002526875
Oxford Blue 50	**0,40925297**
Oxford Blue 150	**0,403224902**
Oxford Blue 250	**0,831172822**

Spirooxazine Ref.	**0,150348211**
Spirooxazine 50	**0,919085087**
Spirooxazine 150	**0,523621425**
Spirooxazine 250	**0,632614145**

Table 45: P-values in a T-test between first and tenth activation in chemically stabilised samples

Ink formulation [wt%] HALS	P-value
Ruby Red 0	0,001749161
Ruby Red 0.05	0,006370431
Ruby Red 0.5	0,001436884
Ruby Red 1.0	0,001225771
Oxford Blue 0	**0,577992877**
Oxford Blue 0.05	0,039752352
Oxford Blue 0.5	**0,477701789**
Oxford Blue 1.0	**0,083669608**
Spirooxazine 0	**0,582846627**
Spirooxazine 0.05	**0,108935533**
Spirooxazine 0.5	**0,661035337**
Spirooxazine 1.0	**0,261591543**

Table 46: P-values in a T-test between first and tenth activation in physically stabilised samples

Ink formulation and coating thickness [µm]	P-value
Ruby Red Ref.	**0,086534189**
Ruby Red 50	0,03282424
Ruby Red 150	0,008580586
Ruby Red 250	**0,842373118**
Oxford Blue Ref.	**0,760204471**
Oxford Blue 50	0,026202081
Oxford Blue 150	0,004474698
Oxford Blue 250	**0,081788281**
Spirooxazine Ref.	**0,332529166**
Spirooxazine 50	0,002890813
Spirooxazine 150	**0,037148316**
Spirooxazine 250	**0,025818881**

Table 47: P-values in a T-test between activation before and after sun-lamp exposure activation

Ink formulation and stabilising	P-value
Varnish	0,011217869
Varnish + 1 wt% HALS	0,02956990
Ruby Red 0 wt% HALS	0,00003425
Ruby Red 1.0 wt% HALS	0,000166986

Oxford Blue 0 wt% HALS	0,003222734
Oxford Blue 1.0 wt% HALS	0,000167062
Spirooxazine 0 wt% HALS	0,00003371
Spirooxazine 1.0 wt% HALS	0,001394937
Ruby Red Ref.	0,000022901
Ruby Red 250 µm coating	0,001582347
Oxford Blue Ref.	0,023016012
Oxford Blue 250 µm coating	0,014070363
Spirooxazine Ref.	0,003909776
Spirooxazine 250 µm coating	0,009870459

Appendix X

Analysis of variance for washing test chemical and physical stabilised samples followed by multiple activations test and sun-lamp exposed samples. Data gathered for qualitative analysis. The ANOVA shows the p-value for HALS concentrations and coating thicknesses significances for fatigue respectively and the washing and multiple activations significances for fatigue respectively.

ANOVA Washing test:

General Linear Model: ΔE-Ruby Red versus HALS; Wash

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
HALS	1	123,36	123,364	161,79	0,000
Wash	1	447,19	447,191	586,49	0,000
Error	45	34,31	0,762		
Lack-of-Fit	13	21,02	1,617	3,89	0,001
Pure Error	32	13,29	0,415		
Total	47	604,87			

General Linear Model: ΔE Oxford Blue versus HALS; Wash

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
HALS	1	27,15	27,149	4,94	0,031
Wash	1	180,65	180,653	32,88	0,000
Error	45	247,21	5,494		
Lack-of-Fit	13	178,73	13,749	6,42	0,000
Pure Error	32	68,48	2,140		
Total	47	455,01			

General Linear Model ΔE spirooxazine versus HALS; Wash

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
HALS	1	68,41	68,415	25,36	0,000
Wash	1	149,81	149,813	55,54	0,000
Error	45	121,39	2,697		
Lack-of-Fit	13	68,85	5,296	3,23	0,003
Pure Error	32	52,54	1,642		
Total	47	339,62			

General Linear Model: ΔE-Ruby Red versus Wash; Coat

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Wash	1	23,325	23,325	15,06	0,001
Coat	3	40,534	13,511	8,72	0,001
Error	19	29,431	1,549		
Lack-of-Fit	3	7,775	2,592	1,91	0,168
Pure Error	16	21,656	1,354		
Total	23	93,290			

General Linear Model: ΔE Oxford Blue e versus Wash; Coat

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Wash	1	0,546	0,5460	0,54	0,472
Coat	3	148,818	49,6061	48,90	0,000
Error	19	19,276	1,0145		
Lack-of-Fit	3	6,948	2,3159	3,01	0,061

Pure Error	16	12,328	0,7705	
Total	23	168,640		

General Linear Model ΔE spirooxazine versus Wash; Coat

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Wash	1	0,886	0,8855	1,02	0,326
Coat	3	228,675	76,2250	87,42	0,000
Error	19	16,567	0,8720		
Lack-of-Fit	3	1,873	0,6244	0,68	0,577
Pure Error	16	14,694	0,9184		
Total	23	246,128			

ANOVA Multiple activations:

General Linear Model: ΔE-Ruby Red versus HALS; Activation

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
HALS	1	5,019	5,0190	15,10	0,001
Activation	1	72,141	72,1413	217,09	0,000
Error	21	6,979	0,3323		
Lack-of-Fit	5	4,058	0,8116	4,45	0,010
Pure Error	16	2,921	0,1825		
Total	23	84,139			

General Linear Model: ΔE Oxford Blue versus HALS; Activation

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
HALS	1	15,244	15,2436	34,01	0,000
Activation	1	9,375	9,3750	20,92	0,000
Error	21	9,412	0,4482		
Lack-of-Fit	5	5,234	1,0468	4,01	0,015
Pure Error	16	4,178	0,2611		
Total	23	34,031			

General Linear Model ΔE spirooxazine versus HALS; Activation

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
HALS	1	1,887	1,8871	2,24	0,149
Activation	1	9,601	9,6014	11,40	0,003
Error	21	17,693	0,8425		
Lack-of-Fit	5	2,261	0,4521	0,47	0,794
Pure Error	16	15,433	0,9646		
Total	23	29,182			

General Linear Model ΔE-Ruby Red versus Activation; Coat

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Activation	1	10,218	10,2181	10,00	0,005
Coat	3	56,680	18,8932	18,49	0,000
Error	19	19,415	1,0219		
Lack-of-Fit	3	5,570	1,8565	2,15	0,135
Pure Error	16	13,846	0,8654		
Total	23	86,313			

General Linear Model: ΔE Oxford Blue versus Activation; Coat

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Activation2	1	11,774	11,774	12,18	0,002
Coat	3	356,780	118,927	123,02	0,000
Error	19	18,367	0,967		
Lack-of-Fit	3	5,862	1,954	2,50	0,097
Pure Error	16	12,505	0,782		
Total	23	386,921			

General Linear Model: ΔE spirooxazine versus Activation; Coat

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Activation2	1	18,780	18,7797	33,53	0,000
Coat	3	164,287	54,7622	97,77	0,000
Error	19	10,642	0,5601		
Lack-of-Fit	3	4,732	1,5772	4,27	0,021
Pure Error	16	5,911	0,3694		
Total	23	193,708			

ANOVA Sun-lamp exposure test

General Linear Model: ΔE-Ruby Red versus HALS; Sun-lamp

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
HALS	1	11,741	11,741	70,18	0,000
Sun-lamp	1	485,522	485,522	2902,15	0,000
Error	9	1,506	0,167		
Lack-of-Fit	1	0,008	0,008	0,04	0,841
Pure Error	8	1,498	0,187		
Total	11	498,769			

General Linear Model: ΔE Oxford Blue versus HALS; Sun-lamp

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
HALS	1	10,360	10,360	21,55	0,001
Sun-lamp	1	107,700	107,700	224,03	0,000
Error	9	4,327	0,481		
Lack-of-Fit	1	0,969	0,969	2,31	0,167
Pure Error	8	3,358	0,420		
Total	11	122,387			

General Linear Model ΔE spirooxazine versus HALS; Sun-lamp

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
HALS	1	5,057	5,057	11,56	0,008
Sun-lamp	1	115,258	115,258	263,37	0,000
Error	9	3,939	0,438		
Lack-of-Fit	1	0,035	0,035	0,07	0,795
Pure Error	8	3,903	0,488		
Total	11	124,254			

General Linear Model: ΔE-Ruby Red versus Sun-lamp; Coat

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Sun-lamp2	1	355,232	355,232	353,98	0,000
Coat	1	6,120	6,120	6,10	0,036
Error	9	9,032	1,004		
Lack-of-Fit	1	6,886	6,886	25,67	0,001
Pure Error	8	2,146	0,268		
Total	11	370,384			

General Linear Model: ΔE Oxford Blue versus Sun-lamp; Coat

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Sun-lamp2	1	48,803	48,803	31,90	0,000
Coat	1	215,731	215,731	141,01	0,000
Error	9	13,769	1,530		
Lack-of-Fit	1	1,374	1,374	0,89	0,374
Pure Error	8	12,395	1,549		
Total	11	278,303			

General Linear Model ΔE spirooxazine versus Sun-lamp; Coat

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Sun-lamp2	1	31,785	31,785	75,66	0,000
Coat	1	104,607	104,607	249,00	0,000
Error	9	3,781	0,420		
Lack-of-Fit	1	2,245	2,245	11,69	0,009
Pure Error	8	1,536	0,192		
Total	11	140,173			