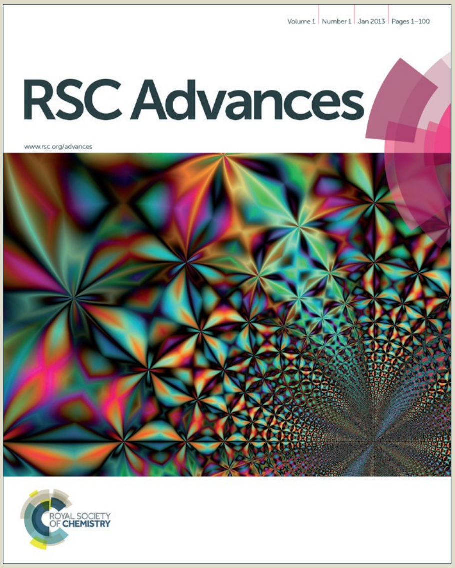
RSC Advances



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

COMMUNICATION

Water-responsive dual-coloured photonic polymer coatings based on cholesteric liquid crystals

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

J.E. Stumpel,[a] D.J. Broer[ab] and A.P.H.J. Schenning[ab*]

This work describes a straightforward method to prepare patterned photonic coatings which alter their colour when exposed to water. Various kinds of dual-coloured patterns were made, which become visible or fade away when placed in water. These effects are reversible and can be repeated many times.

Polymer coatings are widely used for aesthetic purposes, adhesion-promotion/reduction, anti-reflection and/or anti-fouling. Recently stimuli-responsive polymer coatings which can reversibly change their functional properties have received a lot of attention.[1-5] A relatively new class of responsive coatings are based on photonic effects which enable dynamic light effects e.g. by changing their reflection wavelength and/or intensity. Such coating are not sensitive for photobleaching and their colour response can immediately be observed by the naked eye.[6-8] Photonic materials which respond to light-, pH- and temperature or dual stimuli have already been reported showing a single colour change.[7,9-11]

Nature provides us with various kinds of autonomously responsive multi-colour changing phenomena, as observed by chameleons, octopuses, beetles and squids. Inspired by these examples we report now on dual-colour changing polymer coatings that respond to a single stimulus. A recent publication describes vapour-responsive inkjet patterned coatings based on colloidal photonic crystal inks containing nanoparticles of different size.[12] Also, photonic coatings based on bilayer-structures have been prepared where one reflection is responsive, while the other remains unaltered, acting as a control signal.[13] We provide here an alternative fabrication method based on a single coating locally modified by lithographic means.

For this purpose we use a special class of responsive colour-changing materials based on cholesteric liquid crystals (CLCs). The helical organisation of the molecular director leads to selective reflection of incident light, called the selective reflection band (SRB).[14] In CLC polymer films, this helical arrangement is imprinted during the polymerisation process. Such polymer CLCs can be used as stimuli-responsive photonic coatings.[15-19] In earlier work, we reported on water-responsive patterned CLC hygroscopic polymer salt coatings, which alter their topography.[20,21] This response is caused by an increase or decrease in the pitch of the helix due to the absorption or desorption of water. We now show that patterned water-responsive dual-coloured photonic coatings can be prepared in an easy and straightforward method by using this polymer mixture and two subsequent polymerisation steps at different temperatures.[22-24] Subsequently a patterned polymer coating is obtained, which shows multi-colour changes. Such type of coatings are appealing for various kinds of applications, such as moisture responsive decorative coatings, photonic sensors or security and anti-counterfeit features.

A CLC mixture (**M1**, Scheme 1) as earlier reported was used to prepare the water-responsive CLC polymer salt coatings.[21] The mono- and diacrylate LCs (**2** and **3**) induce nematic behaviour in the mixture and compound **2** also forms a chemical network after photopolymerisation. Polymerisable hydrogen-bonded benzoic acid derivatives **4** and **5** were added to make the coating water-responsive. The cholesteric molecular order and corresponding reflection band of the mixture was induced using chiral dopant **1**. Thermal inhibitor **6** was used to establish the thermal stability in the monomer mixture to prevent premature polymerisation during processing at elevated temperatures. The addition of photoinitiator **7** makes the mixture susceptible to photopolymerisation.

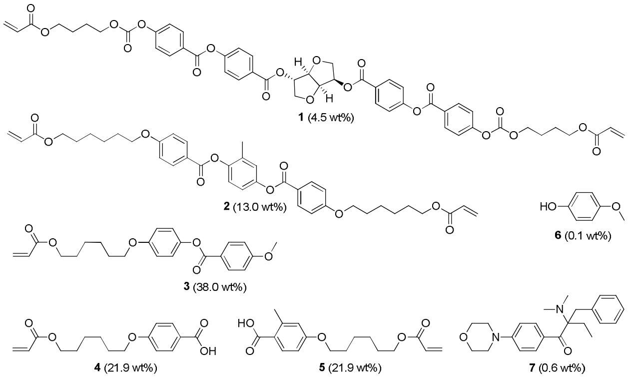
---

[a] *Laboratory of Functional Organic Materials and Devices, Eindhoven University of Technology, Building 14 – HELIX, De Rondom 70, 5612 AP Eindhoven, The Netherlands E-mail: a.p.h.j.schenning@tue.nl*

[b] *Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600MB, The Netherlands*

† *Footnotes relating to the title and/or authors should appear here.*

Electronic Supplementary Information (ESI) available: [preparation and characterisation methods of the coatings]. See DOI: 10.1039/x0xx00000x



Scheme 1 The chemical components used for the preparation of the water responsive cholesteric liquid crystal polymer salt coating. The mixture consists of chiral dopant **1**, nematic mesogens **2** and **3**, benzoic acid derivatives **4** and **5**, thermal inhibitor **6** and photoinitiator **7**. The composition of the various components in mixture (**M1**) is also shown. Homogeneity of the mixture was ensured by the preparation of a solution (20 wt% in THF) prior to use and subsequent evaporation.

The CLC mixture was aligned with the use of shear force between two glass slides and subsequently photopolymerised at a set temperature. Afterwards, this polymer coating with a thickness of ~8 µm was made water-responsive by treatment with an alkaline (0.1 M KOH, 10 h) solution, leading to the disruption of the hydrogen-bonded physical network and the formation of a polymer salt. The conversion of carboxylic acids into the corresponding carboxylate salts was confirmed with the use of FT-IR spectroscopy.[20,21] After this base treatment and subsequent drying, the CLC coating maintained its initial reflection band, which became slightly narrower.

Table 1 Variation in the amount of chiral dopant **1** leads to the reflection of different wavelengths

Mixture	Amount of chiral dopant **1** (wt%)	λ_{refl} dry[a] (nm)	λ_{refl} swollen (nm)
M1	4.5	584	793
M2	5.5	480	632
M3	8.0	350	421

[a] The samples were photopolymerised at 20 °C

In order to prepare materials with an initial green reflection band in the centre of the visible spectrum a mixture (**M1**) with 4.5 wt% of chiral dopant **1** was used. The use of a different concentration of **1** (while the ratio of the other components was kept constant) leads to materials which reflect light with another wavelength. A slight increase in the concentration of chiral dopant results in the reflection of light with a lower wavelength (**M2**) while a higher increase results in UV-reflecting materials (**M3**), as shown in Table 1.

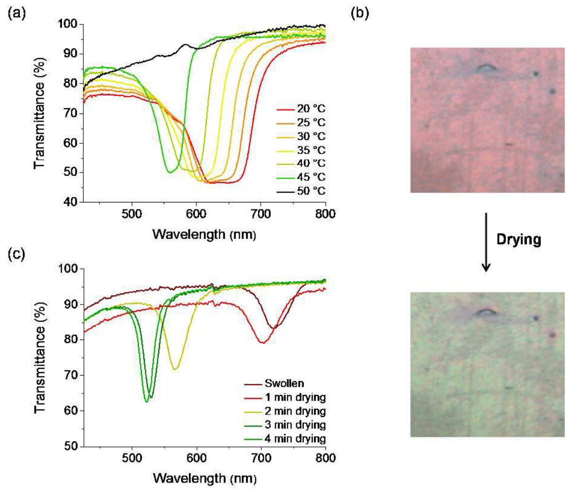


Fig. 1 (a) UV/Vis transmission spectra of unpolymerised **M1** at various temperatures. (b) Optical images of the swollen hygroscopic CLC coating polymerised at 40 °C turning from red to green upon drying in ambient conditions (RH = 40, T = 20 °C) within several minutes. (c) Corresponding UV/Vis transmission spectra showing the changes in the reflection band upon drying of a water-saturated CLC polymer coating.

The SRB of the planarly aligned monomer mixture **M1** is temperature-dependent. Alternation of the polymerisation temperature can therefore be used to produce polymer coatings which reflect various colours. At room temperature, the aligned monomer mixture reflects red light, an increase in temperature leads to a blue shift (Fig. 1a). Up to roughly 50 °C, the mixture is in its cholesteric phase. Above this temperature, the mixture becomes isotropic and the reflection band is lost.[20] The reflected colour can be fixed by photopolymerisation, during which the reflection band undergoes a blue shift.[25] Fig. 1b depicts optical images of a CLC polymer salt coating which was prepared from **M1** at 40 °C in the swollen and dry state. In the wet state, it turns red, while it becomes green again upon evaporation of water in a time scale of several minutes (Fig. 1c).

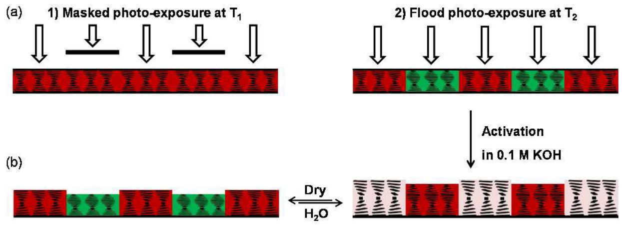


Fig. 2 (a) Schematic representation of the manufacturing method for a patterned CLC coating. The mixture was partially polymerised in a red-reflecting CLC phase at T_1 during the masked photo-exposure step. Subsequent flood exposure at T_2 polymerises a green-reflecting CLC phase and ensures full polymerisation. (b) Activation with an alkaline solution leads to a patterned hygroscopic dual coloured changing CLC polymer coating.

With the use of a photomask and two subsequent photopolymerisation steps at different temperatures below the CLC's clearing point, coatings with different colour-reflecting cholesteric regions were prepared. The preparation method for these patterned CLC-CLC coatings is depicted in Fig. 2a. The mixture was partially polymerised in the red-reflecting CLC phase at room temperature during the masked photo-exposure step. Subsequently the unexposed areas were polymerised at 40 °C in the green-reflecting CLC phase in a flood exposure step. This yields a red-green patterned polymer coating (Fig. 3a). During the masked exposure step migration of the monomers towards the exposed areas occurred, therefore the surface of the coating is not flat (Fig. 3b).

In order to make the coating water-responsive it was treated with a base leading to a hygroscopic patterned photonic polymer salt coating. After this activation step, both regions respond to water. The green regions become red (from 548 to 657 nm) while the red regions shift to the near infrared (from 616 to 702 nm). When the coating was treated with demineralised water, the thickness increased by at least 1 µm over the entire coating (Fig. 3b). The shift in the reflection band of the swollen coating corresponded to the change in thickness[20] In this case, the reflection band increased by a factor 1.15-1.2, while the observed thickness increased by a factor 1.1 (due to evaporation of water during the interferometry experiment, this factor is slightly lower). This behaviour reveals that the optical response is caused by an increase in the pitch of the helix due to the absorption of water.

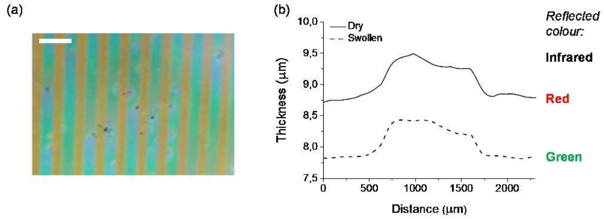


Fig. 3 (a) Optical image showing a patterned dual coloured CLC coating after mask exposure at 20 °C (red areas) and flood exposure at 40 °C (green regions). The scale bar represents 3 mm. (b) A cross section of a part of the corresponding activated coating in the fully swollen and dry (RH = 37%, 20 °C) state (the observed colour at different thicknesses is depicted on the right). Note: the actual height difference is slightly higher, as interferometry cannot be performed in a controlled aqueous environment.

To show the versatility of our method, three coatings having the character "F", and different colour-reflecting regions, were prepared by using a mask containing this character. Mask photopolymerisation of **M1** was performed at 20 °C, followed by flood exposure with the hot plate set at 50 °C (the sample's temperature is just below the clearing point of **M1**). This initially red-green dual-coloured sample reflected dark red and orange light respectively when the coating was swollen (Fig. 4a). In this specific coating, it can be clearly observed that a coloured "F" turned almost colourless. Another coating was prepared with mixture **M2** using an identical procedure which resulted in a dual-coloured coating in both the wet and dry states (Fig. 4b). The initially green "F" turns red, while the purple background turns green. Finally, a sample was prepared which contained both coloured cholesteric and colourless isotropic areas. In this case, the cholesteric areas will change colour when water is present while the isotropic areas remains colourless. Mixture **M3** was subjected to a mask exposure at 20 °C followed by flood illumination at 100 °C, which is above the clearing point of the CLC mixture. In the resulting optically colourless coating, the character "F" appeared in purple when the coating was in contact with water (Fig. 4c).

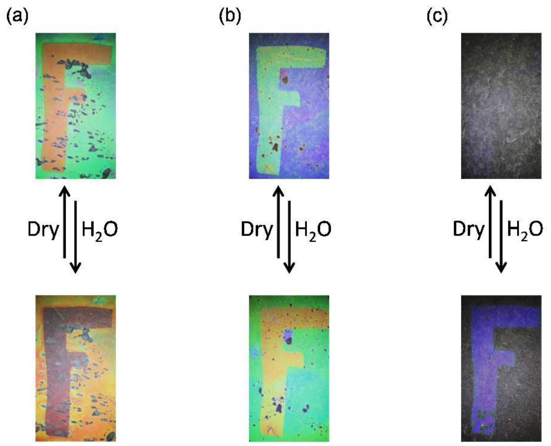


Fig. 4 Optical images showing three different polymer salt coatings with the letter "F" in ambient conditions (RH = 40, T = 20 °C) and in the wet state. The coatings were made as follows: (a) **M1**, 20 °C mask; 50 °C flood exposure, (b) **M2**, 20 °C mask; 50 °C flood exposure and (c) **M3**, 20 °C mask; 100 °C flood exposure. The size of the images is 17 x 9 mm. Note: these are the temperatures of the hot plate, the actual temperature of the monomer mixtures is slightly lower.

The time scale for the change in the optical properties of these three dry coatings was ~30 seconds when placed in a wet environment and slightly longer (2-3 minutes) when the sample was drying at ambient conditions. After six months of storage in open air where the relative humidity fluctuated between 30 and 50%, the response was still fully reversible and similar to the fresh samples, indicating that these materials are stable in time.

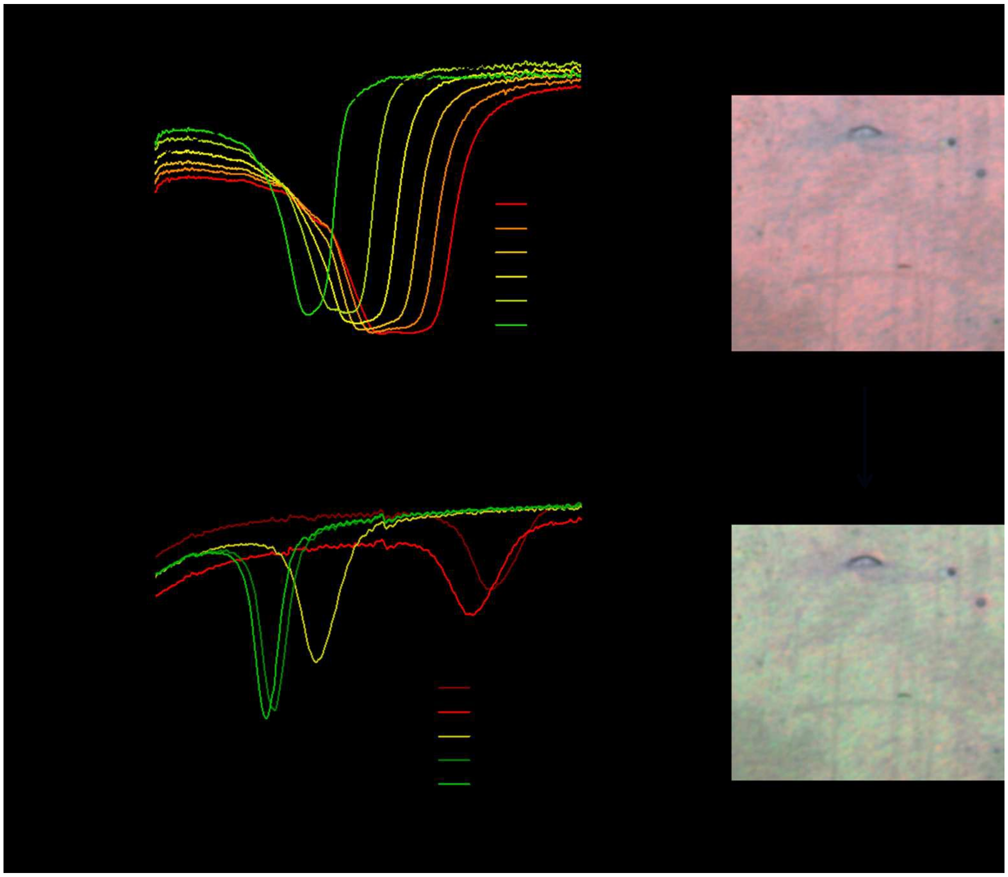
Conclusions

We have prepared responsive cholesteric liquid crystal dual-colour changing coatings via a straightforward method in which we use a single monomer mixture and two subsequent photoexposure steps. With the use of a masked and subsequent flood exposure at two different temperatures, patterned coatings with two distinct coloured regions were prepared. These photonic polymer coatings change their colour reversibly upon exposure to water. The difference between the thickness of the swollen and dry cholesteric areas corresponds to the difference in reflected wavelength as the reflection band is dependent on the length of the pitch. Various kinds of dual-coloured patterned coatings were prepared by varying the amount of chiral dopant and the polymerisation temperature. Moreover, coatings were produced that changed from colourless to coloured when placed in water.

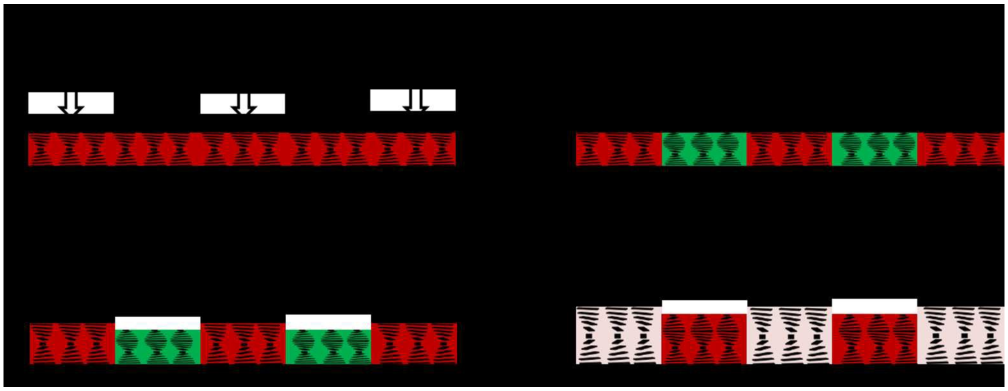
Overall, our straightforward method allows in principle the preparation of bioinspired responsive multi-coloured polymer coatings which are potentially interesting for a variety applications. Such kind of coatings could give rise to materials which autonomously undergo multiple optical changes upon variations in the environment.

References

1. C. Alexander and K. M. Shakesheff, *Adv. Mater.*, 2006, **18**, 3321-3328.
2. H. Meng and J. Hu, *J. Intell. Mater. Syst. Struct.*, 2010, **21**, 859-885.
3. R. Byrne, F. Benito-Lopez and D. Diamond, *Mater. Today*, 2010, **13**, 16-23.
4. Q. Li, *Intelligent Stimuli-Responsive Materials*, John Wiley & Sons, Inc., 2013.
5. V. A. Ganesh, A. Baji and S. Ramakrishna, *RSC Adv.*, 2014, **4**, 53352-53364.
6. J. Ge and Y. Yin, *Angew. Chem., Int. Ed.*, 2011, **50**, 1492-1522.
7. J. E. Stumpel, D. J. Broer and A. P. H. J. Schenning, *Chem. Commun.*, 2014, **50**, 15839-15848.
8. Y. Gao, X. Li and M. J. Serpe, *RSC Adv.*, 2015, **5**, 44074-44087.
9. E. Kim, S. Y. Kim, G. Jo, S. Kim and M. J. Park, *ACS Appl. Mater. Interfaces*, 2012, **4**, 5179-5187.
10. E. Tian, J. Wang, Y. Zheng, Y. Song, L. Jiang and D. Zhu, *J. Mater. Chem.*, 2008, **18**, 1116-1122.
11. C. Liu, C. Yao, Y. Zhu, J. Ren and L. Ge, *Sens. Actuators, B*, 2015, **220**, 227-232.
12. L. Bai, Z. Xie, W. Wang, C. Yuan, Y. Zhao, Z. Mu, Q. Zhong and Z. Gu, *ACS Nano*, 2014, **8**, 11094-11100.
13. J. Zhang, S. Yang, Y. Tian, C.-F. Wang and S. Chen, *Chem. Commun.*, 2015, **51**, 10528-10531.
14. G. Chilaya, in *Chirality in Liquid Crystals*, eds. H.-S. Kitzerow and C. Bahr, Springer New York, 2001, pp. 159-185.
15. V. Shibaev, *Polym. Sci., Ser. A*, 2009, **51**, 1131-1193.
16. D. Liu and D. J. Broer, *Langmuir*, 2014, **30**, 13499-13509.
17. D. J. Broer, C. M. W. Bastiaansen, M. G. Debije and A. P. H. J. Schenning, *Angew. Chem., Int. Ed.*, 2012, **51**, 7102-7109.
18. R. J. Carlton, J. T. Hunter, D. S. Miller, R. Abbasi, P. C. Mushenheim, L. N. Tan and N. L. Abbott, *Liq. Cryst. Rev.*, 2013, **1**, 29-51.
19. D.-J. Mulder, A. P. H. J. Schenning and C. W. M. Bastiaansen, *J. Mater. Chem. C*, 2014, **2**, 6695-6705.
20. J. E. Stumpel, D. J. Broer, C. W. M. Bastiaansen and A. P. H. J. Schenning, *Organic Photonics VI*, 2014, **9137**.
21. N. Herzer, H. Guneysu, D. J. D. Davies, D. Yildirim, A. R. Vaccaro, D. J. Broer, C. W. M. Bastiaansen and A. P. H. J. Schenning, *J. Am. Chem. Soc.*, 2012, **134**, 7608-7611.
22. D. Liu, C. W. M. Bastiaansen, J. M. J. den Toonder and D. J. Broer, *Macromolecules*, 2012, **45**, 8008-8012.
23. D. Liu, C. W. M. Bastiaansen, J. M. J. den Toonder and D. J. Broer, *Angew. Chem., Int. Ed.*, 2012, **51**, 892-896.
24. M. E. Sousa, D. J. Broer, C. W. M. Bastiaansen, L. B. Freund and G. P. Crawford, *Adv. Mater.*, 2006, **18**, 1842-1845.
25. J. Guo, J. Sun, L. Zhang, K. Li, H. Cao, H. Yang and S. Zhu, *Polym. Adv. Technol.*, 2008, **19**, 1504-1512.

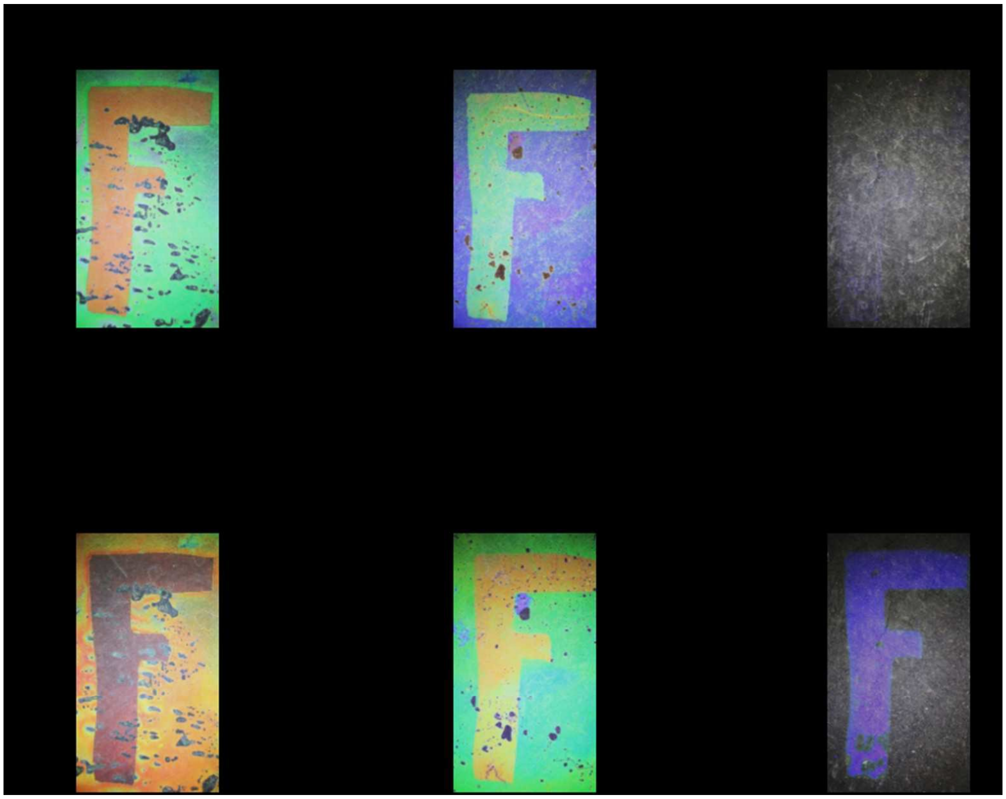


194x169mm (150 x 150 DPI)

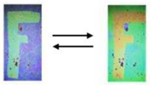


236x90mm (150 x 150 DPI)

240x85mm (150 x 150 DPI)



155x122mm (150 x 150 DPI)



338x190mm (96 x 96 DPI)