Green developers for heat-sensitive layers of thermal paper

Dissertation with the aim of achieving a doctoral degree
at the Faculty of Mathematics, Informatics and Natural Sciences
Department of Biology
University of Hamburg

Submitted by

Taiwo Kayode Fagbemigun

BSc. (Hons.) Industrial Chemistry – University of Ado-Ekiti, Nigeria

MSc. Analytical Chemistry – University of Ibadan, Nigeria

Hamburg, 2021

Evaluators of the dissertation:

Prof. Dr Bodo Saake
Hamburg University
Institute for Wood Sciences
Haidkrugsweg 1
22885 Barsbüttel-Willinghusen
Germany.

Associate Professor Clemens Altaner
University of Canterbury
School of Forestry
Private Bag 4800
Christchurch 8140
New Zealand.

Date of the oral defense: 08th June 2021

Eidesstattliche Versicherung/Declaration on oath

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Dissertationsschrift selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

I hereby declare upon oath that I have written the present dissertation independently and have not used further resources and aids than those stated.

Hamburg, 28th February 2021 **Unterschrift/Signature**

Taiwo Kayode Fagbemigun

I. Acknowledgement

Firstly, I wish to express my profound gratitude to my late supervisor, PD Dr. habil Jürgen Odermatt, for initiating this project and counting me worthy and fit to handle its execution. Furthermore, I am grateful for the opportunity to work under his supervision. His passionate support, engaging opinions, wise and valuable contributions were in no little way instrumental to the success of this work. Beyond academics, Jürgen, his wife, Elke, and adorable Children Anton and Clara ensured that my integration in Hamburg was enjoyable. His impact on my life and the time we spent together will forever remain with me.

Many thanks to Dr. Mayowa Azeez of Ekiti State University, Nigeria, through whom I knew Jürgen Odermatt. His constant admonition and words of advice got me going all through the journey, particularly in difficult moments.

I appreciate Prof. Bodo Saake for ensuring a steady successful completion of this research. His support and contributions were a great incentive in my study and work endeavour.

I appreciate Mrs. Connie Herman, who gave me valuable laboratory support during the first year of my research. She made it possible for me to have a good start in a new working environment.

Thank you to Mrs. Martina Heitmann for the innumerable DSC and FTIR measurements. I am grateful for her consistent tutorials on the use of these instruments. Her expertise and patience were valuable to the achievement of good and quality results.

I also thank Mr. Bernard Ziegler for the NMR measurements. His calmness and willingness to help are great virtue worthy of emulation.

Thank you to Mrs. Anna Knoepfle for her support with the UV-Vis spectroscopy measurements. Equal thanks to Jil Rüter of the Institute for Physical Chemistry, Department of Chemistry, the University of Hamburg for her exceptional support of UV reflection analysis.

My thanks to Dr. Valentina Becerra, Dr. Nora Wilke, and Jensen Svenja of Mitsubishi HiTec Paper Europe GmbH for the thermal printing tests and their valuable contributions to the success of this research.

Thank you to the Fachagentur Nachwaschsende Rohstoffe (FNR) for funding this research work. I am also grateful to the University of Hamburg for the financial support provided through the Merit Scholarship Award.

I am grateful for the privilege to work with the members of my research group, Jens Berger and Max Flaig, Birte Buske. They both created a great working environment and were instrumental to the smooth running of my research. Thank you to Jens Berger for providing technical and personal support all through my research journey. I appreciate Birte Buske for being available all the time to respond to my request and provide technical supports in the laboratory.

Thank you to Patrick Eidman, who always gave me a helping hand, particularly searching for essential laboratory wares, setting up instruments, and providing valuable ideas. I appreciate his constant concern about my welfare and my family. I do not take any of it for granted.

Words may not be enough to thank Niklas Schroettke, who picked me up at the airport on my first day in Hamburg. He was a great buddy. Through my early days in Hamburg, he stood by me and provided terrific personal support that aided my Hamburg survival. In a similar vein, I appreciate Max Flaig and Felix, who gave good help to my family and me on different occasions.

Finally, I would like to extend my gratitude to the employees and fellow Ph.D. students of the Thünen Institute and the Wood Chemistry group of the University of Hamburg for the excellent cooperation, valuable support, and the creation of a friendly and pleasant working environment atmosphere. Everything I learned from them would be helpful as I soldier on in life.

II. Dedication

This doctoral thesis is dedicated to the memory of my late supervisor, colleague, friend, and brother, Jürgen Odermatt, whose intellectual acumen, immense support, trust, and valuable mentorship were instrumental to the initiation, execution, and success of this work.

Also, to my parents, Chief and Mrs. Dele Fagbemigun, for their unrelenting investment and personal sacrifices towards my academic growth and achievements.

To my darling wife and daughter, Alice and Jemima, thank you for your patience, understanding, and support throughout the years. I love you.

III. Abstract

Bisphenol A (BPA) in the manufacturing of several consumer products has implications on human health and the environment. In particular, the exposure to BPA used as a developer in thermal paper is a known cause of endocrine disruption in humans and non-humans. For this reason, local, national, and global regulations have been put in place to reduce or eliminate BPA in thermal paper. However, several known and commercially available alternatives to BPA have similar health and environmental-threatening effect occasioned by their structural similarity to BPA.

This work aimed to assess the potential of bio-based substances to function as an alternative developer in the heat-sensitive layer of thermal paper. These substances are called 'green developers.' The interactions between fluoran dye, ODB-2, and green developers selected from the class of organic carboxylic acids, tannin, and lignin-derived monomers in colour-developing compositions were evaluated in this study. Spectroscopic techniques such as UV-Vis, NMR, and FTIR were employed to monitor these interactions. The thermal and colourimetric behaviour of these compounds in a ternary mixture containing solvent was also studied. Furthermore, phenol resins and phenol-amine complex of high thermal stability were synthesised using methanol extracts of vegetable tannin and pure tannin model compounds. Finally, the performance of these green developers in thermal paper was evaluated as a function of their print density.

The NMR, FTIR, and UV spectroscopy investigation confirmed the lactone ring-opening interaction between fluoran dye and green developers. Most of the studied compounds produced black colour on interacting with fluoran dye under the influence of heat. These compounds also showed potential for utilisation in thermochromic systems like thermal paper.

Of the organic carboxylic acids studied, ascorbic acid, ascorbyl palmitate, and citric acid produced clear colour-forming dispersion and optical print density of 1.1, 0.79, and 0.25, respectively, in thermal paper. The print from the ascorbic acid-coated thermal paper was, however, unstable. Within seven days of printing, 90% of the density was lost. In addition, exposure to oil, water, and solvent led to an 80% reduction in colour density. Also, the unprinted citric acid-coated paper appeared greenish-grey with a whiteness value of 79% - about 11% less than the target value

(≥90%). This relatively low whiteness caused a poor contrast between the printed and unprinted paper. On the other hand, ascorbyl palmitate-coated paper produced a fine, solid, legible, and more stable print.

The thermal paper produced with vanillin gave a characteristic sweet smell on printing, suggesting a partial sublimation of the phenol compound on heating. However, under a higher humid condition of 90% RH, the printout faded and was unrecognizable. Also, the printed image with vanillin displayed an irregular and heterogeneous pattern different from the smooth surface of a BPA-coated paper. Other vanillin derivatives such as vanillic acid, isovanillic acid, and isovanillin showed a weak interaction in colour forming composition and could not be used in thermal paper.

The optical densities of print obtained with thermal paper coated with commercially available tannin compounds such Tanal 02, Tanex 20, Tanal 40, and tannin were 0.66, 0.07, 0.55, and 0.64 respectively. Methanol extract of mimosa tannin gave a low print density of 0.40, while other extracts from mimosa-sulphite and grape seed showed a weak thermal reaction on printing. Application of external heat through flame markedly improved the optical print density of papers coated with the tannin compounds. However, this showed that the applied temperature might not be sufficient to achieve an optimum print density with the tannin compounds. A higher applied printing temperature, unsuitable for energy-efficient technical applications, would be required to achieve a deeper colouration and higher print density.

The amine complex produced from resorcinol and Hexamethylenediamine (HMDA) melted like BPA. The thermal paper made from this coat gave an optical print density of 0.50. Thus, the resorcinol-amine complex might help ease premature colour formation associated with phenol-based thermal paper. Other phenol-amine complexes did not produce colour, possibly due to high thermal stability, requiring printing temperature greater than achievable with the thermal printer.

Some phenol-glyoxal polymers showed promising potential as a developer in a thermal paper. For example, the thermal paper produced from the polymer of grape seed extract gave a print density of 0.24.

Alternatively, the use of a mixture of developers in thermal paper was considered and simulated. The colour density of mixtures containing vanillin and vanillic acid varied from 1.2 to 1.9. The highest colour density was obtained when vanillin and vanillic acid were combined in mole ratio 3:1. The black colour showed average moisture resistance of 80% after 24 hours in 50% relative humidity. The values of colour density also revealed that higher colour density and potentially higher stability could be achieved when organic carboxylic acids, lignin monomers, or tannin model monomers were mixed with phenol-glyoxal polymers in varying ratios.

This study showed that several bio-based compounds offer a route to a safer and environmentally friendly alternative to BPA as a developer in thermal paper. These substances can be used either in pure form, modified form, or building blocks for higher valued chemicals. The use of various commercially available tannins and phenol polymers as a developer in thermal paper comes with many advantages. Tannin is a high molecular weight polymer with little or no known toxicity. In addition, high molecular weight compounds such as tannin and phenol polymers are associated with low dermal migration potential. Thus, they may help overcome the skin-penetration and bioaccumulation problem associated with BPA, Bisphenol S (BPS), and similar compounds. The use of phenolic polymers in thermal paper is recommended because these polymers are easy to synthesise with commercially available compounds. Their high thermal stability could be an advantage. In addition, it ensures that prints are only produced at end-use temperature. However, more work is still needed to improve the properties of these polymers to ensure their suitability as a developer in thermal paper.

The synthesis of more bio-based high molecular weight and high thermally stable phenol resins from bio-based phenols and simple aldehydes, which could function as a developer in thermal paper, is worth further investigation.

IV. Table of contents

I. Acknowledgement....iv
II. Dedication....vi
III. Abstract....vii
IV. Table of contents....x
V. Abbreviations....xiii
VI. List of Tables....xv
VII. List of Figures....xvii
1 **Introduction**....1
1.1 Background....1
1.2 Research Objectives....4
2 **The current state of knowledge**....5
2.1 Functional papers....5
2.2 Thermal paper....6
2.2.1 History of thermal paper....6
2.2.2 Production and consumption of thermal paper....7
2.2.3 Component and design of thermal paper....9
2.2.4 Sensitivity of thermal paper....13
2.2.5 Thermal printing....14
2.3 Dyes....15
2.3.1 Classification of dyes....16
2.3.2 Functional dyes....17
2.3.3 Leuco dyes....17
2.4 Developers....20
2.5 Dye-developer interaction....25
2.5.1 Dye-developer interaction in a binary system....25
2.5.2 Dye-developer interaction in a three-component system....26
2.5.3 Spectroscopic properties of a dye-developer-based system....29
2.6 Properties and application of Bisphenol A (BPA)....32
2.6.1 Exposure to BPA....33
2.6.2 Dietary exposure to BPA....33
2.6.3 Non-dietary exposure to BPA....34
2.6.4 Impacts of BPA exposure on human health and the environment....36
2.6.5 Regulation of BPA....37

2.7 BPA alternatives in thermal paper 40
2.7.1 Petrol-based alternatives 40
2.7.2 Wood-based alternatives to BPA – Green Developers 43
2.8 Alternative technologies 53
3 **Experimental** 55
3.1 Materials 55
3.2 Sample preparation 55
3.2.1 Preparation of ternary mixtures for colour forming reactions. 56
3.2.2 Preparation of ternary mixtures for Job's method 58
3.2.3 Preparation of a mixture of plural developers 59
3.3 Acetone test 59
3.4 Dispersion test 60
3.5 Purification of tannin extracts 60
3.6 Synthesis of phenol-amine complex 61
3.7 Synthesis of phenol polymer 61
3.8 Characterization and instrumental analysis 62
3.8.1 FTIR spectroscopy 62
3.8.2 UV-VIS spectroscopy 62
3.8.3 Differential scanning calorimetry (DSC) 63
3.8.5 Carbohydrate content 64
3.8.6 Total phenolic content 64
3.8.7 Ash content 64
3.8.8 Colour measurement 64
3.8.9 Colour determination 65
3.9 Thermal printing test 66
4 **Results and discussion** 67
4.1 Electronic absorption spectroscopy of ODB-2 based system. 67
4.1.1 Effect of solvent mixture on the electronic absorption of ODB-2 based system. 69
4.1.2 Effect of acid on the electronic absorption of ODB-2 based system. 71
4.1.3 Effect of alkali on the electronic absorption of ODB-2 based system 74
4.2 Colour-Forming Interaction between ODB-2 and green developers 75
4.2.1 Acetone Test: Interaction of ODB-2 and developer in acetone 75
4.2.2 Dispersion Test: Interaction of ODB-2 and developer in dispersion 79
4.3 FTIR Spectra of ODB-2 and green developer 82
4.4 ^{13}C NMR spectra of ODB-2 and green developers 83

4.5 Thermal and colorimetric behaviour of thermochromic mixtures 86
4.5.1 Thermochromism in ODB-2/vanillin/tetradecanol mixtures 87
4.5.2 Thermochromism in ODB-2/vanillic acid/tetradecanol mixtures 90
4.5.3 Effect of excess solvent and developer on the colour properties of a thermochromic mixture 92
4.5.4 DSC of vanillin and vanillic acid-based thermochromic composites 93
4.6 Exploring the use of tannin as a developer in thermal paper. 96
4.6.1 Tannin purification and characterization 96
4.6.2 Synthesis of hydrogen-bonded phenol-amine complex 98
4.6.3 Synthesis of phenol polymers 101
4.6.4 Characterization of phenol-amine complexes and phenol polymers 102
..... 109
4.6.5 Colour-forming reaction of tannin compounds with ODB-2 109
4.7 Colour density of green developer-based mixtures 115
4.7.1 Colour density of the mixture of ODB-2 and phenol compounds 115
4.8 Colour density of the mixture of ODB-2 and plural developers. 118
4.8.1 Colour density of the mixture of vanillin and vanillic acid 118
4.8.2 Colour density of the mixture of phenol-amine complex with co-developers. 120
4.8.3 Colour density of the mixture of phenol polymers with co-developers 124
4.9 Application of green developers in thermal paper 131
4.9.1 Organic carboxylic acids-based thermal paper 132
4.9.2 Monomeric phenols-based thermal paper 133
4.9.3 Tannin-based thermal paper 134
4.9.4 Phenol-amine complex-based thermal paper 136
4.9.5 Phenol-glyoxal polymer-based thermal paper 137
5 **Conclusions and recommendations** 138
6 **Literature** 148
7 **Appendix** 174

V. Abbreviations

ATM	Automated teller machine
BisOPP-A	4,4’-Isopropyllidenebis(2- phenylphenol)
BPA	Bisphenol A (2,2-bis(p-hydroxyphenyl)propane)
BPAP	Bisphenol AP (4,4’-(1-Phenylethylidene)bisphenol)
BPC	Bisphenol C (2,2’-Bis(4-hydroxy-3- methylphenyl)propane)
BPF	Bisphenol F (Bis(4-hydroxyphenyl)methane)
BPS	Bisphenol S (4-Hydroxyphenyl sulfone)
BPS-MAE	Phenol,4-[[4-(2-propen-1- yloxy)phenyl]sulfonyl]-
BPS-MPE	4-Hydroxy-4’- benzyloxydiphenylsulfone
BTUM	4,4'-bis(N-carbamoyl-4- methylbenzenesulfomide)diphenylmethane
CVL	Crystal violet lactone
DD-70	1,7-bis(4-Hydroxyphenylthio)-3,5- dioxaheptane
D8	4-Hydroxyphenyl 4-isoprooxyphenylsulfone
D2T2	Dyes for diffusion thermal transfer
D-90	Phenol, 4,4’-sulfonylbis-, polymer
DEAMAF	(2′-anilino-6′-diethylamino-3′-methylspiro[isobenzofuran-1(3H) ,9′-[9H]xanthene]-3-one
DEAMCF	2′-chloro-6′-diethylamino-3′-methylspiro[isobenzofuran-1(3H), 9′-[9H]xanthene]-3-one
DSC	Differential scanning calorimetry
FD	Fluoran dye
FTIR	Fourier transform infrared
HD	1-hexadecanol
HOMO	Highest occupied molecular orbital
LG	Lauryl gallate
LUMO	Lowest unoccupied molecular orbital
MBHA	Methyl bis(4-hydroxyphenyl)acetate
MGL	Malachite green lactone

MO	Molecular orbital
NMR	Nuclear magnetic resonance
OD	Optical print density
OD	1-octadecanol
ODB-2	One dye black-2 (of 2’-anilino-6’-diethylamino-3’-methylfluoran)
OG	Octyl gallate
OH	Hydroxyl
PG	Propyl gallate
PHBB	Benzyl 4-hydroxybenzoate
pKa	Dissociation constant
POS	Point of sale terminal
PU18	1-(4-hydroxyphenyl)-3-octadecylurea
PVA	Polyvinyl alcohol
TD	1-tetradecanol
TDI	Tolerable daily intake
TG-SA	Bis-(3-allyl-4-hydroxyphenyl) sulfone
TPC	Total phenolic content
TPM	Triphenylmethane
T_g	Glass transition temperature
UU	Urea urethane
UV	Ultraviolet
λ_{max}	UV Absorption maxima
ε	Molar extinction coefficient

VI. List of Tables

Table 1. Worldwide manufacturers of thermal paper. 8

Table 2. Properties of developer for a functional and marketable thermal paper 24

Table 3. Concentration of BPA in thermal paper cash receipts..... 34

Table 4. Worldwide regulations and restrictions of BPA in thermal paper and consumer products 38

Table 5. Absorption maxima of UV-visible absorption spectra of ODB-2 in protic and aprotic solvents 68

Table 6. Effects of pH on the electronic absorption of ODB-2 in acetonitrile..... 72

Table 7. Effects of pH on the electronic absorption of ODB-2 in ethanol 73

Table 8. Composition of an aqueous dispersion of ODB-2 80

Table 9. Composition of ODB-2 based thermochromic mixtures with vanillin as developer 86

Table 10. Composition of ODB-2 based thermochromic mixtures with vanillic acid as developer..... 87

Table 11. Value of colour parameters of vanillin-based ternary composites..... 88

Table 12. Value of colour parameters of vanillic-acid-based ternary composites. 91

Table 13. Enthalpies of the phase transition of thermochromic mixtures in the defined molar rations..... 95

Table 14. Total yield of tannin extracts and their phenolic, and ash compositions. 97

Table 15. Monomeric composition of carbohydrates in industrial tannin extracts and their purified fractions (% w/w on dry extract)..... 98

Table 16. Composition and properties of the phenol-amine complexes. 99

Table 17. Hydroxyl values of phenol-glyoxal polymers 105

Table 18. Colour density of colour-forming mixtures with vanillin and vanillic acid as developer and co-developer..... 118

Table 19**.** Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and vanillic acid as developer and co-developer, respectively 120

Table 20. Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and vanillin as developer and co-developer, respectively..... 121

Table 21. Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and tannic acid as developer and co-developer, respectively..... 122

Table 22. Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and citric acid as developer and co-developer, respectively..... 122

Table 23. Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and ascorbic acid as developer and co-developer, respectively..... 123

Table 24**.** Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and salicylic acid as developer and co-developer, respectively 123

Table 25. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and vanillic acid as co-developer. 125

Table 26. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and vanillin as co-developer. 125

Table 27. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and tannic acid as co-developer. 125

Table 28. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and citric acid as co-developer..... 126

Table 29. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and ascorbic acid as co-developer..... 126

Table 30. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and salicylic acid as co-developer..... 126

Table 31. Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and vanillic acid as co-developer. 128

Table 32. Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and vanillin as co-developer. 128

Table 33. Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and tannic acid as co-developer. 128

Table 34. Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and citric acid as co-developer. 129

Table 35. Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and ascorbic acid as co-developer..... 129

Table 36. Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and salicylic acid as co-developer..... 129

Table 37. Design and optical density of tannin-based thermal papers 134

Table 38**.** Performance evaluation of green developers in thermal paper 143

VII. List of Figures

Figure 1. Supermarket receipt printed with thermal paper. 1

Figure 2. The design of thermal paper. 10

Figure 3. Direct thermal printing. Based on Bradbury [40]. 14

Figure 4. Hypothetical absorption band of an organic dye describing the various shifts. Adapted from [56] 16

Figure 5. Classes of dyes based on the nature of their chemical chromophore. 17

Figure 6. Structure of fluoran. (*Adapted from* Huneke [17]). 19

Figure 7. 2-anilino-6-diethylamino-3-methylfluoran 19

Figure 8: Solid-state colour change of fluoran dyes (at warm and cool) with bisphenol-A and methyl stearate. Copyright: *Oh et al.,* [128]. 27

Figure 9. Subdivision of thermochromic materials. Reproduced based on Hong [139].. 28

Figure 10. Structures of (a) bisphenol A and (b) oestradiol. 32

Figure 11. The use of BPA and its alternatives in thermal paper between 2014 and 2017. (*Adapted from* ECHA *[256, 257]*) 41

Figure 12. Structure of Bisphenol S 42

Figure 13. Chemical classes of potential green developers. 44

Figure 14. Structure of (a) vanillin and (b) vanillic acid. 47

Figure 15. Structure of (a) coumaric acid and (b) diphenolic acid. 48

Figure 16. Structural examples of sugar-based developers (a). g-d-trichloroethylidene-d-gluconic acid (furanose type); (b) 9-trichloroethylidene-d-gluco-furanose and (c) g-(di-trichloroethylidene)-d-gluco-furanose. (*Reproduced based on* Kosche [305]) 52

Figure 17. Samples of ternary mixtures prepared with carboxylic acids, ODB-2, and tetradecanol. (a) mixtures in the unheated state, (b) mixtures heated on a hotplate, and (c) coloured state of the mixtures after cooling. 56

Figure 18. Set-up for the investigation of colour behaviour of a dye-developer mixture. (*Reproduced from* Huneke [17]). 57

Figure 19. Images of capillary tubes containing a micro quantity of a mixture of ODB-2, vanillic acid, and tetradecanol in (a) unheated and (b) heated form. 58

Figure 20. Magnified images of capillary tubes containing (a) unheated vanillin, (b) unheated ODB-2, (c) unheated mixture of vanillin & ODB-2, (d) heated mixture of vanillin & ODB-2, (e) heated mixture of reference developer, BPA &ODB-2... 58

Figure 21. Mixture of vanillic acid and ODB-2 in acetone 59

Figure 22. Wet dispersion of ODB-2, PVA and (1) vanillin, (2) vanillic acid, (3) isovanillic acid and (4) isovanillin. 60

Figure 23. Soxhlet extraction of mimosa extract. 61

Figure 24. Image capturing of a cooled mixture of vanillin, ODB-2, and tetradecanol with a digital camera..... 65

Figure 25. ODB-2 in aprotic and protic solvents. (1) tetrahydrofuran, (2) acetonitrile, (3) toluene, (4) acetone, (5) methanol, (6) ethylacetate, (7) hexane, (8) diethyl ether, and (9) ethanol 67

Figure 26. UV/VIS spectra of ODB-2 in (a) tetrahydrofuran (1.54 x 10^{-3}mol/l), acetone (1.65x 10-3 mol/l), acetonitrile (1.12 x 10^{-3} mol/l), diethylether (1.39 x 10^{-3} mol/l),ethylacetate (0.56 x 10^{-3} mol/l), hexane (1.24 x 10^{-3} mol/l), and toluene (0.97x 10^{-3} mol/l); (b) methanol (1.63 x 10^{-3} mol/l) and ethanol (1.63 x 10^{-3}mol/l). 68

Figure 27. UV/VIS spectra of ODB-2 in toluene (0.93 x 10-2mol/l) with (a) 0.1mol, (b) 0.2mol, (c) 0.3mol, (d) 0.4mol, (e) 0.5mol, (f) 0.6mol, (g) 0.7mol, (h) 0.8mol, (i) 0.9mol, and (j) 1mol of methanol 70

Figure 28. UV/VIS spectra of ODB-2 in acetonitrile (1.87 x 10-2 mol/l) with (a) 0.1mol, (b).. 0.2mol, (c) 0.3mol, (d) 0.4mol, (e) 0.5mol, (f) 0.6mol, (g) 0.7mol, (h)...0.8mol, (i) 0.9mol, and (j) 1mol of ethanol. 70

Figure 29. UV/VIS spectra of ODB-2 in acetonitrile (4.49 x 10^{-3}M) at pH (a) 5, (b) 4.69, (c) 4.52, and (d) 4.39. 72

Figure 30. UV/VIS spectra of ODB-2 in ethanol (0.94 x 10^{-2} M) at pH (a) 5, (b) 4.69, (c) 4.52, and (d) 4.39..... 73

Figure 31. UV/VIS spectra showing effect of NaOH concentration of (a) 0.2 x 10^{-5}M, (b) .... 0.4 x 10^{-5}M, (c) 0.8 x 10^{-5}M and (d) 1.0 x 10^{-5}M on the absorbance of ODB-2 in ethanol (0.47 x 10^{-2} M)..... 75

Figure 32. Mixture of vanillin and ODB-2 in acetone. (a) Before and (b) after evaporation... 76

Figure 33. Mixture of BPA and ODB-2 in acetone. (a) Before and (b) after evaporation. . 76

Figure 34. Mixtures of tannin compounds and ODB-2 in acetone. (a) Tanal 02, (b) Tanex 20, (c) Tanex 40 and (d) tannin and ODB-2 in acetone..... 76

Figure 35. Mixture of ascorbic acid and ODB-2 in solvent. (a) Undissolved ascorbic acid in acetone and (b) solution of ascorbic acid and ODB-2 in a mixture of acetone and ethanol. 77

Figure 36. Coloured species formed from the reaction of ODB-2 and vanillic acid, vanillin, . isovanillic acid and isovanillin. 77

Figure 37. Coloured species formed from the reaction of ODB-2 and resorcinol, pholorglucinol, citric acid, ascorbyl palmitate, salicylic acid, ascorbic acid, succinic acid, and acetylsalicylic acid. 78

Figure 38. Coloured species formed from the reaction of ODB-2 and tannin compounds (Tanal 02, Tanex 20, Tanex 40, tannin, d-catechin) and BPA..... 79

Figure 39. Interaction of ODB-2 and green developer in a dispersion. (1a) vanillin in wet dispersion, (2a) vanillic acid in wet dispersion, (3a) isovanillic acid in wet

dispersion, (4a) isovanillin in wet dispersion, (1b) vanillin in dried dispersion, (2b) vanillic acid in dried dispersion, (3b) isovanillic acid in dried dispersion, (4b) isovanillin in dried dispersion. 80

Figure 40. Interaction of ODB-2 and green developer in a dispersion. (1a) ascorbic acid in wet dispersion, (2a) citric acid in wet dispersion, (3a) ascorbyl palmitate in wet dispersion, (1b) ascorbic acid in dried dispersion, (2b) citric acid in dried dispersion, (3b) ascorbyl palmitate in dried dispersion..... 81

Figure 41. Interaction of ODB-2 and green developer in a dispersion. (1a) Tanal 02 in wet dispersion, (2a) Tanex 20 in wet dispersion, (3a) Tanal 40 in wet dispersion, (4a) tannin in wet dispersion, (1b) Tanal 02 in dried dispersion, (2b) Tanex 20 in dried dispersion, (3b) Tanal 40 in dried dispersion, (4b) tannin in dried dispersion..... 81

Figure 42. FTIR spectra showing the opened and closed lactone ring form of ODB-2..... 82

Figure 43. FTIR spectra of the coloured form of ODB-2 obtained from the interaction with green developers. The green developers are inscribed on the spectra. 83

Figure 44. Molecular structure of ODB-2 84

Figure 45. ^{13}C NMR spectra of (a) ODB-2, (b) reaction product of ODB-2 and ascorbic acid, (c) reaction product of ODB-2 and vanillin, (d) reaction product of ODB-2 and resorcinol in $CDCl_3$ over the range 85 to 175 ppm..... 85

Figure 46. Thermochromic mixtures with vanillin as developer at room temperature. The composition of the samples is presented in **Table** 9..... 88

Figure 47. Variation of colour densities with the number of moles of vanillin the ternary mixtures **(VI–VXI)**..... 89

Figure 48. Variation of colour densities with the number of moles of ODB-2 in the ternary mixtures **(VI–VXI)**..... 89

Figure 49. Colour transition of a thermochromic mixture of tetradecanol, vanillin and ODB-2 (2.3:1) with heating and cooling temperature. 90

Figure 50. Thermochromic mixtures with vanillic acid as developer at room temperature. The composition of the samples is presented in **Table** 10..... 90

Figure 51. Variation of colour contrast with the number of moles of vanillic acid in the ternary mixtures **VAI – VAXI** 91

Figure 52. Variation of colour contrast with the number of moles of ODB-2 in ternary mixtures **VAI – VAXI** 92

Figure 53. Composites containing ODB-2, tetradecaonol and excess vanillic acid (15×10^{-5}mol) as developer showing coloured solid state at 25^{o}C and melt darkened behaviour at 50^{o}C. 93

Figure 54. DSC curves showing (a) heating and (b) cooling of the thermochromic composites with vanillin as developer and tetradecanol as solvent. 94

Figure 55. DSC curves showing heating (a) and cooling (b) of the thermochromic composites with vanillic acid as developer and tetradecanol as solvent. 95

Figure 56. Images of phenol-amine complexes during filtration. GSE-H = Phenol-amine complex from grape seed extract, MIM-H = Phenol-amine complex from mimosa extract, MIM-S-H = Phenol-amine complex from mimosa sulphite extract, TA-H = Phenol-amine complex from tannic acid, CAT-H = Phenol-amine complex from catechin, PH-H = Phenol-amine complex from phloroglucinol, RES-H = Phenol-amine complex from resorcinol. 100

Figure 57. Structure of hexamethylenediamine 101

Figure 58. Phloroglucinol-glyoxal polymer (PH-CP2) (a) before milling and (b) after milling 102

Figure 59. FTIR spectra of pure resorcinol (RES) and resorcinol-amine complex (RES-H) 103

Figure 60. FTIR spectrum of (a) phloroglucinol-glyoxal polymer (PH-CP2, PH-CP2-12, PH-CP2-25 and PH-CP2-40 are polymers produced with 10ml, 12ml, 25ml and 40ml of glyoxal respectively), and (b) tannin-glyoxal polymer..... 104

Figure 61. DSC curves of amine complex and polymers of (a) mimosa extract (MIM), and .. (b) mimosa sulphite extract (MIM-S) 107

Figure 62. DSC curves of amine complex and polymers of (a) grape seed extract (GSE), ... and (d) resorcinol (RES) 108

Figure 63. DSC curves of phloroglucinol-glyoxal polymers and BPA..... 109

Figure 64. Mixture of mimosa extract (MIM) and ODB-2 in acetone. (a) before evaporation and (b) after evaporation..... 110

Figure 65. Coloured species formed from the reaction of ODB-2 and purified tannin extracts: (a) mimosa extract (MIM) (b) mimosa sulphite extract (MIM-S) (c) grape seed extract (GSE) 110

Figure 66. Interaction of ODB-2 and tannin in a dispersion. (1a) mimosa extract (MIM) in wet dispersion, (2a) mimosa sulphite extract (MIM-S) in wet dispersion, (3a) grape seed extract (GSE) in wet dispersion, (1b) mimosa extract (MIM) in dried dispersion, (2b) mimosa sulphite extract (MIM-S) in dried dispersion, and (3b) grape seed extract (GSE) in dried dispersion..... 111

Figure 67. Interaction of ODB-2 and phenol-amine complex in a dispersion. (1a) tannic acid-amine complex (TA-H) in wet dispersion (2a) mimosa sulphite extract (MIM-S) in wet dispersion, (3a) mimosa extract (MIM) in wet dispersion, (4a) resorcinol-amine complex in wet dispersion, (1b) tannic acid-amine complex (TA-H) in dried dispersion, (2b) mimosa sulphite extract (MIM-S) in dried dispersion, (3b) mimosa extract (MIM) in dried dispersion, and (4b) resorcinol-amine complex in dried dispersion 112

Figure 68. Interaction of ODB-2 and phenol polymer in a dispersion. (1a) mimosa-glyoxal polymer at pH 2 (MIMCP2) in wet dispersion (2a) mimosa sulphite-glyoxal polymer at pH 2 (MIM-S-CP2) in wet dispersion, (1b) mimosa-glyoxal polymer at pH 2 (MIMCP2) in dried dispersion, (2b) mimosa sulphite-glyoxal polymer at pH 2 (MIM-S-CP2) in dried dispersion..... 112

Figure 69. Interaction of ODB-2 and phenol polymer in a dispersion. (1a) tannic acid-glyoxal polymer at pH 2 (TA-CP2) in wet dispersion, and (1b) tannic acid-glyoxal polymer at pH 2 (TA-CP2) in dried dispersion 113

Figure 70. Interaction of ODB-2 and phenol polymer in a dispersion. (1a) grape seed extract-glyoxal polymer at pH 2 (GSE-CP2) in wet dispersion (2a) grape seed extract-glyoxal polymer at pH 9 (MIM-S-CP9) in wet dispersion, (1b) grape seed extract-glyoxal polymer at pH 2 (GSE-CP2) in dried dispersion, (2b grape seed extract-glyoxal polymer at pH 2 (GSE-CP9) in dried dispersion..... 113

Figure 71. Interaction of ODB-2 and phloroglucinol polymer produced at pH 2 in a dispersion. (1a) PHCP2 in wet dispersion, (2a) PHCP2-12 in wet dispersion, (3a) PHCP2-25 in wet dispersion, (4a) PHCP2-40 in wet dispersion, (1b) PHCP2 in dried dispersion, (2b) PHCP2-12 in dried dispersion, (3b) PHCP2-25 in dried dispersion, (4b) PHCP2-40 in dried dispersion. 114

Figure 72. Colour densities of phenol-amine complexes and phenol polymers..... 115

Figure 73. Colour density of (a) RES-H, and (b) MIM-CP2 before and after aging for 24 hours at 25^{o}C/50% R.H. 116

Figure 74. Colour density of (a) MIM-S-CP2, and (b) GSE-CP9 before and after aging for 24 hours at 25^{o}C/50% R.H. 116

Figure 75. Colour density of (a) GSE-CP2, (b) PH-CP2 before and after aging for 24 hours at 25^{o}C/50% R.H..... 117

Figure 76. Colour density of (a) PH-CP2-12, and (b) PH-CP2-40 before and after aging for 24 hours at 25^{o}C/50% R.H. 117

Figure 77. Colour density of BPA before and after aging for 24 hours at 25^{o}C/50% R.H. 117

Figure 78. Colour density and moisture resistance of a colour forming composition with a mixture of vanillin and vanillic acid as developer. VV = mixture of vanillin and vanillic acid. 119

Figure 79. Variation of colour density of colour forming composition with vanillin and vanillic acid mixture as a developer over 10 days. VV = mixture of vanillin and vanillic acid. 119

Figure 80. Variation of colour density of colour forming compositions with a mixture of resorcinol-amine complex and vanillic acid as developer over 10 days. The compositions of RESH-VA1 – RESH-VA9 are presented in the appendix (page 174). 124

Figure 81. Variation of colour density of colour forming compositions with a mixture of phloroglucinol-glyoxal polymer (PHCP2) and vanillic acid as developer over 10 days. The compositions of PHCP2-VA1 – PHCP2-VA9 are shown in appendix (page 173). 127

Figure 82. Variation of colour density of colour forming compositions with a mixture of phloroglucinol-glyoxal polymer (PHCP2-40) and vanillin as developer over 10 days. The compositions of PHCP2-40-V1 – PHCP2-40-V1 are shown in the appendix (page 173). 127

Figure 83. Thermal Printing Test: Variation of print density of green developer-based thermal papers with applied energy 131

Figure 84. Thermal Printing Test: Ascorbyl-palmitate based thermal paper showing the print density. 132

Figure 85. Microscopic image of a vanillin-based thermal paper 133

Figure 86. Thermal Printing Test: Tanal 40-based thermal paper after flame application. 135

Figure 87. Thermal Printing Test: Mimosa extract (MIM)-based thermal paper. 136

Figure 88. Thermal Printing Test: Resorcinol-amine complex (RES-H)-based thermal..... paper showing the print density..... 136

Figure 89. Thermal Printing Test: Grapeseed extract (GSE)-based thermal paper (a) GSE-CP2, and (b) GSE-CP9 showing the print density. 137

1 Introduction

1.1 Background

Thermal papers or heat-sensitive papers are a class of functional papers that produce colour, image, or print under the influence of heat. They are also called ‘self-contained papers’ because the print produced results from the chemical interaction involving an in-built chemical mixture [1]. Consequently, unlike conventional printing technology, thermal printing is without inks. This attribute makes thermal printers portable, compact, easy to maintain and has influenced their expanding utilization. Typical thermal paper applications include cash receipts, bank tellers, industrial barcodes, self-adhesive labels, transport tickets, parking tickets, travel luggage tags, point of sale (POS) terminal receipts, ATM receipts, etc. (**Figure 1).**

Figure 1. Supermarket receipt printed with thermal paper.

The colour forming composition in thermal paper consists of a colourless dye, developer, binder, sensitizer, and pigments. While these substances play a complementary role in determining the output print quality, the developer has attracted the highest level of attention. The most widely used developer in thermal paper is

Bisphenol A (4, 4'-isopropylidenediphenol). The industrial utilization of BPA in thermal paper is due to its efficient colour development, excellent thermal response, low cost, and availability. BPA constitutes about 1- 2% by weight (%) of a whole thermal paper receipt [2]. However, owing to its low molecular weight and unbound nature, significant amounts of BPA can be released into the human skin simply by touching and holding thermal papers [3, 4]. The effect of this exposure has generated controversies and conflicting scientific reports. Most of these reports have implicated exposure to BPA as the root cause of health-related diseases such as cancer, obesity, infertility, respiratory irritation, and cardiovascular degeneration, while others have expressed opposing views [5]. For these reasons, public concerns about BPA toxicity and unfavourable health and environmental effects have increased in recent times.

Consequently, regulations that seek to reduce or remove BPA from thermal paper have been proposed. In January 2020, the European Commission's regulation aimed at restricting BPA in thermal paper in concentrations of 0.02% or more by weight came into effect [6]. With this regulation, thermal paper manufacturers and stakeholders worldwide need to switch to safer alternatives.

Several BPA alternatives such as bisphenol C, bisphenol F, bisphenol S, bisphenol AP, D8, and TG-SA cause similar endocrine-disrupting effects. Also, the toxicity, health, and environmental hazard of other non-structurally similar alternatives are currently unknown [7]. More so, most petrol-based chemicals are hazardous to the health and environment. Impediments to the switch from BPA to alternatives are cost, technical performance, and compatibility with current industrial processes and installations.

In the quest for 'Green developers,' bio-based, safer, renewable, and environmentally friendly alternatives to BPA in thermal paper, substances belonging to the class of carboxylic acids, fatty acids, sugars, mono, and polymeric phenols, etc. may provide a sustainable solution since most of these substances can be isolated from natural sources and are commercially available [8]. Also, considering their structures, such as reactive OH groups, their direct utilization in colour forming compositions either in pure or modified form is a possibility. These substances could also be used as building blocks to compounds of improved properties. Unfortunately, there is little technical information in the public domain on using these compounds as

alternative developers in a thermal paper except for organic acids and synthetic phenols, which is well mentioned in patent literature [9, 10].

Natural phenols from wood-derived lignin and biomaterials are known to be safer alternatives to petrol-based phenols. Of these lignin phenols, vanillin and its derivatives like vanillic acid seem the most attractive phenols for use as a developer in thermal paper. Interestingly, there is no technical information on using these compounds in thermal paper at any level. In the same vein, tannins are plant-based polyphenolic compounds with similar structures to synthetic phenols. They are green and sustainable alternatives to synthetic phenols. Tannins are used in their native forms or subjected to various modifications [11]. The use of tannins as developers in thermal paper has not been thoroughly considered except for a few mentions in patents [12]. Besides, tannins offer several potential advantages over BPA. They possess numerous reactive OH groups, which may influence the intensity of prints. They are non-crystalline and thermally stable with high degradation and glass transition temperature influenced by other constituents such as carbohydrates and other oligomeric polysaccharides [13]. The high molecular weight of tannins suggests that when used as a coating in thermal paper, there is a very low likelihood of sublimation or crystallization and premature colour formation, unlike what is obtainable with synthetic monomeric phenols and some organic carboxylic acids. Tannins are high molecular weight compounds with limited dermal migration potential. They are of no known toxicity to man and are commercially available [14].

Attempts have been made to substitute BPA with eco-friendly phenol-formaldehyde resins [15] and hyperbranched polymers [16] produced from a mix of commercially available bio-based monomers. But there is no information on the commercial viability/application of these substances. Perhaps, this could be attributed to their inability to replace BPA or potential toxicity effectively. On the other hand, it could also be due to confidentiality in a highly competitive thermal paper market. Nonetheless, tannins could be utilized as alternatives to synthetic phenols to synthesize these bio-based phenolic resins for use as developers in thermal paper. This is an area of research that is worth further exploration.

Furthermore, for the effective utilization of green developers as alternatives to BPA in thermal paper, it is imperative to ascertain their capacity to react with colour

formers to produce the desired colour effectively. Several spectroscopic methods such as FTIR and NMR can be utilized to give more precise information about the functionality of these substances. This spectroscopic investigation may serve as a complementary study to the recently described preliminary rapid screening method for green developers in a leuco dye-based system [17].

1.2 Research Objectives

Research on the use of bio-based and eco-friendly alternative developers in thermal paper is not common in public literature. However, recent regulations have called for the urgent need to introduce safer BPA alternatives to the market. Therefore, the motivation behind this project is to search for bio-based developers termed ‘green developers’ that can function as alternatives to BPA.

The objectives of this project were therefore

- To carry out spectroscopic investigations of the interaction between green developers and fluoran dye, with a focus on organic carboxylic acids, lignin-derived compounds (vanillin and vanillic acid), vegetable tannin, and tannin model compounds (resorcinol and phloroglucinol).
- To explore the use of lignin-derived compounds such as vanillin and vanillic acid as developers in thermochromic systems like thermal paper
- To synthesise and characterise phenolic polymers from tannin and tannin model compounds.
- To evaluate the technical performance of green developers in thermal paper.

2 The current state of knowledge

2.1 Functional papers

The rapid global trend in technology has led to the development of functional materials that respond to external stimuli such as light, pressure, and heat. For example, paper products that respond to stimuli are termed functional or smart papers [18].

The first generation of functional papers was the pressure-sensitive carbonless copy papers or pressure-sensitive recording materials, which develops image or print using pressure or mechanical impacts such as writing strokes or typewriter impression. The configuration of a typical pressure-sensitive paper is described in the patent literature [19, 20]. To produce this kind of paper, the colourless dye, known as colour former, is encapsulated into microcapsules of diameter about 3- 5 μm. The microcapsules are produced as a finely dispersed emulsion droplet in an organic solvent or oil and coated on the upper layer of a paper substrate. The under layer of a second paper substrate is coated with a developing coat containing a colour-developing agent or developer. The two papers are then placed upon one another such that the microcapsule coated layer and the developer coated layer are in a contiguous position to one another. Upon applying pressure on the upper sheet either by writing, marking, or striking with a typewriter or ballpoint pen, the microcapsules are destroyed to release the in-built dye precursor. The dye precursor then transfers to the developer layer resulting in a colour development reaction. In this application, microcapsules are very important because they prevent colour formation until the interaction is initiated between the colour former and the developer by mechanical force. Different configurations of the microcapsule and developer layer are possible [21] by altering the microcapsule layer's combination and composition [22]. Typical encapsulating materials used in microencapsulation include water-soluble or water-dispersible materials such as gelatin, cellulose, and gum Arabic. Microencapsulation is generally done through complex coacervation [23] and interfacial polymerization [24].

Photosensitive papers produce an image on exposure to light energy of a specific wavelength. In this type of paper, a photosensitive coat is applied on a paper substrate either in the form of microcapsules or liquid suspension. On irradiation with

UV light, the capsules are ruptured and colour forming substances are released to interact with one another leading to image development. Photosensitive papers tend to exhibit reversible coloured or discoloured appearance under the influence of light of varying wavelengths and therefore have broad applications in photography, photocopying, and photolithography [25].

The commonly used functional papers are those which produce an image under the influence of heat. They are called thermal paper, heat-sensitive papers, or thermal recording materials [26]. Thermal paper is structurally multi-layered, consisting of a supporting base (paper), a base coating, and a thermosensitive layer [27]. The colour-forming chemicals are embedded in the thermosensitive coating, which upon heating to a pre-determined temperature, melt-react to develop the desired print or image. Although other components of the coating, such as pigments, binder, lubricants, play complementing roles, characteristics, and quality of image/print formed, are majorly determined by the nature of the colour former and the developer. The design of the developing component of thermal paper and the mechanism of colour formation is the focus of this research.

2.2 Thermal paper

2.2.1 History of thermal paper

The earliest type of heat-sensitive paper was developed and marketed by the Minnesota Mining and Manufacturing (3M) Corporation under the trade name ScotchMark [28]**.** These papers utilized the reaction of a metal salt such as iron stearate with phenolic compounds. They were designed to function as heat-sensitive copying paper to reproduce printed materials such as the printed pages of books, pencilled notes, sketches, drawings, type-written letters, etc. They were also used extensively in barcode production. An original copy of printed material is irradiated with intense radiant energy to achieve the copying process, which is absorbed and converted to heat energy to generate the printed or the coloured areas of the original.

A more advanced dye-developer thermal paper was invented by the National Cash Register Corporation (NCR) and described in a patent [29]**.** A temperature-sensitive record material that functions based on the heat-initiated reaction between a colourless crystal violet lactone dye and phenolic compound such as diphenols was described in this patent. Coatings made from aqueous dispersions of the colourless

dye and phenol are applied separately on sheets of papers. These papers are then placed face to face with one another such that once heat is applied, the components of the two dispersions are liquefied/vaporised to interact and produce the expected colour. These papers were stable up to 60^{o}C and produced a blue-coloured image when heated between 100-150^{o}C. Many other improved and more sophisticated thermal papers have been produced based on similar principles, formulations, and technological processes [30, 31]. Commonly used dye-developer thermal paper now requires a single coating application on a pre-coat paper rather than a separate coating on two sheets. The dye-developer thermal paper is the most used and most marketed worldwide due to its improved technical capability [32].

2.2.2 Production and consumption of thermal paper

Various organisations have reported an estimated current and future value of the global thermal paper market. The thermal paper market was valued at USD 1.5 – 1.6 bn in 2006 [33], USD 1.02 billion in 2014, USD 2.69 billion in 2017 [34], USD 3.54 billion in 2018 and it is expected to reach USD 4.77 billion by 2022 [35] and USD 5.52Billion by 2025 [36]**.** Reports also show that over 3.1 million tons of thermal papers were sold globally in 2018, and consumption was likely to grow at a subdued rate of 2.7% in 2019 [37]. That is partly due to the reduced supply of commonly used colour former. The retail industry is the largest end-user of thermal paper, accounting for over half of global demand during the studied period. In the report by Grandview research, about 82% of the global volume share in 2015 was utilized in POS. Tags and label segment generated revenue worth USD 258.0 million, and it is expected to rise for the foreseeable future.

Many factors back the increase in the demand for thermal paper. One such is the rising demand for point of sale (POS) terminals as an alternative to cash registers in various sectors of the economy, such as in the coffee shops, restaurants, hospitality, and craftsman shops. This is attributed mainly to the growth and advancements of the global retail industry. In addition, an increase in online purchases of products will also require an increase in the use of thermal paper for labelling. Furthermore, the future growth projection of the global thermal paper market assumes continuous development of innovative and improved thermal paper products. Therefore, manufacturers are constantly working to offer consumers of thermal papers improved quality such as high image density, moisture, heat, UV, and plasticiser resistance. For

instance, thermal papers with standard sensitivity that can last a minimum of 15 - 25 years are currently in the market. This and many other developments, including the incorporation of inherent security features to thermal paper to prevent counterfeiting and the ability to provide multi-colour images, has expanded the utilization scope of thermal paper in a specialized and extensive range of fields such as in the preparation of sensitive legal documents, and medical documents like electrocardiograms (ECGs), and prescription labels.

Table 1. Worldwide manufacturers of thermal paper.

Company	**Country**
Koehler Paper	Germany
Mitsubishi HiTech Paper	Germany
Mitsubishi Paper Mills	Japan
Jujo Thermal Paper	Finland
Appvion	US
Oji Paper Company	Japan
Shandong ChenMing Paper Holdings Ltd	China
Henan Jianghe Paper Co. Ltd.	China
Guangdong Guanhao High Tech Co. Ltd	China
Jiangsu Papers Co. Ltd	China
Ricoh Industry	Japan
Hansol	Korea
NCR Corporation	US
Kanzan Specialty Papers GmbH	Germany
Nashua Corporation	US

[33].

The current thermal paper market is highly competitive, oligopolistic, and controlled by a handful of major paper producers. The top key players in the global thermal paper market in no particular order are presented in **Table** 1. While China is currently the largest thermal paper producer due to lower production costs, the largest thermal paper enterprise is spread across Japan, Europe, and the USA. Germany is

the largest producer of thermal paper in Europe. Emerging markets, including Mexico, Brazil, China, and Thailand, are expected to contribute significantly to the future demand for thermal paper.

Pricing for thermal paper is often not in the public domain. Still, the relatively stiff competitive nature of the thermal paper suggests that price variations from one producer to the other are not likely to be high. Furthermore, thermal paper products are usually not sold directly to end consumers but to paper converters in the form of paper rolls, receipt rolls, thermal paper rolls, cash register rolls, or jumbo rolls. Before use, paper rolls are carefully stored and protected from moisture, water, and dust. Under normal storage conditions, information printed on thermal paper can be preserved for many years. However, certain oils, moisture, sunlight, or mechanical friction make images less legible. As such, the stability of prints on thermal paper is still being developed.

2.2.3 Component and design of thermal paper

Thermal paper is generally like a plain white sheet of paper. It is, however, smoother, thinner, and more sophisticated than regular paper. Thermal paper is a specialty paper consisting of a high-quality base paper matrix, a heat-sensitive layer, undercoat, topcoat, and back coat [38]. The base paper is specially sized [26]. The prototype design of a thermal paper is shown in **Figure 2**. The heat-sensitive layer, also called the thermo-reactive layer, thermosensitive layer, or colour-producing layer houses the compositions that produce colour during printing. This layer and the base paper matrix are separated by a pre-coat which prevents heat transfer through the lower layers of the paper during printing. This pre-coat is also known as Z-coat or undercoat. Thermal papers are divided into three categories based on their base weight [39]:

1. fax and sales slips (average base weight: 58 g/m^2)

2. labels and tickets (average base weight: 80 g/m^2)

3. heavy tickets (average base weight: 120 g/m^2)

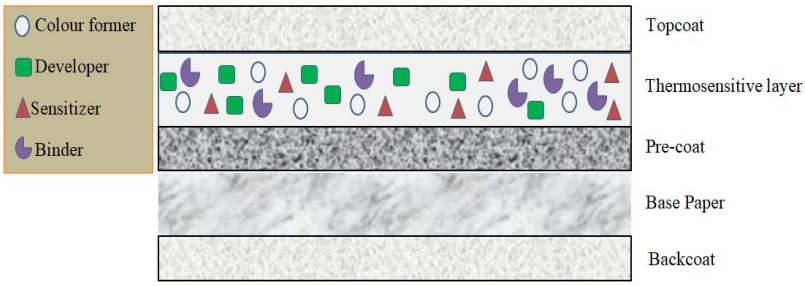


Figure 2. The design of thermal paper.

2.2.3.1 Thermosensitive layer

The thermosensitive layer is an essential part of thermal paper. The components of this layer include a colourless chromogenic dye (colour former), a developer that can change the dye to its coloured form when heated. Also included are binders, pigments, sensitizer, minerals, optical brightener, UV absorber, and other additives which impart various properties to the finished thermal paper. The thermosensitive layer can have a thickness between 5-10μm [40].

A chromogenic dye precursor is characterized by its colourless or off-white appearance and ability to change to its coloured state after a heat-initiated reaction with a developer occurs. Without the developer, the dye remains in its colourless state. Commonly used dyes in thermal paper are fluoran dyes, which produce a variety of colours depending on the structure and the operating temperature. Other examples of classes of colour formers are triarylmethanephthalide, pyridylphthalide, leucoauramine, and phenothiazine compound [41]. A suitable developer must be weakly acidic. A strong acid can also develop colour with the dye, but this may lead to a permanent colour formation which is undesirable for erasable thermal printing technology [42]. Therefore, phenols and phenol derivatives are commonly used as developers in this application. The amount of developer in a colour composition is usually more than the dye; therefore, it has a greater influence on the optical density of the image formed.

The temperature of colour formation is generally dependent on the melting temperature of the dye and developer. However, since this is mostly high and leads to low energy efficiency, a compound that lowers the colour development temperature is added to the colour composition. This compound is known as a sensitizer. Owing to

its lower melting temperature, sensitizers act as a medium to enhance the rapid interaction between the dye and developer. Furthermore, the sensitizer dissolves the dye and developer, thereby lowering the colour reaction temperature. Examples of sensitizers include benzyl-2-naphthyl ether and dimethyl terephthalate, stearic acid amide, palmitic acid amide, etc.

Furthermore, essential for a coating composition for a thermosensitive layer is a binder. Binder act as a vehicle for the dissolution of the dye and developer. It also acts as a glue that firmly holds the coating composition's components on the paper matrix. In addition, the binder acts as a delimiter which keeps the dye and developer away from each other to prevent premature colour development. The quantity of the binder, which depends on the physical nature or characteristics of the dye, developer, and other components of the coating composition, determines the viscosity or flow characteristics of the dispersion. Examples of binders in this application are polyvinyl alcohol and polyvinyl alcohol derivatives. Also, polyvinyl pyrrolidone, polyacrylamide, polyvinyl butyral, hydroxyethylcellulose, and carboxymethyl cellulose.

Furthermore, a UV stabilizer may be added to the coating composition to enhance the UV or photostability of thermal paper. The stabilizer helps prevent colour fading on exposure to light and increases the shelf life of the print. In addition, some stabilizers impact long-term paper storability or image preservability [43].

Other components of a heat-sensitive layer may include fillers or inorganic or organic pigment such as calcium carbonate, aluminium hydroxide, silica, kaolin, calcined kaolin, talc, zinc oxide, aluminium oxide, or urea resin emulsion. They also prevent the melted components from sticking to the thermal head. Lubricants such as metal soaps (zinc or calcium stearate) minimize the friction of the surface of the thermosensitive layer so that the paper runs smoothly over the roll. Anti-pressure agents like paraffin wax are added to the thermosensitive layer so that the paper can be easily calendered. Fluorescent brightening agents, anti-sticking agents, defoaming agents, viscosity modifiers, dusting preventives, lubricants, and water-proofing agents are other additives added to the coating formulation a thermosensitive layer. Depending on the design, quality, and end application, a thermosensitive layer may contain several dozens of chemicals. It may also be a multi-layered structure.

2.2.3.2 Preparation of thermal paper

In the preparation and design of thermal paper, the coating formulation is prepared as an aqueous dispersion of the colourless dye, developer, and other additives [44]. Dye and developer are ground separately in an aqueous suspension with a binder. The diameter of the particles is between 1-10μm using a wet grinding apparatus such as a ball mill, attritor, and sand grinder. The slurry is ground until the desired particle size is attained. The smaller the particle size, the higher the interaction between the dye and developer.

The aqueous dispersion of the dye and developer are mixed in a pre-determined ratio. Generally, the weight ratio of developer to leuco dye varies between 0.1:1 to 10:1, depending on the expected output. Sensitizers and other additives are also added and pulverized. The balance of the combination of the dye, developer, and sensitizer determines the optical density of the colour image. It may also influence the scan properties and the durability of the thermal paper [45]. The pulverised mix of the dispersion is then distributed on a pre-coat base paper by a coating method using a roller, coating machine, blade, or ruler. A printing method such as gravure can also be used to apply the coating composition on the paper. After the coat is applied, a convective or radiation-type dryer is used immediately to speed up the drying of the wet coat to avoid disruption of the coat. A topcoat may be optionally added to act as a sealant and protect the papers from premature colour formation under physical abrasion, chemical or environmental influences. The topcoat also helps prevent the paper from sticking to the thermal head and mitigates fading by fat, solvent, or plasticizer**.** Also, a back coat may be added to offer additional protection during the lamination or printing process. It improves the flatness of the thermal paper and serves as a barrier against migrating adhesives. In addition, the back coat preserves the paper's integrity during mechanical transportation within a thermal printer [46]. The final step is the calendaring of the paper to afford a certain degree of smoothness. Calendering produces a smooth surface and ensures reproducibility. During calendaring, care is taken to avoid colour development due to excessive pressure. Preferably, a white paper background is desired after the application of the coat.

The Colour produced when the thermal paper is heated depends on the nature of the dye and the chemical composition of the coat. However, over 95% of marketed thermal paper produced worldwide develops a single black print on heating. To create

two colours, two heat-sensitive layers with two different dyes are applied to the base paper. In between the two heat-sensitive layers is an extinguishing layer which selectively destroys the image of the upper, first melted layer to allow for the appearance of the image of the second layer. In this system, an image is created based on the different melting points of the two heat-sensitive layers [47].

2.2.4 Sensitivity of thermal paper

Thermal paper is simple to the eye but sophisticated in design. The shelf life, durability, and application performance of thermal paper depend on strength, surface, absorption properties, and sensitivity. Technically, the quality of thermal paper is described in terms of sensitivity.

Sensitivity is a measure of the degree of response of thermal paper to thermal energy. There are two forms of sensitivity – static and dynamic sensitivity. Static sensitivity is defined as the temperature at which colour/image begins to form on thermal paper. A thermal paper has low sensitivity when it produces an image at a high temperature, while it has high sensitivity when it produces an image at a relatively low temperature, typically between 70^{o}C and 75^{o}C. Static sensitivity is of high importance, particularly when the thermal paper is designed to be used in a high-temperature environment and when a high degree of colouration is required in a short time of heating. This enhances energy efficiency in thermal printers. Low static sensitivity ensures that images are not produced due to exposure to the sun or other external heat-producing sources. The topcoat plays a critical role in this regard.

On the other hand, dynamic sensitivity explains how fast a thermal printer can operate with the thermal paper and the required energy level. Dynamic sensitivity is used to evaluate the speed at which the thermal paper can be printed on to attain the maximum colouration. All other conditions constant; the higher the dynamic sensitivity of the thermal paper, the faster the printer can run. In other words, thermal paper with high dynamic sensitivity takes a shorter printing time than thermal paper with low dynamic sensitivity.

The sensitivity of thermal paper is significant when selecting the paper for specific applications. Knowledge of the sensitivity of thermal paper helps determine the appropriate environment or thermal condition for the application. For high-end

applications such as passenger tickets, medical measurements, barcodes, parking receipts, ATM receipts, and POS (Point of Sale) labels, thermal papers that produce an image of high colour density with relatively high speed at sufficiently low temperatures are desired.

2.2.5 Thermal printing

The utilization of thermal paper is enabled via the use of a thermal printer. The thermal printing process relies on the transfer of heat from the thermal head to the paper to create a text or image. It is an ink-free technology with no need for an external ink supply or ink recovery mechanism [48]. The ink-free system differentiates thermal printers from conventional inkjet or LaserJet printers. Thermal printers are usually small in size and portable in design [49] and relatively inexpensive, durable, rapid, highly reliable, and produce no noise during use. In addition, they require low energy for operation.

The early direct thermal printing technique invented in the 1930s involved using an unsophisticated and straightforward image production process. In this process, as shown in **Figure 3**, writing is done on a black coated base paper with a heated stylus. Then, the coating wax is melted with heat application, revealing the black base paper [50].

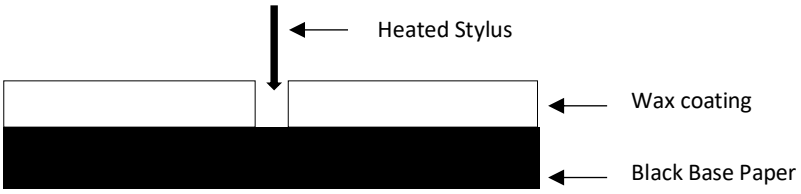


Figure 3. Direct thermal printing. Based on Bradbury [40].

The most essential component of a direct thermal printer is the thermal head equipped with many heating elements arranged in a predetermined pattern [51, 52]. Each heating element has an approximate size of 0.1 x 0.1 mm and can be switched on and off independently of the other elements. Heat is supplied to the heating elements via an input voltage. Heat application from the thermal head causes the localised melting of the component mixture resulting in colour or image formation. A

thermal head must have a low heat retention capacity for an effective application enough to allow continuous rapid heating and cooling cycles. This is important because thermal printing usually lasts for about several milliseconds with the elements heated as high as 300^{o}C.

2.3 Dyes

Dyes are compounds used to impart colour to a substance and appear coloured when they absorb light of wavelengths in the visible region of the UV spectrum. They are mostly soluble organic compounds whose use for the colouration and improvement of the aesthetic properties of substances is influenced by the presence of colour bearing chromophores. Chromophores are responsible for the absorption of energy. Colour can be produced via different phenomena: colour from the scattering process, colour arising from absorption or transmission of specific frequencies of light from an incident beam, and colour by emission from a source. Colour arising from organic dyes is due to energy absorption in the visible region of the light spectrum and is best explained by the molecular orbital theory [53].

In this theory, it is understood that absorption of energy in the visible region of the light spectrum leads to the transition of an electron from the highest occupied molecular orbital (HOMO) *ground state* to higher energy lowest unoccupied molecular orbitals (LUMO) *excited state*. Some molecular orbitals, including bonding and antibonding orbitals of the σ and σ* or π and π* type or *n*-type nonbonding orbitals, are involved in this transition. Organic dyes have extended π -bonding networks which allow for long conjugation lengths and small HOMO-LUMO excitation energies [54]. The energy gap between the HOMO and LUMO is controlled by the degree of delocalization of the π-bonding [55]. The longer the conjugation lengths, the narrower the energy gaps between molecular orbital, promoting the shift in the absorption energy of the valence electrons from the UV region into the visible region of the spectrum. Possible transitions in this regard from the smallest energy level to higher energies include n-π*, π–π*, n–σ*, and π–σ* transitions.

Some dyes have chromophores but only absorb energy in the ultraviolet region and therefore produce no colour. In this case, substituent groups called auxochromes meaning *colour increasers,* are attached to modify the electronic structure of the chromophore. Modification of the chromophore is achieved either by adding or

removing electron density to the chromophore because auxochromes are electron-donating or electron-withdrawing groups. Examples of auxochromes are -NO_2, -CH_3, -OH, -OR, -NH_2, -NHR, -NR_2, -BR, -Cl. The addition of these auxochromes alters the dye's physicochemical properties and enhances the shift of the absorption band to the visible region (**Figure 4**). It may lead to the shifting of absorption to a longer (*bathochromic or red shifting)* or shorter wavelength *(hypsochromic or blue shifting*), increase in the intensity of the colour (*hyperchromic*), or decrease in the colour intensity (*hypochromic*). Bathochromic auxochromes can also be hyperchromic, resulting in both increased colour intensity and a shift to longer wavelengths. Most dyes have resonance structures, and the more resonance structures are present, the larger the expected bathochromic and hyperchromic shifts.

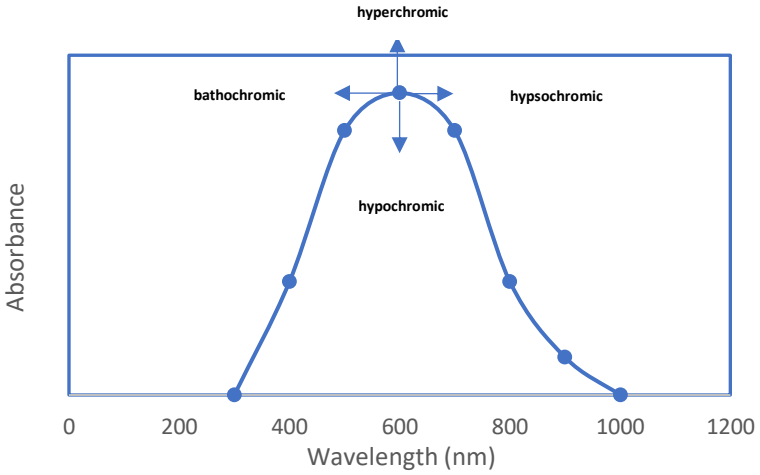
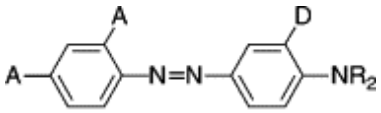


Figure 4. Hypothetical absorption band of an organic dye describing the various shifts. Adapted from [56]

2.3.1 Classification of dyes

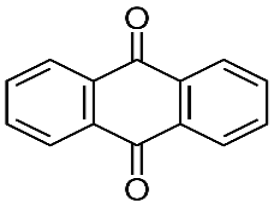
Dyes may be classified based on the nature of their chemical chromophores and based on applications. Chromophores have a profound effect on the characteristic properties of the dye. Examples of chromophore-based dyes include azo, anthraquinone, indigoid, and phthalocyanines dyes (**Figure 5**).



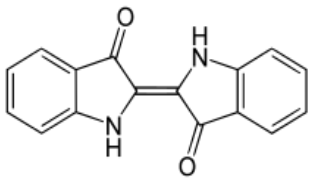
Acceptor (A) = NO_2, CN

Donor (D) = OH. NHR, NR_2

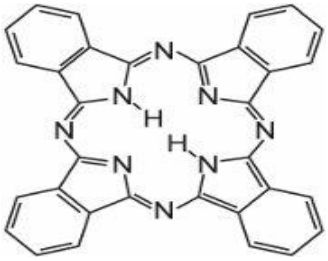
Azo dyes



Anthraquinone dyes



Indigoid dyes



Phthalocyanines

Figure 5. Classes of dyes based on the nature of their chemical chromophore.

Based on usage or application, dyes are classified as acidic, metal-complex, reactive, dispersive, direct, vat, sulphur, disperse dyes, cationic (basic) dyes, etc.[57]. These dyes are possible in textile materials (cellulosic fibres, wool, silk, polyamide fibres) and non-textile applications such as leather, fur, paper, foods, writing inks, photography indicators, drugs, and hair, etc.

2.3.2 Functional dyes

Functional dyes are described as dyes that possess the ability to change form in response to chemical and physical interactions with external forces such as pH, electricity, heat, pressure, electromagnetic radiation, touch, body heat, etc. A wide array of high-technology products in areas such as thermal imaging, electrography, liquid crystal display, molecular switches, sensors, and probes for analytes systems have been designed and commercialised based on the ability of functional dyes to alter their form in a different medium or under varying conditions [50]. Leuco dyes are one of the most widely researched and applied classes of functional dyes.

2.3.3 Leuco dyes

Leuco is from the Greek word *leukos,* meaning white. Leuco dyes, also called colour formers, are characterised by their white, colourless, or off-white appearance. A typical leuco dye has the potential to exhibit two reversible chemical forms; (a)

colourless, off-white or leuco form and (b) an intense coloured state. Structurally, reversible changes in the electronic absorption of these dyes occur depending on the nature of the external influence and the structural and molecular properties of the dyes [58]. These properties also play a vital role in the colour produced, the stability of colour, and their scope of applications. For example, based on the colour-forming reaction with acid developers, some leuco dyes are used in the production of thermal paper. Adsorption or interaction with a cellulose fibre can also initiate colour formation [59]. Also, the coloured form of leuco dye can be achieved by the change in the polarity of the dye environment or interaction with metal ions [60].

For use as a colour former in thermal paper and related materials, leuco dye properties such as high molar extinction coefficients, solubility in acceptable solvents for coating, high-temperature stability to withstand the temperature of the thermal head, good fastness properties, good image stability, low cost of preparation, good chemical stability of both the coloured and colourless form, nontoxicity, non-mutagenicity are critical to achieving a product of quality characteristics. Furthermore, depending on the target application, quality, and economic feasibility, a mixture of leuco dyes can be used. The use of such a mixture in ink formulation has been investigated and found to have a significant effect on the density of colour formed [61]. Leuco dyes can be divided into spiropyran, quinone, thiazine/oxazine/phenanzine, phthalide, triarylmethane, fluoran, and tetrazolium dyes. In this work, the focus is placed on leuco dyes belonging to the family of fluoran dyes used in thermal papers.

2.3.3.1 Fluoran leuco dyes

Fluoran is the name for the compound spiro[2-benzofuran-3,9'-xanthene]-1-one. It is characterized by a xanthene moiety core with a planar geometry in a perpendicular position to a phthalide moiety (**Figure 6)** [62].

The xanthene moiety comprises two phenyl ring bridges with an oxygen atom. In the presence of an acid, the lactone ring is cleaved, leading to the extension of the conjugated double bond system, lowering the energy of the π-π* transition, forming a zwitterionic structure colour development. The remarkable ability of flouran dyes to produce a variety of colours is a distinguishing property that has influenced their high-volume utilization in thermosensitive recording materials [63] and erasable inks [64].

Examples of fluoran dye include rhodamine B lactone [65], eosin Y [66], and fluorescein [67].

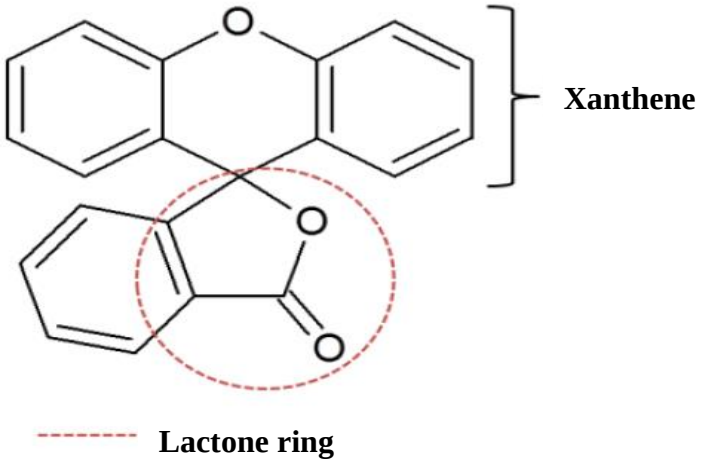


Figure 6. Structure of fluoran. (*Adapted from* Huneke [17]).

Commonly known fluoran leuco dye, which produces singly black colour is 2-anilino-6-diethylamino-3-methylfluoran (**Figure 7**).

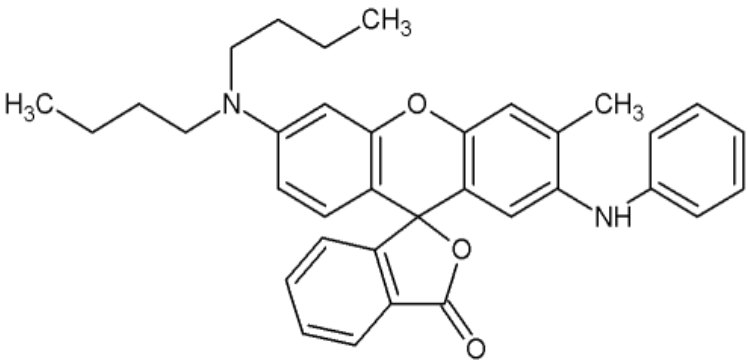


Figure 7. 2-anilino-6-diethylamino-3-methylfluoran

The single black formation makes it valuable in thermal paper production. ODB-2, as being called in the market, utilizes the steric hindrance of a methyl group at the 3'-position of the xanthene moiety to develop black colour. X-ray structural analysis of this compound has shown that the xanthene moiety is slightly bent along the central spiro-carbon (C*) and oxygen atoms. The phthalide moiety is as with the parent fluoran compound perpendicular to the xanthene moiety. The carbonyl C*-O* length is about

1.527Å which is approximately 0.1Å longer than the usual C-O length [68]. The elongation in the C*-O bond of 2'-anilino-6'-diethylamino-3'-methylfluoran enhances its cleavage.

All black colour-developing leuco dyes, though with unique individual characteristics, are derivatives of ODB-2. Several of such derivatives have been synthesised and investigated in binary and thermochromic systems [69, 70]. They develop a wide variety of colours like yellow, orange, red, blue, and green, depending on the attached substituent(s). In addition, thermally activated fluoran dye, which produces colour without a developer [71], was recently developed. These dyes are characterised by the presence of both allyloxy and amino groups and produce colour via Claisen rearrangement and intramolecular acid-base reaction.

2.4 Developers

The term developers are used to describe compounds with the ability to cause colour development in the presence of a co-reactant. Developers were first described in colour photography, where latent images were developed through a redox-based process called *chromogenic development* [72]. In this process, a colour developing compound like pyrogallol, catechol, hydroquinone, p-phenylenediamine, or p-aminophenol acting as a reducing agent reacted with silver halide to convert it to its metal form. The oxidized developer compound then reacted with couplers to form a wide variety of colours depending on the component groups. Finally, through additional processing means, a final photographic image was obtained. The developer's reduction of the silver ion enhanced by the transfer of an electron from the developer was the determining factor in the rate of colour development.

Colour developers play a central role in colour and image development in thermal paper. They are a critical part of the thermosensitive layer. Developers partake in the heat-initiated reaction with a colourless colour former to produce the coloured form of the dye with accompanying image/print. Developers used in thermal paper are typically weak acids and electron acceptors with readily accessible hydrogens or active protons. Compounds with acidic functional groups or phenolic hydroxyl groups are examples of developers use in heat-sensitive papers. Compounds modified by the addition of substituents & groups are also used as developers. Substituent groups in these type of developers include halogens [73], amino [74],

phenylureido [26], ester [75], aromatic carboxyl [76], sulphate [77], sulphonamide [78], thiourea [79], phenylurea [80], thiourea [81], urea-urethane [82], alkyl [83, 84], alkoxy [85], ether [86], heteroaryl [87], triazole [88], metal salt [89], ureido and imido moiety [90].

Compounds with the structural capacity to release acid when heated to certain temperatures have also been used as a developer. In these compounds, called hindered phenols, the hydroxyl group is chemically prevented from taking part in the reaction with leuco dye until a specific temperature is reached. To hinder a phenol, the phenolic compound may be reacted with a coupler to form a thermally stable complex. Typical examples are phenol-amine complexes [91-94]. A hydrogen-bonded complex produced from phenol and a suitable amine prevents premature colour formation. Images are produced when the thermal dissociation temperature of the complex is reached. Acid precursors can also function as developers. These substances' structure and molecular configuration are altered under heat, thereby releasing the acid functionality to partake in the dye-developer reaction. Salts of acids are examples of acid precursors. Blocked acids are another type of developer.

A typical example is the amine salt of p-toluenesulfonic acid. In this compound, the amino group acts as the blocking group. Therefore, heating the compound splits the ion pair, thereby regenerating the acid functionality.

The earliest developers used in pressure and heat-sensitive systems are inorganic acids such as activated acid clay; acid clays such as attapulgite, zeolite, bentonite, kaolin, silica [95, 96]; and acid-treated molecular sieve [97]. Though relatively inexpensive, problems associated with these compounds arose from their ability to adsorb gas and moisture from the air during storage resulting in yellowing reduced colour density. In addition, the colour developed from these substances was vulnerable to fading on exposure to sunlight. Nowadays, the commonly used developer in thermal paper is Bisphenol A (BPA) and structure-like compounds. It is associated with high image density and stability [98]. However, problems associated with its environmental and health toxicity have necessitated the call for its restriction and development of alternatives [99].

The quality of thermal paper during application is generally a function of the quality of the image produced, which depends largely on the characteristics of the

developer used. Owing to the increased demand for thermal paper in high-tech applications, the quality threshold of its developer component and other substances is very high. **Table 2** highlights the expected properties of a potential developer needed to produce a functional and marketable thermal paper.

Generally, the developer used in thermal paper is expected to be colourless in a similar fashion as the colour former. This is because the presence of colour in the background of a thermal paper may interfere with the quality of the image/print formed. Developers can be used either in solid, semi-solid, liquid, or condensate form. However, widely used developers are in solid form. The solid nature of the developer allows for easy and good miscibility with the colour former during the preparation and application of the coat.

The melting temperature is also an important quality of developers for consideration. The colour formation is dependent on the temperature of the colour developing mixtures. When the melting temperature of the developer is too high, an equally high temperature will be needed to cause the melting of the developer. This makes the process energy inefficient. On the other hand, if the temperature is too low, the possibility of premature colour formation may be high.

Furthermore, since thermal paper is a consumer product and the potential for dermal migration has been suggested, the developer must have little or no environmental and human bioaccumulation hazard potential.

Colour developers must also have good thermal stability at end-use temperature. Images/prints produced with a developer are expected to be stable against external factors such as light, moisture, heat, plasticizer, oil, solvent, and other forms of chemicals. These are the main characteristics that determine the longevity of the image. Modifications of developer compounds or the use of a mixture of developers may be considered to achieve the pre-determined developer and image characteristics. For instance, with the use of a plurality of developers, such as a mixture of diphenolic compounds and at least one polyphenolic compound, increased image density, image stability, image sensitivity, and resistance to external factors, was achieved [100]. This mixture also led to the reduction of the eutectic point of the dye-developer mixture. An irreversible high-density image was achieved with a developer mixture consisting of diphenyl sulfone derivatives in combination [101] with an organic acid such as ascorbic acid, citric acid, coumaric acid, salicylic acid, vanillic

acid, cinnamic acid, o-acetyl salicylic acid, etc. [30]. A modifier compound was optionally added to the heat-sensitive composition**.** Suga and co-workers reported the use of a mixture of phenolic condensate and bisphenol sulfone to obtain a thermal recording material with improved colour sensitivity and image stability [102].

Furthermore, an image of higher density and stability was created with a mixture of phenolic resin with phenol [103], metal salts of aromatic carboxylic acid [1], and vinylic or acrylic resin [104]. Furthermore, a mixture of kaolin clay, zinc-modified phenol-formaldehyde resin, and urea-formaldehyde resin pigment accorded improved print speed and image intensity [20, 105]. Finally, in a bid to obtain highly detailed images of adequate density and stability, the use of a colour developing mixture of a leuco dye and either of linear, branched, or copolymers of polyhdrostyrene, alone or in combination with a co-developer such as BPA, benzyl paraben, phenolic resins, polymeric and oligomeric hydroxy sulfones was proposed [106].

In addition, metal ions, particularly polyvalent metal ions, have played a vital role in improving the image quality of a recording material. Yamaguchi and co-workers attempted the combined use of a multivalent-metal-modified salicylic acid resin and a polycondensation resin to overcome the challenges associated with using metal salts of aromatic carboxylic acid, which exhibited premature colour formation and poor resistance to water, plasticizers, and light [107]. Although the challenges were not eliminated, an improved recording sheet was obtained. Similarly, a colour-developing layer having both an electron donor and a metal double salt of a higher fatty acid of 16-35 carbon atoms as a developer was designed [89]. It was reported that the combination of a long-chain fatty acid iron salt such as iron stearate and iron myristate and a phenolic compound such as tannic acid, gallic acid, and ammonium salicylate yielded a heat-sensitive adhesive sheet of improved properties [108]. In addition, a mixture of a metallic salt of carboxylic acid, hydroxyl-containing polymer, and melamine or urea resin was employed to improve the water-resistance of the recording sheet [109]. Chelate-type colour-forming systems with at least one leuco dye and at least one urea-based developer produced print images having a printing sensitivity remarkably better than with the use of the individual developer [110].

Table 2. Properties of developer for a functional and marketable thermal paper

Properties	Description
Colourless	No inherent colour to prevent background imaging of the thermal paper during storage and before use.
Good solid morphology	Required for good miscibility with colour former during the preparation of coating dispersion and to enhance effective reaction
Low water solubility	Slightly soluble or water-insoluble preferred. Allows for easier coating preparation and application. It also preserves the water stability of print.
Clear/legible print	Formation of clear and legible print.
High sensitivity	Ability to produce an image of high colour density with relatively high speed at sufficiently low temperature.
Image stability	Image density sufficiently unchanged over a pre-determined period.
High/optimum resistance to external factors	High resistance to light, oil, moisture, plasticiser, solvent, and other chemicals
Thermal stability	Stable to heat and temperature at the end-use
Economic/commercial viability	Preparation should be inexpensive for large-scale commercial production.
High molecular weight	Sufficiently high molecular weight to limit dermal migration
Toxic-free	Low environmental and human bioaccumulation hazard potential.

In the last decade, the use of a mixture of urea-based compounds to prepare a heat-sensitive paper has been described [111]. Ten thermal papers were produced from the combination of the two developers from a ratio of 99:5 to 85:15. While the background whiteness before aging and after aging of the thermal paper changed with varying proportions of the developer mixture, the optical density of the image formed was essentially unchanged.

2.5 Dye-developer interaction

Colour development in a leuco dye-based system such as thermal paper is premised on the heat-initiated chemical reaction between an electron donor (colour former) and an electron acceptor (developer). The developer, as earlier discussed, is mostly known to be a weak acid with the ability to donate a proton which triggers the opening of the hitherto closed lactone ring of the dye leading to a structural rearrangement and visible colour formation. The visible colour change represents the new structural forms of the dye and developer [112]. This colour formation process is a fundamental feature of the thermal printing process. In thermal printing, multiple competing interactions occur depending on the components' characteristics, thermal history, and operating conditions. This section focuses on the interactions and the mechanisms thereof.

2.5.1 Dye-developer interaction in a binary system

In both thermal paper and carbonless copy paper, the equilibrium reaction and strength of the bond between dye and developer is central to the application output. While the dye-developer complex formed in carbonless copy paper is irreversible, the equilibrium reaction between dye and developer in thermal paper is reversible depending on the prevailing operating conditions [113].

The first test of the efficacy of a dye and developer is the production of colour when fused under the influence of heat. On this note, previous work done by our group focused on the design of a rapid preliminary screening test to investigate the colour forming potential of over 50 bio-based, renewable compounds and fractions spread across 15 different classes [17]. Substances tested were carboxylic acids, fatty acids, sugar, sugar acids, tannin, proanthocyanins, etc. Most of the binary mixtures studied produced characteristic black colour on heating, albeit at different temperatures. For instance, the white/off-white colour of carboxylic acids such as citric acid, ascorbic acid, salicylic acid, succinic acid, acetylsalicylic acid, and fatty acids such as myristic acid and stearic acid was retained in their unheated mixture with ODB-2. On the application of heat, black colour was observed between 40 – 180^{o}C. The colour remained constant when heated to a higher temperature and after cooling. Heated mixtures of monomeric phenols and ODB-2 also produced characteristic black colour on heating between 60 and 170^{o}C.

For a closer look at the nature of the coloured substances, organic acids like citric acid were heated with ODB-2 on an aluminium dish. As the temperature increased, a thick black viscous liquid was formed. On cooling in ice, the black coloured substances turned glassy. Microscopic image showed that similar glassy coloured substances formed between crystal violet lactone and dodecyl gallate were solid, opaque, and lacked distinct attributes [114]. The coloured state represents a metastable dye: developer aggregate structure [115].

2.5.2 Dye-developer interaction in a three-component system

A three-component system called a ternary system or thermochromic system consisting of a solvent, dye, and developer exhibits different colouring behaviour. In a thermochromic system, contrary to a binary system where one irreversible state is mainly attainable, two reversible states can be alternatively maintained by altering the temperature conditions, thereby offering the possibility of recording and erasing in application materials [86, 116]. Alteration of operating temperature influences interactions such as dye-developer interaction and developer-solvent interaction, and by extension, the colouring characteristics of a thermochromic mixture [117].

Solvent plays a vital role in the thermochromic system. It can facilitate or inhibit the colourimetric characteristics of the system. Low-melting organic, non-volatile, and hydrophobic compounds belonging to the class of long-chain alkyl alcohols from 1-octadecanol (OD) to dodecanol [118, 119], esters [84], fatty acids [120, 121], aliphatic ethers, [85], ketones [122], amides [88], acid amides, thiols, sulphides and disulphides [123] are used as solvents in thermochromic mixtures. Depending on the nature of the solvent and condition of use, it can act as a decolourising-accelerating agent [116], phase separation controlling agent [86], activator [124], reversible agent [125], and sensitizing agent [126].

Several investigations have been carried out to study the structure, thermal and colourimetric properties of thermochromic systems [69, 118, 127-129]. While the application temperature of a binary mixture was largely dependent on the melting point of the developer, the temperature at which the solvent changes from solid to liquid or vice versa influences the operating temperature of the thermochromic mixture [130]. This temperature can be set over a wide range of low to high temperatures because solvent compounds are thermally stable over a long heating and cooling cycle.

For instance, Oh *et al*., [128] studied the reversible thermochromic properties of six tert-butyl substituted fluoran-based leuco dyes. The three-component system design with methyl stearate and 1-dodecanol underwent a phase transition from red to colourless and vice versa at 40ºC and 20ºC, respectively (**Figure 8)**. The melting points of the solvents also influenced this.

In general, depending on the prevailing colour characteristics, the operating temperature of a thermochromic system may be termed activation temperature [131], clearing temperature [69], discolouration temperature [117], transition temperatures [124]; switching temperature [132], or a more general term – thermochromic temperature [123]. Below this temperature, they are mostly coloured, and above the temperature, they are colourless or possess a light hue.

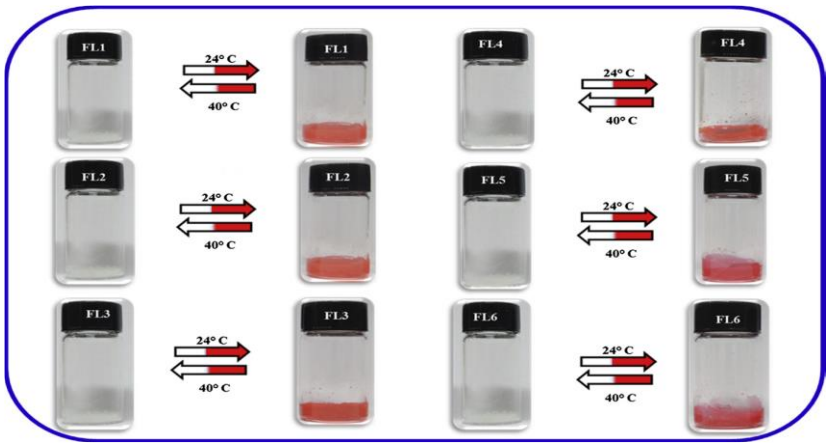


Figure 8. Solid-state colour change of fluoran dyes (at warm and cool) with bisphenol-A and methyl stearate. Copyright: *Oh et al.,* [128].

Thermochromic systems have been exploited to design temperature-sensitive commercial products termed thermochromic materials [133], functional materials, or smart materials [134]. These materials change colour with temperature changes. **Figure 9** summarises the different classes of thermochromic materials.

Colour formation and erasing in thermal paper is thermochromism [38, 135]. This mechanism has been studied and remains an open matter for continuous debate. However, most studies have supported the phase separation mechanism [136] and pH-dependent molecular arrangement [70]. According to the phase separation mechanism of thermochromism, when a three-component thermochromic system as found in thermal paper is heated to the melting temperature of the solvent, the solvent melts, bringing the dye and developer into solution. In this state, the dilution effect of

the solvent enhances the developer and solvent interaction. This inhibits the interaction of the developer with the dye and results in a 'no-colour ring-closing state.' However, a melt-coloured state can also be achieved depending on the compatibility of the solvent and developer [137]. Conversely, when the system's temperature is reduced either via cooling on ice or under liquid nitrogen or via quenching [138], the solubility of the dye and developer is decreased gradually, leading to their crystallization and subsequent coloured ring-opened state. In this state, the interaction between the dye and the developer outweighs the developer: solvent interaction due to the solvent's dye and developer phase separation.

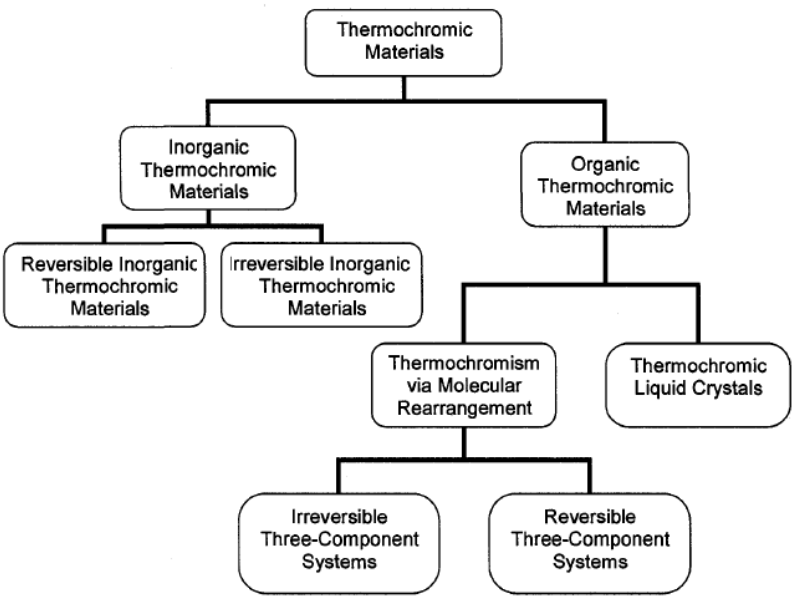


Figure 9. Subdivision of thermochromic materials. Reproduced based on Hong [139].

In line with the phase separation mechanism, Ibata *et al*.,[140] divided the colour formation process in thermal printing application into three steps:

(1) Dissolution – the process in which the dye and developer dissolve in the molten solvent at increased temperature.
(2) Fixation – the metastable dye-developer colour complex is rapidly fixed on the substrate at a lowered temperature.
(3) Stabilization – the colour formed is finally stabilized by weak intermolecular interactions such as H-bonding and van der Waals forces.

To achieve precise thermochromism in thermal paper, each developer requires a compatible solvent. The solubility of the developer in the mixture during the transition from one state to the other is important for effective application. Also, colourimetry characteristics are dependent on a good formulation. Typically, the composition of dye and developer may vary from 5 to 15% or more by mass, respectively. The solvent can be as high as 80% or more, depending on the target print quality. The quantity of solvent used is essential for the stability and durability of colour. Too much solvent may lead to a dilution effect which inhibits the crystallisation of the dye and developer in transition. As a result, a low colour density is achieved in such a situation. On the other hand, when the quantity of solvent is too low, the dissolution of the dye and developer on solvent melting will be hindered, thereby affecting the targeted colour changes.

Based on this understanding, the first design rule for the optimization of rewritable thermochromic properties was proposed [141]. According to the rule, the contrast between the coloured and non-coloured state must be high at ambient temperature. Secondly, the rate at which colour changes in transition must be fast enough to lead to a metastable state. The rate of transition from colourless to coloured state in thermal printing is very rapid. Lastly, the metastable state of the colour formed must be stable over a long period with no significant change in density at ambient temperature.

2.5.3 Spectroscopic properties of a dye-developer-based system

FTIR, NMR, UV spectroscopy, and X-ray crystallography analysis have been used to study the interaction between leuco dyes and developers. Leuco dyes are characterised by carbonyl (C=O) absorption vibration peaks between 1740cm^{-1} and 1760 cm^{-1} in the FTIR spectra [118]. Typically, the transfer of a proton from the developer initiates the formation of a hydrogen bond between the carboxylate anion (COO-) of the dye and the hydroxyl groups (OH) of the developer leading to the opening of the lactone ring [142]. Takahashi *et al*., [143] studied the coloured species formed from the fusion of S-205 dye and BPA and confirmed that the opening of the lactone ring of the dye led to the formation of a colour-developing complex (CDC). This CDC comprised the dye and developer in a defined mole ratio and stabilized by hydrogen bonding [144]. Tsutsui *et al*., [145] called the coloured species a

supramolecular complex. The stoichiometric molar ratios of complexes of various dyes and developers have been determined [140, 146, 147].

The first attempt to isolate the colouring species of dye and developer was reported in the early ’90s [148]. In this work, a well-defined complex was obtained from the interaction of CVL with either zinc or cadmium iodide in acetone. According to the X-ray crystallography, the CVL with its opened carboxylate structure is embedded in a carrier matrix built of the metal and iodine atoms forming alternately six and four-membered rings linked together in a spiro-arrangement. Single crystals of the complex were later obtained with intercalated acetone molecules [149]. It was revealed that the leuco dye takes on a different structural formation when transiting from the colourless to the coloured state and vice versa [62, 68, 150-152].

Furthermore, Takaoka *et al*., [153] showed that the diethylaniline ring to the xanthene moiety of the fluoran dye has a quinoid structure in the coloured state. In contrast, in the decoloured state, the xanthene moiety is folded at about 180^{o} around the central C-O axis. As reported by Horiguchi and co-authors, the mixture of 6′-(Diethylamino)-3′-methyl-2′-(phenylamino)spiro[isobenzofuran-1(3H),9′-[9H]-xanthene]-3-one (ODB) and the long-chain developer, N-(4-hydroxyphenyl)docosanamide (PA21) molecule exhibited different layered structures between the coloured to decoloured state signalling a degree of intercalation and deintercalation of the leuco dye [154].

Also, based on X-ray diffraction of the colouring species obtained from Rhodamine B and phenolic colour developers, two main types of interactions were observed. Firstly, a hydrogen bond between the OH groups of developers to form a dimer (in developers with less than two OH groups, such interaction was not evident) and secondly, a π-π stacking interaction between xanthene moieties of the dye [155]. The xanthene moieties overlapped parallel to each other across an inversion centre, indicating the extension of the electronic conjugation in the colouring species.

This is similar to the results of the X-ray diffraction analysis of the interaction between fluoran leuco dye and Bisphenol-S (BPS), in which one molecule of BPS was found to be hydrogen-bonded to four different neighbouring ones to form a two-dimensional hydrogen bond network [156]. One of these hydrogen bonds formed the dye/BPS system, while the remaining three hydrogen bonds act as network stabilizers.

Essentially, these studies emphasised the importance of hydrogen bonding in dye-developer interaction. Hydrogen bonding plays a key role in the stability of the colouring species, and the presence of multiple hydrogen bonding may increase the stability of the complex [82]. Notably, it has been opined that the ability to participate in hydrogen bonding is one of the prerequisites for a developer in a leuco dye-based system [82, 157].

Dye-developer interactions have also been extensively monitored with NMR spectroscopy. Based on ^{1}H-NMR, Hojo *et al*., [158] showed that the cleavage of the C-O bonds of Rhodamine B base and the formation of stable zwitterions in the presence of alkali or alkaline-earth metal ions is confirmed by a shift in the band of the xanthene of the fluoran dye to a lower magnetic field from the coloured and colourless states. ^{13}CNMR signals confirmed the formation of the sp^2 hybridized carbon centre of the black colour former. In a study of the reversible ring-opening and ring-closing interaction between fluoran leuco dye (DEAMCF) and $CDCl_3$ with a developer using ^{13}CNMR, Endo *et al*., [112] showed that in the presence of an acid such as H_2SO_4, some signals of the dye shifted to a lower field while some shifted to a higher field. Most of these signals were found in the shift range of the normal benzene-ring carbons of about 110-150 ppm, suggesting a change of the xanthene ring to a planar structure. Signal shifts varied with an increasing amount of the acid [159].

UV spectroscopic analysis provides information about the characteristic absorption spectra of a dye in the coloured and colourless state [60]. The coloured form of some fluoran leuco dyes exhibits two absorption maxima (λmax) and an identical molar absorption coefficient. For instance, two strong complementary absorption peaks at 453nm and 595nm representing yellow and violet colours are produced when ODB-2 interacts with a developer. The additivity of the complementary colours develops black colour [154]. In its ground state, CVL is colourless with λmax at 280nm. In the presence of a developer, CVL showed absorption peaks at 620nm with a shoulder at about 570nm when it changed to its characteristic blue colour [139]. The coloured state of Rhodamine B also had an intense absorption maximum at a wavelength between 510nm and 570nm [160].

2.6 Properties and application of Bisphenol A (BPA)

Bisphenol A [4,4′-(propane-2,2-diphenyl propane)], commonly called BPA, is a petrol-based chemical with an estimated high production volume of about 8 billion tonnes per annum worldwide [161]. BPA is commonly used as a plasticizer in the production of polycarbonate, epoxy resins and as a component of the flame retardant tetrabromobisphenol-A due to its relatively high heat resistance and transparency [162]. In addition, BPA is a major component of various plastic products, including baby toys, feeding bottles, dental sealants, drinking bottles, cookware, plates, storage containers, sport, and electronic equipment. Also, BPA is widely used in the production of printing ink and thermal paper for receipts, self-adhesive labels, lottery tickets, and fax paper, where it functions as a developer responsible for image production.

Owing to the ubiquity of BPA in various everyday products, it has been detected in many environmental media, non-humans, and humans. As such, public concerns about its toxicity and related environmental implications have been raised. Furthermore, BPA is a known environmental pollutant [163] and with the potential to disrupt the normal functions of the endocrine system in humans and non-humans [164]. Consequently, its estrogenic activity and detrimental health effects *in vitro* and *in vivo* have been the focus of a large body of research [165-168].

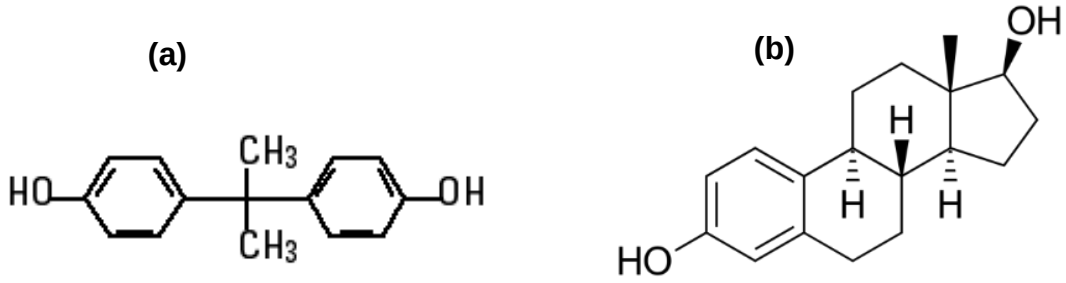


Figure 10. Structures of (a) bisphenol A and (b) oestradiol.

Hormones play a vital role in many processes in the body, including the development of organs. Enhanced by the structural similarity to oestrogen (**Figure 10**), BPA binds with the nuclear estrogenic receptor and modifies gene expression under oestrogen control [169]. Thus, BPA mimics endogenous hormones to act as a hormone antagonist, leading to a false increase in the available hormone in the body. In principle, BPA interferes with the synthesis, secretion, transport, and binding action of natural hormones, including the development of the central nervous system

responsible for the maintenance of homeostasis, reproduction, development, and behaviour [170]. Disruption of the endocrine system can lead to the breakdown of communication between body cells and organs, thereby posing a significant effect on health stability.

2.6.1 Exposure to BPA

Exposure to BPA can either be through dietary or non-dietary routes. Dietary exposure is associated with BPA exposure through contact with food products and food packaging, such as food and beverage containers, while non-dietary exposure refers to exposure through contact with non-food substances.

2.6.2 Dietary exposure to BPA

Food, particularly canned food, is an important source of BPA exposure and was recently one of the highlights of the Scientific Opinion released by the European Food Safety Authority [171]. Epoxy resins are used as internal coatings of food and beverage cans to prevent the cans from corrosion and to prevent the migration of metal ions into the food, thereby protecting the integrity of the container and the organoleptic properties of the food. Epoxy resins are synthesised by the condensation of BPA with epichlorohydrin to create BPA diglycidyl ether. However, residual free BPA monomers from the polymerization process can leach from the epoxy resin and contaminate stored foods and drinks [172].

A review of several studies conducted worldwide to determine BPA concentration in canned foods and beverages [173] shows that BPA migrates from coated cans to foods including vegetables, fish, meat, beans, soup, milk, fruit, and infant formula [174]. These studies showed large variations in the BPA concentrations depending on the food type, food brands, coating compositions, and make-up of the cans [175]. Food packaged in glass, plastic paper, and laminated paperboard also contained some level of BPA, although significantly lower than the amount detected in their canned counterparts [176]. Lids for glass containers contain epoxy resins, and most packaging papers are made from recycled papers, which may contain BPA. The migration of BPA from these containers into food is increased during storage and is greatly influenced by heat and temperature [177]. As such, when foods stored in BPA-containing packages are microwaved at high temperatures, the BPA can be released from the packaging material into the food [178]. For this reason, the use of plastics in

microwave or filling of plastics with hot substances has been discouraged. In addition, since epoxy resins are key components of household pipes and fittings, the probability of BPA exposure through household water, especially in hot climate conditions, is also high [172].

Furthermore, an investigation of the urine samples of those who either consumed canned soup or canned vegetables showed a substantial difference in BPA level compared with those who did not consume canned foods [179, 180]. On the other hand, a reduction in the urinary BPA concentration was reported for volunteers subjected to a 3-day uncanned or unpackaged ‘’fresh food’’ diet [181]. Thus, although intake of BPA through food was less than the tolerable daily intake set by the food authorities, humans of different age groups remain at risk of the cumulative effect of BPA through food exposure [182].

2.6.3 Non-dietary exposure to BPA

Only about 3% of the produced polycarbonate and 10% of the epoxy resins are used in materials intended to contact food substances [183]. Therefore, non-dietary sources of BPA exposure such as inhalation of contaminated air or dust in homes, offices, and laboratories [184], medical devices [162], dental materials [185], sewage treatment effluents [186], and thermal paper are a genuine cause for concern.

Table 3. Concentration of BPA in thermal paper cash receipts (LOQ = Limit of quantification)

Country	Concentration of BPA **(range)** (µg /g)	Reference
Switzerland	13500 **(5600 -30400)**	[187]
China	13940 **(160 – 26750)**	[188]
USA	15400 **(4500 – 42600)**	[189]
	15100 **(<LOQ-17000)**	[190]
	12500 **(3000 – 17000)**	[191]
	9310 **(<LOQ-13900)**	[192]
Belgium	15000 **(100 – 21000)**	[193]
Denmark	11400 **(8700 – 17000)**	[32]
Brazil	16300 **(5000 – 23200)**	[194]
Germany	15530 **(15000 – 15900)**	[98]

BPA exposure through contact with thermal paper receipts is one of the single largest non-dietary sources of BPA in humans [195]. The European Thermal Paper Association (ETPA) reported that 70-80% of all thermal paper sold in the EU contained BPA [196]. At the turn of the millennium, an estimated 1,400 tons of BPA was used to produce 105,000 tonnes of thermal paper [197]. This suggests that the thermal paper contains about 13,000 µg/g BPA. Furthermore, a 35% increase was reportedly used between 2005-2006 [32]. A further survey and investigation of thermal paper receipts show that about 1-2% by weight of the whole thermal paper receipts is made up of BPA [2]. In addition, several country-specific studies have identified several BPA concentrations in thermal paper. The results of these studies are summarised in **Table 3.**

Exposure to BPA from thermal paper can occur via several routes. Firstly, during manufacturing, workers are exposed to high dosages of BPA via inhalation. Secondly, consumers and particularly cashiers who touch receipts frequently, are exposed to BPA through skin contact. Contrary to other applications, BPA in thermal paper is present in a free, unbound, non-polymerized form which enhances dermal absorption or medium transfer when contact is made. Lastly, exposure to BPA can occur during the recycling of used thermal paper and other BPA-coated papers. BPA ends up in paper recycling sites through trimmed, discarded, and re-pulped thermal papers. Paper products made from these recycled papers like kitchen rolls, hand tissue, books, magazines, and serviette papers are potential carriers of BPA and a route of exposure.

Dermal absorption of BPA through the handling of receipts and other papers such as banknotes is significant. It could run to about several hundreds of micrograms per day, depending on certain factors. A study by Biedermann *et al.,* [190] assessed the level of *'paper to skin transfer'* of BPA in occupationally exposed people such as supermarket cashiers and showed that more than 1.1µg BPA could be transferred daily to each of the two exposed fingers if the skin was dry and ten times more if the skin was wet or greasy. The study further predicted that the BPA level might rise to a worst-case of 71µg/day if all ten fingertips repeatedly touch the thermal paper during a 10h work shift. 27% of this BPA is likely to penetrate the skin. A Danish study predicted a realistic worst-case scenario of a daily uptake of 240µg, assuming the receipts were touched with humid fingers [32]. According to this study, the immersion

of the receipts in artificial sweat for 5 seconds showed a BPA migration of 7-21µg BPA/cm^2, equivalent to 10-37% of BPA content in the receipts. An increase in the amount of BPA transferred to the skin was also observed when touched first with ''normal'' conditioned fingers (0.8µg BPA /finger) and later with moistened fingers (35µg BPA/finger) [98]. Alcohols used in hand creams and sanitizers could also act as an enhancer of the '*paper to skin transfer'* of BPA. Direct contact of BPA-exposed unwashed hands with food, mouth, or any other item may also lead to increased exposure. Geens and co-researchers [193] estimated the daily intake of the BPA exposure in a population at 0.4 mg/day, and in a worst-case scenario, this could rise to about 1.3 mg/day. A slightly higher value of 1.4mg/day was predicted by Rocha and co-authors [194], while Zalko *et al.,* [198] set the amount of bioavailable BPA at 6.6mg/day. The level of exposure depends on which side of the thermal paper was frequently touched because only the front side of the thermal contains BPA. *Paper-to-skin transfer* from the backside of the thermal paper could be attributed to contamination.

2.6.4 Impacts of BPA exposure on human health and the environment

Human and non-human exposure to BPA is ubiquitous, and the aftermath effects of this exposure have been extensively reviewed [5, 99, 165, 166, 168]. Mielke and co-authors systematically simulate BPA concentrations in human body organs like kidneys, liver, and blood after dermal and oral exposure to BPA. Results confirmed the transfer of BPA through the skin into the target organs at varying concentrations. Accordingly, an estimated amount between 10% and 60% of BPA coped from external exposure could find its way to the internal tissues and fluids [199, 200]. A large body of evidence from epidemiological studies have therefore implicated BPA levels in body fluids in wildlife, [201] and humans in many health challenges such as infertility [202], breast cancer [203], type 2 diabetes [204], obesity [205], attention deficit hyperactivity disorder [206], neurodegeneration [207], unfavourable brain development and behaviour [208], and numerous cardiovascular diseases and metabolic disorders [204, 209].

A higher BPA level was associated with poorer ovarian response in women undergoing IVF treatment [210]. An increase in BPA level in serum of women and Asian men also caused a decrease in the probability of fertilization [211]. Cases of premature delivery (less than 37 weeks) reportedly occurred in Mexican pregnant

women due to elevated BPA levels [212]. Children with BPA-exposed mothers had significantly lower birth weight than children of unexposed mothers. Furthermore, increased urinary BPA was associated with premature puberty in 9-year old girls [213]. Higher urinary BPA in pregnant women and offspring was implicated in girls' increased externalizing behaviours at two years of age, but the same was not found in boys [214]. High urinary BPA led to higher body mass index and obesity in adults and school children [215, 216]. In males, exposure to BPA was associated with decreased serum levels, low sperm count, sperm motility, and rapid increase in sperm DNA damage [207, 217, 218]. These effects could be irreversible, long-lasting, and transgenerational, surviving several future generations [219].

The level at which BPA produces harmful effects in humans and non-humans is still a subject of debate and research. Some studies suggested that a low dosage of BPA at about 10 to 100ng/kg could produce profound and adverse health effects in animals [220, 221]. For example, Wang *et al*., [222] claimed that low-dose BPA exposure was responsible for breast cancer. On the other hand, more studies have reported contrary opinions, suggesting that a low dosage of BPA has no significant effect in humans [223, 224]. Nonetheless, very low doses of chemical pollutants could have profound effects on the exposed. Furthermore, the mixture of BPA with other chemical pollutants in the environment could lead to compounded effects in the exposed [225].

2.6.5 Regulation of BPA

Despite the high number of scientific reports in the public domain, the overall effects of BPA exposure on BPA levels in the human body fluids and health implications remain a complex matter of controversial discussion in the health and regulatory space. Some scientists have argued that the various epidemiological studies on BPA are limited in approach and cannot be accepted. Some of the limitations of BPA-focused studies include the questionable criteria for the selection of studies for risk assessment, the insignificant correlation between *in vitro* and *in vivo* investigations, inaccuracy of the levels of human exposure, lack of clarity in the mechanisms of action, uncertain routes of human exposure, and the limited scope and volume of the studied populations [5, 226-228].

Table 4. Worldwide regulations and restrictions of BPA in thermal paper and consumer products

Year	Country/Organisation	Regulation	Reference
2001	Japan	Prohibited the use of BPA in thermal paper	[229]
2008	European Food Safety Authority (EFSA)	Sets a tolerable daily intake of 0.05mg/kg/day for BPA.	[230]
2010	Canada	Became the first country to ban BPA in baby bottles	[231]
2010	Institut National de la Santé Et de la Recherche Médicale – (INSERM)	Classified BPA as a reproductive toxic substance of category 3	[232]
2010	Trade Union Priority List	Included BPA in Trade union priority list as reprotoxic and endocrine-disrupting compound.	[233]
2011	Taiwan; Connecticut, USA, Belgium	Banned BPA in thermal papers	[234, 235]
2011	European Union	Banned BPA from infant feeding bottles across EU	[236-238]
2012	German Federal Environmental Agency	Set a reference value of 7µg/l BPA for 20-29-year-old adults	[239]
2012	France	Officially passed a law suspending the production, trade, and marketing of food containers containing BPA	[240]
2013	Suffolk County, New York	Signed the ‘’Safer Sales Slip’’ act into law to ban thermal receipt paper coated with BPA in Suffolk County, New York	[241]
2014	French Agency for Food, Environmental and Occupational Health and Safety (ANSES)	Submitted a restriction proposal for the use of BPA in thermal paper.	[6]
2015	European Food Safety Authority (EFSA)	Lowered the TD) of BPA from 50 to 4µg/kg BW per day	[171, 242]
2016	Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH)	Announced the restriction of BPA in thermal paper on the European market at a concentration equal to or greater than 0.02% by weight after January 2, 2020, under the EU regulation (EU) 2016/2235	[243]
2017	European Chemicals Agency (ECHA)	Listed BPA in the candidate list of substances of very high concern (SVHCs)	[244]
2017	Institut national de l'environnement industriel et des risques (INERIS)	Developed the certification ‘’BPA Free’’ and ‘’No Phenols added’’	[245]

Furthermore, the genuineness of the results of the research has been questioned. According to vom Saal et al., [246], the outcome of most scientific investigations relating to BPA is influenced by social issues, legislation, and, more importantly, the source of research funding – industry-funded or public-funding. For example, an evaluation of about 115 studies showed that industry-funded studies did not find significant effects of low doses of BPA. In contrast, over 90% of public-funded studies reported significant results. Regardless, governmental, and non-governmental institutions worldwide have taken steps and measures to reduce or eliminate the widespread exposure to BPA in many consumer products. **Table 4** lists BPA regulations of various countries and organisations.

The first ban on BPA in thermal paper was in Japan in 2001. Similar restrictions on the manufacturing, sale, or distribution of thermal receipt paper or cash register receipt paper and other consumer products containing BPA have been enacted in Taiwan [247], and some states in the USA like Minnesota [248] [249], New York, Connecticut and more recently, Illinois [250]. Many other states are expected to follow the same route [235].

Due to the health risks of BPA on pregnant women and consumers, in June 2014, the French Agency for Food, Environmental and Occupational Health and Safety (ANSES) submitted a restriction report proposal to the European Chemicals Agency (ECHA) on the use of BPA in thermal paper [6]. This proposal seeks to ban the use of BPA in thermal paper in concentrations equal to or higher than 0.02%. In response, the European Commission carried out a thorough assessment of the proposal and decided that the requested ban was admissible and might be utilized as an EU-wide measure to reduce the risk for human health. Consequently, a draft amendment to the REACH regulation regarding the use of BPA was made to set a limit for BPA in thermal paper. In December 2016, after passing through several legislations, the European Commission added BPA to the list of restricted substances (regulation (EC) No. 1907/2006). Equally, in June 2017, ECHA's member state committee announced their support for the French proposal to additionally identify BPA as a substance of very high concern because of its endocrine-disrupting properties. The entry was updated in January 2018. Therefore, it was decided that BPA may not be placed on the European Market in thermal paper at a concentration equal to or greater than 0.02% by weight after January 2, 2020. This regulation applies

to all producers of thermal paper in the EU and imported thermal papers. In principle, there is a ban on BPA in thermal paper for the European market from 2020 and onwards [251].

In response to the new BPA regulations, there has been an increased effort by EU countries, notably Belgium [252] and the Netherlands [253], to search for safer BPA alternatives of similar or improved technical competence. For example, through its National Competence Centre for Industrial Safety and Environmental Protection (INERIS), France developed a ‘’BPA Free’’ and ‘’No Phenols added’’ label - to guarantee the absence of BPA and other phenolic compounds in thermal papers. This initiative is one of the French government’s National Strategic Plan against Endocrine Disruptors [254]. Many manufacturers have adopted this move in the EU as a way of emphasising their commitments to the removal of BPA and related substances of health and environmental concern from the production of several consumer goods and thermal papers.

2.7 BPA alternatives in thermal paper

2.7.1 Petrol-based alternatives

Few studies have sought to address the quality of alternatives to BPA in thermal paper and other consumer products. In 2012, the United States Environmental Protection Agency (USEPA) released a draft assessment of the existing 19 alternatives to BPA in thermal paper [255]. This was a response to the chemical action plan for BPA released by the Environmental Protection Agency (USEPA), which tasked the Design for the Environment (DfE) branch to conduct an alternatives assessment for BPA in thermal paper. The assessment carried out in conjunction with a consortium of stakeholders, including NGOs, chemical experts, supply chain companies, green chemistry, and technical experts, and international governmental organisations focused primarily on the chemical and physical properties of the substances, their production, use, hazard profile, toxicity potential, predicted bioaccumulation and persistence in the environment. Out of the 19 studied substances, 12 were Bisphenol-based (BPA, BPF, BPC, MBHA, BisOPP-A, BPAP, PHBB, BPS, 2,4-BPS, TGSA, BPS-MAE, and BPS-MPE), bisphenol-free but phenol-based developers were 3 (D-8, D-90, DD-70) and 3 were phenol-free developers (Pergafast 201, BTUM, and UU). The final report of the assessment released in 2015 [195] revealed that none of the 19 substances was fit enough to be a safer alternative

to BPA. All these substances are petrol-based, and most have a moderate to high probability to impact human health and/or aquatic systems and therefore did not pass the health safety assessment test. The report stressed that substitution with these alternatives is questionable and can result in the need for additional substitution in the future.

Despite these revelations, petrol-based BPA and many of these compounds are still being highly used as developers in thermal paper. Investigation of colour developers in thermal papers placed in the EU market between 2014-2016 shows that BPA is the most used developer. However, an increase in the use of other developers was reported from 2014 to 2017 (**Figure 11**).

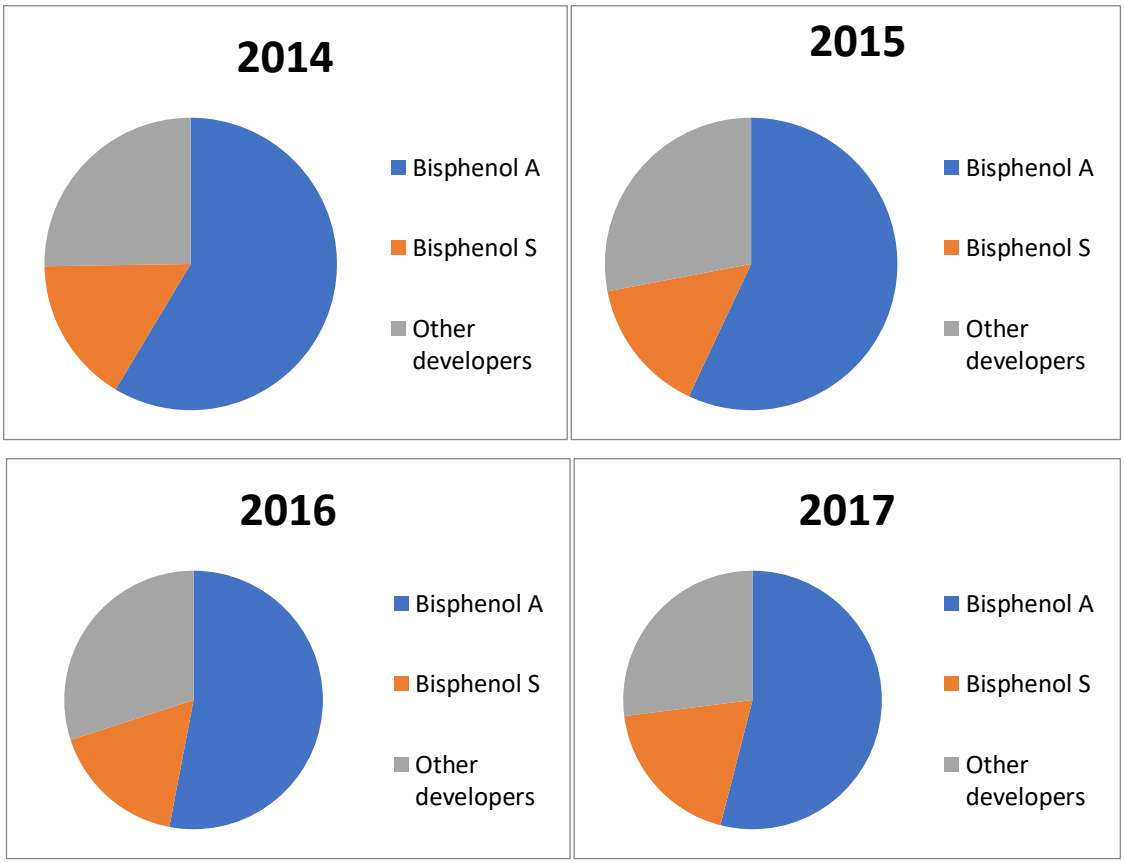


Figure 11. The use of BPA and its alternatives in thermal paper between 2014 and 2017. (*Adapted from* ECHA *[256, 257]*)

A study of BPA alternatives in thermal papers from the Netherlands, Spain, Sweden, and Norway revealed the presence of BPS, Pergafast 201, and D-8 [4, 258].

BPA is the main developer in cash receipts, while D-8 is commonly used in other thermal paper products such as cinema tickets, boarding passes, and luggage tags. Similarly, in a recent study on the developer contents of thermal papers in the German market between 2014 -2017 [98], 5 out of the 19 colour developers listed by the US EPA were detected in about 311 thermal papers investigated. BPA found in almost 50% of the samples was still the most frequently used colour developer, while phenol-free Pergafast 201 was the most used alternative. Bisphenol analogues such as BPS and D8 were found to be less common. Between 2015 and 2017, supermarkets and grocery stores were observed to have moved from BPA to other alternatives. Businesses like gas stations and clothing stores still use thermal paper containing BPA, while event tickets, parking tickets, and self-adhesive labels were mostly produced with D8. The most widely known BPA alternative in thermal paper is Bisphenol S – the sulphur-containing structural analogue of BPA (**Figure 12**).

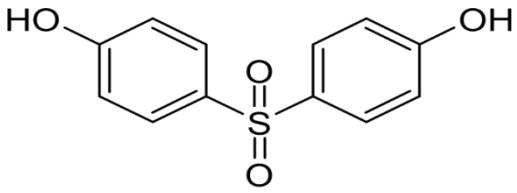


Figure 12. Structure of Bisphenol S

A recent study shows that receipt papers coated with BPS accounted for about 88% of human's BPS exposure [259]. Due to structural similarity to BPA, BPS, and other bisphenol compounds like bisphenol C (BPC), bisphenol F (BPF), bisphenol AF (BPAF), bisphenol AP (BPAP), and TGSA have been predicted to pose a similar risk and threat to human and aquatic life [7, 260]. These compounds possess estrogenic activity and genotoxicity with the potential to be more potent than their parent compound [261]. They have been detected in various environmental media [262] and waste paper samples [263] in concentrations higher than BPA. They have also been implicated in many health-deteriorating challenges. BPS disrupts cell signalling at an extremely low dosage [264], causes severe eye irritation, reproductive and developmental hazards [255], and may even be more persistent in the environment than BPA [265].

Phenol-free alternatives like D-8, D-90, and Pergafast 201 offer better performance than BPA [8]. Compared to BPA and BPS-based thermal paper, image

stability, printability, oil, and sunlight resistance is higher for D-8 and D-90 and much higher for Pergafast 201. Substituting BPA for these compounds comes with little or no technical challenges in the production process and adaptability with the existing thermal printers. A phenol-free, urea-urethane (UU) compound produced from the condensation of phenols and aromatic isocyanate is also used as a developer in thermal paper [266]. The UU developer has no acidic protons but promotes the opening of the dye fluoran ring and stabilises the dye/developer complexes through hydrogen bonding [82]. UU developers and related compounds effectively produce thermal paper with good surface whiteness and high thermal sensitivity. In addition, they develop images of high density, high stability, and high resistance to hydrophobic substances [87, 267, 268].

Thermal paper made with Pergafast 201 is the most expensive alternative [269]. This is due to the fact the market for this developer is monopolistic. It is produced by one manufacture – BASF. Secondly, its complex structure also suggests that a considerable amount of investment in material resources is needed for its production. Thermal paper with alternatives other than Pergafast 201 is about twice as expensive as BPA-based thermal paper. The use of isocyanate compounds considered a health and environmental hazard in the production of urea-based developers poses a great challenge. Pergafast 201 and UU are known to be environmentally persistent and toxic to aquatic life with long-lasting effects. Although, due to its higher molecular weight, dermal migration of Pergafast 201 might be considerably lower than BPS and BPA.

On the other hand, Pergafast 201 does not possess significant estrogenic activity [187]. The potential for carcinogenicity cannot, however, be ruled out. The human toxicity of Pergafast 201 and D-8 is considered very low to moderate and low to moderate, respectively [195]. Meanwhile, the aquatic toxicity of Pergafast 201 is high and may cause long-term adverse effects in the aquatic environment. Therefore, their use as a developer in thermal paper, born out of necessity to adhere to regulations, should be considered cautiously. Moreover, BPA-free thermal papers are not necessarily safer if substitutes of related chemical and toxic properties are used as developers [270].

2.7.2 Wood-based alternatives to BPA – Green Developers

Considering the challenges associated with the use of petrol-based chemicals as developers in thermal paper, bio-based, food-grade, natural, and commercially

available substances belonging to the class of carboxylic acids, fatty acids, sugars, biopolymers, mono & polymeric phenols (**Figure 13**) may be considered an alternative route to a safer and sustainable substitution because they are mostly isolated and purified from natural sources of little or no known toxicity. Also, they possess inherent multifunctional and structural features that are amenable to modifications, thereby making them useful either in pure form, in combination with other substances or as building blocks to a higher value chemical.

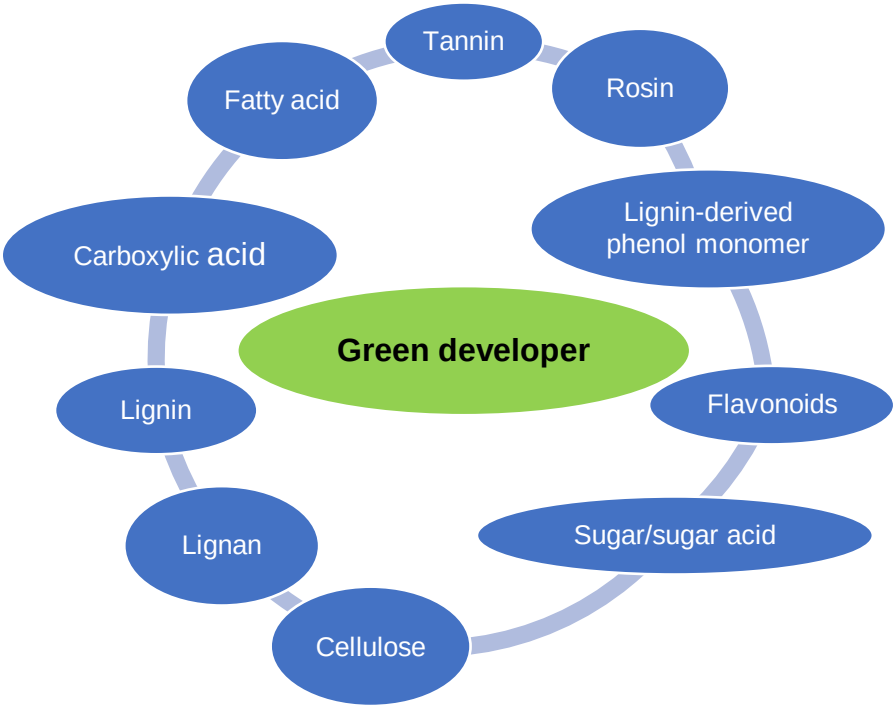


Figure 13. Chemical classes of potential green developers.

2.7.2.1 Organic acids

The most frequently patented bio-based substances used as colour developers in thermal papers are organic acids - either aliphatic or aromatic - such as salicylic acid, oxalic acid, maleic acid, benzoic acid, citric acid, sorbic acid, oleic acid, succinic acid, tartaric acid, phosphonic acid, ascorbic acid and the likes [30, 44]. Carboxylic organic acids are weak acids characterized mainly by one or more carboxylic groups – COOH. They can act as both hydrogen-bond acceptors (-C=O) and hydrogen-bond donors (-OH) [271]. Carboxylic organic acids are pervasive. They can be isolated from wood and wood by-products [272, 273] and are also produced industrially on a large scale.

One critical problem associated with the use of organic carboxylic acids as a developer in thermal paper is that they crystallise during the coating application resulting in a semi-opaque coating [107]. Separate crystallisation of organic acid developer and dye is easily influenced by high humidity leading to a print of low moisture resistance. Secondly, aromatic organic acids tend to sublime and decompose, leading to an unwanted premature colour reaction. To mitigate these problems, the use of organic acid derivatives [274] or modified forms of the organic acids such as their polyvalent metal salt, esters, and copolymers have been considered [9]. Metal salts of aromatic carboxylic acids considerably improved the image quality and resistance to yellowing [275]. Still, their ability to produce colour at very low temperatures was a limitation. Poor light fastness is an additional problem.

Recently, an environmentally friendly thermal recording material consisting of a phosphate modifier used in conjunction with leuco dye and organic acids like citric acid, salicylic acid, or ascorbic acid acting as an activator was proposed [45]. Under the influence of heat, the phosphate modifier facilitates colour formation.

Thermal paper produced from the use of ascorbic acid (vitamin C) as a developer was recently announced [276]. This paper appears yellowish, and it is reportedly accepted and used by organic food retailers in some parts of the United States. Meanwhile, an analytical investigation into the constituent makeup of this paper revealed that there was no trace of vitamin C in the thermal paper. However, two pharmacologically active chemicals, dapsone, and tolbutamide were detected in the paper [98]. These same compounds were used as developers in a thermal recording patent [101]. No other information as regards the technical feasibility of ascorbic acid is available in the public domain.

Nonetheless, ascorbic acid is a naturally occurring antioxidant present in fruits and other plant products. However, its hydrophilic nature has limited its use in life science, food and pharmaceutical industries and could also pose a challenge when used as a developer in thermal paper [271]. Alternatively, ascorbic acid ester like ascorbyl palmitate could offer improved performance. Ascorbyl acid esters are potential surfactants and antioxidants. The presence of the long-chain alkyl group in the molecular structure imparts new chemical properties such as higher melting and low water solubility, both of which are key to the performance of developers in thermal paper. The application of this compound as a developer will be investigated in this work.

2.7.2.2 Phenols

Phenols have long been used as developers in heat-sensitive materials due to their efficacy attributed to active protons for colour formation and sufficiently high colour density and relative stability due to their inherent aromatic backbone. Monomeric, dihydric, and polyhydric phenols are the most commonly used phenol types as developers. Examples include hydroxybenzoate, bisphenols, trisphenols, m-cresols, xylenols, m-ethoxyphenol, m-chlorophenol, 2,4'-methylene-diphenol, tert-butyl phenol, octylphenol, phenyl phenol, 4-hydroxybenzoic ester, catechol, resorcinol, phloroglucinol, pyrogallol, hydroxyhydroquinone, and related compounds [277]. These compounds have been used in their native monomeric or polymeric form, as derivatives and polymeric resins. The use of these phenolic compounds poses several challenges. For instance, colours produced from certain phenols fade under light and during storage in the dark [103]. Fading is caused by the crystallisation of the phenol compound and dye under the influence of humidity and temperature. Thermal papers produced from phenols are known to be of low sensitivity and characterised by background staining. The hydrophobic nature of phenols makes them susceptible to moisture erasure, thereby limiting the application stability. More importantly, phenols are known to be hazardous to human health and the environment. Naturally occurring monomeric and polymeric phenols isolated from natural sources are, however, environmentally friendly, and biodegradable. These phenol types could serve as an upgrade to petrol-based phenols.

Wood-derived lignin is a good source of natural phenols and chemicals for value-added applications. Lignin, the second most available renewable raw material, is a complex three-dimensional biopolymer arising from the polymerization of three cinnamyl alcohols: p-hydroxycinnamyl alcohol, coniferyl alcohol, and sinapyl alcohol. The production of phenols from lignin through depolymerisation techniques has been extensively discussed in many publications [278-282]. Through these processes, lignin is fragmented into a complex mixture containing different lignin model compounds belonging to various chemical groups, including phenols, aldehydes, and hydrocarbons. The resulting mixtures are then separated or purified using a variety of techniques. Lignin phenolic compounds dissolve in cooking solutions during the pulping process can also be isolated from the liquor. In addition to their favourable

properties, lignin phenolic compounds are environmentally friendly with good pharmacological and antioxidant properties [283].

Of these lignin phenols, vanillin and its derivative like vanillic acid seem the most attractive phenols for use as a developer in thermal paper. Vanillin (4-hydroxy-3-methoxy benzaldehyde) (**Figure 14**) is a food-grade substance majorly used as a preservatives and flavouring agent in food and cosmetic products because of its antioxidant and antimicrobial properties. It is also extracted from Vanilla orchid pods. However, the composition of Vanillin from this source is complex and contains many side compounds, which make it unadaptable for industrial use. Vanillin can also be produced through biological means using ferulic acid [273], another natural phenolic compound with high industrial potential. With its free phenolic hydroxyl group, Vanillin can act as a proton donor to leuco dye and participate in hydrogen bonding.

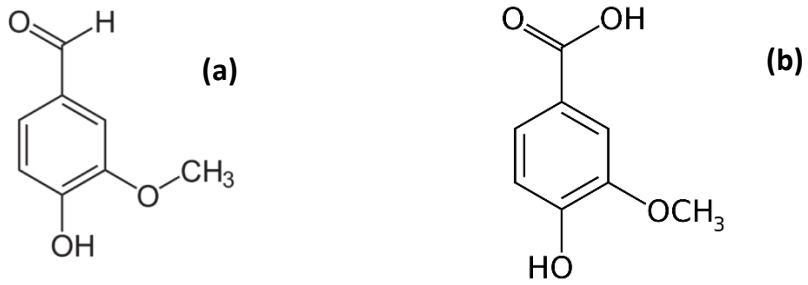


Figure 14. Structure of (a) vanillin and (b) vanillic acid.

Vanillin can be used in its pure form or as a building block for higher-value renewable materials [284]. One of the challenges that might limit the utilization of vanillin in thermal paper is the competition with food and cosmetic application, which may inevitably lead to increased costs in the international market. Chemically, vanillin is also hydrophilic absorbing moisture on exposure to air. This may impact its effectiveness as a developer in thermal paper.

In 2014, a ‘green alternative’ to BPA from lignin was reported by a research group in the USA [285]. The lignin fragments vanillyl alcohol and guaiacol were converted to isomers of bisguaiacol-F (BGF) via an acid-catalyzed electrophilic aromatic substitution. The synthesised resins had a similar structure to BPA, high thermal stability, and additional methoxy substituents [286]. The endocrine activity of these BGF compounds recently investigated [287] revealed that BGF isomers have a

lesser endocrine disruptive impact than BPA. BGFs are, however, designed to be used in plastics. Information on their application as a developer in thermal paper is still unavailable.

The lignin-based coumaric acid and its derivatives, such as caffeic acid, ferulic acid, and phloretic acid, are also a potential bio-based alternative to BPA. For example, coumaric acid (**Figure 15a**) has free phenolic hydroxyl groups and sufficiently high melting points. In addition, diphenolic acid (**Figure 15b**), a renewable bisphenol derivative produced from the condensation reaction of phenol with levunilic acid – a by-product from the biorefinery process – has the physical and chemical properties to act as a BPA substitute [288].

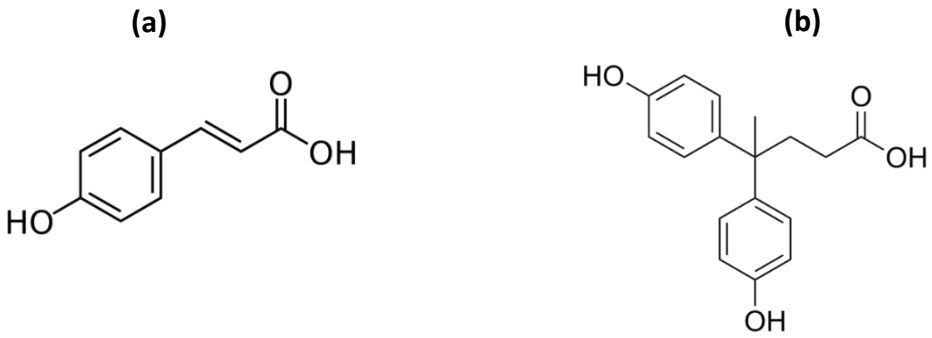


Figure 15. Structure of (a) coumaric acid and (b) diphenolic acid.

2.7.2.3 Tannins

Second only to lignin, tannins are the most abundant source of natural polyphenols and aromatic biomolecules. Tannins are high molecular weight substances from bark, leaves, roots, branches and also obtained as by-products of some agricultural wastes such as tea [289], coffee [290], and fruit residues [291]. Tannins are commonly obtained from wood species such as quebracho wood, pine, oak, mimosa, etc. The chemical properties of tannins are dependent on extraction conditions such as the method of extraction, extraction time, extractant type, the particle size of the sample, and extraction temperature [292]. In woody plants, tannins perform a wide variety of defensive roles. They defend the wood against infections, fungi, bacteria, and insect attacks. In addition, tannins give fruits and leave astringent taste making them less appealing to herbivores. Through molecular mechanisms, tannins also offer protection against UV rays and free radicals.

Tannins are classified into two major groups - condensed tannins and hydrolysable tannins. Another class of tannins is the phlorotannins which are derivatives of phloroglucinol. Hydrolysable tannins are esters of gallic or ellagic acids and sugar. The term 'hydrolysable' simply means that weak acids or bases can hydrolyse these tannins to produce carbohydrates and phenolic acids. Hydrolysable tannins are commercially extracted from Chinese gall (*Rhus semialata*), Sumac (*Rhus coriara*), Turkish gall (*Quercus infectoria*), tara (*Caesalpinia spinosa*), Myrobalan nuts (*Terminalia chebula*), and Chestnut (*Castanea sativa*). They can also be isolated from pomegranate peel, alder leaves, myrobolans, and divi-divi extracts. Hydrolysable tannins are characterised by low nucleophilicity and a macromolecular structure dependent on extraction methods [14]. These attributes affect their chemical and economic importance. Condensed tannins, known as proanthocyanidins, are the most common commercially available tannins. They constitute about 90% of the total global production of commercial tannins and are mostly concentrated in tree bark.

There is little information on the use of tannins as a developer in heat-sensitive paper. Although a handful of patents have mentioned tannic acid [12, 293, 294] and tannin model compounds like resorcinol, phloroglucinol, and catechin as potential developers, no technical information is provided to ascertain their effectiveness. Gallic acid (3,4,5-trihydroxy benzoic acid) is the most widely mentioned form of tannin used as a developer in thermal-responsive materials. In addition, the developing potential of esters of gallic acid such as stearyl gallate, lauryl gallate, octyl gallate, dodecyl gallate, ethyl gallate, butyl gallate, and propyl gallate has also been studied [117, 137, 141].

The use of tannins as developers in thermal paper may offer several advantages over BPA. Tannins are bio-based polyphenolic antioxidants with similar structures to synthetic phenols. They are veritable, green, and sustainable alternatives to synthetic phenols. They possess numerous reactive OH groups and chemical properties, making them amenable to modifications and reactions for wide industrial applications [11, 13]. Tannins are non-crystalline and thermally stable [295]. Their thermal stability is influenced by other constituents such as carbohydrates [296]. The non-crystallinity of tannins could lead to a very low likelihood of sublimation or crystallization, a problem encountered with monomeric phenols. High thermal stability of tannin could also help overcome the limitations associated with phenolics, such as

premature colour formation and colour instability. Tannins are high molecular weight compounds with limited dermal migration capacity. They are of no known toxicity to man and are commercially available.

2.7.2.4 Phenolic resins

Phenolic resins or condensates are produced from the condensation of phenol and aldehydes, typically formaldehyde. There are two main classes of phenol-formaldehyde resins – novolac or resole produced under either acidic or alkaline conditions, respectively. The use of high molecular weight phenolic polymer/resins like novolac and resole as a developer in pressure and heat-sensitive paper was patented [297-299]. The use of phenol-formaldehyde as a developer was invented to mitigate the volatile capacity of phenols in coating formulations. Para-substituted phenol-formaldehyde polymers and similar derivatives were highly effective as developers in heat-sensitive papers and are known to have excellent colour-producing ability and high fading resistance. However, paper sheets coated with phenol-formaldehyde polymers underwent yellowing and produced colour marks, thereby becoming significantly faded upon exposure to sunlight or during storage. Metal-modified phenolic polymer produced by the melt condensation of phenolic resin with metal salt in the presence of an acid catalyst provided improved performance in print fade resistance, light stability, and intensity [300, 301]. Metalation of resin could be achieved by adding zinc, copper, aluminium, tin, cobalt, and nickel salt. While phenol-formaldehyde polymers have shown capability as a developer in functional papers, the environmental incompatibility of formaldehyde is a challenge. Like BPA, exposure to formaldehyde in humans and animals is a known problem. For this reason, attempts have been made to produce environmentally friendly polymers for use as developers in thermal papers.

Recently, Jang *et al*.,[16] synthesised hyperbranched polyester copolymers through a one-pot polycondensation reaction involving phloroglucinol, terephthaloyl chloride, and adipoyl chloride. The resultant highly insoluble copolymers characterised by a high degree of branching and reactive OH groups, induced a colour in a leuco dye system. The copolymers, however, displayed inferior developing performance compared to BPA when used as a developer in thermal paper. In addition, an increase in the proportion of alkyl groups by varying the ratio of terephthaloyl chloride and

adipoyl chloride in the polymer backbone had a negative effect on the developing properties of the polymers.

Similarly, Choi *et al*.,[15] synthesised and investigated the developing properties of eco-friendly phenol-formaldehyde novolac and resole polymers using phenols and BPA. While other polymers work as developers, thermal paper produced from BPA-based novolac resins showed the highest developing potential and sensitivity. However, the presence of BPA in the polymer casts doubt on its ability to replace BPA effectively.

One of the advantages of phenolic polymeric resin is that they are of high molecular weight, which tends to overcome skin absorption problems associated with BPA. This is because most high molecular weight compounds are less mobile in biological and environmental systems, limiting their migration through biological membranes [3]. Phenolic resin derivatives are also easy to synthesise with associated low cost and possess multiple phenol groups. Furthermore, hyperbranched polymers are an interesting proposition because, contrary to linear polymers, they possess many active groups owing to their highly branched architectures. In addition, they are highly insoluble in solvents which may also reduce bioaccumulation through dermal absorption [302]. Finally, they possess a high melting temperature which may improve the archiving stability of the printed image.

As aforementioned, tannin and tannin model compounds have been used as a substitute for phenol in phenolic resin [303], but their use in thermal paper has not been mentioned anywhere in the literature. Also, in place of formaldehyde, simple and lower aliphatic aldehydes such as acetaldehyde, propionaldehyde, butyl aldehyde, glyoxal may be used in the synthesis of cross-linked phenolic resin [304]. Therefore, such polymeric resins may also be useful as a developer in thermal paper.

2.7.2.5 Sugars

The simplest forms of sugar are monosaccharides. These include glucose, fructose, and galactose. Commonly used table sugar, sucrose are disaccharides of glucose and fructose, while higher molecular weight sugars are oligosaccharides. Sugars are naturally present in plant tissues, fruits, and vegetables. Sucrose is commercially isolated from sugar cane and sugar beet. Structurally, sugars are organic compounds containing hydroxyl, aldehyde, or ketone groups.

The first sugar compound used as a developer in thermal paper was produced by reacting the organic hydroxyl group of sugars, uronic acids, sugar acids, or sugar alcohols with electro negatively substituted mono- or poly aldehydes **(Figure 16 a-c)** [73, 305]. These developers possess excellent colour developing properties with high thermal, acid, and air resistance. In their unreactive state, they are slightly soluble or insoluble in water, virtually colourless and odourless, eliminating background staining. In addition, their production is relatively inexpensive. Not much is, however, known of either the commercial utilization of these compounds.

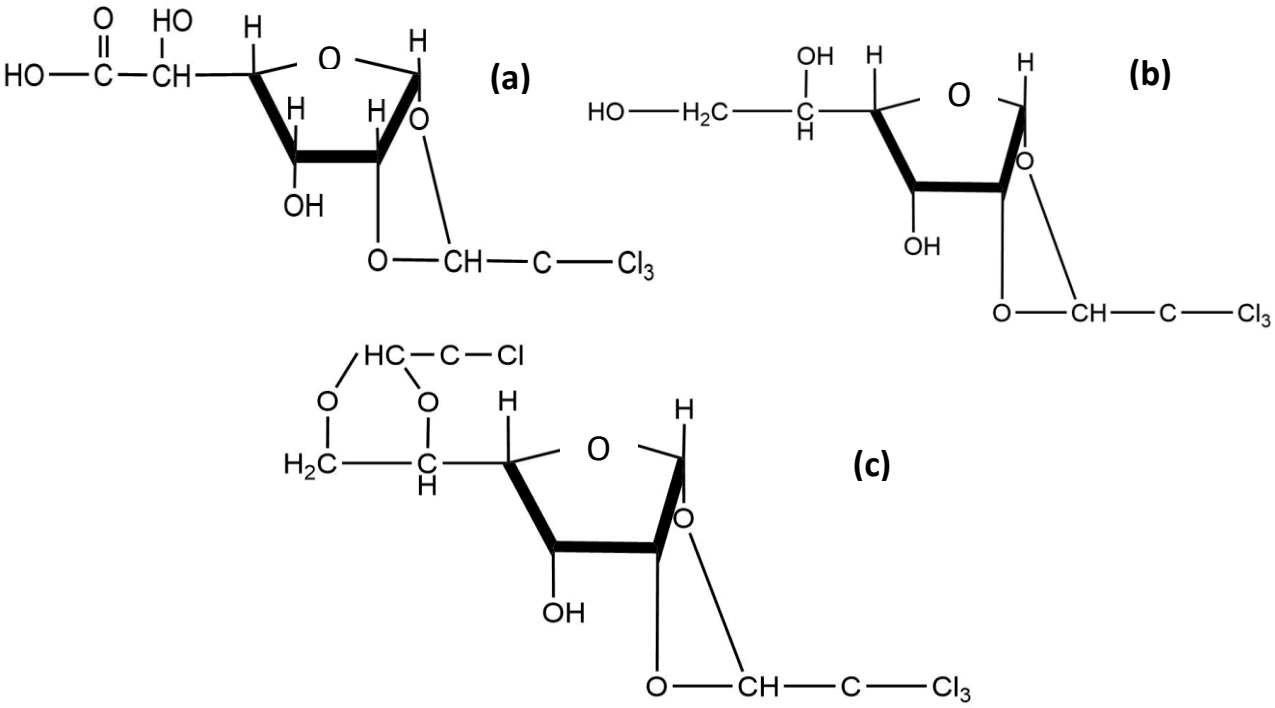


Figure 16. Structural examples of sugar-based developers (a). g-d-trichloroethylidene-d-gluconic acid (furanose type); (b) 9-trichloroethylidene-d-gluco-furanose and (c) g-(di-trichloroethylidene)-d-gluco-furanose. (*Reproduced based on* Kosche [305])

The commonly used sweetening agent, saccharin, and its derivatives like saccharin, 1'-bromo saccharin, 1'-nitro saccharin, 1'-amino saccharin, and saccharin 5'-carboxylic acid have were applied as developers [306]. These compounds produced colour with all studied colour formers. The chemical structure of the derivatives largely determined the intensity and stability of the colour developed. The colour formed by saccharin derivatives was largely irreversible, limiting the erasure of print and recyclability of the thermal paper produced with such developers.

2.7.2.6 Urea-based compounds

Commonly known, non-phenolic developers with urea and urethane functionalities are petrol-based. However, substances with urea functionalities are also present in nature. Uracil, caffeine, and uric acid are three biobased compounds possessing aromatic urea functionalities. They are weakly acidic, have high melting points, and are commercially available. These compounds, in addition to glycolylurea, could function as a developer in thermal paper.

2.8 Alternative technologies

While the search for healthier alternatives to BPA is being intensified, alternative technologies which promote the drastic reduction in exposure to BPA via thermal paper have been proposed. For instance, the Safe-by-Design (SbD) concept by the Netherlands encouraged scientists, paper manufacturers, and policymakers to look not only at chemical replacements for BPA but also consider non-chemical, technological, and environmentally friendly solutions during the design of products [253]. Danish authorities also recommend several alternative technologies. The alternative technologies centered on adopting a cashless payment system with custom applications, mobile web payments, SMS payments, electronic ticketing/receipts, label-less self-service check-in, and check-out system in supermarkets and airports. Retailers are advised to offer consumers the option of not collecting receipts and paperless transactions. Challenges associated with the e-receipt system are mostly about data protection. Coverage of customers who do not use smartphones may also be a challenge. Besides, the subscription cost for some mobile application features may be an additional burden on customers.

The Koehler paper group recently began marketing an innovative eco-friendly thermal paper that functions without the traditional dye and developer. According to the manufacturer, the paper produces colour through a physical process [307]. It was designed with thermo-responsive polymeric hollow-sphere pigments (HSP) as light scattering centres to generate the functional layer's necessary hiding power/opacity. During the thermal process, the heat responsive layer of the paper can switch between an opaque and transparent state. *Blue4est* paper significantly reduced the chemical load of low molecular weight chemicals because no colour-forming functional chemicals are present in the coating. It can be manufactured with standard paper

coating technologies/equipment. The paper works with conventional thermal printers and standard printer settings with excellent long-lasting print. *Blue4est* has become the first thermal paper to be verified and approved for direct contact with food. However, the thermal paper is more expensive than conventional BPA thermal paper. For this new development, Koehler and Dow were awarded the US Green Chemistry Award 2017 [308].

3 Experimental

3.1 Materials

All chemicals were obtained commercially and used without further purification, except otherwise stated. The colour former, 2-anilino-6-dibutylamino-3-methylfluoran (Pergascript Black 2C) and an aqueous solution of polyvinyl alcohol (12.5% PVA 15-99), were obtained from Mitsubishi paper Hi-tech Europe. For this study, the leuco dye colour former would be referred to as ODB-2 ("One Dye Black 2").

Raw tannin industrial extracts: mimosa and mimosa sulphite were obtained from Otto Dille GmbH & Co. KG and Christian D. Markmann GmbH, respectively. The Grape seed extract was obtained from C.E. Roeper GmbH.

The following reagents and solid solvents were obtained from Sigma Aldrich: Folin-Ciocalteu's phenol reagent, (2N); tannic acid, 99.3%, CAS [1401-55-4]; hexadecanol, 99%, CAS [36653-82-4]; octadecanol, 95%, CAS [112-92-5]; catechin hydrate, 96%, CAS [225937-10-0]; hexamethylenediamine, 96%, CAS [124-09-4]; and BPA, 98%, CAS [80-05-7].

Lauric acid, 99.0%, CAS [143-07-7]; resorcinol, 93%, CAS [108-46-3]; and phloroglucinol, 95%, CAS [108-73-6] were obtained from Merck KGaA.

The following reagents were obtained from Alfar Aesar: vanillin, 99%, CAS [121-33-5]; vanillin acid, 98% CAS [121-34-6]; and tetradecanol, 97+%, CAS [112-72-1].

Solvents and reagents such as hexane, ethyl acetate, dimethylformamide (DMF), dimethylsulphoxide (DMSO), acetone, acetonitrile, 1-butanol, chloroform, dichloromethane, ethanol, ethyl acetate, hexanes, methanol, and toluene were obtained from Sigma Aldrich and used without further purification. In addition, ascorbic acid, salicylic acid, citric acid, and ascorbyl palmitate were obtained from Alfa Aesar, while deuterated chloroform (chloroform-d1) was obtained from Deutero GmbH.

3.2 Sample preparation

Ternary mixtures containing developer materials, ODB-2, and solvents were prepared to:

1. Study the colour forming reaction of green developers with ODB-2.

2. Investigate the thermal and colourimetric properties of ternary mixtures containing lignin-based compounds (vanillin and vanillic acid) as developers using Job's method of continuous variation [147, 309].

3.2.1 Preparation of ternary mixtures for colour forming reactions.

An appropriate quantity of the developer was weighed into a glass vial containing ODB-2 and solvent of known weights **(Figure 17)**. The mixture was thoroughly mixed with the aid of a shaker. Tetradecanol was used as the solvent. Developers are citric acid, ascorbic acid, salicylic acid, ascorbic palmitate, vanillin, vanillic acid, resorcinol, phloroglucinol, phenol-amine complex, and phenolic copolymers. The synthesis and characterisation of phenolic polymers are explained in section 3.6.

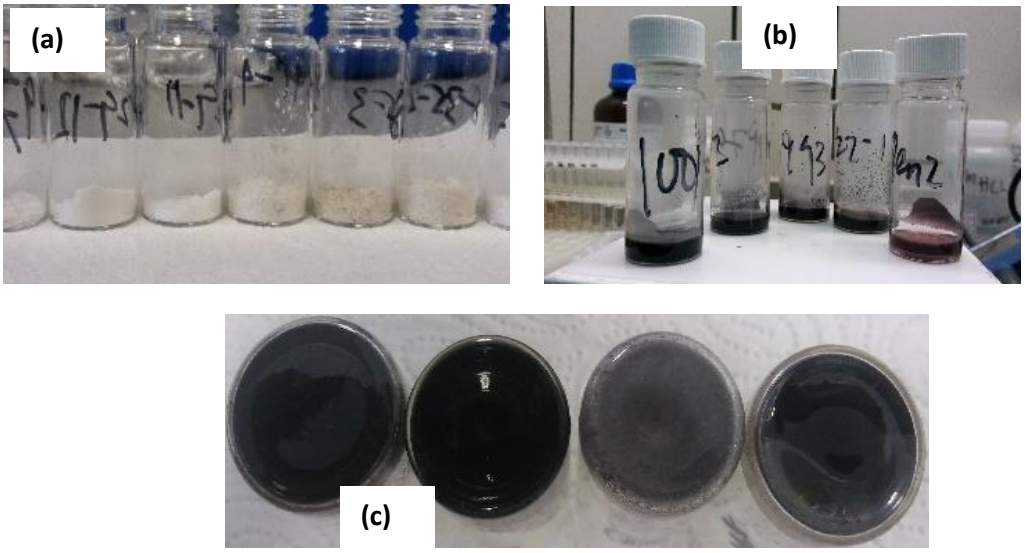


Figure 17. Samples of ternary mixtures prepared with carboxylic acids, ODB-2, and tetradecanol. (a) mixtures in the unheated state, (b) mixtures heated on a hotplate, and (c) coloured state of the mixtures after cooling.

In the case of phenol polymers, the polymer samples were first ground into small particles with a ball mill because smaller particles are known to increase the interaction between developer molecules and leuco dye. On the other hand, the phenol-amine complex only required mortar and pestle. The samples were then heated on a hotplate at about 170^{o}C for 2 mins. A homogenous mixture was obtained on heating due to the complete melting of the solvent. The mixtures were then gradually cooled in a water bath. A change in the colour of the samples was achieved on cooling.

To study the temperature of colour change, a binary mixture of the developer and ODB-2 was introduced in an Eppendorf tube before heating and mixed with a shaker. A micro quantity of this mixture was charged into a transparent glass capillary of 1.5 mm internal diameter, 80mm length to a height of 3mm. The capillary tube was gently tapped to allow for the settling of the mixture in the base. The mixtures' colour developing characteristics were monitored using the rapid screening test method previously developed [17]. **Figure 18 and Figure 19** show the schematic diagram of the set-up for the screening test and a representative sample in a capillary.

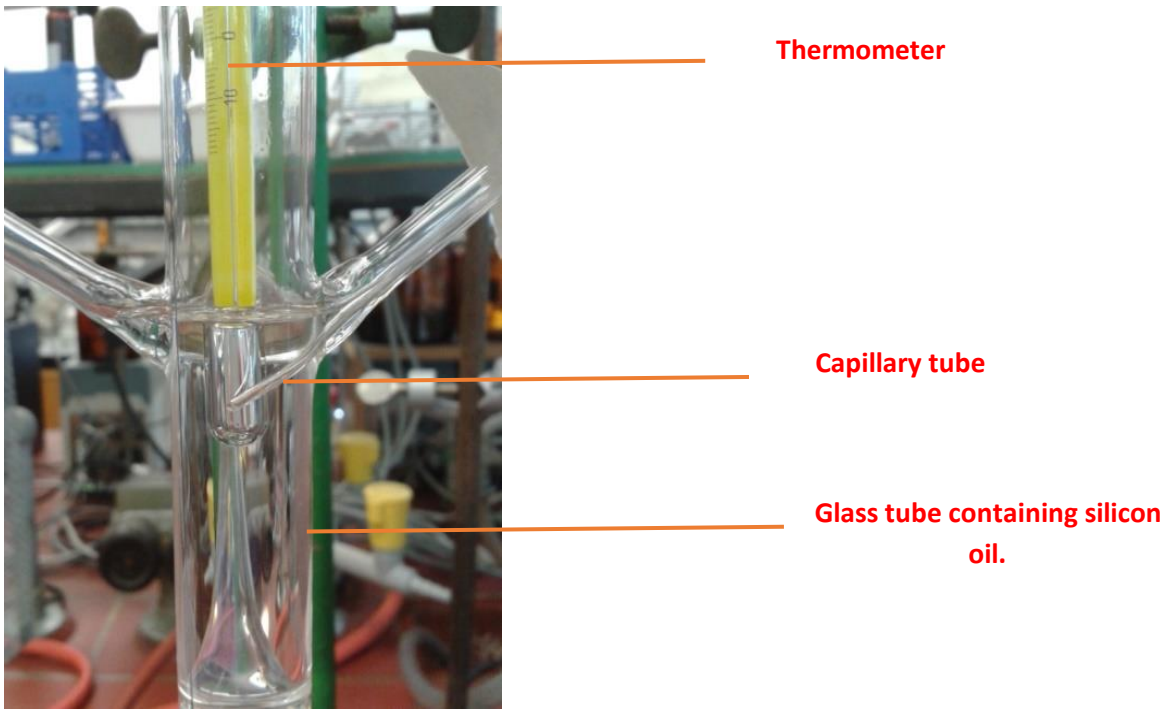


Figure 18. Set-up for the investigation of colour behaviour of a dye-developer mixture. (*Reproduced from* Huneke [17]).

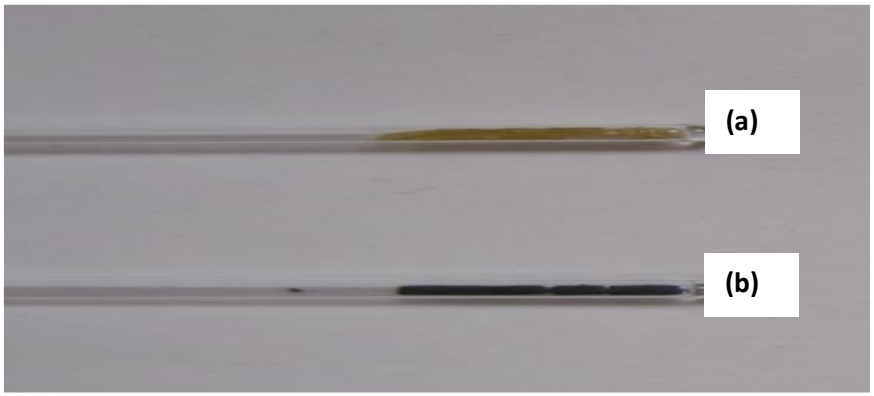


Figure 19. Images of capillary tubes containing a micro quantity of a mixture of ODB-2, vanillic acid, and tetradecanol in (a) unheated and (b) heated form.

With the aid of a hand-held magnifying lens, the temperature characteristics of thermochromic mixtures in relation to the solvents were visually observed on the thermometer. After treatment, the capillary tubes were cooled in air. Magnified images of the capillary tubes were captured with a VHX-500FD Keyence digital microscope (**Figure 20**). Image processing was done with Microsoft Office Picture Manager 2010. The colour formed and temperature of colour formation was compared to reference substance – BPA.

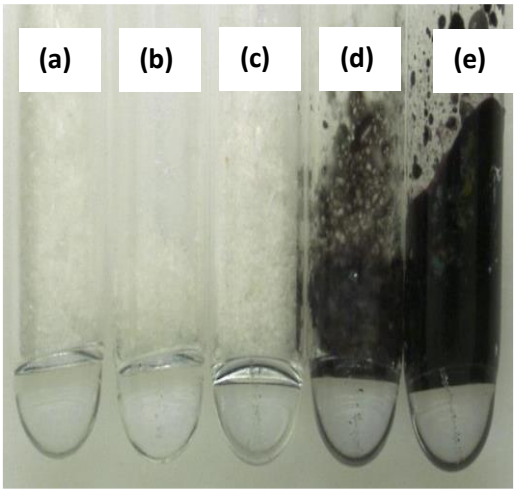


Figure 20. Magnified images of capillary tubes containing (a) unheated vanillin, (b) unheated ODB-2, (c) unheated mixture of vanillin & ODB-2, (d) heated mixture of vanillin & ODB-2, (e) heated mixture of reference developer, BPA &ODB-2.

3.2.2 Preparation of ternary mixtures for Job's method

Twenty-eight ternary mixtures containing the lignin-based model compounds, vanillin, and vanillic acid, were prepared by weighing the known quantity of ODB-2,

developer, and solvent into a glass vial (50 ml) such that the total amount of the composition was kept constant at 3.75×10^{-5} mol. The samples were then subjected to a heating and cooling cycle in a water bath with gentle agitation. The water bath had an in-built temperature regulation. To cool, the glass vials were placed inside a glass dish of iced water. With this method, multiple samples were subjected to identical thermal treatment.

3.2.3 Preparation of a mixture of plural developers

To investigate the effect of a mixture of developers on colour density and colour stability, developers were mixed in an aluminium pan in a ratio ranging from 5:95 to 50:50 (w/w). One developer was assigned as the main developer and the other as the co-developer. Tetradecanol was used as the co-solvent. The developer mixture was introduced into the melted solvent and heated to 200^{o}C on a hot plate for 60min. After heating, the aluminium pan was immediately transferred into an iced water bath to cool.

3.3 Acetone test

Developer samples were subjected to the acetone test using the method described by Rihs and Weis [148]. This test allows for the isolation of the coloured form of ODB-2. Typically, 0.00532g, 0.01mmol, ODB-2 was added to 20ml acetone. Unless otherwise stated, 0.04mmol of developer sample was added to the mixture and allowed to stand for 5 days. Acetone was removed via rotary evaporation, and the solid black crystal obtained was left to dry in the flask. A mixture of vanillic acid and ODB-2 in acetone is shown in **Figure 21**.

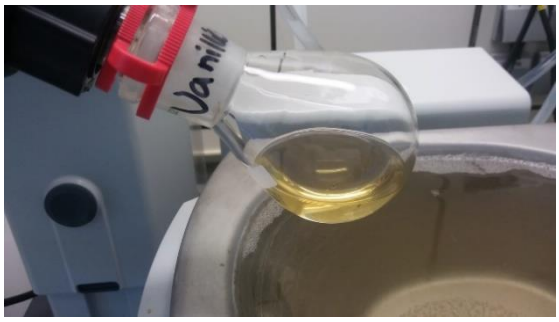


Figure 21. Mixture of vanillic acid and ODB-2 in acetone

3.4 Dispersion test

The colour forming reaction of developer samples in a dispersion containing ODB-2, developer, and polyvinyl alcohol (PVA) was investigated in the wet and dry states. Firstly, a suspension of ODB-2 was prepared by mixing an appropriate amount of ODB-2 in water and PVA. Then, the composition was thoroughly dispersed using an ultra-turrax.

An appropriate amount of developer was added to about 1g of ODB-2 suspension in an aluminium pan. The mixture was allowed to stand for a few minutes (**Figure 22**). Afterward, the sample was dried to a constant weight in a drying oven at 120^{o}C. During the drying process, the mixture's water component was removed, and the dye and developer fused to produce the corresponding colour.

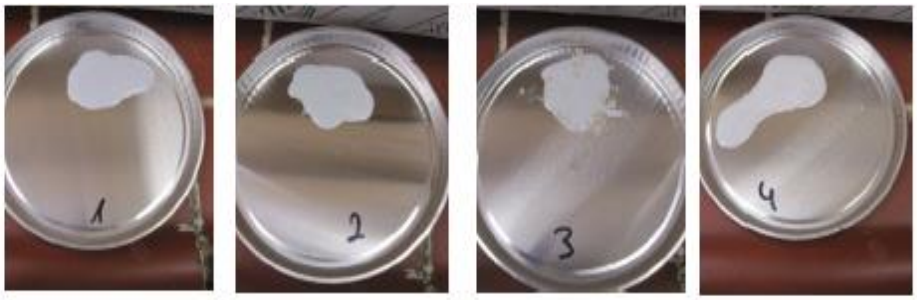


Figure 22. Wet dispersion of ODB-2, PVA and (1) vanillin, (2) vanillic acid, (3) isovanillic acid and (4) isovanillin.

3.5 Purification of tannin extracts

Purification of raw tannin extracts (mimosa extract, mimosa sulphite extract, and grape seed extract) was carried via soxhlet extraction with methanol as solvent (**Figure 23**). For the purification, approximately 25g of oven-dried raw tannin industrial extract was introduced into the extraction thimble, placed in a soxhlet, and extracted with 150ml of methanol for 8hrs. After extraction, the solvent was recovered via rotary evaporation, and the extracts were dried in an oven at 70^{o}C. The concentrated extracts were then cooled in a desiccator. For each sample, purification was done in six and repeated three times. The percentage yield of extract yield was calculated with equation 1.

$$Yield\ of\ extract\ (Y\ \%) = \frac{Weight\ of\ purified\ extract\ (g)}{Initial\ weight\ of\ raw\ tannin\ extract\ (g)} X\ 100 \qquad \textbf{Equation 1}$$

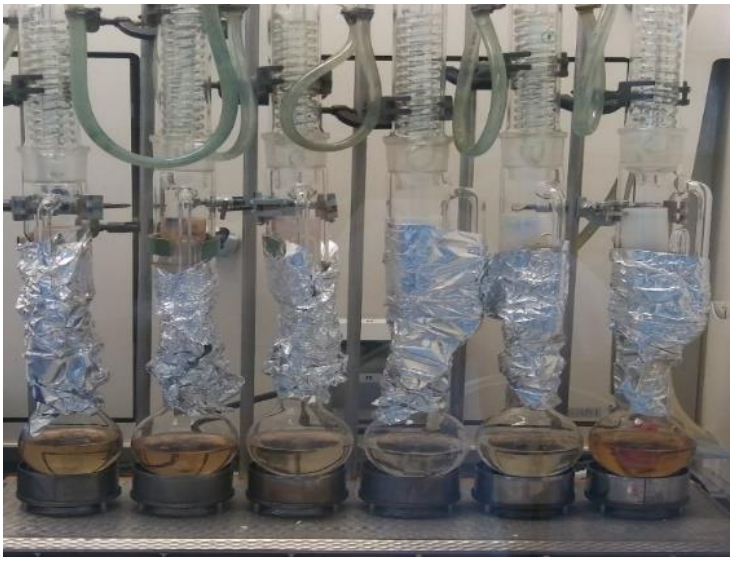


Figure 23. Soxhlet extraction of mimosa extract.

3.6 Synthesis of phenol-amine complex

Phenol-amine complexes of purified tannin extracts (mimosa, mimosa-sulphite, grape seed), tannic acid, and tannin model compounds (resorcinol and phloroglucinol) were synthesised using the method described by Lawton [310].

In a typical reaction, 1mol of the phenolic compound was dissolved in aqueous methanol to form a 25% solution. An appropriate quantity of solid HMDA crystals was added to the alcoholic solution in molecular equivalent corresponding to the functional hydroxyl groups in the phenolic compound. The mixtures were stirred for a few minutes until they became homogeneous. The reaction mixture was separated via filtration with Whatman filter paper, and the residue was washed thoroughly with methanol. The number of hydroxyl groups in mimosa and mimosa sulphite was calculated based on the structure of the predominant flavonoid unit, probinetinidin. Tannic acid is hydrolysable tannin with gallic acid as its basic structure.

3.7 Synthesis of phenol polymer

Copolymers of purified tannin extracts (mimosa, mimosa sulphite, grape seed), tannic acid, and tannin model compounds (resorcinol and phloroglucinol) were synthesised through reaction with glyoxal according to the method described by Tondi [304].

Phenol copolymers were prepared in plastic 50ml test tubes by reacting with different amounts of glyoxal at varying pH and temperature conditions. Generally, 30% phenol solution was prepared by dissolving an appropriate amount of the phenol compound in distilled water. To 20g of phenol solution, 10ml of glyoxal solution (40%) was added, and the pH was adjusted to 2, 7, and 9. The acid, neutral and alkaline pH was obtained by adding an aqueous solution of H_2SO_4 and NaOH (0.001 M). After formulation, the plastic test tubes were screw-capped and vigorously mixed on a shaker to ensure dissolution/homogenous distribution. The samples were then kept at ambient temperature for 24h and thereafter subjected to heating at successively increasing temperature, 50, 70, 90, 100, 120^{o}C in the oven. Samples were removed from the oven after a solid mass was obtained. The hardening temperature was recorded for every sample. The solid was milled into a fine powder and washed with ethyl acetate, acetone, and ethanol. The washed polymer was then dried in a desiccator. For each sample, polymerisation was done in triplicate. The yield was presented as the percentage of the weight of dried polymer over the initial weight of the phenol compound.

3.8 Characterization and instrumental analysis

3.8.1 FTIR spectroscopy

FTIR spectra of pure ODB-2, black composite, phenol-amine complex, and phenol copolymers were recorded at ambient temperature on a Bruker Vector 33 ATR instrument from 3750 to 530cm−1 with 60 cumulative scans a resolution of 4cm^{-1}.

3.8.2 UV-VIS spectroscopy

The UV analyses of ODB-2 and developer substances were carried out with a Perkin Elmer Lambda 650 UV-Vis spectrometer. Dilute solutions of ODB-2 in an appropriate solvent (acetonitrile, ethanol, methanol, ethyl acetate, toluene, hexane, diethyl ether, acetone, and tetrahydrofuran) were prepared from the stock solution. A 2-3ml aliquot of the solution was introduced into a 10mm quartz cuvette and measured. The spectra were scanned at ambient temperature in the range of 220 - 500nm. In addition, molar absorptivity was calculated from the absorbance value obtained using the Beer-Lambert relationship:

$$\varepsilon = \frac{A}{C\ x\ L}$$ **Equation 2**

Where;

ε = molar absorptivity

A = absorbance

C = concentration of the solute in moldm^{-3} (M)

L = path length of the light.

3.8.3 Differential scanning calorimetry (DSC)

3.8.3.1 DSC of ternary mixtures

The thermal behaviour of ternary mixtures was studied by DSC analysis following the method described by Panak *et al.,* [311]. Approximately 5mg of the coloured composite was weighed and enclosed in an aluminium pan. A Mettler Toledo DSC 3+ differential scanning calorimeter was used at a scan rate of 2^{o}C/min over a temperature range of 10 to 50^{o}C. Results obtained were evaluated using the STARe software. The second heating cycle was used for the result evaluation to minimize the effect of sample preparation and its thermal history.

3.8.3.2 DSC of Phenol copolymer and phenol-amine complex

Glass transition temperature (T_g) and melting properties of the different phenol copolymer and the phenol-amine complexes were determined using a Mettler Toledo DSC 3+ differential scanning calorimeter at a scan rate of 10^{o}C/min over a temperature of 50 to 400^{o}C. Before the measurement, samples were dried in a vacuum overnight to remove residual water. Approximately 5 mg was weighed and enclosed in an aluminium pan. T_g, defined as the midpoint of the temperature at which the change in heat capacity occurred, was evaluated using the STARe software.

3.8.4 ^{13}CNMR spectroscopy of ODB-2

The molecular structures of the colourless and the coloured form of ODB-2 were determined by ^{13}C-NMR spectroscopy at 25^{o}C with $CDCl_3$ as a solvent and as standard. For NMR measurement, about 100mg of coloured or colourless solid of ODB-2 was weighed in a glass vial. Then, $CDCl_3$ was added, and the sample was

thoroughly dissolved on a shaker. NMR spectroscopy was performed on a Varian Mercury 400 MHz spectrometer. Acquisition parameters: 40^{o}C, 25,000 Hz spectral window, 150 scans, a 2.0s acquisition time, and 10s delay between pulses.

3.8.5 Carbohydrate content

The amount and monomeric composition of carbohydrates in the raw and purified tannin extracts were analyzed by two-step hydrolysis, followed by Borate-high-performance anion-exchange chromatography with post-column derivatization (Borat-HPAEC) described by Bianchi *et al*., [312].

3.8.6 Total phenolic content

The total phenolic content (TPC) in raw and purified tannin extracts was measured using a modified Folin-Ciocalteau method [313, 314] and estimated as gallic acid equivalents. In this assay, 100µl of 4N Folin-Ciocalteau reagent were added to 20µl of each tannin sample (50mg/l) in a cuvette containing 1550µl of distilled water. This mixture was allowed to react for about 5min before the addition of 300µl of 10% sodium carbonate. The reaction mixture was stirred gently inside the water bath at 40^{o}C for about 30min before measuring the absorbance at 765nm against the blank using a UV–visible spectrophotometer Agilent 8453 (Agilent Technologies, USA). The total phenol content was calculated using a standard calibration curve of gallic acid and expressed in milligram equivalents of gallic acid per gram of extract (mgGAE/g). For the calibration, dilute solutions of gallic acid (0–500mg/l) were prepared by dissolving 0, 1, 2, 3, 5, and 10ml of stock solution of gallic acid in ethanol (50mg/ml) into a 100ml volumetric flask. All analyses were done in triplicates.

3.8.7 Ash content

The ash content was determined according to Tappi Standard T211om-02.

3.8.8 Colour measurement

Digital images of the thermochromic mixtures in a glass vial were captured at different temperatures using a digital camera (**Figure 24**). The glass vials were removed from the water bath, dried, and captured from the bottom over a white rectangular-shaped spectralon disc. The white spectralon disc helped to normalize the brightness of the image, eliminate variations in the posture of the sample, settings of the camera, and the presence or absence of stray light from room lighting. Firstly, the

Microsoft office picture manager was used to crop the image to remove unwanted areas. ImageJ software was then used to measure the colour of each sample at a variety of spots.

Figure 24. Image capturing of a cooled mixture of vanillin, ODB-2, and tetradecanol with a digital camera.

For dried dispersions in aluminium pans, images were obtained using the data colour ELREPHO 450x with measurement geometry 45c/o. A round-shaped white-surface-coated aluminium plate was used as the measuring cell. A few mg of each sample was melted on the cell at a temperature of 120^{o}C and then covered with glass to avoid change in sample thickness during measurement. The sample was cooled to room temperature before measurement. The measuring cell was placed on a white rectangular-shaped spectralon disc and then positioned under the instrument aperture. Thus, the 34 mm aperture covered almost all measuring cells with the sample while ensuring that the light source was directed on the sample. The measurement was performed four times.

3.8.9 Colour determination

Colour values from ImageJ were in the RGB colour space, while colour values from the data colour instrument were obtained as CIE *Lab* values*. The CIE *Lab** colour space is the closest representation of the observed colour of objects. There are three axes in this colour space; the *a** axis spans from red (*a** > 0) to green (*a** < 0), the *b** axis spans from yellow (*b** > 0) to blue (*b** < 0) and the *L** axis relates the lightness of the sample (*L** = 100 indicates a pure white sample, *L** = 0 indicates a pure black sample). To obtain the colour density, colour values were converted to

standard trichromatic values CIE *XYZ* values through computing methods described by the International Commission on Illumination (CIE 1964) standard colourimetric method [315].

Colour densities were calculated as the negative logarithm of trichromatic value Y.

$$CD = -\log\left(\frac{Y}{100}\right) \qquad \textbf{Equation 3}$$

where *CD* is the colour density and *Y* is the *Y* coordinate of the CIE *XYZ* colour space.

3.9 Thermal printing test

The thermal printing test was done at Mitsubishi Hi-tech Paper GmbH. Coating dispersions were produced from the developers and ODB-2. Developer substances were first grounded into a reduced particle size. The particle size obtained was in the range of 50±5µm. Then, the milled samples were dissolved in water using a magnetic stirrer. A dispersion consisting of finished coating colour former without a developer was prepared separately. The finished coating formulation consists of colour former, inorganic pigments, waxes, and binder.

A known weight of the coating dispersion was measured into a laboratory cup then the developer solution was added while stirring to produce a fine mixture. The weight ratio between developer and colour former varied with the developer. Binder content also varied between 7%-10%, depending on the consistency of the dispersion. The coating mixture was applied on a pre-coated paper with the aid of a laboratory paint coater and dried with a hairdryer at a temperature of 55^{o}C to prevent a premature colour reaction before printing. The coated sheets were printed with an Atlantek 400 test printer. The printer printed ten fields with increasing energy levels from 3 to 15 mJ/mm^{2}. In addition, the field with the maximum optical print density was recorded and compared to the reference thermal paper produced with BPA as a developer.

4 Results and discussion

4.1 Electronic absorption spectroscopy of ODB-2 based system.

Figure 25 shows the colour properties of ODB-2 in protic and aprotic solvents. In aprotic solvents, such as acetonitrile, tetrahydrofuran, toluene, acetone, and hexane, ODB-2 did not produce any colour. On the other hand, ODB-2 turned black in protic solvents, ethanol, and methanol.

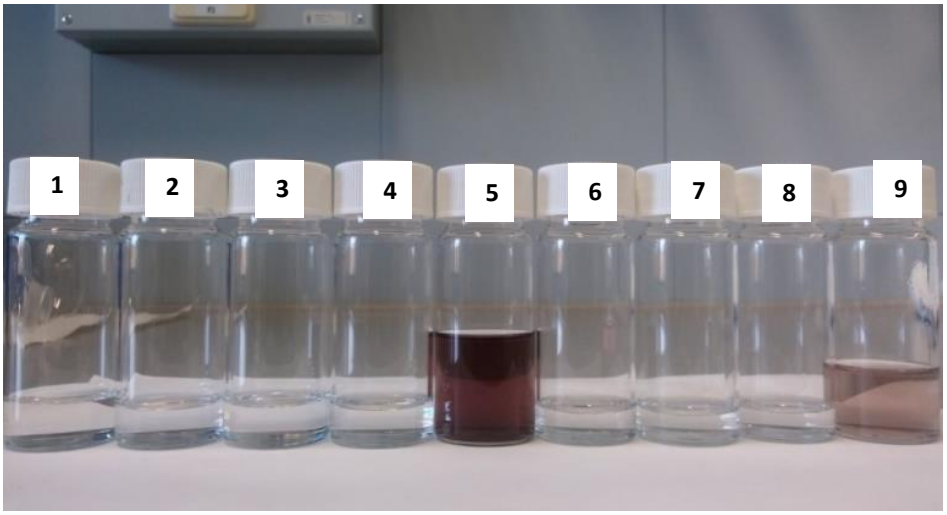


Figure 25. ODB-2 in aprotic and protic solvents. (1) tetrahydrofuran, (2) acetonitrile, (3) toluene, (4) acetone, (5) methanol, (6) ethylacetate, (7) hexane, (8) diethyl ether, and (9) ethanol

The formation of characteristic black colour resulted from the cleavage of the lactone ring of ODB-2 triggered by the transfer of a proton from the solvent to the dye. On the other hand, the dye appeared in its colourless form in the aprotic solvents because solvents such as acetone and acetonitrile cannot participate in solvent-to-solute hydrogen bond interactions due to their inability to act as proton donors [316].

Furthermore, the interaction of ODB-2 with protic solvent led to the formation of its resonance form with an increased degree of conjugation in the chromophore and subsequent reduction in the energy of π-π* transition. This resonance form absorbed radiation in the visible region of the electromagnetic spectrum. The effect of polar solvent on the absorption maxima of ODB-2 was evident in the UV/vis absorption spectra (**Figure 26**). The absorption maxima are shown in **Table 5.**

Table 5. Absorption maxima of UV-visible absorption spectra of ODB-2 in protic and aprotic solvents

Solvent	**λ_{max}**	**λ_{max}**
Ethanol	458	570
Methanol	461	564
Ethylacetate	-	-
Toluene	-	-
Hexane	275	
Diethylether	-	-
Acetonitrile	-	-
Acetone	-	-
Tetrahydrofuran	-	-

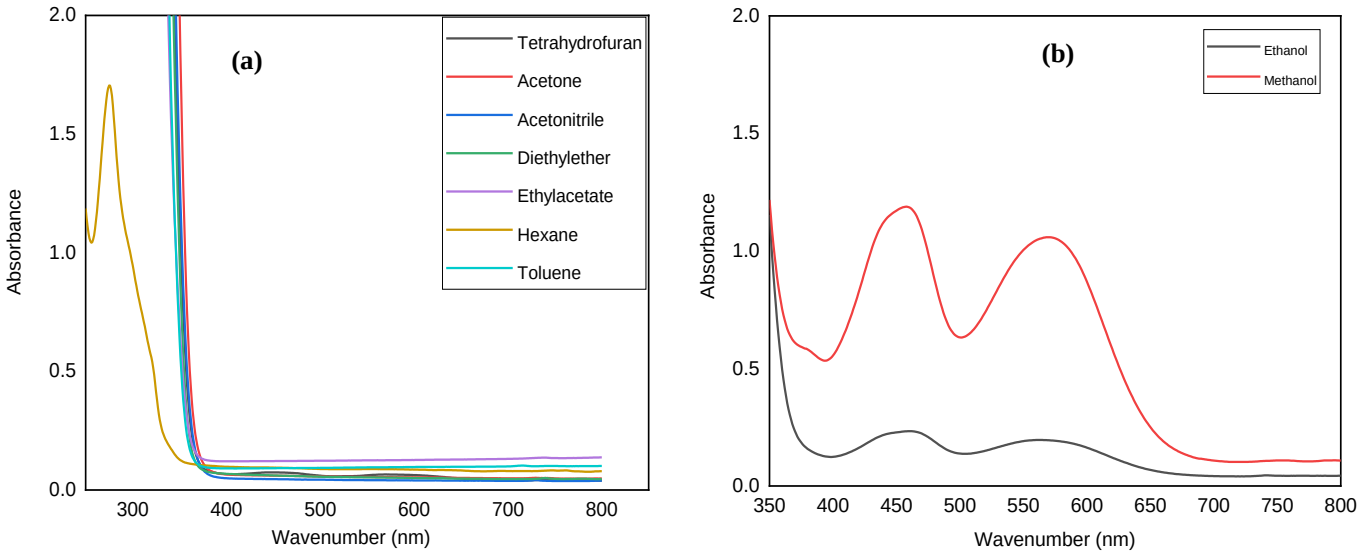


Figure 26. UV/VIS spectra of ODB-2 in (a) tetrahydrofuran (1.54 x 10^{-3}mol/l), acetone (1.65 x 10-3 mol/l), acetonitrile (1.12 x 10^{-3} mol/l), diethylether (1.39 x 10^{-3} mol/l), ethylacetate (0.56 x 10^{-3} mol/l), hexane (1.24 x 10^{-3} mol/l), and toluene (0.97 x 10^{-3} mol/l); (b) methanol (1.63 x 10^{-3} mol/l) and ethanol (1.63 x 10^{-3}mol/l).

ODB-2 showed two strong absorption peaks λ_{max} at 458nm and 570nm in ethanol and λ_{max} at 461 nm and 564 nm in methanol. A shift in the band was observed with increasing polarity from ethanol to methanol**.** The two bands in the spectra representing characteristic π-π* transition involving the whole π-electron system are complementary, and their additivity produced the visible black colour. Though of the

same concentrations (1.63 x 10-^{3}mol/l), the black colour formed by methanol was visibly deeper than the colour obtained with ethanol. The higher polarity of methanol was responsible for this variation.

Moreover, the polarizability of solvents is known to influence the molecular and electronic behaviour of solutes [317]. Related studies reported similar results for fluoran dye [159] and aryl azo dyes [318] in varying solvents. Noticeably, a single absorption band was observed at 275nm in the spectrum of hexane (**Figure 26a**). The reason for this was unclear. It was first assumed to be a product of interference from impurity, but after multiple measurements, the band remained unchanged. A similar effect was reported in the spectrum of fluoran dye in toluene [319]. This was attributed to the presence of the lactone form of the dye.

4.1.1 Effect of solvent mixture on the electronic absorption of ODB-2 based system.

The behaviour of leuco dye in a neat solvent is different from its behaviour in a mixed binary solvent system. Various solvent-solute interactions may alter the molecular characteristics of the dye resulting in spectra shifts of varying degrees [320]. The electronic absorption of ODB-2 was further investigated in a binary solvent mixture of methanol-toluene and ethanol-acetonitrile. Increasing amount of methanol and ethanol (0.1mol – 1mol) was added to a mixture of ODB-2 in toluene (0.93 x 10^{-2}mol/l) and acetonitrile (1.87 x 10^{-2} mol/l), respectively.

As reported in section 4.1, ODB-2 had no absorption in the visible region in toluene and acetonitrile but developed black colour in methanol and ethanol. In the toluene-methanol binary mixture, the characteristic absorption bands of ODB-2 at 460 nm and 570 nm were well resolved (**Figure 27**). A redshift of 12nm on the long wavelength was observed upon the addition of 0.3 mole methanol. This shift remained constant until the maximum amount was added. The change in the shorter wavelength was of the order of 1nm. Absorbance continued to rise at a steady rate with an increase in the amount of methanol. Maximum absorption was attained on the addition of 1mole methanol.

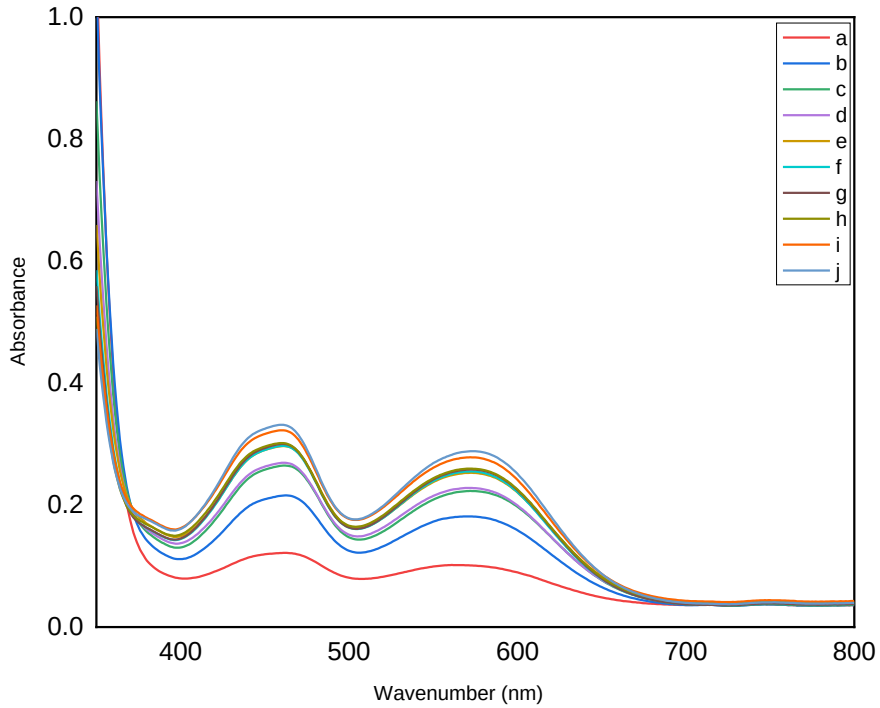


Figure 27. UV/VIS spectra of ODB-2 in toluene (0.93 x 10-2mol/l) with (a) 0.1mol, (b) 0.2mol, (c) 0.3mol, (d) 0.4mol, (e) 0.5mol, (f) 0.6mol, (g) 0.7mol, (h) 0.8mol, (i) 0.9mol, and (j) 1mol of methanol

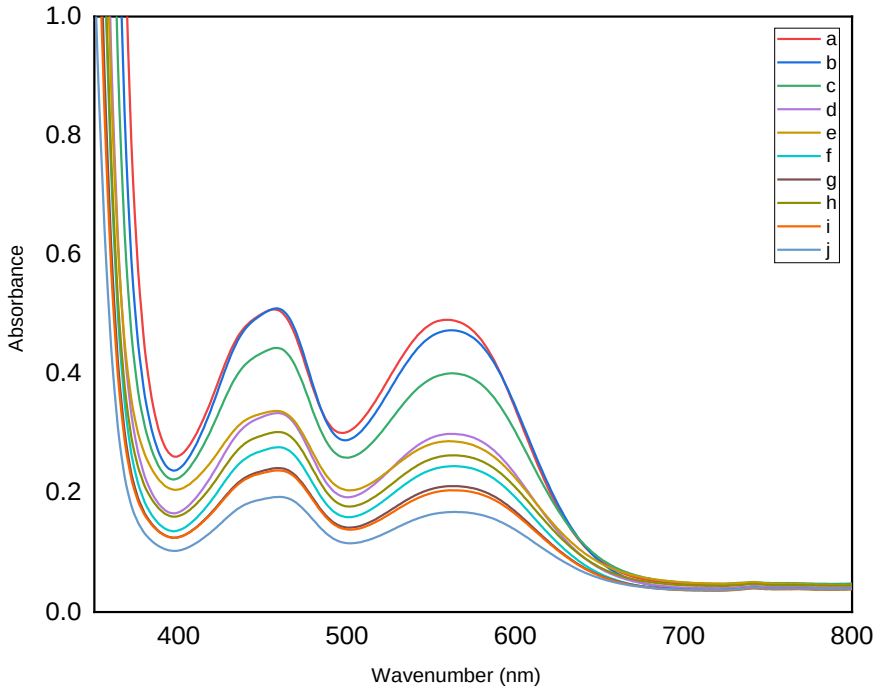


Figure 28. UV/VIS spectra of ODB-2 in acetonitrile (1.87 x 10-2 mol/l) with (a) 0.1mol, (b) 0.2mol, (c) 0.3mol, (d) 0.4mol, (e) 0.5mol, (f) 0.6mol, (g) 0.7mol, (h) 0.8mol, (i) 0.9mol, and (j) 1mol of ethanol.

Like the toluene-methanol mixture, the characteristics absorption bands of the ODB-2 in acetonitrile-ethanol were also well resolved (**Figure 28**). A lower redshift of 4nm was observed in the long wavelength with 1mole ethanol, while a 3nm red shift occurred in the short wavelength.

The change in absorbance and intensity of absorption may be attributed to an alteration in the ratios of the coloured and colourless form of ODB-2 in the solvent mixture [321]. The leuco dye existed in its colourless state in nonpolar solvent and produced colour when the polar solvent was added. A direct relationship between the coloured form of the dye and the polarity of the solvent may be inferred because absorbance is known to be typically affected by the distribution of the solvents between two phases: the bulk and the solvation shell of the dye. This may lead to differential solvation of the ground and the first excited state of the chromophore.

4.1.2 Effect of acid on the electronic absorption of ODB-2 based system.

Figure 29 and **Table 6** show the UV-visible spectra changes of ODB-2 (4.49 x 10^{-3}M) with hydrochloric acid solution and the peak wavelengths of absorption, respectively. The addition of 1.0 x 10^{-5}M hydrochloric acid (HCl) to the solution of ODB-2 in acetonitrile produced an intense black colour. This signalled the opening of the lactone ring of ODB-2 and the formation of the zwitterion form of the dye. Two characteristic absorption bands of ODB-2 at λ_{max} 448nm and λ_{max} 587nm were observed in the visible region of the spectrum. The positions of the bands were unchanged, but their absorbance increased with the increasing concentration of HCl. Related spectroscopic studies on the interaction of fluoran dye and tin (IV) chloride in methyl alcohol showed similar results [98]. A third peak was observed at a lower wavelength between λmax 279nm and 311nm for all HCl concentrations. This peak increased with an equivalent increase in the other two absorption peaks. This may be attributed to the mono-protonation of the aniline- or dialkylamino-group in the molecule of ODB-2 [60].

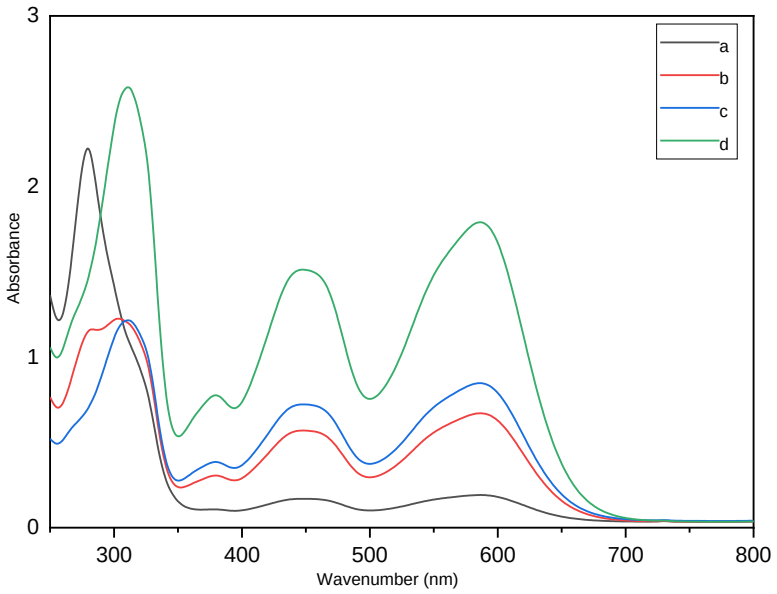


Figure 29. UV/VIS spectra of ODB-2 in acetonitrile (4.49 x 10^{-3}M) at pH (a) 5, (b) 4.69, (c) 4.52, and (d) 4.39.

Table 6. Effects of pH on the electronic absorption of ODB-2 in acetonitrile

pH	λ^1_{max} (nm)	λ^2_{max} (nm)	λ^3_{max} (nm)
5	279	448	587
4.69	303	448	588
4.52	311	448	586
4.39	311	447	587

Investigation of the concentration dependence of the coloured forms of spirobenzopyran in nonpolar solvents had earlier showed that additional absorption bands and a shoulder appeared on the shorter wavelength side [322]. Likewise, the appearance of three peaks when heterocyclic substituted fluoran compounds were dissolved in 95% acetic acid was reported [323]. The authors opined that the three peaks might be due to the co-existence of the quinone, zwitterion, and lactone forms of the dye.

The addition of a high concentration of HCl to ODB-2 in ethanol caused an instant saturation of the black colouration, which was not measurable in UV. The experiment was done with lower concentrations of HCl (0.5 x10^{-5}M – 2.0x10^{-5}M) in a mixture of ODB-2 in ethanol (0.94x10^{-2}M). The UV absorption spectra and peak wavelengths of absorption are reported in **Figure 30** and **Table 7**, respectively.

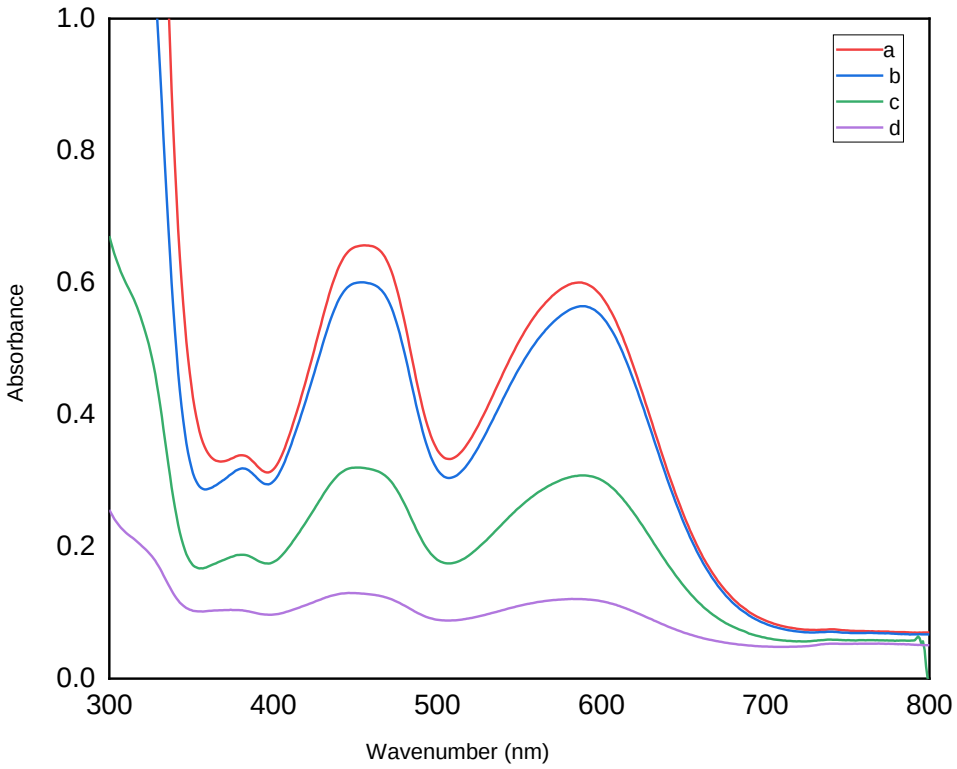


Figure 30. UV/VIS spectra of ODB-2 in ethanol (0.94 x 10^{-2} M) at pH (a) 5, (b) 4.69, (c) 4.52, and (d) 4.39

Table 7. Effects of pH on the electronic absorption of ODB-2 in ethanol

pH	λ^1_{max} (nm)	λ^2_{max} (nm)	λ^3_{max} (nm)
5	381	455	587
4.69	381	452	589
4.52	384	452	588
4.39	391	447	582

In the long-wavelength (λ_{max} 587nm), a hypsochromic shift of 18nm occurred from the neutral ethanol solution by adding 0.5 x 10^{-5}M HCl, indicating the formation of the cationic form of ODB-2. A small shift in peak wavelength was observed when the amount of HCl was doubled. However, with further addition, there was a decrease in the black colour. Consequently, there was a decrease in the intensity of the bands close to the intensity of ODB-2 in neutral ethanol. The black colour receded by adding 1.5 x 10^{-5}M HCl, and the colour was completely lost when HCl was increased to 2.0 x

10^{-5}M. Further addition of either HCl or ethanol did not return the colour of the solution. Absorbance, therefore, remained at its minimum with more addition. Unlike in non-polar solvent, no additional peaks were observed in ethanol.

A selective and random change in the $\boldsymbol{\lambda_{max}}$ absorption of fluorescein was observed when hydrogen chloride was mixed with its neutral alcoholic solution [324]. The authors reported that while one band became stronger, the other turned weaker, and the remaining part of the spectrum appeared like the neutral dye. Further increase in the hydrogen chloride content completely changed the character of the absorptions. Hojo *et al*., [60] reported a similar trend when trifluoromethenesulfonic acid was added to fluoran dye in acetonitrile. With a mono-equivalent amount of the acid, the black colour was developed. However, further addition of the acid led to a decrease in the black colour. Other acidic substances tested in the study gave varying results [60].

4.1.3 Effect of alkali on the electronic absorption of ODB-2 based system

To investigate the effect of alkali on the absorption spectra of ODB-2, increasing amounts of NaOH were added to a fresh mixture of ODB-2 in ethanol (0.47 x 10^{-2}M). **Figure 31** shows that a shift in the peak wavelength (λ^1_{max} 457-455nm; λ^2_{max} 566-568nm) was observed on the addition of NaOH. The coloured zwitterionic form remained constant when the concentration of NaOH was up to 0.4 x 10^{-5}M (ε = 7.3 x 10^4 M^{-1} cm^{-1} at λmax 457nm; ε = 6.4 x 10^4 M^{-1} cm^{-1} at λmax 568nm). However, when NaOH was increased to 0.8 x 10^{-5}M, the intensity of the bands was reduced. With further addition to 1.0 x 10^{-5}M NaOH, the black colour became more intense. Further addition of NaOH did not lead to any further change in the absorption. Colour formation in the presence of amines and potassium hydroxide, respectively, have been previously reported [60, 324]. This was attributed to salt formation caused by solute-solvent interaction.

Based on the above results, it can be concluded that the colour-forming capacity and protonation-deprotonation of ODB-2 can be influenced by the polarity of solvents and the strength of the acid or alkali [325]. In a polar solvent, protonation of the dye chromophore is achievable, while a non-polar solvent does not participate in the proton-transfer reaction. Acid and alkali can also alter the behaviour of the zwitterionic chromophore in polar solvents to varying degrees.

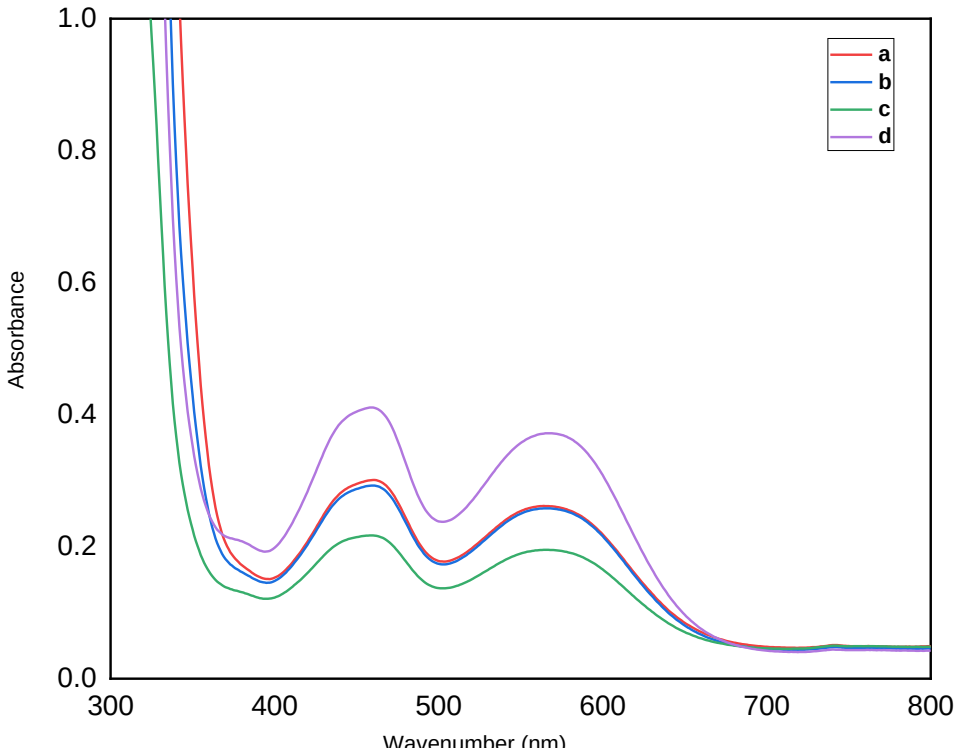


Figure 31. UV/VIS spectra showing effect of NaOH concentration of (a) 0.2 x 10^{-5}M, (b) 0.4 x 10^{-5}M, (c) 0.8 x 10^{-5}M and (d) 1.0 x 10^{-5}M on the absorbance of ODB-2 in ethanol (0.47 x 10^{-2} M).

4.2 Colour-Forming Interaction between ODB-2 and green developers

A rapid screening method developed in our group was previously used to study the colour forming potential of a catalogue of bio-based substances in the presence of ODB-2 [17]. In this study, an acetone test, dispersion test, FTIR and NMR were utilized further to ascertain the reaction between ODB-2 and green developers.

4.2.1 Acetone Test: Interaction of ODB-2 and developer in acetone

As shown in **Figure 32**, ODB-2 and vanillin dissolved in acetone to produce a transparent colourless solution. Similar solutions were produced with other studied compounds like vanillic acid, isovanillin acid, isovanillinic acid, and BPA (**Figure 33**). Tannin substances such as Tanal 02, Tanex 20, and Tanex 40 dissolved in acetone to produce a light-yellow solution, while Tannic acid solution had a slight purple colour (**Figure 34**). Ascorbic acid and its derivative, ascorbyl palmitate, were only sparingly soluble in acetone. The acetone solution was transferred to a larger round bottom flask and the sediment dissolved with ethanol. Ascorbic acid was also only slightly soluble in ethanol. The blackish solvent mixture (**Figure 35**) was then removed from the round bottom flask in two fractions in the rotary evaporator. Acetone was evaporated at 40°C and 300mbar, and ethanol at 60°C.

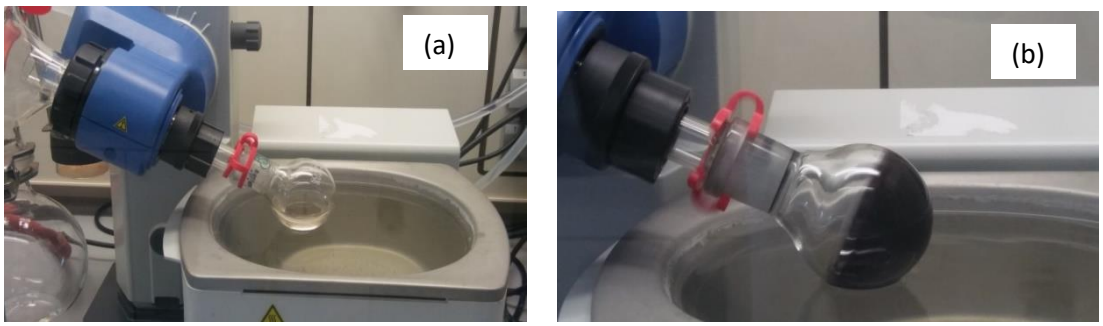


Figure 32. Mixture of vanillin and ODB-2 in acetone. (a) Before and (b) after evaporation

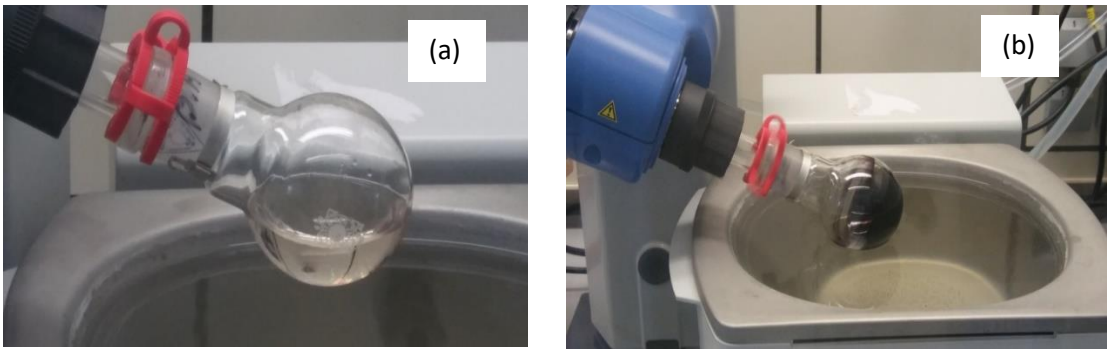


Figure 33. Mixture of BPA and ODB-2 in acetone. (a) Before and (b) after evaporation.

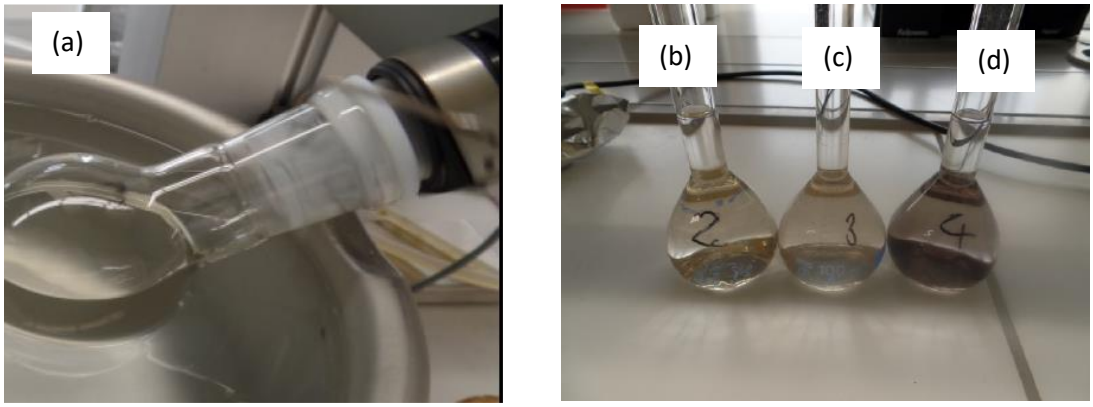


Figure 34. Mixtures of tannin compounds and ODB-2 in acetone. (a) Tanal 02, (b) Tanex 20, (c) Tanex 40 and (d) tannin and ODB-2 in acetone.

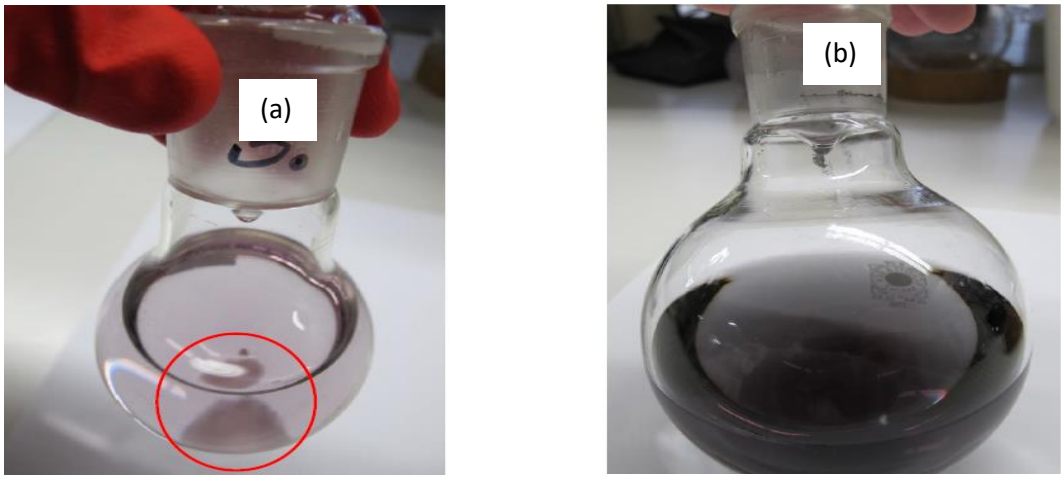


Figure 35. Mixture of ascorbic acid and ODB-2 in solvent. (a) Undissolved ascorbic acid in acetone and (b) solution of ascorbic acid and ODB-2 in a mixture of acetone and ethanol.

On evaporation of acetone, the colour formed with vanillic acid and isovanillin compounds was relatively lighter, suggesting weaker interaction with the colour former (**Figure 36).**

Figure 36. Coloured species formed from the reaction of ODB-2 and vanillic acid, vanillin, isovanillic acid and isovanillin.

In acetone, the solid powder of dye and developer dissolved to produce a transparent solution. Acetone acted as a sensitizing agent by initiating the mobilization of the dye and developer molecules into the solution for efficient interaction. After evaporation of the solvent, a solid black coloured substance was produced. The absence of colour in acetone suggested that the dye molecules were strongly bonded to the acetone and unavailable for interaction with the developer molecules. Acetone could also be said to act as an inhibitor. The reversed situation ensued when acetone was removed. A coloured species representing a dye-developer complex with an open

lactone structure was produced. This coloured substance confirmed a good reaction with ODB-2.

Further addition of acetone dissolved the complex and returned the dye to its colourless form. Conversely, acetone played the role of a decolourising-accelerating agent or reversible agent. These complexes also dissolved finely in other solvents such as methanol, ethanol, and dimethyl sulfoxide, confirming their thermodynamically metastable properties.

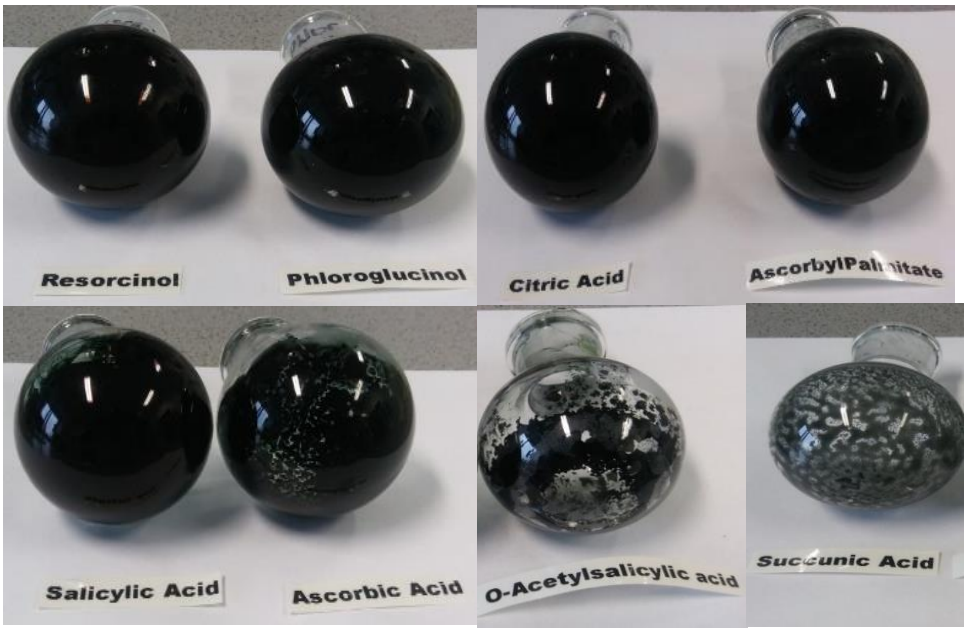


Figure 37. Coloured species formed from the reaction of ODB-2 and resorcinol, pholorglucinol, citric acid, ascorbyl palmitate, salicylic acid, ascorbic acid, succinic acid, and acetylsalicylic acid.

In the case of citric acid, resorcinol, salicylic acid, and tannin compounds, the reaction of ODB-2 with the developer already took place in the acetone solution. After evaporation of the solvent, the black colour became more intense (**Figure 37 and 38**). All colour formed in solid states were stable, suggesting a stable colour complex. The colour developed in the solution confirmed the transfer of a proton from the developer to the dye to open the lactone ring. Citric acid, salicylic acid, resorcinol, and tannic acid produced colour in solution because of their stronger acidic nature. In addition, a higher proportion of hydroxyl groups in substances like tannic acid made the solution more acidic, and hence colour was produced. This same effect was reported when fluoran dye was dissolved in hydrochloric acid solution [143]. With a lower

concentration of hydroxyl groups in the solution, the equilibrium position moved in the direction of the acetone, maintaining the colourless form of the dye. The higher concentration of the hydroxyl groups shifted the equilibrium in the direction of the coloured form of the dye.

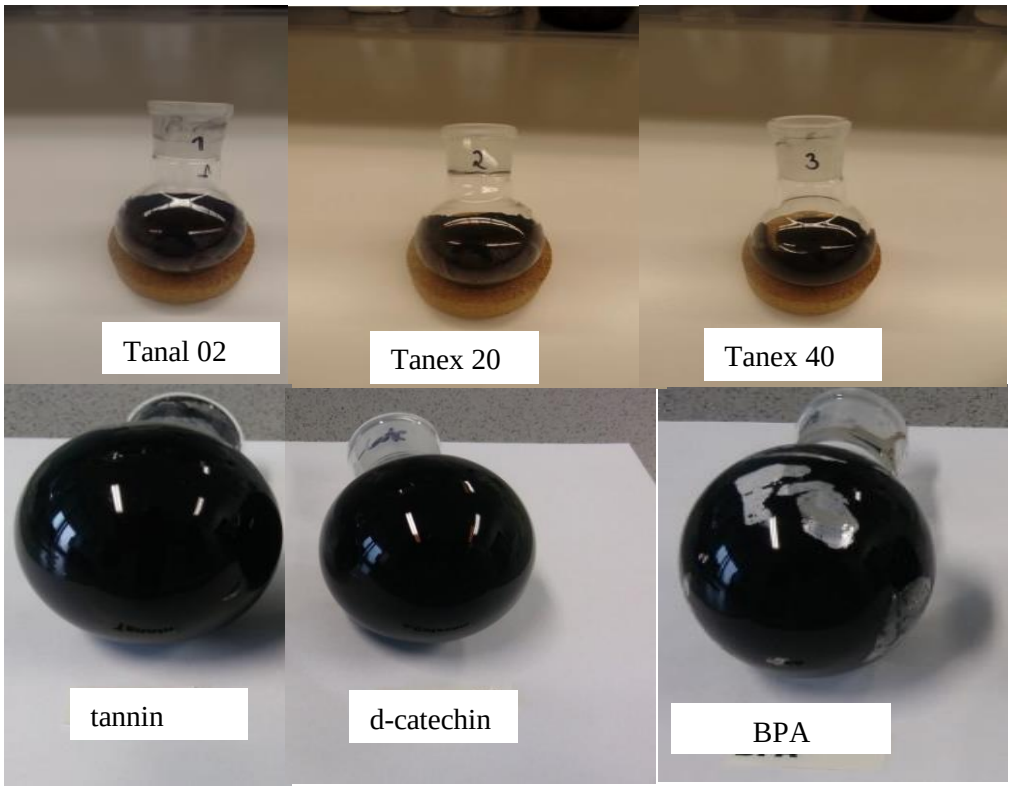


Figure 38. Coloured species formed from the reaction of ODB-2 and tannin compounds (Tanal 02, Tanex 20, Tanex 40, tannin, d-catechin) and BPA.

4.2.2 Dispersion Test: Interaction of ODB-2 and developer in dispersion

The dispersion test mimicked the reaction environment in a commercial thermal paper. In this test, a coating dispersion containing ODB-2, the developer samples, and binder was prepared as used in thermal paper and tested for colour formation both in wet and dried form. The composition of the aqueous dispersion of ODB-2 is shown in **Table** 8.

Table 8. Composition of an aqueous dispersion of ODB-2

Component	**Weight (g)**
ODB-2	201.54
10% aq. solution of polyvinyl alcohol (PVA)	101.62
Water	750

The results of the dispersion test of vanillin, vanillic acid, and their derivatives are shown in **Figure 39**. The mixture of vanillin, vanillic acid, isovanillin, and isovanillic acid with ODB-2 in the aqueous phase resulted in no colour reaction. As the suspensions were dried, the reaction between dye and vanillin was initiated to yield a black colour. Vanillic acid and isovanillin developed a slightly grey colour. In the case of isovanillic acid, there was no change in colour. In the wet state, citric acid, ascorbic acid, and salicylic acid produced a grey colouration, suggesting that a reaction was initiated. This reaction intensified during the drying of the suspension. This coincides with the result obtained with the organic acids in acetone described in section 4.2.1. Ascorbyl palmitate showed no reaction in a wet suspension. After drying, a grey colour was observed, confirming the reaction with ODB-2 (**Figure 40**). With all the tannin samples, a reaction with ODB-2 already occurred in the wet phase. The reaction with Tanal 40 was the strongest. After drying, the dispersion took on a deeper black colour. There were no obvious differences between the compounds (**Figure 41**).

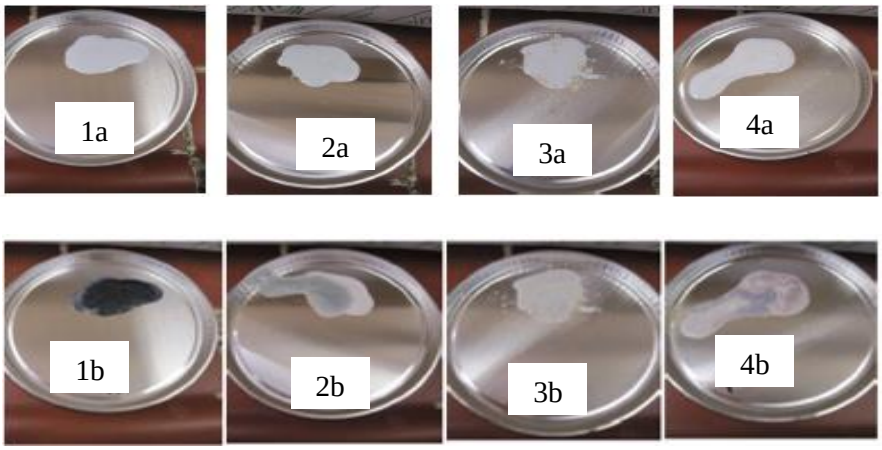


Figure 39. Interaction of ODB-2 and green developer in a dispersion. (1a) vanillin in wet dispersion, (2a) vanillic acid in wet dispersion, (3a) isovanillic acid in wet dispersion, (4a) isovanillin in wet dispersion, (1b) vanillin in dried dispersion, (2b) vanillic acid in dried dispersion, (3b) isovanillic acid in dried dispersion, (4b) isovanillin in dried dispersion.

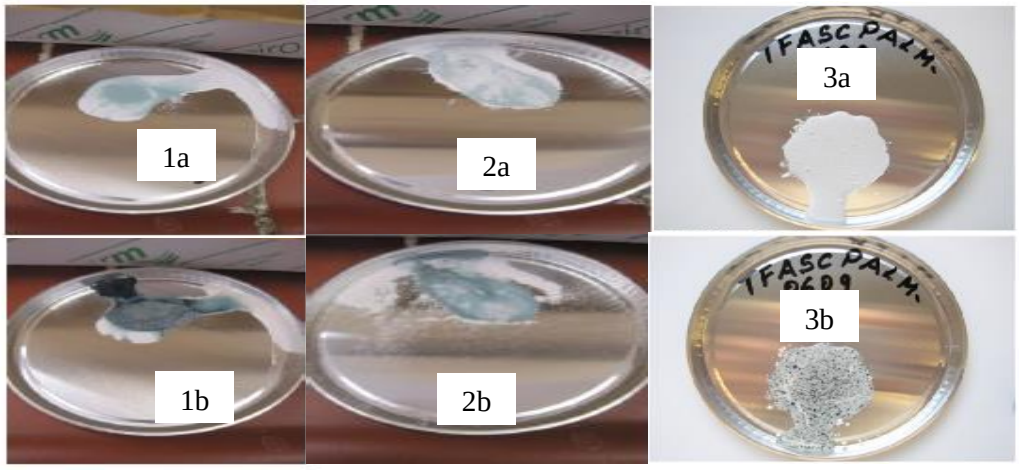


Figure 40. Interaction of ODB-2 and green developer in a dispersion. (1a) ascorbic acid in wet dispersion, (2a) citric acid in wet dispersion, (3a) ascorbyl palmitate in wet dispersion, (1b) ascorbic acid in dried dispersion, (2b) citric acid in dried dispersion, (3b) ascorbyl palmitate in dried dispersion.

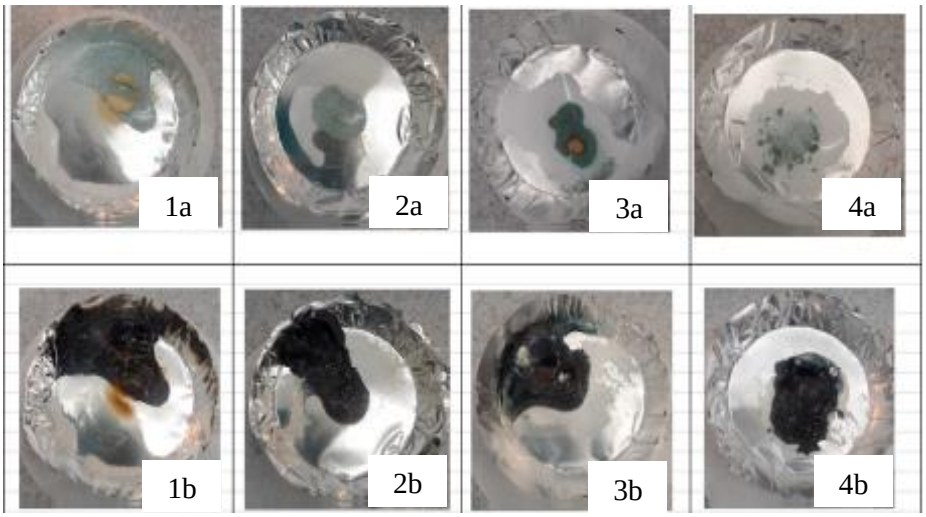


Figure 41. Interaction of ODB-2 and green developer in a dispersion. (1a) Tanal 02 in wet dispersion, (2a) Tanex 20 in wet dispersion, (3a) Tanal 40 in wet dispersion, (4a) tannin in wet dispersion, (1b) Tanal 02 in dried dispersion, (2b) Tanex 20 in dried dispersion, (3b) Tanal 40 in dried dispersion, (4b) tannin in dried dispersion.

Colour formation in the wet state is not beneficial for thermal paper. It risks premature colour formation during storage. This underlines the limitations of organic acids such as salicylic acid and citric acid as developers in thermal paper.

4.3 FTIR Spectra of ODB-2 and green developer

The FTIR spectra of pure ODB-2 with the closed lactone ring and the reaction product of ODB-2 and BPA with the opened lactone ring are shown in **Figure 42**. BPA was used as a control to monitor the interaction of ODB-2 with green developers. FTIR confirmed the reduction or total disappearance of the lactone ring of ODB-2. Three major peaks were present in the spectrum of pure ODB-2, the characteristic carbonyl (C=O) vibration of lactone ring in ODB-2 at 1745cm$^{-1,}$ and the C-C stretching of aromatic rings at 1598 cm^{-1} and 1620cm^{-1} [326]. The sharp carbonyl vibration peak showed that the fluoran dye was in its closed state. Studies on ODB-2 observed the C=O vibration peak at 1744cm^{-1} [327] while being present at 1751cm^{-1} and 1760 cm^{-1} in other fluoran dyes like S-205 and benzofluoran dye, respectively [69, 143]. In Crystal violet lactone dye, this band is present in the range 1734cm^{-1} and 1754cm^{-1} [146, 328, 329].

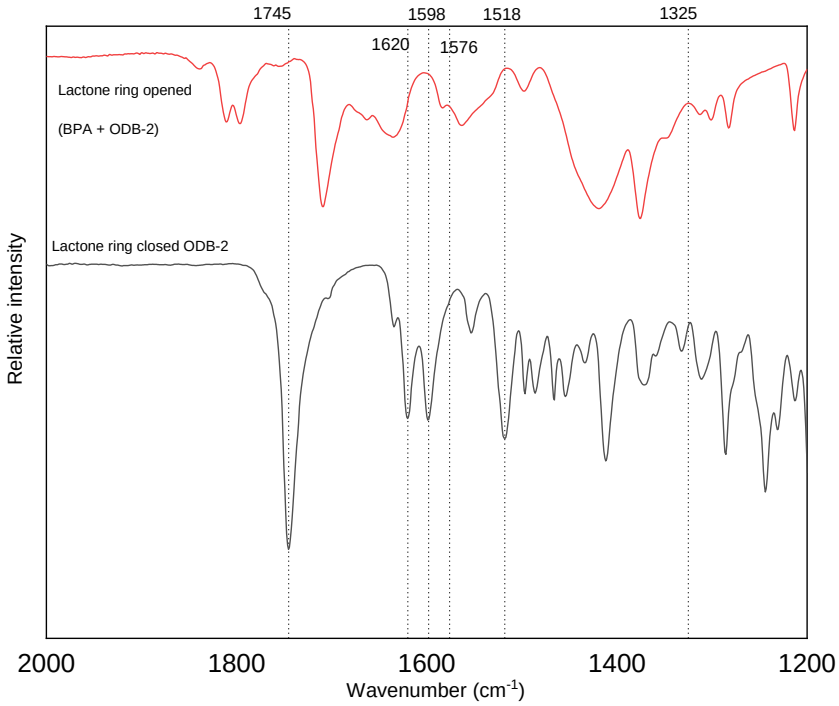


Figure 42. FTIR spectra showing the opened and closed lactone ring form of ODB-2.

The cleavage of the lactone ring by monomeric phenols was confirmed by the disappearance of the carbonyl band in the FTIR spectrum (**Figure 43**). This band was replaced by two new carboxylate bands: 1325 cm^{-1} (symmetric) and 1576 cm^{-1} (anti-symmetric). Carboxylate bands also appeared at 1722 cm^{-1} (vanillic acid), 1708cm^{-1} (vanillin) and 1703 cm^{-1} (resorcinol & phloroglucinol). Furthermore, when the lactone ring was opened, two vibrations, the symmetric and the asymmetric stretching of the COO^- group, were formed [326]. The symmetric band was very weak in vanillic acid and appeared as broadband in phloroglucinol. The weak band in vanillic acid could be attributed to the instability of the black colour. A strong peak attributed to asymmetric vibration was observed in salicylic acid at 1640cm^{-1}. This peak was also evident in ascorbyl palmitate but weak in citric acid and ascorbic acid.

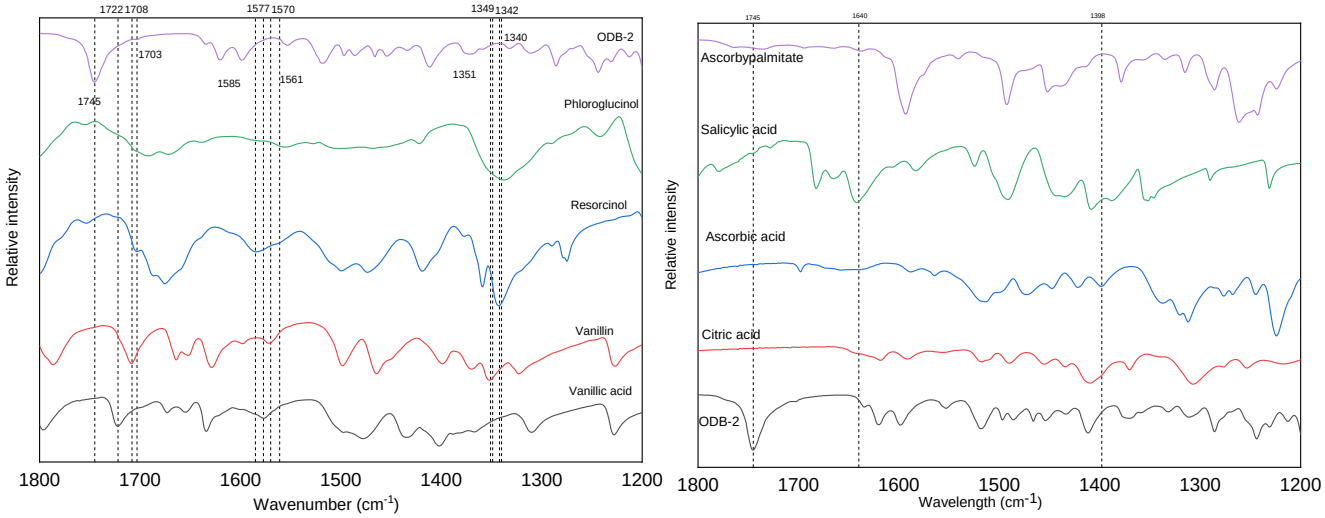


Figure 43. FTIR spectra of the coloured form of ODB-2 obtained from the interaction with green developers. The green developers are inscribed on the spectra.

4.4 ^{13}C NMR spectra of ODB-2 and green developers

The molecular structures of the colourless lactone of ODB-2 and the coloured zwitterions formed from the interaction with green developers were identified by ^{13}C NMR spectroscopy. The numbering of each carbon atom in the central structure of ODB-2 is shown in **Figure 44.**

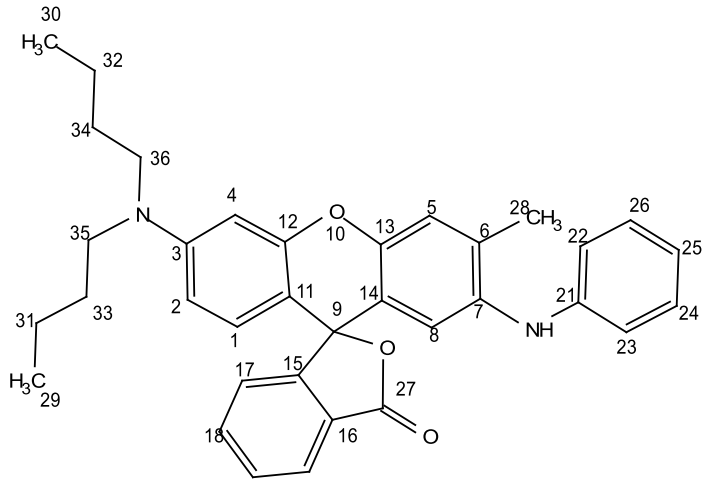


Figure 44. Molecular structure of ODB-2

The position of **C_9** in NMR spectra is typical of sp^3, quaternary carbon (∂ = 75–85ppm) [112], and it was used to monitor the interaction of ODB-2 with green developers (**Figure 45).** The spiro carbon (C9) signal of ODB-2 appeared at 84.12 ppm, which suggested that ODB-2 existed as colourless lactone in chloroform-d ($CDCl_3$) [158]. The spectra show that ascorbyl palmitate, citric acid, ascorbic acid, vanillin, vanillic acid, salicylic acid, resorcinol, and phloroglucinol transferred a proton to ODB-2, leading to the opening of the lactone ring of the dye. In response, the spiro carbon (**C_9**) and the surrounding carbon atoms shifted to varying magnetic fields. The difference in the chemical shift ($\Delta\partial$) of the spiro carbon in the black $CDCl_3$ solution produced from ascorbyl palmitate, citric acid, and resorcinol was 12.89, 13.31, 11.80, respectively *(details in Appendix, page 188*). For these compounds, **C_9** was in the range of about 97–110ppm. Higher shifts to 152 – 169 ppm were recorded for ascorbic acid ($\Delta\partial$ = 78.04), vanillin ($\Delta\partial$ = 68.71), and salicylic acid ($\Delta\partial$ = 85.41). The appearance of ^{13}C signals at lower magnetic fields in the presence of these compounds respectively gave evidence of the formation of the sp^2 hybrid carbon centre for the black colour former. It confirmed the formation of the zwitterions form of ODB-2 [158].

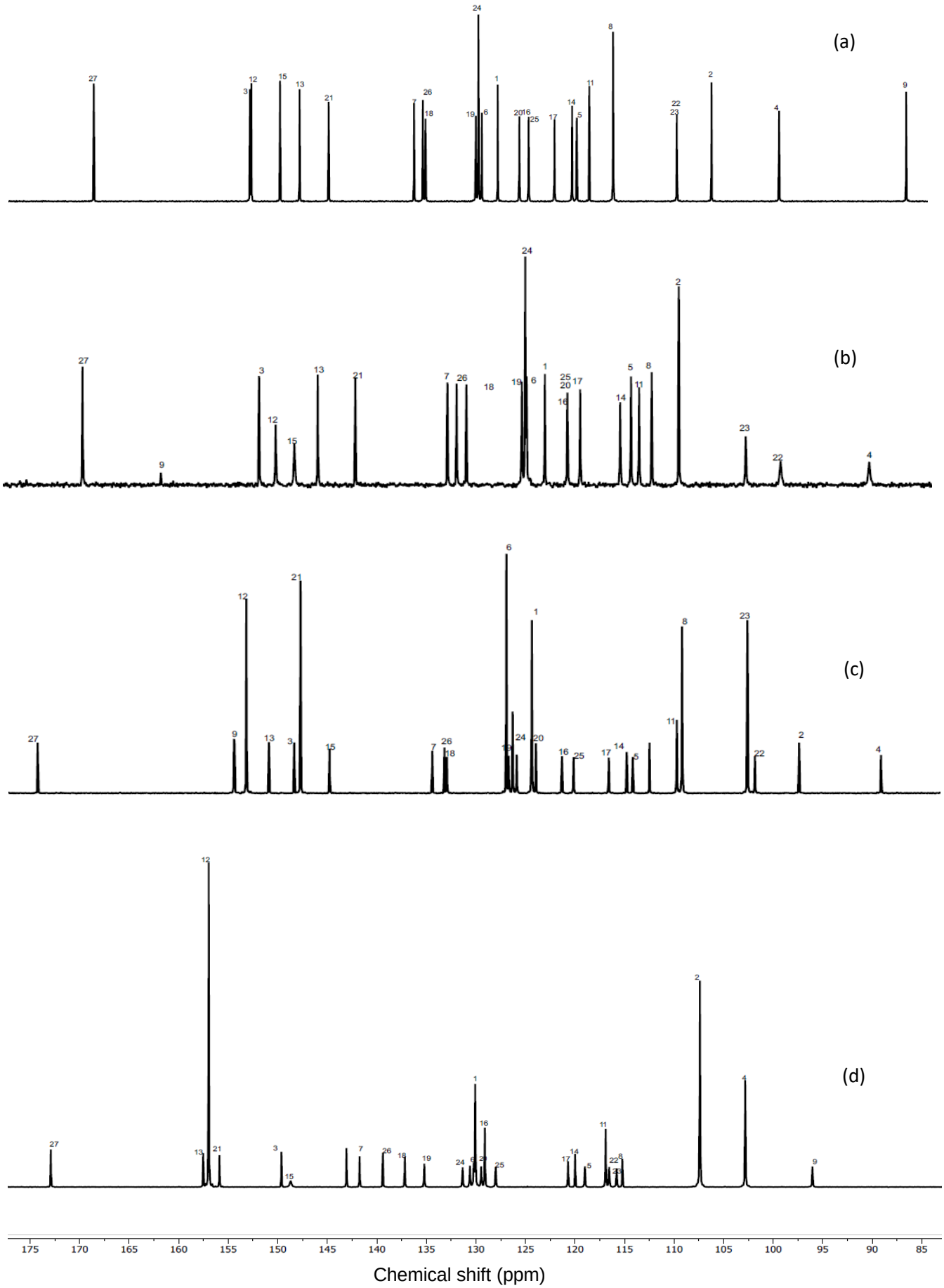


Figure 45. ^{13}C NMR spectra of (a) ODB-2, (b) reaction product of ODB-2 and ascorbic acid, (c) reaction product of ODB-2 and vanillin, (d) reaction product of ODB-2 and resorcinol in $CDCl_3$ over the range 85 to 175 ppm

4.5 Thermal and colorimetric behaviour of thermochromic mixtures

The effect of stoichiometric relationships on the thermal and colour properties of ternary composites containing lignin-based monomers (vanillin and vanillic acid) as developers in the presence of tetradecanol was investigated using Job's method of continuous variation. Tetradecanol was selected as a solvent because it possesses an alkyl chain of intermediate length which is suitable to provide the required solubility of the dye and developer on melting and colour development during crystallisation [146, 328].

In the solid state, vanillin and tetradecanol are crystalline white, while ODB-2 and vanillic acid bear a somewhat off-white appearance. ODB-2 and developer were mixed with the molten tetradecanol to give a colourless or weakly coloured homogenous mixture. The melt solidified when cooled on ice resulting in an instant generation of colour. The colour forming reaction was reversible when mixtures were heated and cooled. All composites showed colour reversibility around 38^{o}C. Most of the composites showed a high contrast between density in the coloured state and the sufficiently low colour density in a decoloured state. The Colour produced was dependent on the molar ratio of the components. **Tables 9** and **10** show the composition of the samples. While the total number of moles in the composition was kept constant, the number of moles of ODB-2, vanillin, and vanillic acid were sequentially varied.

Table 9. Composition of ODB-2 based thermochromic mixtures with vanillin as developer

Sample code	Amount of TD* (g)	Amount of vanillin (mol)	Amount of ODB-2 (mol)	Total amount of vanillin and ODB-2 (mol)
VI	1.5011	0	3.75×10^{-5}	3.75×10^{-5}
VII	1.0123	0.375×10^{-5}	3.375×10^{-5}	3.75×10^{-5}
VIII	1.0789	0.75×10^{-5}	3.0×10^{-5}	3.75×10^{-5}
VIV	1.0600	1.125×10^{-5}	2.625×10^{-5}	3.75×10^{-5}
VV	1.0142	1.5×10^{-5}	2.25×10^{-5}	3.75×10^{-5}
VVI	1.0283	1.875×10^{-5}	1.875×10^{-5}	3.75×10^{-5}
VVII	1.0489	2.25×10^{-5}	1.5×10^{-5}	3.75×10^{-5}
VVIII	1.0238	2.625×10^{-5}	1.125×10^{-5}	3.75×10^{-5}
VIX	1.0513	3.0×10^{-5}	0.75×10^{-5}	3.75×10^{-5}
VX	1.0186	3.375×10^{-5}	0.375×10^{-5}	3.75×10^{-5}
VXI	1.0258	3.75×10^{-5}	0	3.75×10^{-5}

*TD = Tetradecanol

Table 10. Composition of ODB-2 based thermochromic mixtures with vanillic acid as developer

Sample code	Amount of TD* (g)	Amount of vanillic acid (mol)	Amount of ODB-2 (mol)	Total amount of vanillic acid and ODB-2 (mol)
VAI	1.0290	0	3.75×10^{-5}	3.75×10^{-5}
VAII	1.0631	0.375×10^{-5}	3.375×10^{-5}	3.75×10^{-5}
VAIII	1.0793	0.75×10^{-5}	3.0×10^{-5}	3.75×10^{-5}
VAIV	1.0307	1.125×10^{-5}	2.625×10^{-5}	3.75×10^{-5}
VAV	1.0230	1.5×10^{-5}	2.25×10^{-5}	3.75×10^{-5}
VAVI	1.0630	1.875×10^{-5}	1.875×10^{-5}	3.75×10^{-5}
VAVII	1.0217	2.25×10^{-5}	1.5×10^{-5}	3.75×10^{-5}
VAVIII	1.0554	2.625×10^{-5}	1.125×10^{-5}	3.75×10^{-5}
VAIX	1.0714	3.0×10^{-5}	0.75×10^{-5}	3.75×10^{-5}
VAX	1.0148	3.375×10^{-5}	0.375×10^{-5}	3.75×10^{-5}
VAXI	1.0777	3.75×10^{-5}	0	3.75×10^{-5}

*TD = Tetradecanol

4.5.1 Thermochromism in ODB-2/vanillin/tetradecanol mixtures

As the temperature rises above the melting point of tetradecanol, the mixture melted to give a clear transparent solution. The gradual lowering of the temperature led to the crystallisation of dye and developer from the solvent. At room temperature, colour was formed in most mixtures (**Figure 46**). As the amount of vanillin increased, a more intense colour was observed. A light pink colouration was obtained after cooling sample **VI** containing ODB-2 and TD only. This suggested a reaction occurred, and the ODB-2 potentially had an affinity for TD. Repeated heating and cooling of the mixtures yielded the same result. This process appeared to support the mechanism of phase separation explained in section 2.5.

According to the design rule of thermochromism, the optimum ratio is defined as the ratio at which the deepest colouration, complete discolouration, and high contrast are obtained [141]. Several methods have been used to determine the stoichiometry of the coloured complex formed from the reaction of leuco dye and developer. Luthern and Peredes [309] employed a graphical analysis of thermochromic mixtures' reflectance and absorption values to arrive at an optimal stoichiometric ratio. The optimal ratio was determined as the ratio at which the reflectance was lowest, and absorbance was highest. Absorbance is a function of colour density, and colour density is indirectly proportional to luminosity. The higher the colour density, the lower the luminosity. Therefore, the density and luminosity of

composites may be used as parameters for determining the ratio of highest colour formation.

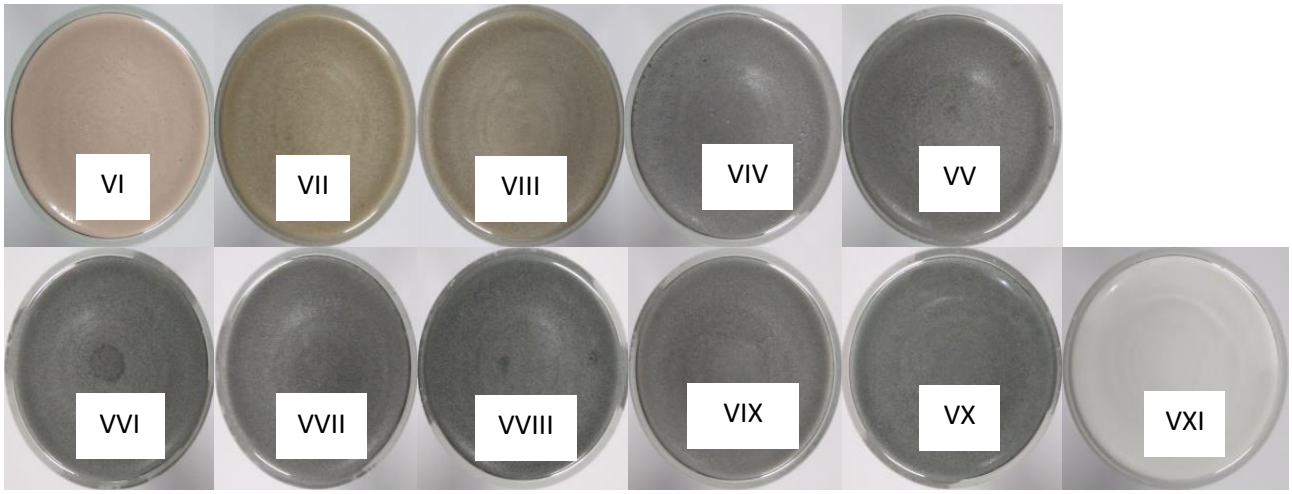


Figure 46. Thermochromic mixtures with vanillin as developer at room temperature. The composition of the samples is presented in **Table** 9.

Table 11. Value of colour parameters of vanillin-based ternary composites.

Sample code	Mole ratio (Vanillin:ODB-2)	L*	a*	b*	C*
VI	0	61.72	5.30	2.73	5.97
VII	1:9	60.13	7.97	4.23	9.02
VIII	1:4	35.07	2.71	-0.39	2.74
VIV	1:2.3	52.90	3.62	1.99	4.14
VV	1:1.5	35.28	1.40	-0.79	-0.71
VVI	1:1	35.54	1.21	-0.71	1.40
VVII	1.5:1	37.01	1.32	0.21	1.34
VVIII	2.3:1	22.06	1.29	-0.93	1.59
VIX	4:1	31.98	0.84	-0.28	0.88
VX	9:1	31.22	0.79	0.43	0.91
VXI	0	74.63	0.37	2.87	2.89

Values of colour parameters obtained for the vanillin-based mixtures are shown in **Table** 11. The luminosity of the samples is represented as L*. The colourimetric values (CIE Lab*) were used to calculate the densities of the thermochromic colours. The variation of densities and colour contrasts with moles of vanillin and ODB-2 is presented in **Figures 47 and 48**. The highest density was obtained at a molar ration 2.3:1 (sample **VVIII**). This molar ratio gave the highest colour density, lowest luminosity, highest solubility of the components in the molten solvent, and the highest

contrast between the coloured and discoloured forms. The colour transition of **VVIII** as a function of temperature is shown in **Figure 49**.

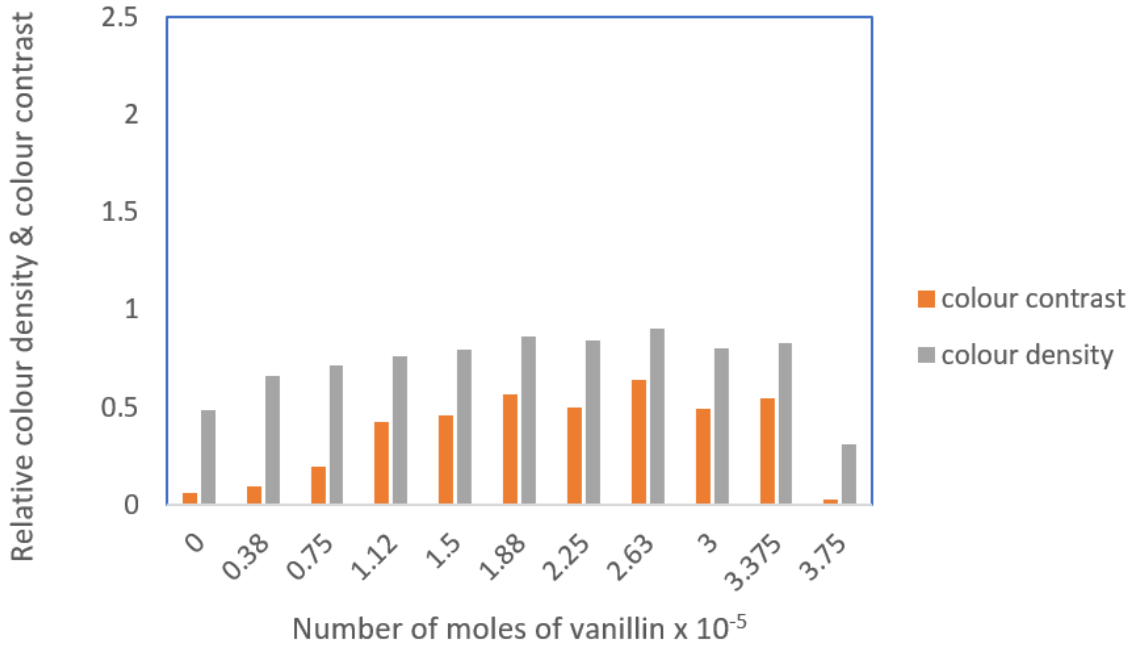


Figure 47. Variation of colour densities with the number of moles of vanillin the ternary mixtures **(VI–VXI)**

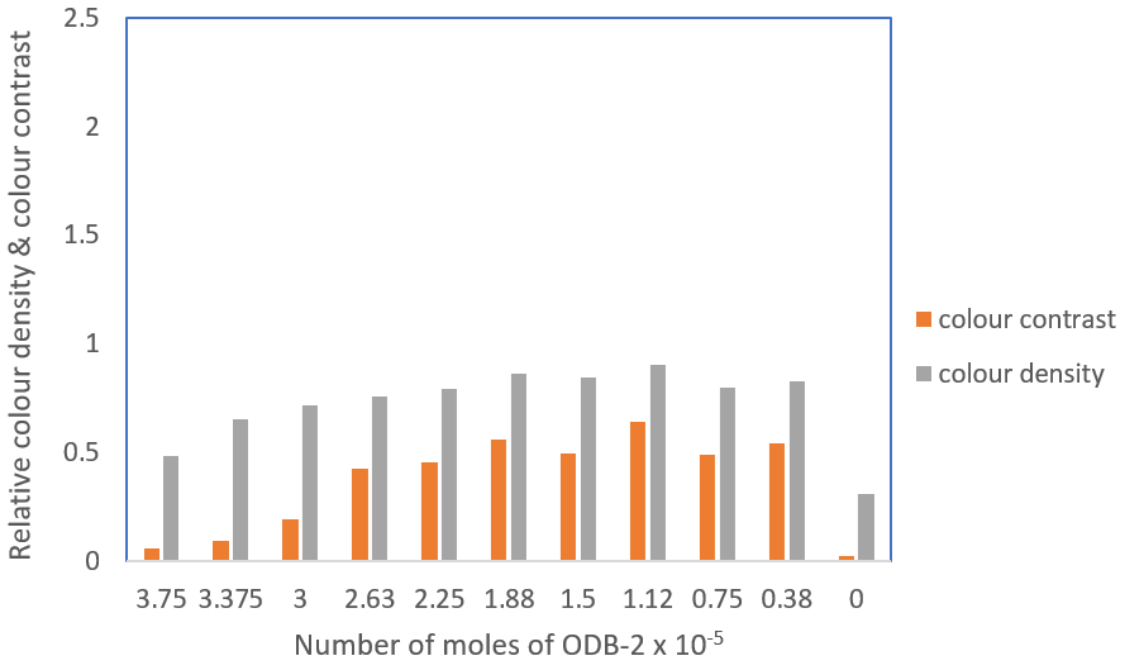


Figure 48. Variation of colour densities with the number of moles of ODB-2 in the ternary mixtures **(VI–VXI)**

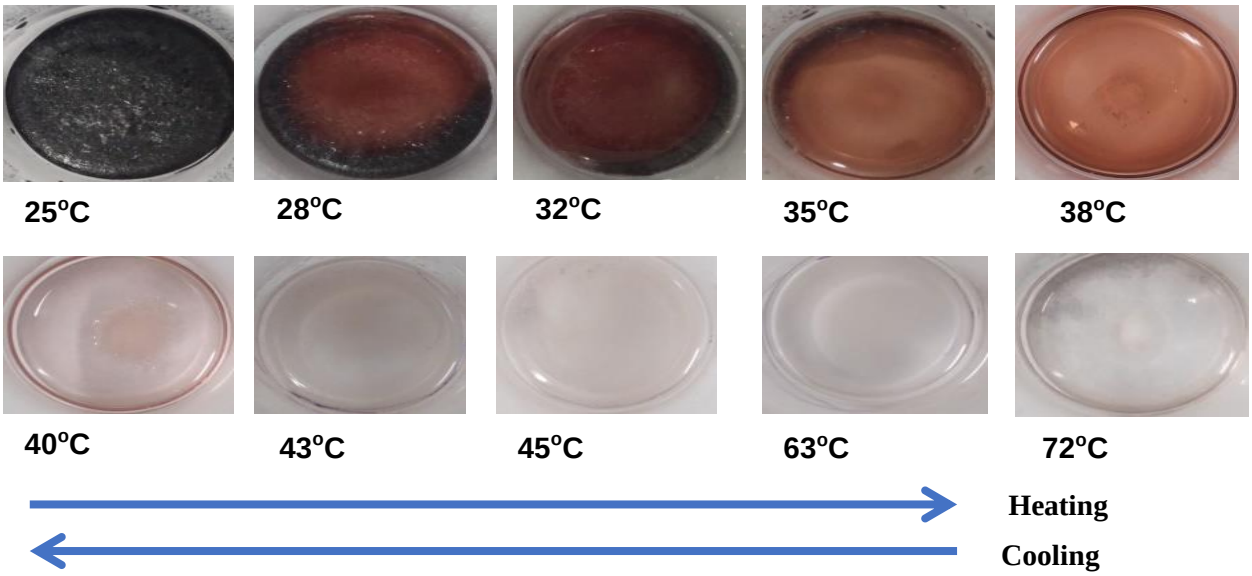


Figure 49. Colour transition of a thermochromic mixture of tetradecanol, vanillin and ODB-2 (2.3:1) with heating and cooling temperature.

4.5.2 Thermochromism in ODB-2/vanillic acid/tetradecanol mixtures

Like vanillin, TD, and ODB-2 (VAI) mixture only produced an off-white colour while other mixtures containing vanillic acid produced colours ranging from grey to black (**Figure 50**). In addition, the colour stability of composites with vanillic acid was relatively low. The Colour faded within an average time of 150 seconds.

Figure 50. Thermochromic mixtures with vanillic acid as developer at room temperature. The composition of the samples is presented in **Table** 10.

The colour parameters of vanillic acid-based composites shown in **Table** 12 indicated that the lowest lightness at room temperature was observed in **VAVI.** Colour transition was also apparent around the melting temperature of tetradecanol.

Furthermore, **VAVI** showed the highest calculated colour density at room temperature (**Figure 51 and 52**). Compared to other samples, it also showed the fastest rate of decolourisation and the highest colour contrast. For vanillic acid-based thermochromic mixture, the optimum ratio of ODB-2: Vanillic acid was estimated at 1:1.

Table 12. Value of colour parameters of vanillic-acid-based ternary composites.

Sample code	Mole ratio (vanillic acid:ODB-2)	L*	a*	b*	C*
VAI	0	65.62	3.01	3.61	4.69
VAII	1:9	63.01	3.33	2.37	4.08
VAIII	1:4	47.84	2.55	2.23	3.39
VAIV	1:2.3	50.49	1.76	1.67	2.42
VAV	1:1.5	39.95	0.64	0.95	1.14
VAVI	1:1	31.02	2.19	-1.55	2.69
VAVII	1.5:1	33.45	0.67	-0.15	0.68
VAVIII	2.3:1	32.66	0.02	-0.34	0.34
VAIX	4:1	37.31	0.29	1.51	1.54
VAX	9:1	57.63	0.83	1.33	1.57
VAXI	0	74.46	-0.38	8.64	8.65

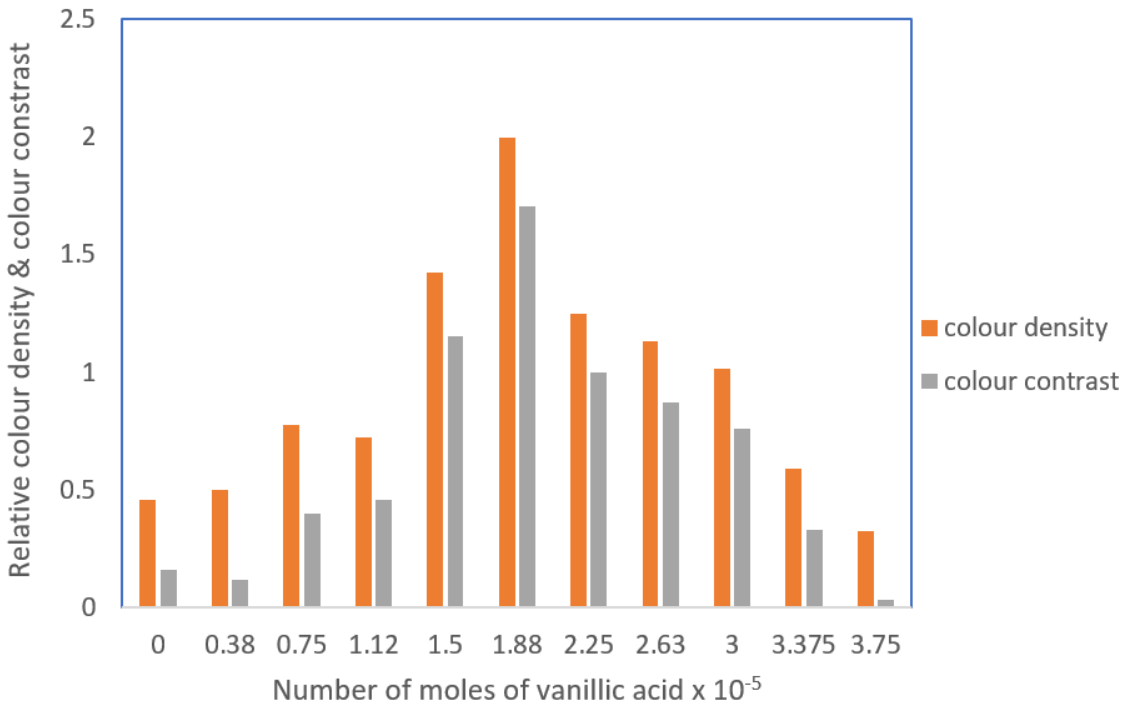


Figure 51. Variation of colour contrast with the number of moles of vanillic acid in the ternary mixtures **VAI – VAXI**

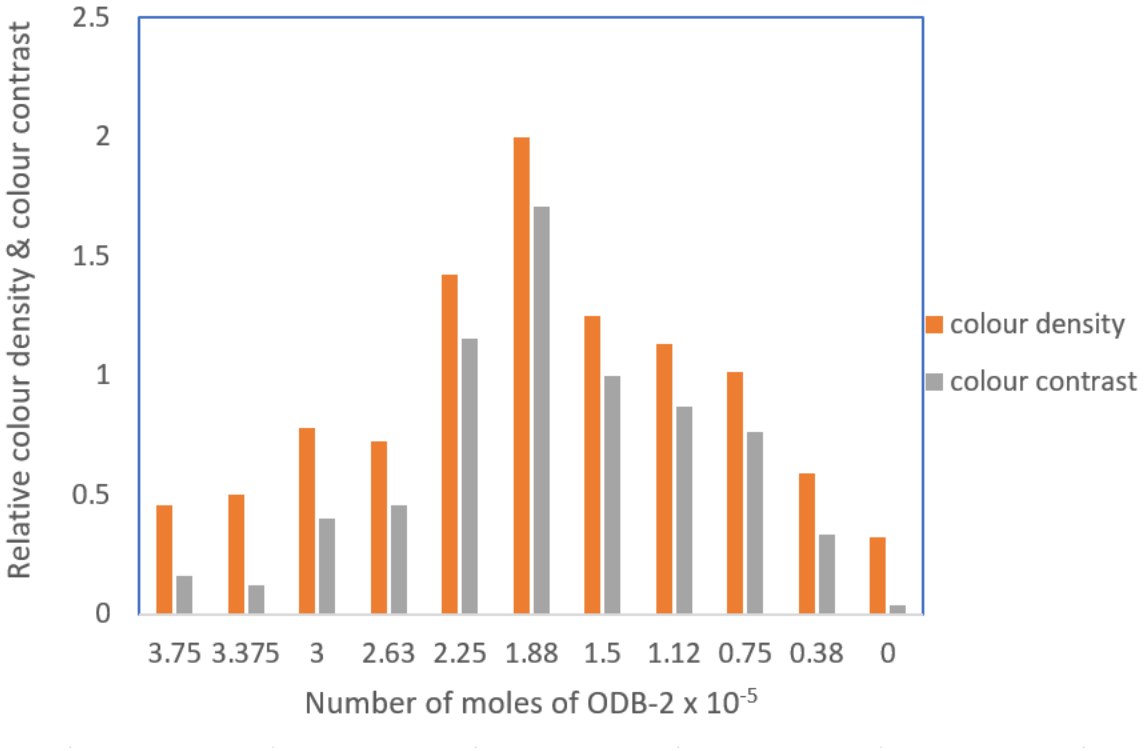


Figure 52. Variation of colour contrast with the number of moles of ODB-2 in ternary mixtures **VAI – VAXI**

The optimum ratios reported for both vanillin and vanillic acid mixtures were estimated with due consideration of all possible interactions that might affect the mixtures' colour and thermal behaviour. Though the transition temperatures were broadly similar, the affinity between developer-dye and developer-solvent, nature, and purity of components are some of the factors that may affect the optimum ratio and, by extension, application conditions of these mixtures in thermochromic systems like pH papers, thermal paper and souvenirs [83, 140, 309].

4.5.3 Effect of excess solvent and developer on the colour properties of a thermochromic mixture

An attempt was made to see how higher solvent and developer concentrations can affect the composites' colorimetric property. With about 5g of tetradecanol added to the mixtures in section 4.5, the colour was entirely lost in both heated and cooled states. A higher amount of tetradecanol led to a dilution effect. In the presence of higher vanillin and vanillin acid contents of about 15 x 10^{-5}mol, low solubility and high colour density were observed at high temperatures. The liquid state was coloured with

high density and showed no thermochromic effect when cooled at 25°C (**Figure 53**). A similar outcome was reported for propyl gallate in CVL and alcohol solvent [141]. A follow-up study described it as melt darkened thermochromism [137]. On the other hand, melt lightened thermochromism was observed when the developer and dye dissolve in the melted solvent without interaction to produce a transparently clear solution.

Figure 53. Composites containing ODB-2, tetradecaonol and excess vanillic acid (15 x 10^{-5}mol) as developer showing coloured solid state at 25°C and melt darkened behaviour at 50°C.

4.5.4 DSC of vanillin and vanillic acid-based thermochromic composites

To study the interconnection between colour change and phase transitions, DSC analysis was carried out on ten thermochromic mixtures prepared with ODB-2 as the colour former, tetradecanol as the solvent, and vanillin or vanillic acid as a developer. Five mixtures were prepared, each for vanillin and vanillic acid as a developer, respectively. In these mixtures, the ratios of tetradecanol/ODB-2/developer were 25/1/1, 25/1/1.5, 25/1/2, 25/1/4, and 24/1/10.

The DSC diagrams and data of colour species formed from mixtures containing vanillin as the developer are summarised in **Figure 54**. A single distinct peak was observed on heating, representing the overlapped solid-solid (S-S) and solid-liquid (S-L) transitions. The melting point of pure tetradecanol is 38.5°C. The addition of vanillin shifted the melting point to lower temperatures around 37°C, leading to a slight broadening of the peak. The endset temperature was stable between 39-40°C with increased developer content. The endset temperature on heating is the temperature at which colour change ends, and this also represents the critical temperature of system application [330]. This is the point at which the dye and developer molecule

dissolves in the molten solvent. No colour forming reactions occurred at this stage, and therefore there was no crystallisation. Discolouration on heating is a product of the formation or destruction of the solvent's low-temperature rigid crystalline structure [115].

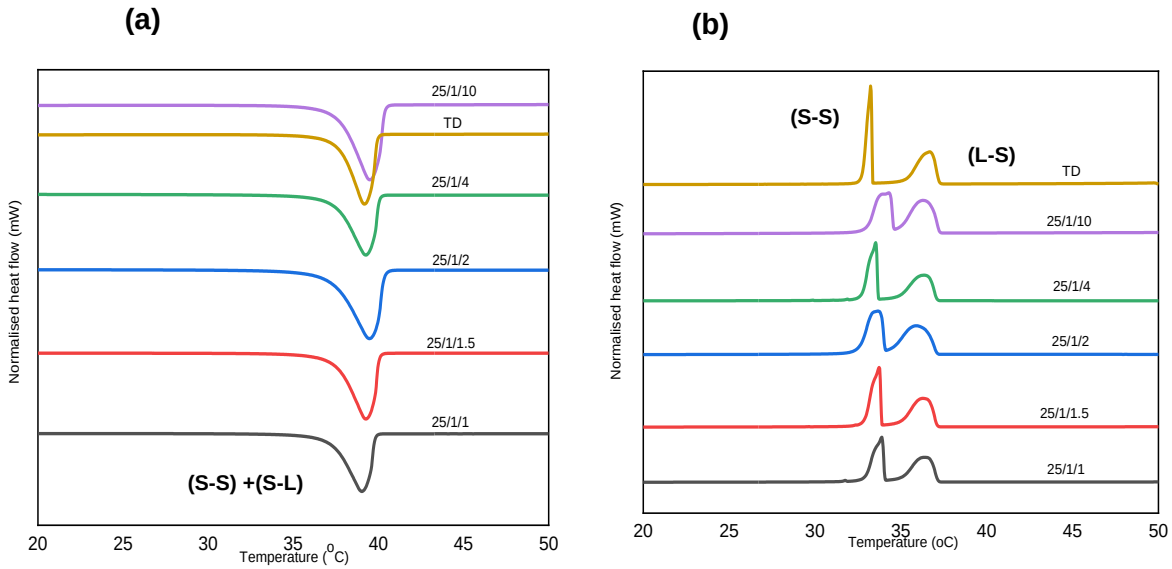


Figure 54. DSC curves showing (a) heating and (b) cooling of the thermochromic composites with vanillin as developer and tetradecanol as solvent.

The transitions on cooling, such as liquid-solid and solid-solid transitions, were well separated. The liquid-solid transition's onset temperature, which represented the solvent's freezing, was almost unchanged, hovering around 37^{o}C, while the solid-solid transition was around 34.5^{o}C. The increasing proportion of the developer had no significant effect on the temperature of the solid-solid transition. The distinct solid-solid transition corresponded to the formation of a stable ß form. This may be attributed to the existence of several crystalline forms [69]. For mixtures containing vanillic acid, the liquid-solid and solid-solid transitions were well separated on cooling (**Figure 55**). The onset temperature varied with an increase in the developer on the order of 1-2^{o}C. An increase in the proportion of vanillic acid led to the prolongation of the liquid-solid transition. This was evident in the broadening of the peaks and can be attributed to the formation of crystallites. It also underlines the interplay between the components in the composite towards the crystal growth process. The corresponding enthalpies of phase transition of tetradecanol and its composites are expressed in **Table** 13.

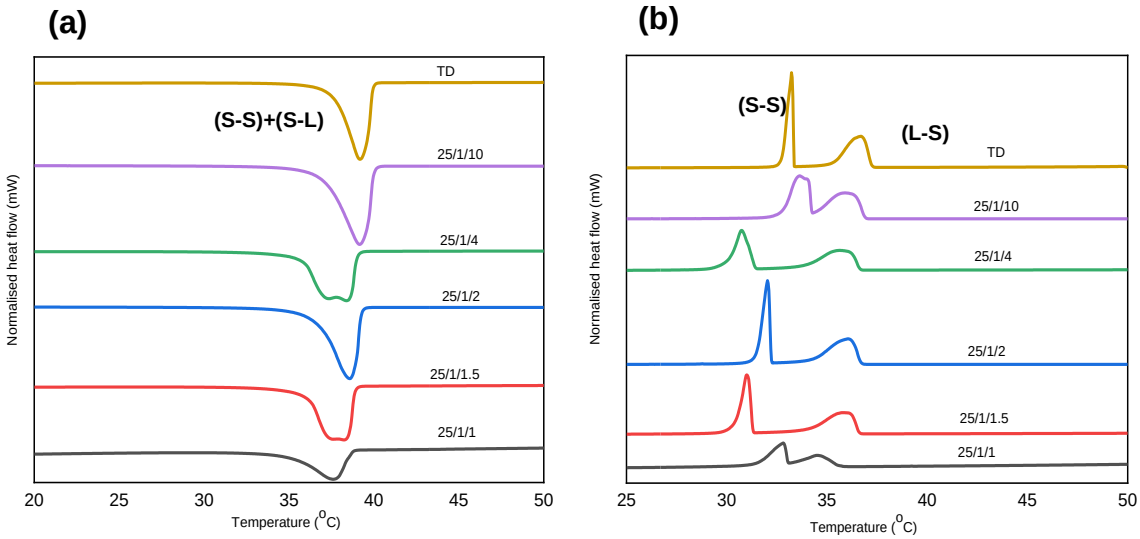


Figure 55. DSC curves showing heating (a) and cooling (b) of the thermochromic composites with vanillic acid as developer and tetradecanol as solvent.

Table 13. Enthalpies of the phase transition of thermochromic mixtures in the defined molar rations.

	Enthalpy of transition (J/g)		
	Heating	Cooling	
Sample	(S-S) + (S-L)	(L-S)	(S-S)
Pure TD	213.85	-108.56	-97.43
(TD/ODB-2/vanillin)			
25/1/1	119.50	-20.40	-52.00
25/1/1.5	197.30	-99.00	-97.01
25/1/2	178.10	-87.52	-83.02
25/1/4	183.10	-75.37	-82.36
25/1/10	203.10	-62.40	-103.57
(TD/ODB-2/vanillic acid)			
25/1/1	189.25	-79.09	-87.47
25/1/1.5	205.21	-92.51	-96.54
25/1/2	195.12	-78.71	-116.10
25/1/4	185.39	-77.16	-81.12
25/1/10	219.26	-88.00	-115.09

TD = Tetradecanol

S-S = solid-solid transition, S-L = solid-liquid transition, L-S= liquid-solid transition; (S-S) + (S-L) represents melting on heating where the (S-S) + (S-L) phase transitions overlap. The data were obtained from the DSC curves in Figure 54 & 55

The above results showed that changes in the appearance of thermochromic systems are a function of the changes in the phase of the component materials. At a temperature higher than the melting temperature of the solvent, little or no interaction occurred between the dye and the developer, thereby producing a transparent and colourless system. However, on cooling to solid-state, the interaction between the dye and developer is initiated to produce colour. This process is evident in thermochromic materials like thermal paper. When thermal paper is introduced into the thermal printer, no colour is formed until the paper is exposed to the air while leaving the printer. The transition between the heated and cooled states, however, takes milliseconds. It must also be mentioned that varying colour-colourless response can be achieved depending on the nature of the solvent, dye, and developer.

4.6 Exploring the use of tannin as a developer in thermal paper.

Tannin extract in its native form contain other substances besides of polyphenols. Sugars, organic acids, gums, and hydrocolloids are some of its other constituents. Therefore, depending on the target application, tannin extract must undergo further purification processes to isolate the preferred components. By doing so, its scope of application can be expanded to higher-value products such as pharmaceuticals, cosmetics, and advanced composite materials.

4.6.1 Tannin purification and characterization

With the focus of this investigation being the use of tannin as a phenol substitute, industrial tannin extracts such as mimosa extract, mimosa sulphite extract, and grape seed extract were purified using Soxhlet extraction with polar organic solvent, methanol. The soluble fraction was recovered after evaporation of the methanol solvent with the rotary evaporator. The methanolic fractions of mimosa, mimosa-sulphite, and grape seed extracts were labelled MIM, MIM-S, and GSE. The industrial raw extracts carried the subscript **R**. The properties of the raw and purified extracts were evaluated through the determination of the total phenolic, ash, and carbohydrate contents (**Table 14 and 15**).

Table 14. Total yield of tannin extracts and their phenolic, and ash compositions.

(Total Phenolic compounds (TPC) expressed as gallic acid equivalent (GAE) (mean ± std. dev., *n* samples))

Tannin samples	Total yield (n=6) (%)	TPC (n =3)	Ash % (n=3)
MIM_R		29.5 ± 0.15	16.4 ± 0.03
MIM	72.5 ± 1.3	44.9 ± 0.32	9.1 ± 0.45
$MIM\text{-}S_R$		31.2 ± 0.25	15.9 ± 0.25
MIM-S	71.5 ± 2.3	46.1 ± 0.10	5.7 ± 0.12
GSE_R		30.3 ± 0.51	6.3 ± 0.05
GSE	74.9 ± 0.4	52.7 ± 0.33	1.4 ± 0.91

Total yields of extraction for MIM, MIM-S, and GSE were 72.5%, 71.4%, and 74.9%, respectively. Tannins are inherently polar, and compatibility with the polarity of the extracting solvent will lead to high efficiency. Purification of mimosa extract with soxhlet extraction in methanol reportedly yielded 82.2% [331]. Lesser yield values were reported for ethyl acetate (6.1%) and hexane (0.2%). The higher the polarity of the solvent, the higher the yield of the extract.

The content of total phenolic compounds (TPC) in the raw industrial extracts and their methanol fractions was determined by Folin-Ciocalteu (FC) assay. TPC of the raw industrial extract of MIM_R, $MIM\text{-}S_{R,}$ and GSE_R was 29.5 ± 0.15 mg, 31.2 ± 0.25 mg, 30.3 ± 0.51 mg of GAE/g of dried raw extract, respectively, while the TPC of their methanol fractions were significantly higher at 44.9 ± 0.32 mg, 46.1 ± 0.10 mg, and 52.7 ± 0.33 mg of GAE/g of methanolic extract. The phenolics were concentrated in the methanol fractions, with the highest concentration found in grape seed extract. These findings agreed with a previous study that reported higher phenolic contents in the methanol extract and butanol extracts of Mimosa, respectively [332]. The polarity of the extracting solvent also influenced the concentration of phenolics [333]. The TPC of GSE fell in the range of values reported by Poudel *et al*., [334], who analysed the TPC of seeds and skins of wild grapes. Rababah *et al*., [335] reported TPC values ranging from 4.66 to 5.12 g of GAE/100g extracts for a different cultivar of grape seed extracts [335]. The TPC of other tannic compounds used in this study like Tanal 40, Tanal 02, Tanex 20, and tannin were 1.03%, 0.99%, 0.86%, and 1.00%, respectively. These values were obtained from the supplier.

The monomeric composition of carbohydrates in the raw and purified extracts shown in **Table** 15 revealed the typical softwood bark polysaccharides. These compounds were also found present in varying amounts in tannins obtained from the bark of European softwoods such as Silver fir, European larch, Norway spruce, Douglas fir, and Scots pine [292]. The total carbohydrate monomers in MIM_R (60.87 ± 1.36%) were slightly higher than MIM-S_R (58.05 ± 1.5%). A similar trend was observed for the methanolic fractions. The highest total carbohydrate concentration was found in GSE_R (65.56 ± 0.93 %). Overall, higher concentrations of carbohydrates were found in the raw industrial tannin compared to the methanolic fractions. This suggested low solubility of these compounds in methanol.

Table 15. Monomeric composition of carbohydrates in industrial tannin extracts and their purified fractions (% w/w on dry extract)

	MIM_R	MIM	**MIM-S_R**	MIM-S	**GSE_R**	GSE
Rhamnose	2.22 ± 0.12	0.88 ± 0.17	1.83 ± 0.31	0.61 ± 0.04	2.12 ± 0.11	0.40 ± 0.31
Mannose	2.71 ± 0.56	0.97 ± 0.89	2.30 ± 0.30	0.86 ± 0.54	2.90 ± 0.10	0.46 ± 0.14
Arabinose	8.36 ± 0.82	5.99 ± 0.98	6.11 ±0.12	5.58 ± 0.13	7.11 ±0.22	2.03 ± 0.18
Galactose	7.66 ± 0.80	1.23 ± 0.03	7.12 ± 1.12	1.51 ± 0.02	6.15 ± 1.12	0.25 ± 0.01
Xylose	0.50 ± 0.01	0	0.40 ± 0.12	0	0.30 ± 0.05	0
Glucose	39.42 ± 0.88	45.39 ± 0.76	40.29 ± 1.16	41.75 ± 0.50	46.98 ± 0.26	55.35 ± 0.33
Total	60.87 ± 1.36	54.47 ± 1.39	58.05 ± 1.5	50.31 ± 0.68	65.56 ± 0.93	58.49 ± 0.03

GSE_R and GSE had significantly lower ash contents 6.25 ± 0.05 and 1.41 ± 0.91%, respectively, compared to mimosa extracts. There was no significant difference in the ash content of both the raw and methanolic extracts of mimosa and mimosa sulphite. The higher concentration of ash in the raw extracts confirmed the enrichment of carbohydrate in the raw extracts.

4.6.2 Synthesis of hydrogen-bonded phenol-amine complex

Hydrogen bonded complexes of phenol were produced by complexation reaction with an amine. Phenols possess one or more hydroxyl groups (-OH) directly connected to the aromatic system. Due to the high electronegativity of the oxygen, phenols have an acidic character and can form phenoxide ion through the loss of H^+. Both phenol and its conjugate base are resonance stabilized. Consequently, alteration of the chemical nature of phenol can be achieved by the addition of varying functional

groups. Properties such as melting point, boiling point, and water solubility can be effectively modified by adding electron-withdrawing groups (-NO_2, -COOH) or electron-donating groups (-NH_2, -OCH_3). Substitution with groups such as amine can form either inter or intramolecular hydrogen bonds, which imparts a new character on the phenol derivative [336]. Several hydrogen-bonded phenol-amine complexes containing different phenols and amines have been synthesised, and their properties studied in the literature [337-339]. The target of this experiment was to produce modified phenol compounds of higher molecular weight and higher thermal stability.

Phenol compounds such as purified tannin extracts (MIM, MIM-S, GSE), tannic acid, and tannin model compounds (catechin, resorcinol, and phloroglucinol) were reacted with hexamethylenediamine (HMDA) at neutral pH to produce hydrogen-bonded complexes. HMDA was mixed with the methanolic solution of the phenol in an amount equivalent to the number of actives OH groups. The molar compositions and properties of the hydrogen-bonded amine complexes are shown in **Table 16**.

Table 16. Composition and properties of the phenol-amine complexes.

*Sample code	Phenol	Weight of phenol (g)	Number of active OH in phenol	Weight of HMDA (g)	Temperature of crystal formation (^oC)	%Yield of crystal
IM-H	MIM	14.22	5	29.15	24	75.4
MIM-S-H	MIM-S	14.05	5	29.14	24	70.3
TA-H	Tannic acid	8.511	4	23.2	24	75.4
GSE-H	GSE	14.31	5	29.23	24	53.42
RES-H	Resorcinol	5.53	2	11.6	60 - 70	97.8
PH-H	Phloroglucinol	6.37	3	17.4	50 - 60	54.1
CAT-H	Catechin	14.26	5	29.01	24	32.45

**See the appendix (page 182) for the description of the samples.*

On addition of HMDA to the alcoholic solution of MIM, MIM-S, GSE, and catechin, a white precipitate was formed immediately at ambient temperature. On the contrary, in phloroglucinol and resorcinol, no precipitate was formed at ambient temperature. The mixture was then subjected to mild heating at about 60^{o}C with vigorous stirring. After about 10mins, solid white crystals began to form. The mixture was cooled in cold water. After cooling, the crystals were filtered on a Whatman filter paper and washed thoroughly with methanol to remove the unreacted HMDA and

phenol compound. The residue, phenol-amine complex, was left to dry in the air overnight (**Figure 56**). On drying in air, complexes of phloroglucinol and GSE turned dark. This may be attributed to air oxidation or incomplete reaction of the phenols with HMDA. Darkening of the complexes of phloroglucinol and GSE rendered them un-useful for the application as developers. The hitherto whitish resorcinol-amine complex turned slightly off-white while MIM and MIM-S complexes were brownish in appearance.

Figure 56. Images of phenol-amine complexes during filtration. GSE-H = Phenol-amine complex from grape seed extract, MIM-H = Phenol-amine complex from mimosa extract, MIM-S-H = Phenol-amine complex from mimosa sulphite extract, TA-H = Phenol-amine complex from tannic acid, CAT-H = Phenol-amine complex from catechin, PH-H = Phenol-amine complex from phloroglucinol, RES-H = Phenol-amine complex from resorcinol.

HMDA (**Figure 57**) was used in this synthesis because it is a di-functional diamine substance. It is widely used in the production of polymeric materials such as nylon66. HMDA can react with flavonoid tannins such as catechin and mimosa in acidic, basic, and neutral conditions to produce dimeric, oligomeric, and polymeric condensates of different proportions [340]. This reaction proceeds via the formation of ionic bonds between protonated amino groups of HMDA and the hydroxyl groups of the flavonoid structure. Mimosa and catechin are slow reacting tannins, while catechol and resorcinol-type tannins have good reactivity. However, phloroglucinol-type tannin

has undesirable characteristics due to its very high reactivity [303]. This may account for the fast darkening of the phloroglucinol-amine complex in air.

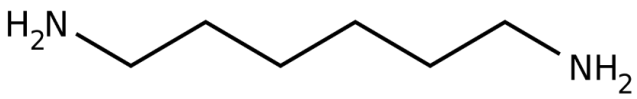


Figure 57. Structure of hexamethylenediamine

4.6.3 Synthesis of phenol polymers

Polymers of phenol; MIM, MIM-S, GSE, tannic acid and resorcinol, and phloroglucinol were synthesised by condensation reaction with glyoxal at acidic and alkaline pH. Several experimental variations were attempted to obtain polymers of these phenolic compounds.

At ambient temperature, mixtures of MIM, MIM-S, GSE, tannic acid (TA), and resorcinol (RES) at pH 2, 7, and 9 remained in the suspension form. Solid polymers of MIM, MIM-S, GSE, TA, and RES were produced when the mixture was treated at 120^{o}C. At 100^{o}C the samples appeared as viscous semi-solid, and below 100^{o}C they remained in liquid form. The hardened solids obtained were either dark or dark brown in appearance. The resulting products were labelled with the name of the phenol and a figure showing the pH of formation, e.g., MIM-CP2 is a copolymer obtained from mimosa tannin at pH 2. MIM-CP2 and MIM-S-CP2 showed a somewhat light appearance. MIM-CP2, MIM-CP7, MIM-CP9, MIM-S-CP2, MIM-S-CP7, MIM-S-CP9 were brittle and could easily be ground into a powder with a mortar and pestle. GSE-CP2 appeared as a glassy solid. The polymer of tannic acid, TA-CP2, was also a glassy solid while TA-CP7 and TA-CP9 looked soft.

Phloroglucinol showed high reactivity with glyoxal at ambient temperature. A soft, lightly coloured solid (PH-CP2) was produced when left standing overnight at ambient temperature. At neutral and alkaline pH, PH-CP7 and PH-CP9 turned glassy when heated to about 90^{o}C for 24hr. Technically, the electrophilic substitution that occurs in the case of tannin and formaldehyde also took place with glyoxal. Glyoxal reacted with the two functional groups in the activated positions of the flavonoid, producing a diolic crosslink or its enol [304]**.** With phloroglucinol, the electron-donating property of the three hydroxyl groups of the phenol placed meta to each other

enhanced the nucleophilic property of the unsubstituted positions of the ring. Thereby increasing its ease of attack by the protonated aldehyde. This outcome agreed with previous works, which showed that aldehydes react rapidly with phloroglucinol in acidic or alkaline solution to form insoluble polymers of appreciably high molecular weight possessing methylene bonds linking the phenol units [341]. The use of glyoxal helps overcome the health challenges associated with formaldehyde because glyoxal is of low toxicity and can be obtained from several natural resources.

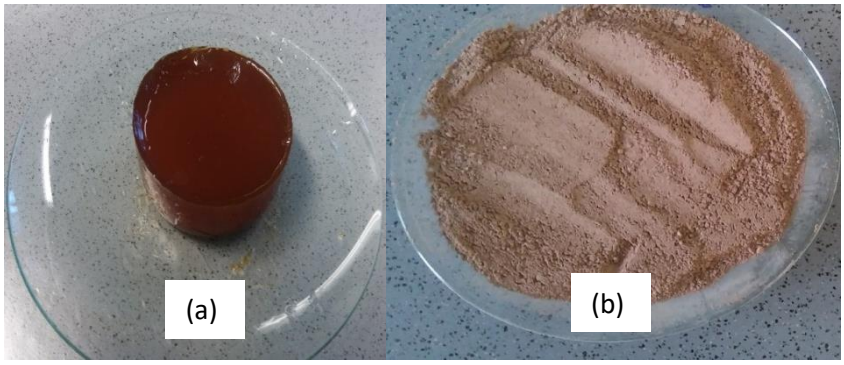


Figure 58. Phloroglucinol-glyoxal polymer (PH-CP2) (a) before milling and (b) after milling

The effect of varying concentrations of glyoxal on phloroglucinol was investigated. 5ml, 12ml, 15ml, 25ml, and 40ml of 40% glyoxal was added to a 30% aqueous solution of phloroglucinol, and the pH adjusted to 2 with 0.001 M H_2SO_4. The mixtures were left for 24hr at ambient temperature. Lightly coloured solid polymers PH-CP2-25 and PH-CP2-40 were obtained with 25ml and 40ml glyoxal at room temperature, respectively (**Figure 58**). The other mixtures remained unchanged until heated to 90^{o}C – 95^{o}C. They were dark-coloured. Increasing the time of polymerization at all temperatures did not yield any significant change. The resulting polymers were ground into a fine powder and subjected to washing: first, with ethyl acetate, then acetone, and ethanol.

4.6.4 Characterization of phenol-amine complexes and phenol polymers

The vibration and thermal characteristics of phenol-amine complexes and phenol polymers were evaluated with FTIR and DSC.

4.6.4.1 FTIR spectroscopy of phenol-amine complexes and phenol polymers

The inactivation of the phenol through the formation of the hydrogen-bonded phenol-amine complex with HMDA was shown in the spectra of pure resorcinol and the reaction product of resorcinol and HMDA (RES-H) in **Figure 59**.

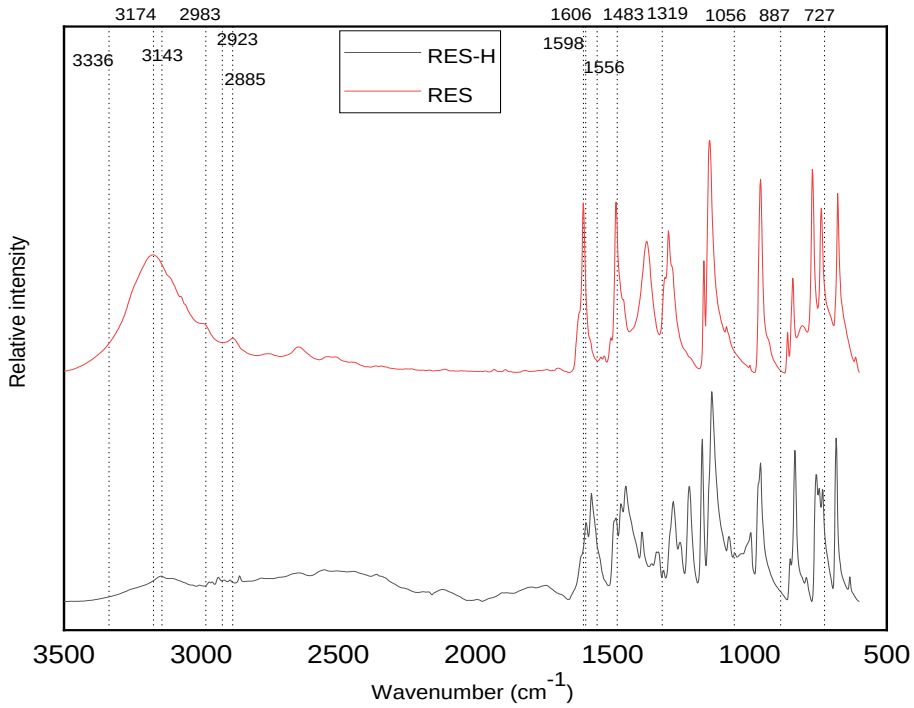


Figure 59. FTIR spectra of pure resorcinol (RES) and resorcinol-amine complex (RES-H)

The band at 3174cm^{-1} is characteristic of –OH groups bonded to the benzene ring in pure resorcinol. The bands at 2983cm^{-1} and 1483cm^{-1} are attributed to the stretching of –CH_2– bonds. The band at 1606cm^{-1} represents aromatic ring stretching. A significant reduction in the intensity of the OH was evident in the spectra of the complex (RES-H). The band at 3336cm^{-1} was assigned to N-H stretching vibration. Bands between 3180cm^{-1} and 2923cm^{-1} were attributed to C-H stretching (aromatic CH), C-H stretching (methylene CH asymmetric stretch in O-CH_3), and C-H stretching (methylene CH symmetric stretch in O-CH_3). The C=C-C stretching (aromatic skeleton) and C=C-C stretching (the aromatic skeleton with C-H bond in methylene) were found at 1598cm^{-1} and 1442cm^{-1} [338].

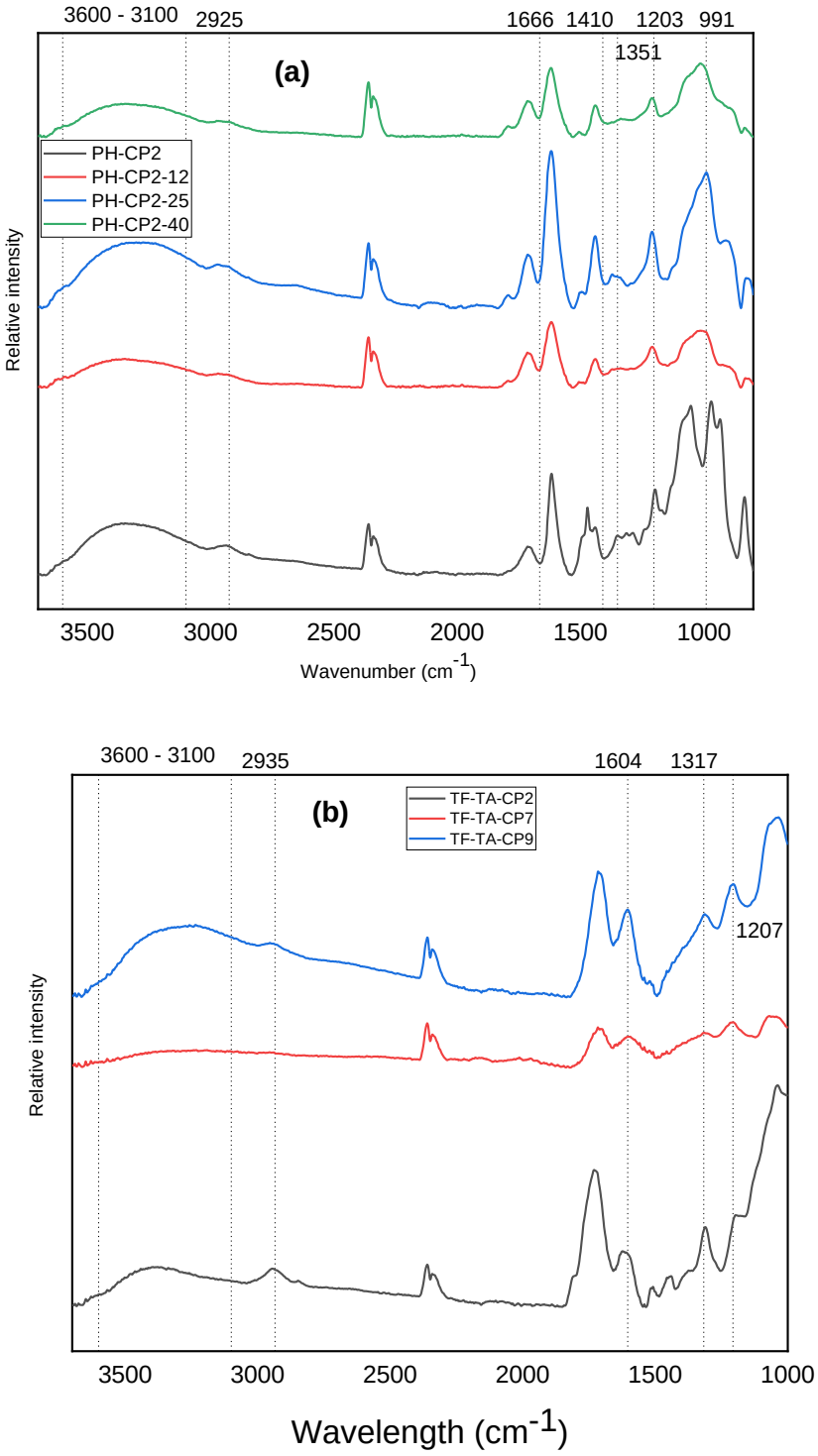


Figure 60. FTIR spectrum of (a) phloroglucinol-glyoxal polymer (PH-CP2, PH-CP2-12, PH-CP2-25 and PH-CP2-40 are polymers produced with 10ml, 12ml, 25ml and 40ml of glyoxal respectively), and (b) tannin-glyoxal polymer.

The FTIR spectra of various phloroglucinol-glyoxal and tannin-glyoxal are shown in **Figure 60a** and **60b**. The peak at about 3600−3100cm^{-1} corresponded to the phenolic OH stretching vibration of the polymers. Other peaks were identified as the C–H stretching vibration bands (2890cm^{-1} and 2935cm^{-1}) from methyl, methoxyl, and methylene groups; the carbonyl groups (1712cm^{-1}); and the ether linkage of methylene groups and ether bonds (1203cm^{-1}) [340].

The hydroxyl values of the obtained polymers in **Table 17** show that the hydroxyl values of the polymers ranged from 515mg – 300mg of KOH/g. These values are lower than the reported hydroxyl value of BPA (660.6 mg of KOH/g) [15].

Table 17. Hydroxyl values of phenol-glyoxal polymers

Phenol polymer	**hydroxyl value (mg of KOH/g)**
MIM	503.5 ± 1.1
MIM-CP2	459.3 ± 0.3
MIM-CP7	441.1 ± 0.5
MIM-CP9	421.5 ± 0.1
MIM-S	514.4 ± 1.5
MIM S-CP2	412.5 ± 0.3
MIM S-CP7	432.3 ± 0.2
MIM S-CP9	413.7 ± 0.5
GSE	515.5 ± 0.5
GSE-CP2	401.5 ± 0.1
GSE-CP7	409.1 ± 0.3
GSE-CP9	391.7 ± 0.2
RES-CP2	321.5 ± 1.5
RES-CP9	300.1 ± 2.2
PH-CP2	454.7 ± 1.4
PH-CP7	412.3 ± 0.8
PH-CP9	448.1 ± 1.2

4.6.4.2 DSC of phenol-amine complex and phenol polymer

As the thermal property of a developer material has a pronounced influence on the colour forming properties of thermal papers, the thermal behaviour of tannins, their complexes, and polymers were observed with DSC. **Figure 61-63** show the DSC curves of the samples obtained at a heating rate of 10^{o}C/min.

The glass transition temperatures (T_g) of MIM, MIM-S, and GSE were 93.8^{o}C, 99.5^{o}C, and 98.3^{o}C. The amine complexes: MIM-H and MIM-S-H showed similar thermal behaviour with T_g values at 103.3^{o}C and 101.9^{o}C. However, the amine complex of resorcinol, RES-H, showed a melting behaviour at 163.2^{o}C. The melting temperature of RES-H is considerably higher than the melting temperature of pure resorcinol (110^{o}C). This confirms that the reaction of resorcinol with HMDA affected the structural configuration of the phenol. The melting property of RES-H, which is similar to that of BPA, would enhance its use as a developer in thermal imaging. This is because higher melting temperatures inhibit premature colour formation and enhances heat resistance in a high-temperature environment. In addition, the melting of a developer enhances the homogenous blending with other coating materials and the effective interaction with the colour former.

Regarding the phenol-glyoxal polymers, none of the polymers showed melting behaviour between room temperature and 300^{o}C. MIM-CP2, GSE-CP2, and PHCP2 had the highest T_g values of 206.5^{o}C, 207.7^{o}C, and 223.8^{o}C, respectively. Other polymers showed T_g values ranging between 101-197^{o}C. The pH of polymerisation had no significant effect on the thermal properties. This indicated that these polymers have high thermal stability and would likely be stable at the end-use and printing temperatures [342].

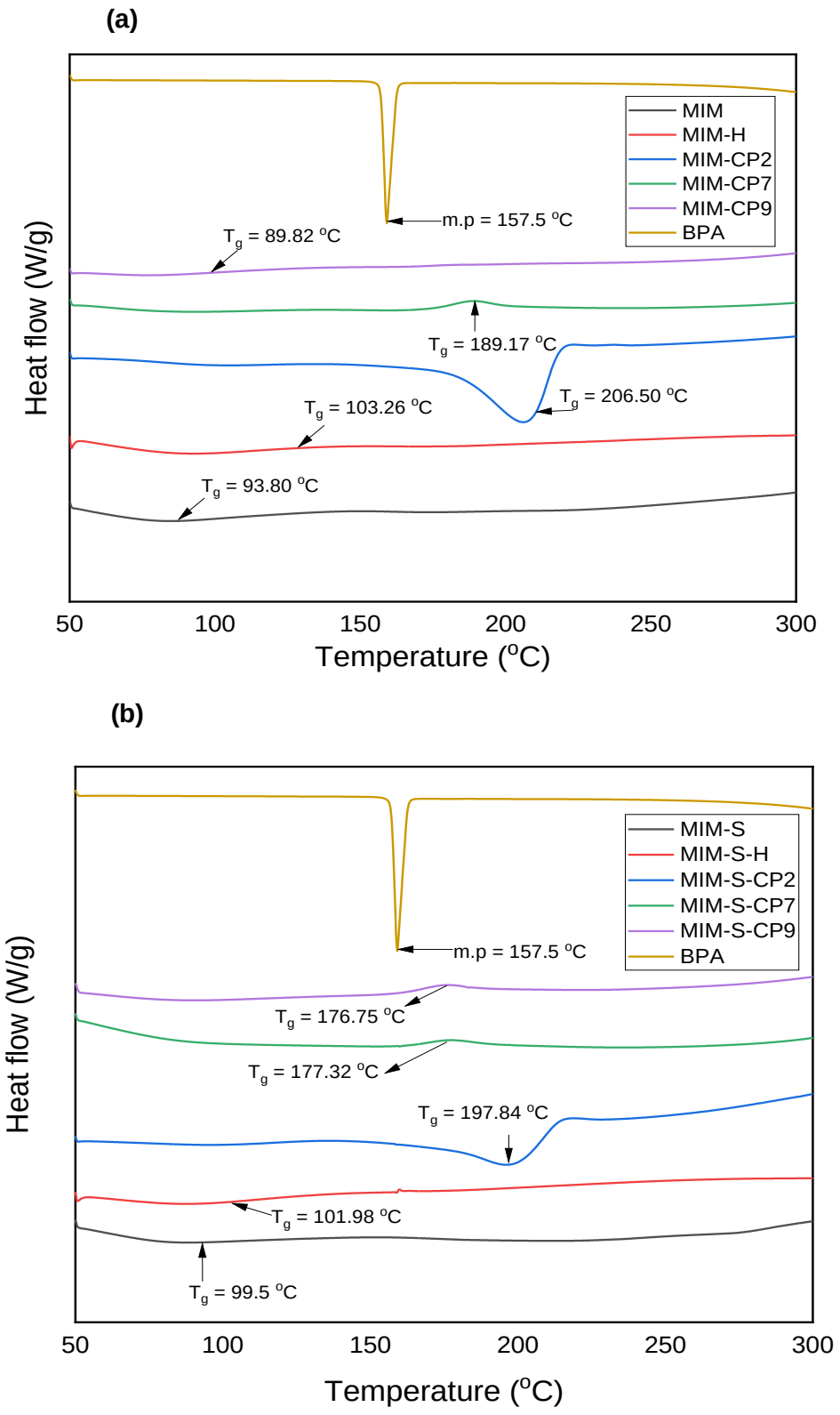


Figure 61. DSC curves of amine complex and polymers of (a) mimosa extract (MIM), and (b) mimosa sulphite extract (MIM-S)

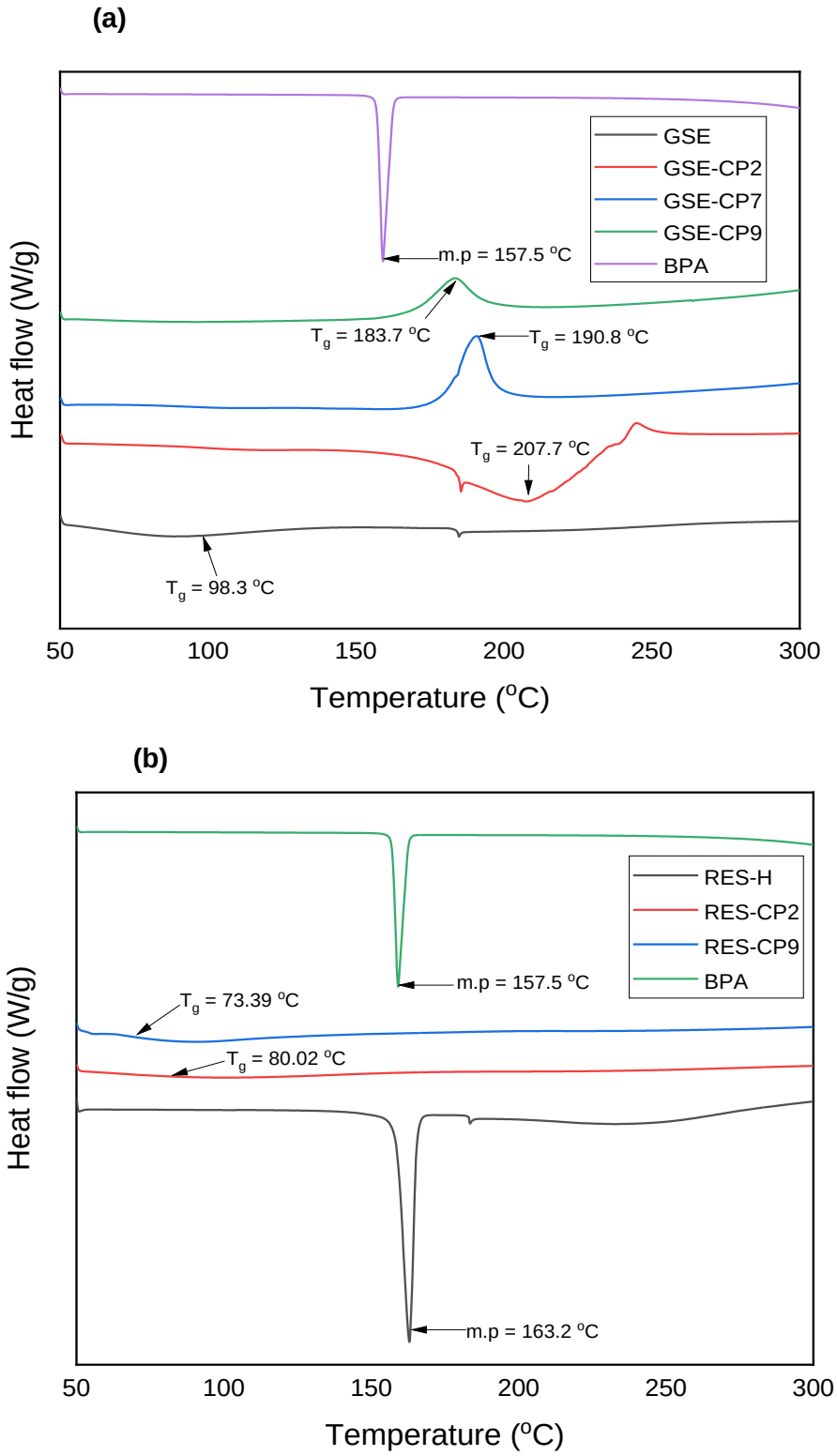


Figure 62. DSC curves of amine complex and polymers of (a) grape seed extract (GSE), and (d) resorcinol (RES)

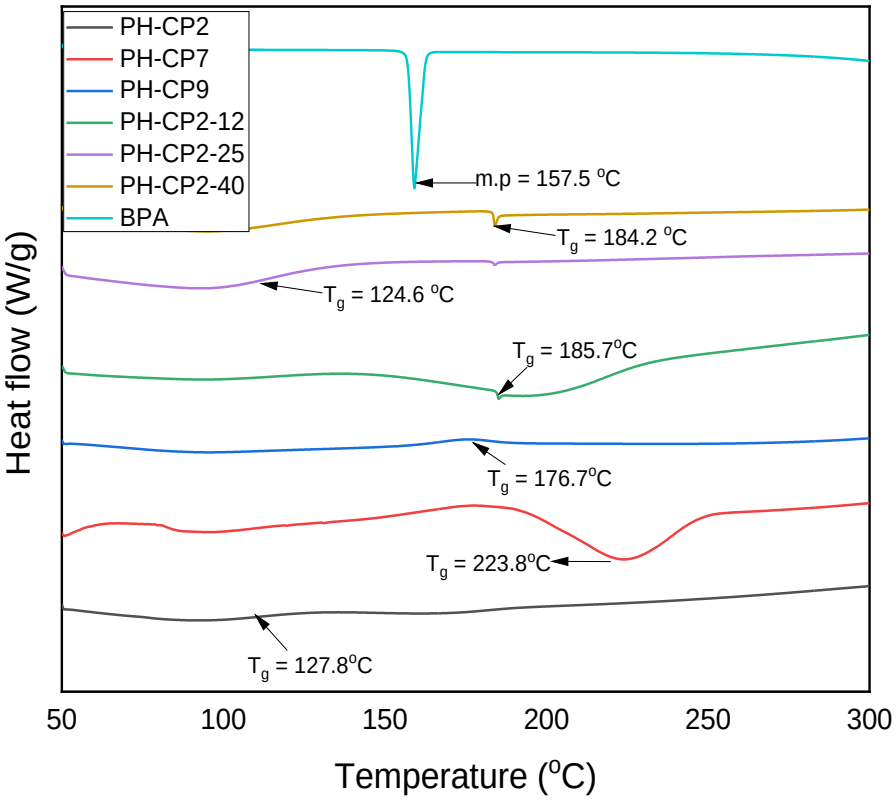


Figure 63. DSC curves of phloroglucinol-glyoxal polymers and BPA

4.6.5 Colour-forming reaction of tannin compounds with ODB-2

4.6.5.1 Colour-forming reaction of ODB-2 and tannin compounds in acetone

Purified tannin extracts and phenol polymers showed brownish colouration in acetone (**Figure 64**) and were largely insoluble. However, on evaporation, they produced sharp black colouration (**Figure 65**). Unlike the pure phenol, all phenol-amine complexes were insoluble in acetone, and no colour was produced after evaporation of the solvent. This indicated that the compounds were in their complex form, and the phenols were not available for reaction. In addition, the temperature of evaporation (40°C) was too low to initiate the decomposition of the complex. This also confirmed the effectiveness of the complexation process.

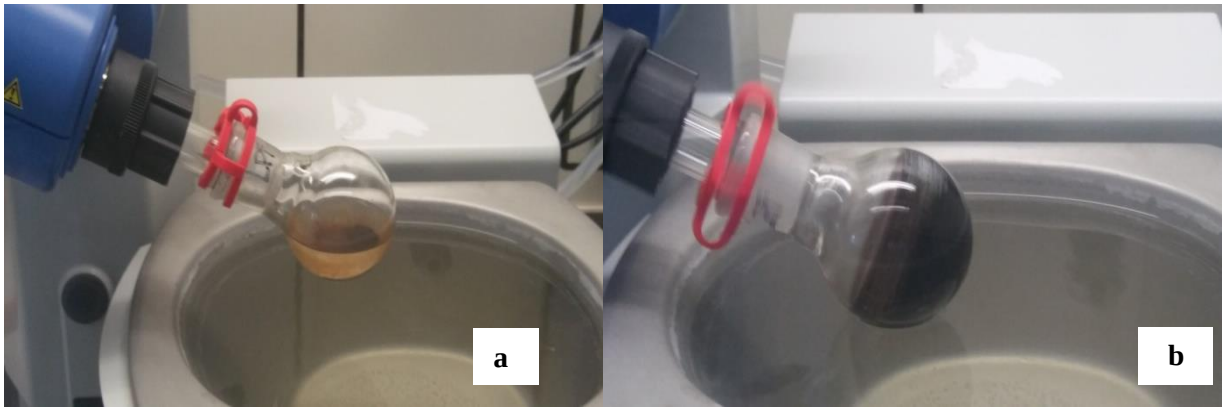


Figure 64. Mixture of mimosa extract (MIM) and ODB-2 in acetone. (a) before evaporation and (b) after evaporation

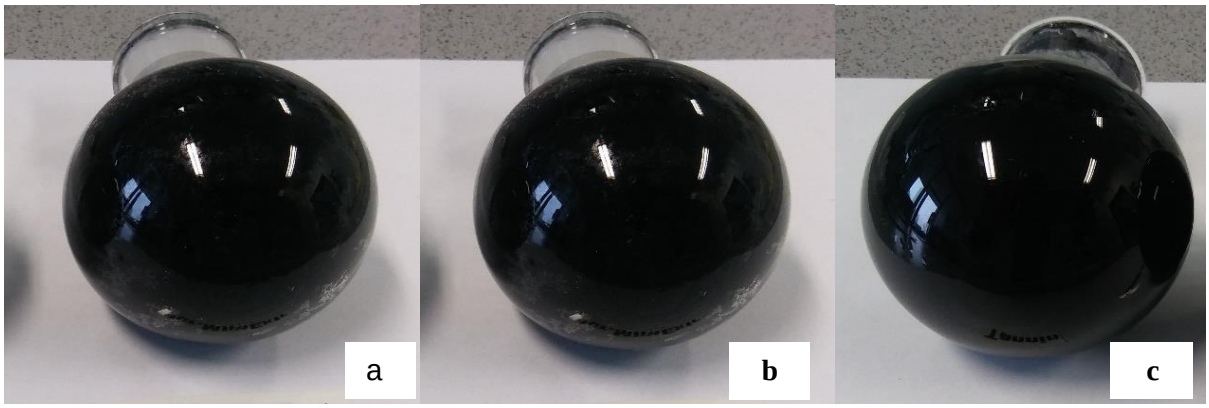


Figure 65. Coloured species formed from the reaction of ODB-2 and purified tannin extracts: (a) mimosa extract (MIM) (b) mimosa sulphite extract (MIM-S) (c) grape seed extract (GSE)

4.6.5.2 Colour-forming reaction of ODB-2 and tannin in dispersion

The results of the dispersion test according to the procedure described in section 4.2.2 are presented in **Figure 66**. The composition of the aqueous dispersion includes ODB-2, 10% PVA, and water. About 1g of this dispersion was thoroughly mixed with the tannin samples for this evaluation. Dispersion prepared with mimosa extract (MIM), mimosa sulphite extract (MIM-S), and grape seed extract (GSE) showed no colour reaction in the aqueous state. The suspensions had the colour of the phenol samples. After drying, a grey/black discolouration was observed. Only MIM showed a somewhat coloured reaction. It may be suggested that MIM-S and GSE underwent thermal degradation leading to burning and darkening.

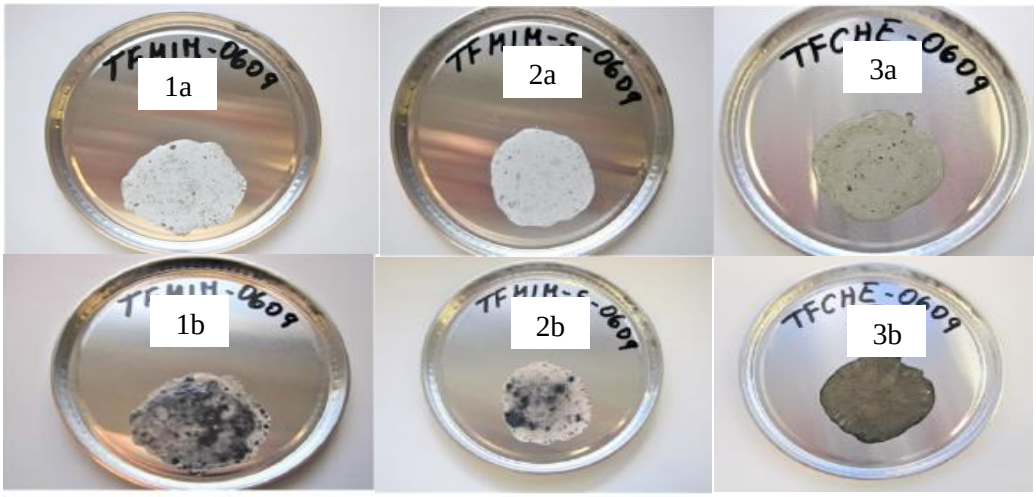


Figure 66. Interaction of ODB-2 and tannin in a dispersion. (1a) mimosa extract (MIM) in wet dispersion, (2a) mimosa sulphite extract (MIM-S) in wet dispersion, (3a) grape seed extract (GSE) in wet dispersion, (1b) mimosa extract (MIM) in dried dispersion, (2b) mimosa sulphite extract (MIM-S) in dried dispersion, and (3b) grape seed extract (GSE) in dried dispersion

The phenol-amine complexes produced from tannic acid (TA-H), mimosa extract (MIM-H), and mimosa-sulphite extract (MIM-H) were grey in the wet dispersion. On drying at 120ºC, brownish colour appeared. TA-H, MIM-H, and MIM-H did not react with ODB-2 to form the expected black colour. An increase in the treatment temperature to 180ºC - 200ºC led to dark colouration. This colour may be attributed to the chemical degradation of the tannin compound (**Figure 67**). The resorcinol-amine complex (RES-H) produced a grey colouration different from the off-white appearance in wet dispersion when dried at about 150ºC–160ºC. RES-H melted at about 163ºC to produce a black colour. The black colour signified a reaction with ODB-2.

The dispersion prepared from the polymer of mimosa extract (MIM-CP2) and mimosa sulphite extract (MIM-S-CP2) appeared light brown taking the colours of the polymers. In the wet dispersion, no reaction was observed. However, after drying to 120ºC – 125ºC, a slight grey/green discolouration was detected, which signified a reaction had taken place (**Figure 68**). However, the samples did not melt, which confirmed the characteristic high thermal stability.

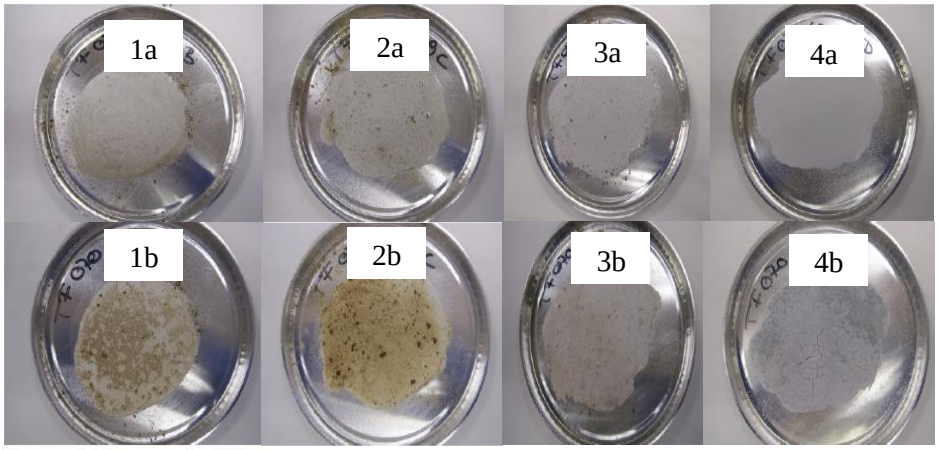


Figure 67. Interaction of ODB-2 and phenol-amine complex in a dispersion. (1a) tannic acid-amine complex (TA-H) in wet dispersion (2a) mimosa sulphite extract (MIM-S) in wet dispersion, (3a) mimosa extract (MIM) in wet dispersion, (4a) resorcinol-amine complex in wet dispersion, (1b) tannic acid-amine complex (TA-H) in dried dispersion, (2b) mimosa sulphite extract (MIM-S) in dried dispersion, (3b) mimosa extract (MIM) in dried dispersion, and (4b) resorcinol-amine complex in dried dispersion

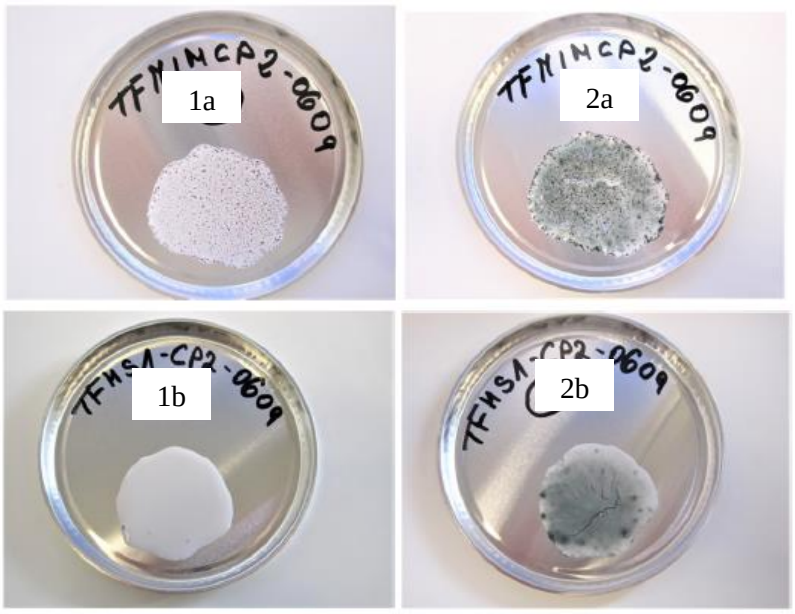


Figure 68. Interaction of ODB-2 and phenol polymer in a dispersion. (1a) mimosa-glyoxal polymer at pH 2 (MIMCP2) in wet dispersion (2a) mimosa sulphite-glyoxal polymer at pH 2 (MIM-S-CP2) in wet dispersion, (1b) mimosa-glyoxal polymer at pH 2 (MIMCP2) in dried dispersion, (2b) mimosa sulphite-glyoxal polymer at pH 2 (MIM-S-CP2) in dried dispersion.

The tannic acid polymer, TA-CP2, was a glassy solid. Therefore, it could not be grounded into fine solid. Similar to MIM, there was no reaction in the wet dispersion. However, drying to about 120^{o}C - 130^{o}C produced a slight grey discolouration without melting (**Figure 69**).

Figure 69. Interaction of ODB-2 and phenol polymer in a dispersion. (1a) tannic acid-glyoxal polymer at pH 2 (TA-CP2) in wet dispersion, and (1b) tannic acid-glyoxal polymer at pH 2 (TA-CP2) in dried dispersion

The polymer synthesised from grape seed extracts, GSE-CP2 and GSE-CP9, the dispersions produced were off-white **(Figure 70).** There was no reaction in the wet dispersion. On heating, GSE-CP2 and GSE-CP9 showed a possible interaction with ODB-2 around 170^{o}C - 180^{o}C. These interactions suggested the potential suitability of these polymers as developers in thermal paper.

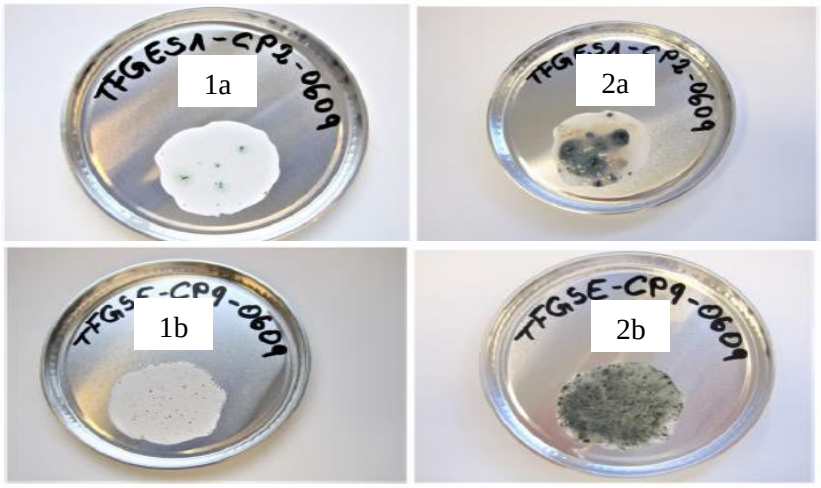


Figure 70. Interaction of ODB-2 and phenol polymer in a dispersion. (1a) grape seed extract-glyoxal polymer at pH 2 (GSE-CP2) in wet dispersion (2a) grape seed extract-glyoxal polymer at pH 9 (MIM-S-CP9) in wet dispersion, (1b) grape seed extract-glyoxal polymer at pH 2 (GSE-CP2) in dried dispersion, (2b grape seed extract-glyoxal polymer at pH 2 (GSE-CP9) in dried dispersion

Phloroglucinol-glyoxal polymers also showed a slight reaction with ODB-2 in the dried dispersion (**Figure 71**). PH-CP2, PHCP2-12, PHCP2-25, and PHCP2-40 showed no reaction in the wet dispersion. On drying at 120^{o}C, PH-CP2, PHCP2-12, and PHCP2-40 showed only a weak reaction with ODB-2 with the slightly grey colouration. On the other hand, PHCP2-25 showed no reaction with ODB-2. All PH-CP2 samples did not, however, melt on heating. These polymeric samples showed high thermal stability.

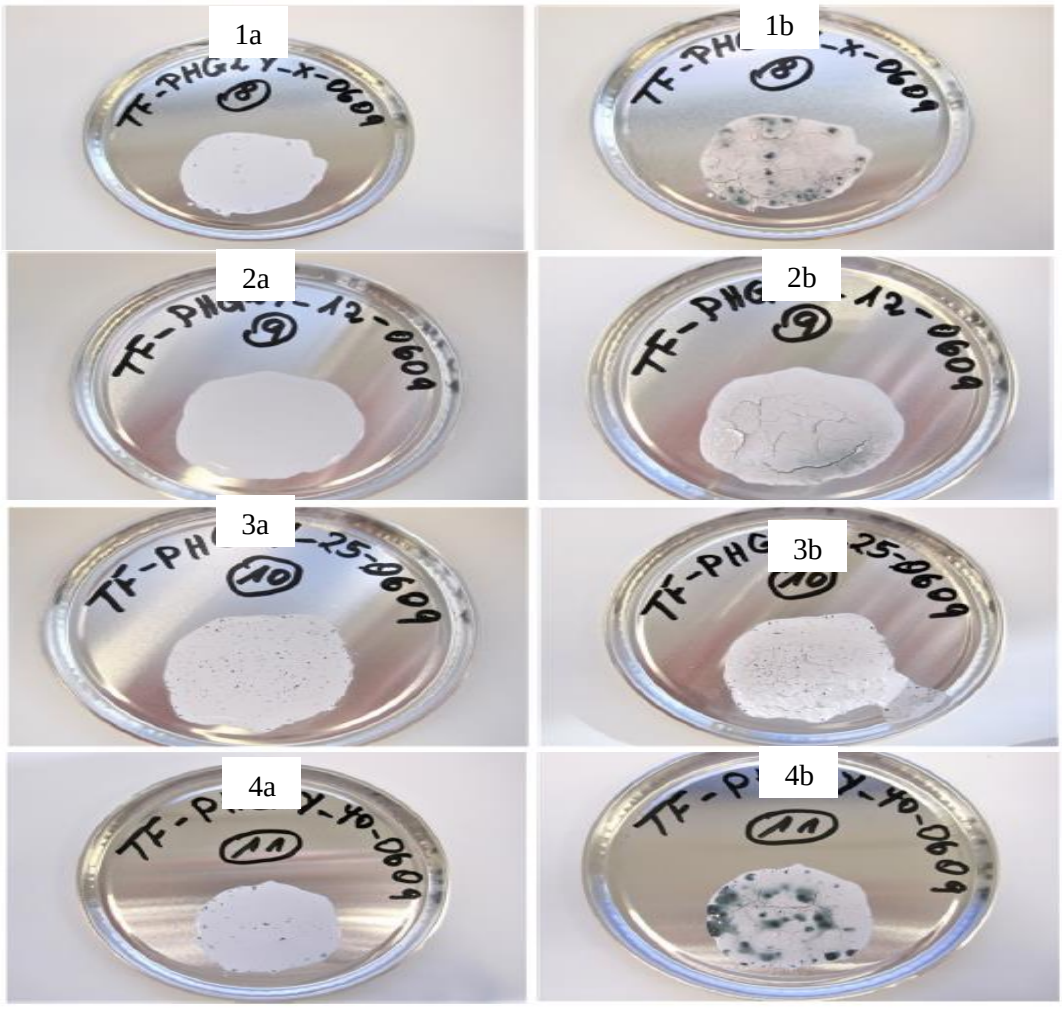


Figure 71. Interaction of ODB-2 and phloroglucinol polymer produced at pH 2 in a dispersion. (1a) PHCP2 in wet dispersion, (2a) PHCP2-12 in wet dispersion, (3a) PHCP2-25 in wet dispersion, (4a) PHCP2-40 in wet dispersion, (1b) PHCP2 in dried dispersion, (2b) PHCP2-12 in dried dispersion, (3b) PHCP2-25 in dried dispersion, (4b) PHCP2-40 in dried dispersion.

4.7 Colour density of green developer-based mixtures

The quantitative evaluation of the colour formed from the mixture of green developers and ODB-2 was carried out by measuring the colour density values. The values obtained were compared to the colour density obtained from mixtures produced with BPA as a developer.

4.7.1 Colour density of the mixture of ODB-2 and phenol compounds

Figure 72 shows the colour densities after heating the mixture of ODB-2 and tannin polymers such as MIM-CP2, MIM-CP2-S, GSE-CP2, GSE-CP9, PH-CP2, and resorcinol-amine complex RES-H.

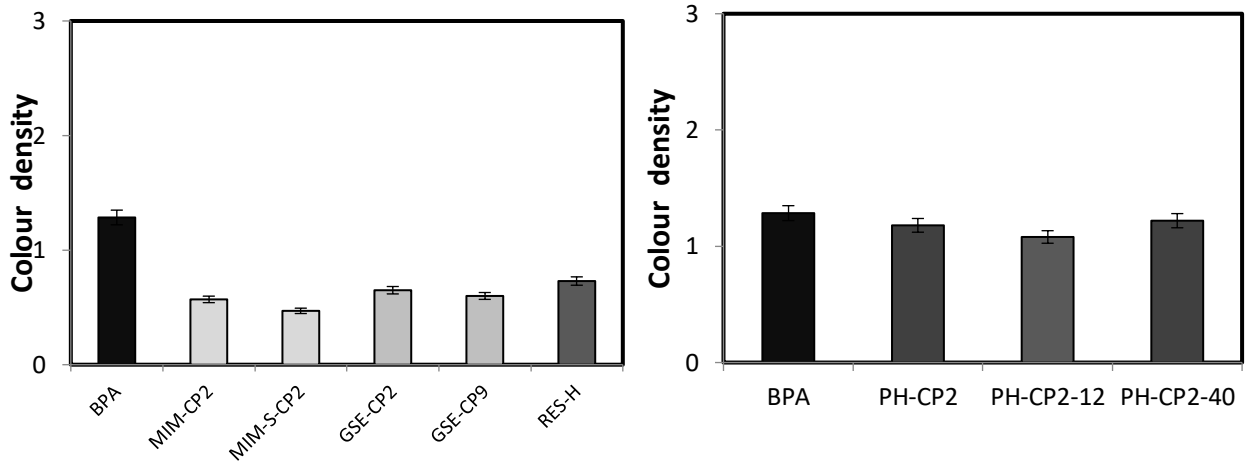


Figure 72. Colour densities of phenol-amine complexes and phenol polymers

The density of RES-H (0.7) was higher than those of MIM-CP2 (0.57), MIM-CP2-S (0.47), GSE-CP2 (0.65), GSE-CP9 (0.6) but still lower than that of BPA (1.2). The densities of PH-CP2, PH-CP2-12, and PH-CP2-40 were 1.18, 1.08, and 1.22, respectively.

Figures 73-77 show the dependency of colour density on the ratio of developer to dye. Colour density achieved increased with an increase in the amount of developers. After aging for 24 hours at 25ºC/50% R.H, all samples showed only slight change in their colour density. In the same vein. The colours were relatively stable over 10 days.

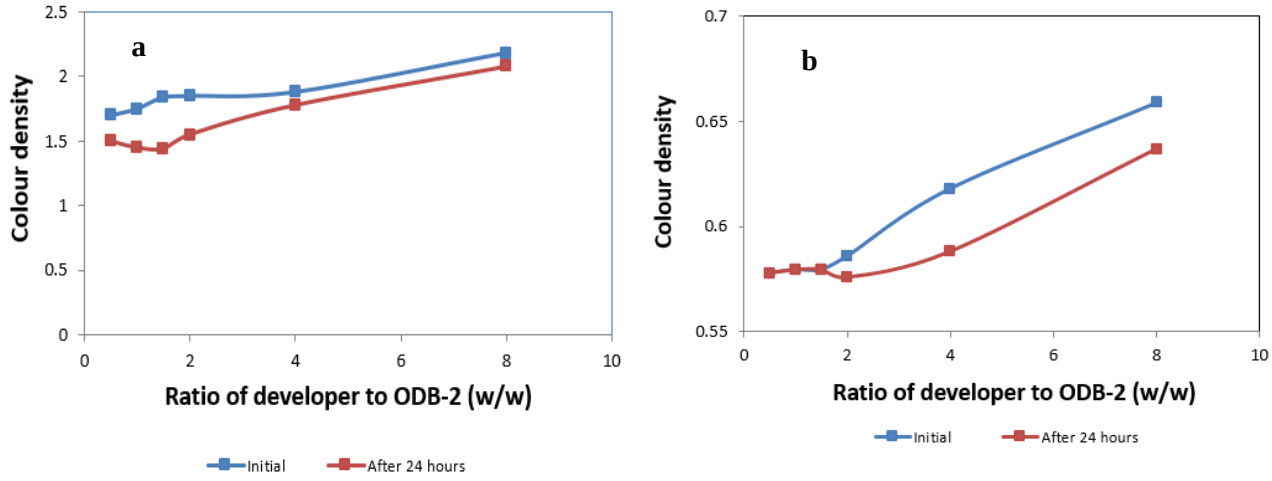


Figure 73. Colour density of (a) RES-H, and (b) MIM-CP2 before and after aging for 24 hours at 25oC/50% R.H.

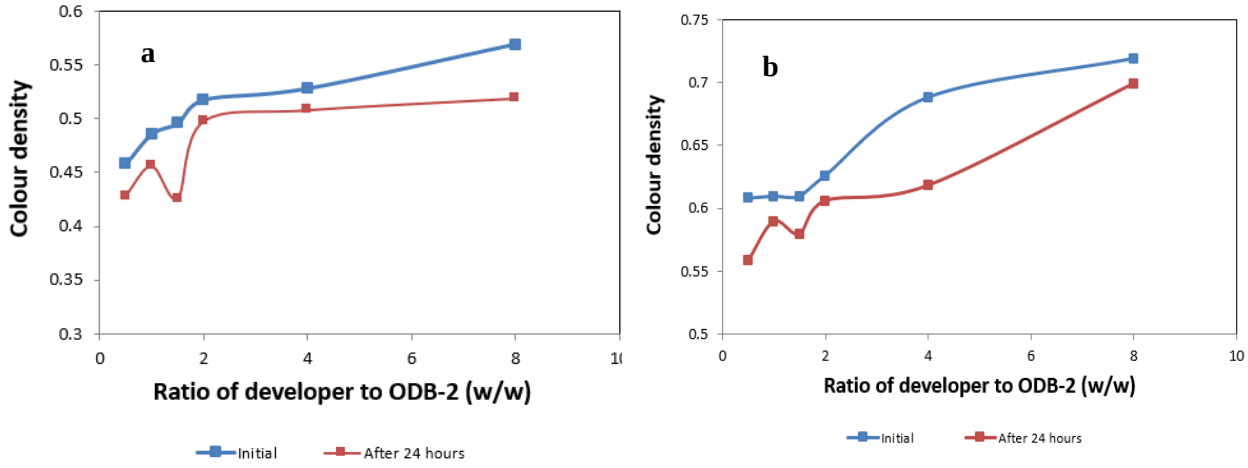


Figure 74. Colour density of (a) MIM-S-CP2, and (b) GSE-CP9 before and after aging for 24 hours at 25°C/50% R.H.

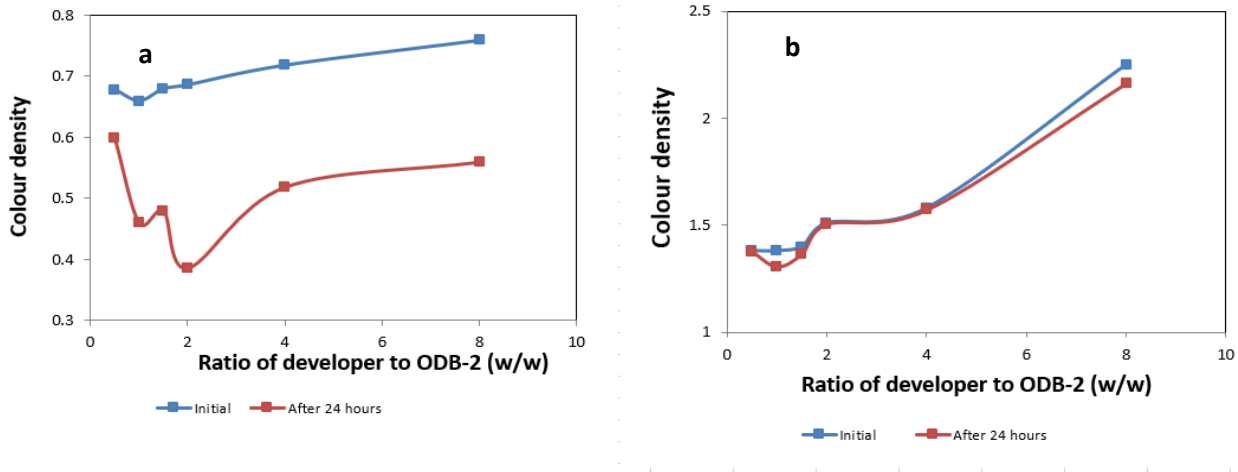


Figure 75. Colour density of (a) GSE-CP2, (b) PH-CP2 before and after aging for 24 hours at 25°C/50% R.H.

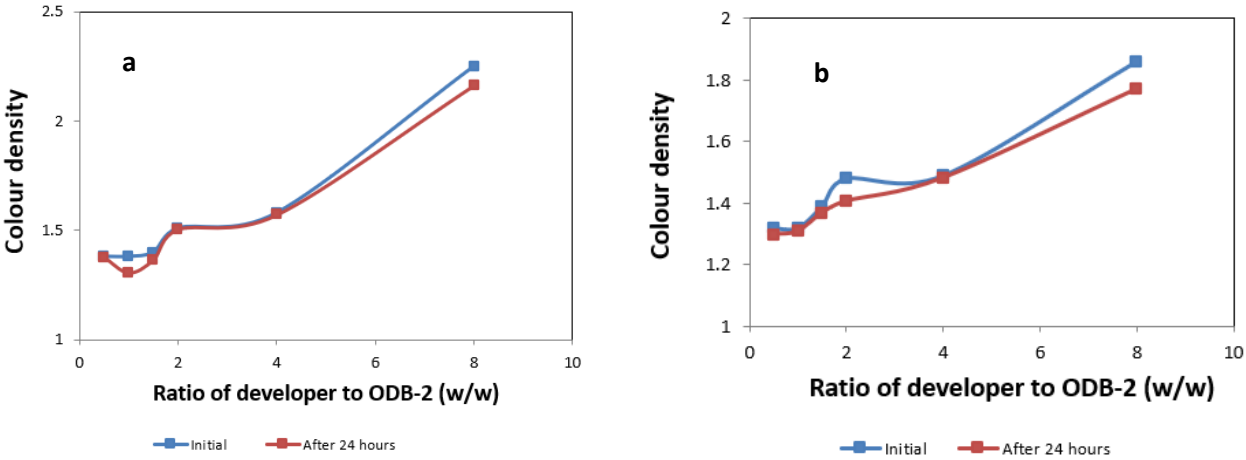


Figure 76. Colour density of (a) PH-CP2-12, and (b) PH-CP2-40 before and after aging for 24 hours at 25°C/50% R.H.

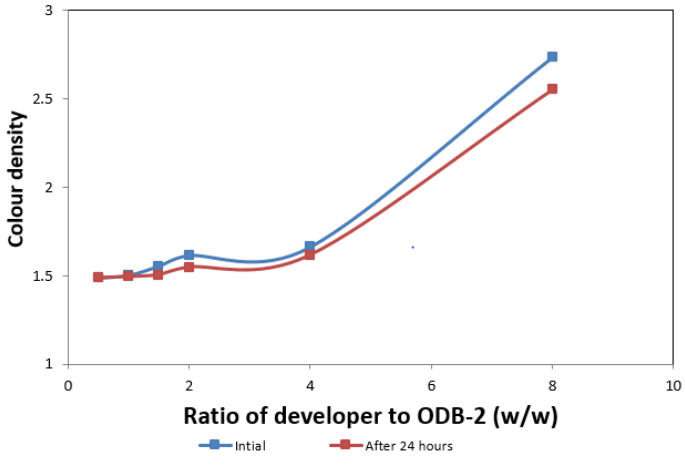


Figure 77. Colour density of BPA before and after aging for 24 hours at 25°C/50% R.H.

4.8 Colour density of the mixture of ODB-2 and plural developers.

To enhance image density and image stability, the use of plural developers in colour forming formulation was explored. The descriptions of the samples are shown in the appendix (page 182).

4.8.1 Colour density of the mixture of vanillin and vanillic acid

The first experiments focused on using a mixture of the monomeric phenols, vanillin, and vanillic acid (VV) as developers. The phenolic compounds were mixed sequentially in mole ratios 1:1, 1:2, 1:3, 1:4, and 1:6. The weight of ODB-2, PVA, and tetradecanol solvents were kept constant for all samples at 0.05g, 2.5g, and 5g, respectively. The colour densities immediately after colour formation and after 24 h in 50% R.H at 25^{o}C are shown in **Table 18** and **Figure 78**. The variation of the colour density for 10 days was also monitored (**Figure 79).**

Table 18. Colour density of colour-forming mixtures with vanillin and vanillic acid as developer and co-developer.

*Sample code	Colour density immediately	Colour density after 24h	Colour density after one week	Moisture resistance (%)
VV1	1.63	1.21	0.81	77.95
VV2	1.38	0.94	0.92	74.14
VV3	1.91	1.87	0.62	91.13
VV4	1.73	1.71	0.78	99.32
VV5	1.75	1.71	0.93	96.03
VV6	1.71	1.53	0.62	87.94
VV7	1.73	1.46	1.14	83.42
VV8	1.65	1.35	0.91	81.43
VV9	1.56	1.32	0.91	85.91

The colour densities of the mixtures ranged from 1.38 to 1.9. The highest colour density for VV3 prepared from the combination of vanillin and vanillic acid in mole ratio 3:1 was 1.9. The average colour density was 1.6. The densities of the mixtures did not follow a particular trend. After 24 hours in 50% relative humidity condition, the densities of VV1 and VV2 reduced to about 25 % of the original values. VV1, VV2, VV6, VV7,

VV8, and VV9 had moisture resistance of 77.9%, 74.1%, 88%, 83.3%, 81.4%, and 86%, respectively. The colours of VV3, VV4, and VV5 were relatively more stable than the other samples. They showed higher resistance to moisture with 91%, 99%, and 96%, respectively. Over 10 days, the gradual fading of the coloured mixtures was noticeable. During this period, an average of 56% of the initial colour densities was lost. This was attributed to the water solubility of the phenol monomers. In comparison, the mixture containing BPA only retained 80% of its initial colour strength after 10 days.

Figure 78. Colour density and moisture resistance of a colour forming composition with a mixture of vanillin and vanillic acid as developer. VV = mixture of vanillin and vanillic acid.

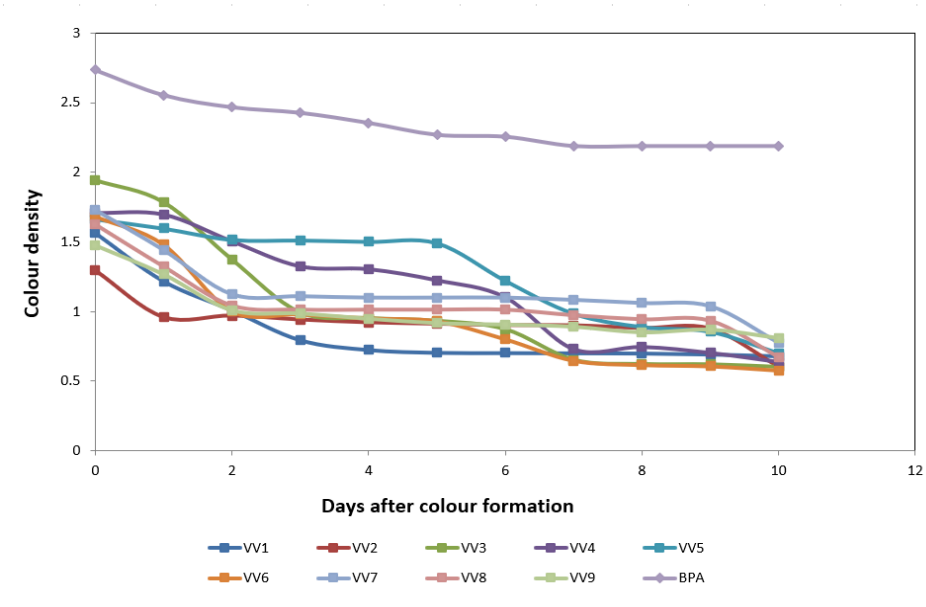


Figure 79. Variation of colour density of colour forming composition with vanillin and vanillic acid mixture as a developer over 10 days. VV = mixture of vanillin and vanillic acid.

4.8.2 Colour density of the mixture of phenol-amine complex with co-developers

The performance of resorcinol-amine complex (RES-H) in a colour-forming mixture containing other co-developers was evaluated by measuring the density of colour formed immediately and the stability for 10 days. The resorcinol-amine complex (RES-H) was mixed with vanillic acid, vanillin, citric acid, ascorbic acid, salicylic acid, and tannic acid in varying ratios produce RESH-VA, RESH-V, RESH-CA, RESH-AS, RESH-SLY, and RESH-TA respectively. The weight of ODB-2, PVA, and tetradecanol solvents were kept constant for all samples at 0.05g, 2.5g, and 5g, respectively. The compositions of the samples are shown in the appendix***.***

As shown in **Table 19,** the highest colour density of the coloured products recorded for RESH-VA4 (1.84), a colour forming mixture produced by the addition of 20% vanillic acid to 30% RES-H. All other samples showed similar colour densities ranging between 1.43–1.75. After 24 hours at room temperature at 50%R.H, the colours were relatively stable. This was evident with the high values of moisture resistance between 91.5 (RESH-VA7) – 99% (RESH-VA1).

Table 19**.** Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and vanillic acid as developer and co-developer, respectively

*Sample code	Colour density immediately	Colour density after 24hr	Colour density after one week	Moisture resistance (%)
RES-H-VA1	1.64	1.63	1.56	99.61
RES-H -VA2	1.66	1.64	1.59	98.32
RES-H -VA3	1.75	1.73	1.54	98.85
RES-H -VA4	1.84	1.81	1.51	98.21
RES-H -VA5	1.65	1.64	1.61	99.34
RES-H -VA6	1.73	1.61	1.22	92.38
RES-H -VA7	1.65	1.51	1.33	91.52
RES-H -VA8	1.43	1.34	1.01	93.72
RES-H -VA9	1.60	1.52	1.39	93.68

**See the appendix (page 174) for the description of the samples.*

In the presence of vanillin, higher colour densities ranging from 1.78 – 2.19 were recorded. RESH-V4 and RESH-V5 showed the highest values of 2.18 and 2.19, respectively (**Table 20**). The density of samples containing tannic acid was in the range of 2.55 (RESH-TA8) – 2.07 (RESH-TA4). Moisture resistance after 24 hours was in the range of 58.6% (RESH-TA) – 99.8% (RESH-TA5). RESH-TA samples showed the highest densities compared to others with phenol and other organic acids (**Table 21**). Amongst the organic carboxylic acids, the addition of citric acid yielded the highest density. The Colour density of RESH-CA samples ranged from 1.89 – 1.99. RES-SLY and RESH-AS samples ranged from 1.69 – 1.77 and 0.8 – 1.42, respectively **(Table 22 – 24)**. After 24 hours, only RESH-AS9 dropped below 50% of its original value.

Table 20. Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and vanillin as developer and co-developer, respectively

*Sample code	Colour density immediately	Colour density after 24hr	Colour density after one week	Moisture resistance (%)
RES-H-V1	2.12	1.66	1.53	78.31
RES-H -V2	2.11	1.59	1.5	75.71
RES-H -V3	2.19	1.59	1.04	72.60
RES-H -V4	2.18	1.7	1.51	77.98
RES-H -V5	2.19	1.65	1.5	75.34
RES-H -V6	1.85	1.8	1.58	97.29
RES-H -V7	1.78	1.65	1.44	92.69
RES-H -V8	1.92	1.81	1.6	94.27
RES-H -V9	1.89	1.78	1.43	94.18

**See the appendix (page 174) for the description of the samples.*

Table 21. Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and tannic acid as developer and co-developer, respectively.

*Sample code	Colour density immediately	Colour density after 24hr	Colour density after one week	Moisture resistance (%)
RES-H-TA1	2.11	1.62	1.61	77.14
RES-H - TA2	2.11	1.61	1.55	76.19
RES-H - TA3	2.07	2.01	2.00	96.29
RES-H - TA4	2.07	1.59	1.55	76.81
RES-H - TA5	2.21	2.20	2.11	99.83
RES-H - TA6	2.43	2.31	2.11	95.06
RES-H - TA7	2.34	2.10	1.89	89.74
RES-H - TA8	2.55	2.31	1.78	90.19
RES-H - TA9	2.11	1.23	0.89	58.57

**See the appendix (page 174) for the description of the samples.*

Table 22. Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and citric acid as developer and co-developer, respectively.

*Sample code	Colour density immediately	Colour density after 24hr	Colour density after one week	Moisture resistance (%)
RES-H-CA1	1.94	1.90	1.87	97.94
RES-H - CA2	1.93	1.91	1.91	98.96
RES-H - CA3	1.91	1.90	1.81	99.48
RES-H -CA4	1.94	1.91	1.78	98.46
RES-H - CA5	1.90	1.88	1.88	98.89
RES-H - CA6	1.89	1.85	1.80	97.88
RES-H - CA7	1.97	1.96	1.80	99.49
RES-H - CA8	1.96	1.92	1.80	97.96
RES-H - CA9	1.99	1.92	1.80	96.48

**See the appendix (page 174) for the description of the samples.*

Table 23. Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and ascorbic acid as developer and co-developer, respectively.

*Sample code	Colour density immediately	Colour density after 24hr	Colour density after one week	Moisture resistance (%)
RES-H-AS1	1.54	1.42	1.24	92.21
RES-H - AS2	1.47	1.31	1.1	89.12
RES-H - AS3	1.47	1.12	1.06	76.14
RES-H - AS4	1.45	1.09	1.00	75.17
RES-H - AS5	1.39	1.11	0.74	79.14
RES-H - AS6	1.46	1.02	0.66	69.86
RES-H - AS7	1.44	1.11	0.66	77.08
RES-H - AS8	1.47	0.91	0.33	61.22
RES-H - AS9	1.48	0.81	0.61	54.05

**See the appendix (page 174) for the description of the samples.*

Table 24**.** Colour density of colour-forming mixture with resorcinol-amine complex (RES-H) and salicylic acid as developer and co-developer, respectively

*Sample code	Colour density immediately	Colour density after 24hr	Colour density after one week	Moisture resistance (%)
RES-H-SLY1	1.69	1.51	1.31	88.76
RES-H-SLY2	1.67	1.31	1.27	77.84
RES-H-SLY3	1.67	1.60	1.51	95.81
RES-H-SLY4	1.66	1.62	1.45	96.39
RES-H-SLY5	1.76	1.71	1.52	97.16
RES-H-SLY6	1.77	1.72	1.65	96.04
RES-H-SLY7	1.72	1.77	1.63	98.83
RES-H-SLY8	1.70	1.66	1.62	97.65
RES-H-SLY9	1.71	1.62	1.41	94.74

**See the appendix (page 174) for the description of the samples.*

Over 10 days, the colour of RESH-VA4 was reduced by a further 20%. The densities of RESH-VA1 and RESH-VA2 were decreased by 8% (**Figure 80**). The highest reduction in colour density was observed in RESH-VA9, with about 50% of the original colour left after 10 days. In contrast, the densities of RESH-V samples were almost similar all through the first 9 days. After the tenth day, all samples showed an average reduction in the density of 30%. Only RESH-V3 showed a decrease in density up to 53%. RESH-TA samples generally showed about 50% resistance after 10 days.

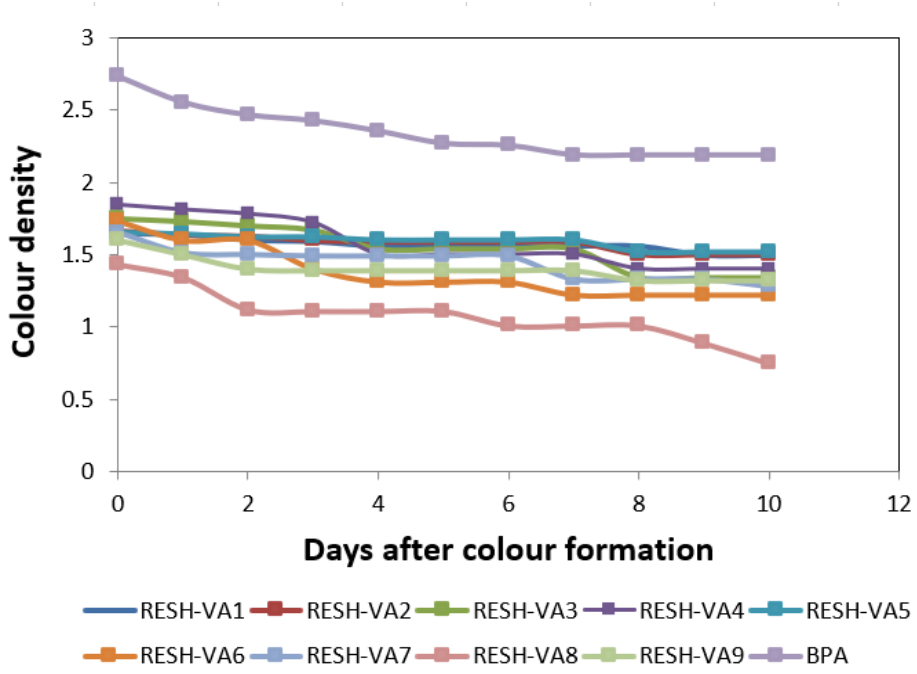


Figure 80. Variation of colour density of colour forming compositions with a mixture of resorcinol-amine complex and vanillic acid as developer over 10 days. The compositions of RESH-VA1 – RESH-VA9 are presented in the appendix (page 174).

4.8.3 Colour density of the mixture of phenol polymers with co-developers

The addition of vanillic acid or vanillin to phloroglucinol polymer (PHCP2) significantly increased the polymer's colour density. The colour density of PHCP2-VA samples ranged between 2.07 – 2.17, while PHCP2-V ranged between 2.95 and 4.69. In the presence of tannic acid and other organic carboxylic acids, such as citric acid, ascorbic acid, and salicylic acid, colour densities were similar (**Table 25-30**). During the first 5 days, most samples remain relatively stable while few reduced in density steadily. There were not large differences recorded when vanillic acid was added in a varying amount to PHCP2-12.

Table 25. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and vanillic acid as co-developer.

Sample code	Colour density immediately	Colour density after 24 hr	Colour density after one week	Moisture Resistance (%)
PHCP2-VA1	2.08	2.08	1.32	99.78
PHCP2-VA2	2.16	2.05	2.00	95.10
PHCP2-VA3	2.13	2.11	2.10	99.16
PHCP2-VA4	2.17	2.15	2.10	99.16
PHCP2-VA5	2.17	2.11	1.19	96.97
PHCP2-VA6	2.13	2.10	1.70	98.41
PHCP2-VA7	2.21	2.12	1.52	95.91
PHCP2-VA8	2.13	2.12	2.00	99.58
PHCP2-VA9	2.12	2.05	1.87	96.91

**See the appendix (page 174) for the description of the samples.*

Table 26. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and vanillin as co-developer.

Sample code	Colour density immediately	Colour density after 24 hr	Colour density after one week	Moisture Resistance (%)
PHCP2-V1	4.70	4.66	4.66	99.17
PHCP2-V2	2.95	2.21	2.21	74.58
PHCP2-V3	3.76	3.31	3.31	87.54
PHCP2-V4	4.70	4.10	4.10	87.17
PHCP2-V5	3.31	2.14	2.14	64.85
PHCP2-V6	4.12	3.89	3.89	94.42
PHCP2-V7	4.32	4.01	4.01	92.76
PHCP2-V8	2.98	2.09	2.09	70.41
PHCP2-V9	3.78	3.38	3.38	89.60

**See the appendix (page 174) for the description of the samples.*

Table 27. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and tannic acid as co-developer.

Sample code	Colour density immediately	Colour density after 24 hr	Colour density after one week	Moisture Resistance (%)
PHCP2-TA1	4.32	2.42	2.42	56.01
PHCP2-TA2	4.24	2.33	2.33	55.02
PHCP2-TA3	4.56	4.32	4.32	94.76
PHCP2-TA4	4.39	4.12	4.12	93.85
PHCP2-TA5	4.78	4.53	4.53	94.67
PHCP2-TA6	4.01	3.97	3.97	99.00
PHCP2-TA7	4.22	4.12	4.12	97.63
PHCP2-TA8	4.38	4.21	4.21	96.20
PHCP2-TA9	4.98	4.71	4.71	94.61

**See the appendix (page 174) for the description of the samples.*

Table 28. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and citric acid as co-developer.

Sample code	Colour density immediately	Colour density after 24 hr	Colour density after one week	Moisture Resistance (%)
PHCP2-CA1	4.72	3.42	3.42	72.46
PHCP2-CA2	4.42	3.33	3.33	75.25
PHCP2-CA3	4.32	3.32	3.32	76.84
PHCP2-CA4	4.12	3.12	2.22	75.66
PHCP2-CA5	4.32	3.53	3.13	81.72
PHCP2-CA6	4.23	2.96	1.76	70.18
PHCP2-CA7	4.56	4.12	3.82	90.39
PHCP2-CA8	4.39	4.21	3.41	95.91
PHCP2-CA9	4.78	4.71	3.55	98.46

**See the appendix (page 174) for the description of the samples.*

Table 29. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and ascorbic acid as co-developer.

Sample code	Colour density Immediately	Colour density after 24 hr	Colour density after one week	Moisture Resistance (%)
PHCP2-AS1	3.01	2.08	1.68	68.89
PHCP2-AS2	3.22	2.05	1.65	63.75
PHCP2-AS3	4.38	2.11	1.71	48.15
PHCP2-AS4	2.98	2.15	1.45	72.19
PHCP2-AS5	3.12	2.11	1.33	67.59
PHCP2-AS6	3.32	2.10	1.76	63.10
PHCP2-AS7	2.98	1.92	1.52	64.46
PHCP2-AS8	3.78	2.12	1.72	56.16
PHCP2-AS9	2.32	2.05	1.83	88.52

**See the appendix (page 174) for the description of the samples.*

Table 30. Colour density of colour-forming mixture with phloroglucinol-glyoxal polymer (PHCP2) as developer and salicylic acid as co-developer.

Sample code	Colour density Immediately	Colour density after 24 hr	Colour density after one week	Moisture Resistance (%)
PHCP2-SLY1	4.24	4.21	3.72	99.41
PHCP2-SLY2	4.56	4.45	3.15	97.59
PHCP2-SLY3	3.40	3.21	2.41	94.61
PHCP2-SLY4	4.30	4.21	3.11	95.99
PHCP2-SLY5	3.87	3.77	3.00	97.41
PHCP2-SLY6	4.32	4.21	3.30	97.41
PHCP2-SLY7	4.08	3.91	2.57	95.83
PHCP2-SLY8	4.18	4.01	3.32	95.69
PHCP2-SLY9	4.32	4.31	3.21	99.77

**See the appendix (page 174) for the description of the samples.*

At the end of 10 days, a 40% - 50% reduction in the density of most of the measured samples (**Figure 81 & 82**).

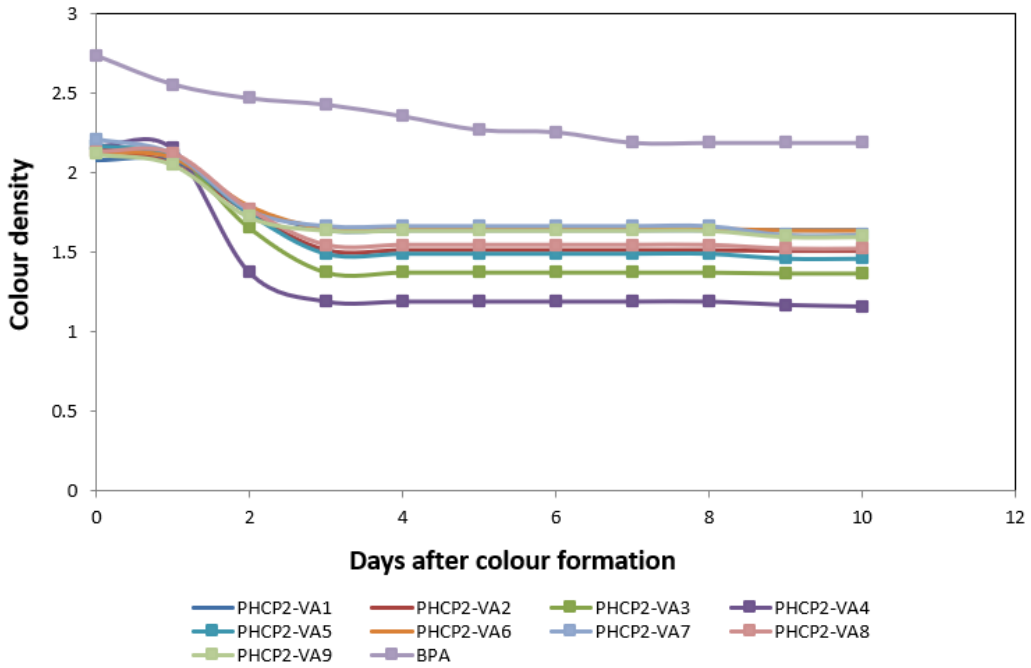


Figure 81. Variation of colour density of colour forming compositions with a mixture of phloroglucinol-glyoxal polymer (PHCP2) and vanillic acid as developer over 10 days. The compositions of PHCP2-VA1 – PHCP2-VA9 are shown in appendix (page 173).

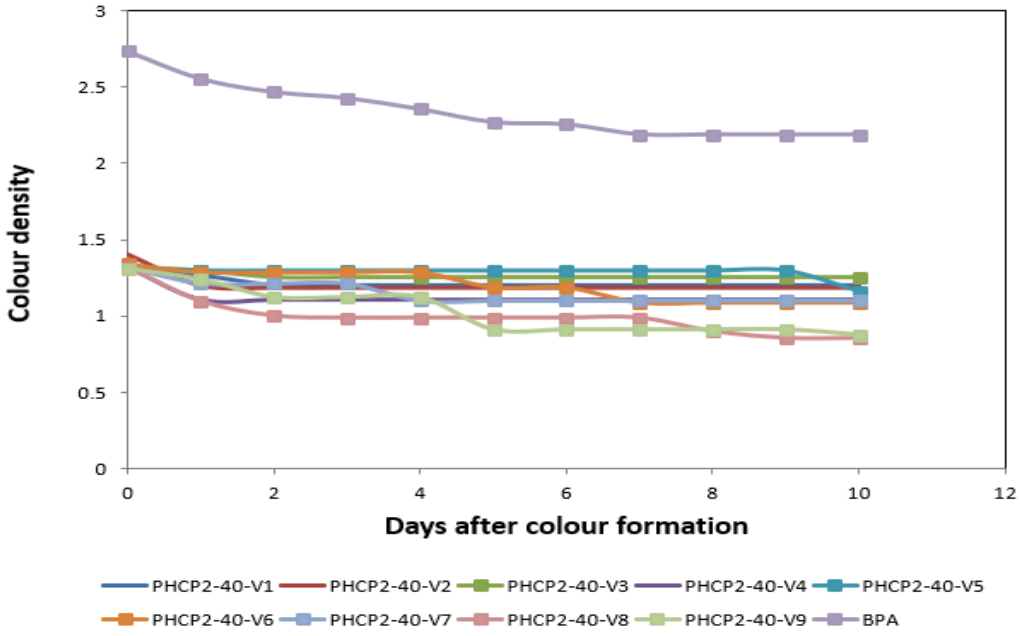


Figure 82. Variation of colour density of colour forming compositions with a mixture of phloroglucinol-glyoxal polymer (PHCP2-40) and vanillin as developer over 10 days. The compositions of PHCP2-40-V1 – PHCP2-40-V1 are shown in the appendix (page 173).

Table 31 Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and vanillic acid as co-developer.

Sample	Colour density immediately	Colour density after 24 hours	Colour density after one week	Moisture Resistance (%)
MIM-CP2-VA1	0.37	0.2	0.12	56.8
MIM-CP2-VA2	0.33	0.22	0.09	67.6
MIM-CP2-VA3	0.33	0.26	0.16	82.3
MIM-CP2-VA4	0.34	0.23	0.13	68.5
MIM-CP2-VA5	0.37	0.26	0.08	71.1
MIM-CP2-VA6	0.37	0.28	0.09	76.6
MIM-CP2-VA7	0.38	0.23	0.13	59.7
MIM-CP2-VA8	0.36	0.21	0.11	59.1
MIM-CP2-VA9	0.39	0.26	0.19	67.4

**See the appendix (page 174) for the description of the samples.*

Table 32 Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and vanillin as co-developer.

Sample	Colour density immediately	Colour density after 24 hours	Colour density after one week	Moisture Resistance (%)
MIM-CP2-V1	0.33	0.15	0.11	45.7
MIM-CP2-V2	0.34	0.21	0.10	59.2
MIM-CP2-V3	0.32	0.21	0.11	62.9
MIM-CP2-V4	0.32	0.14	0.07	45.5
MIM-CP2-V5	0.35	0.21	0.11	60.3
MIM-CP2-V6	0.35	0.29	0.13	83.3
MIM-CP2-V7	0.37	0.32	0.07	87.0
MIM-CP2-V8	0.32	0.23	0.16	72.3
MIM-CP2-V9	0.38	0.21	0.12	55.5

**See the appendix (page 174) for the description of the samples.*

Table 33 Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and tannic acid as co-developer.

Sample	Colour density immediately	Colour density after 24 hours	Colour density after one week	Moisture Resistance (%)
MIM-CP2-TA1	0.44	0.33	0.14	75.0
MIM-CP2-TA2	0.44	0.23	0.06	52.3
MIM-CP2-TA3	0.44	0.39	0.12	88.6
MIM-CP2-TA4	0.44	0.35	0.12	79.5
MIM-CP2-TA5	0.44	0.32	0.18	72.7
MIM-CP2-TA6	0.44	0.31	0.22	70.5
MIM-CP2-TA7	0.44	0.33	0.21	75.0
MIM-CP2-TA8	0.44	0.34	0.17	77.3
MIM-CP2-TA9	0.44	0.34	0.16	77.3

**See the appendix (page 174) for the description of the samples.*

Table 34 Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and citric acid as co-developer.

Sample	Colour density immediately	Colour density after 24 hours	Colour density after one week	Moisture Resistance (%)
MIM-CP2-CA1	0.51	0.40	0.18	79.0
MIM-CP2-CA2	0.51	0.38	0.21	74.4
MIM-CP2-CA3	0.51	0.27	0.15	53.1
MIM-CP2-CA4	0.51	0.28	0.16	54.1
MIM-CP2-CA5	0.51	0.27	0.14	53.7
MIM-CP2-CA6	0.51	0.28	0.15	55.9
MIM-CP2-CA7	0.51	0.36	0.12	69.8
MIM-CP2-CA8	0.51	0.36	0.11	69.8
MIM-CP2-CA9	0.51	0.48	0.13	93.3

**See the appendix (page 174) for the description of the samples.*

Table 35 Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and ascorbic acid as co-developer.

Sample	Colour density immediately	Colour density after 24 hours	Colour density after one week	Moisture Resistance (%)
MIM-CP2-AS1	0.33	0.29	0.14	87.9
MIM-CP2-AS2	0.33	0.27	0.11	81.8
MIM-CP2-AS3	0.33	0.19	0.12	57.6
MIM-CP2-AS4	0.33	0.12	0.03	31.5
MIM-CP2-AS5	0.33	0.11	0.03	34.2
MIM-CP2-AS6	0.33	0.13	0.04	40.9
MIM-CP2-AS7	0.33	0.12	0.03	35.4
MIM-CP2-AS8	0.33	0.12	0.02	33.0
MIM-CP2-AS9	0.33	0.22	0.11	66.4

**See the appendix (page 174) for the description of the samples.*

Table 36 Colour density of colour-forming mixture with mimosa extract-glyoxal polymer (MIM-CP2) as a developer and salicylic acid as co-developer.

Sample	Colour density immediately	Colour density after 24 hours	Colour density after one week	Moisture Resistance (%)
MIM-CP2-SLY1	0.48	0.31	0.10	64.6
MIM-CP2-SLY2	0.48	0.33	0.11	69.0
MIM-CP2-SLY3	0.48	0.35	0.19	73.1
MIM-CP2-SLY4	0.48	0.36	0.19	75.2
MIM-CP2-SLY5	0.48	0.32	0.18	66.9
MIM-CP2-SLY6	0.48	0.31	0.14	64.8
MIM-CP2-SLY7	0.48	0.33	0.11	69.0
MIM-CP2-SLY8	0.48	0.31	0.19	64.8
MIM-CP2-SLY9	0.48	0.34	0.14	71.0

**See the appendix (page 173) for the description of the samples.*

The addition of vanillic acid to MIM-CP2 as a co-developer deepened the black colour of the phenol polymer when heated. The colour density of the mixture ranged from 0.31 (MIM-CP2-VA3) to 0.38 (MIM-CP2-VA7) **(Table 31-36)**. The average colour density of MIM-CP2-V samples was also in a similar range with MIM-CP2-VA samples. The lowest and highest colour density was observed for MIM-CP2-V4 (0.30) and MIM-CP2-V9 (0.38), respectively. The addition of tannic acid, citric acid, and salicylic acid to MIM-CP2 yielded an average colour density of 0.44, 0.51, and 0.48. There was only a minute change in the density of the samples as the ratio of combination varied. On the other hand, MIM-CP2-AS samples gave an average colour density of 0.33. This was the lowest in the evaluated batch.

After 24 hours in 50% RH at room temperature, MIM-CP2-VA showed moisture resistance of 70%. MIM-CP2-VA1, MIM-CP2-VA7, and MIM-CP2-VA8 had the lowest values with 56.8%, 59.7%, and 59.1%, respectively. MIM-CP2-V1, MIM-CP2-V4, and MIM-CP2-V5 had moisture resistances of 45.7%, 45.5%, and 55.5%, respectively. With tannic acid, only MIM-CP2-TA3 had moisture resistance beyond 80%. Other related samples showed moisture resistance of about 70% and below. For example, 40% of MIM-CP2-AS samples had moisture resistance of about 35%, while MIM-CP2-SLY and MIM-CP2-CA samples had an average moisture resistance of 70% and 62%. Organic acid samples were relatively stable. MIM-S-CP2-CA samples with moisture resistance ranging from 86% - 99% after 24 hours. MIM-S-CP2-AS samples were considerably lower, with average moisture resistance of 45%.

The above results showed that individual monomeric compounds such as vanillin, vanillic acid, and the studied organic carboxylic acids could be used as co-developers to prepare thermal paper to achieve products of varying qualities. In addition, the use of co-developers has the potential to increase the optical density of the print.

4.9 Application of green developers in thermal paper

To evaluate the practical usability of studied green developers in thermal paper, coating dispersions of the developers were produced by mixing with ODB-2 suspension and PVA. The coat was then applied on the paper substrates as the heat-sensitive layer of the resulting thermal papers. The details of the preparation of the thermal coating dispersion and thermal papers are in section 3.9. The development of black colour on the thermal papers was observed after heating with a thermal printer. The density of the print produced was compared to the density of BPA-coated thermal paper (**Figure 83)**.

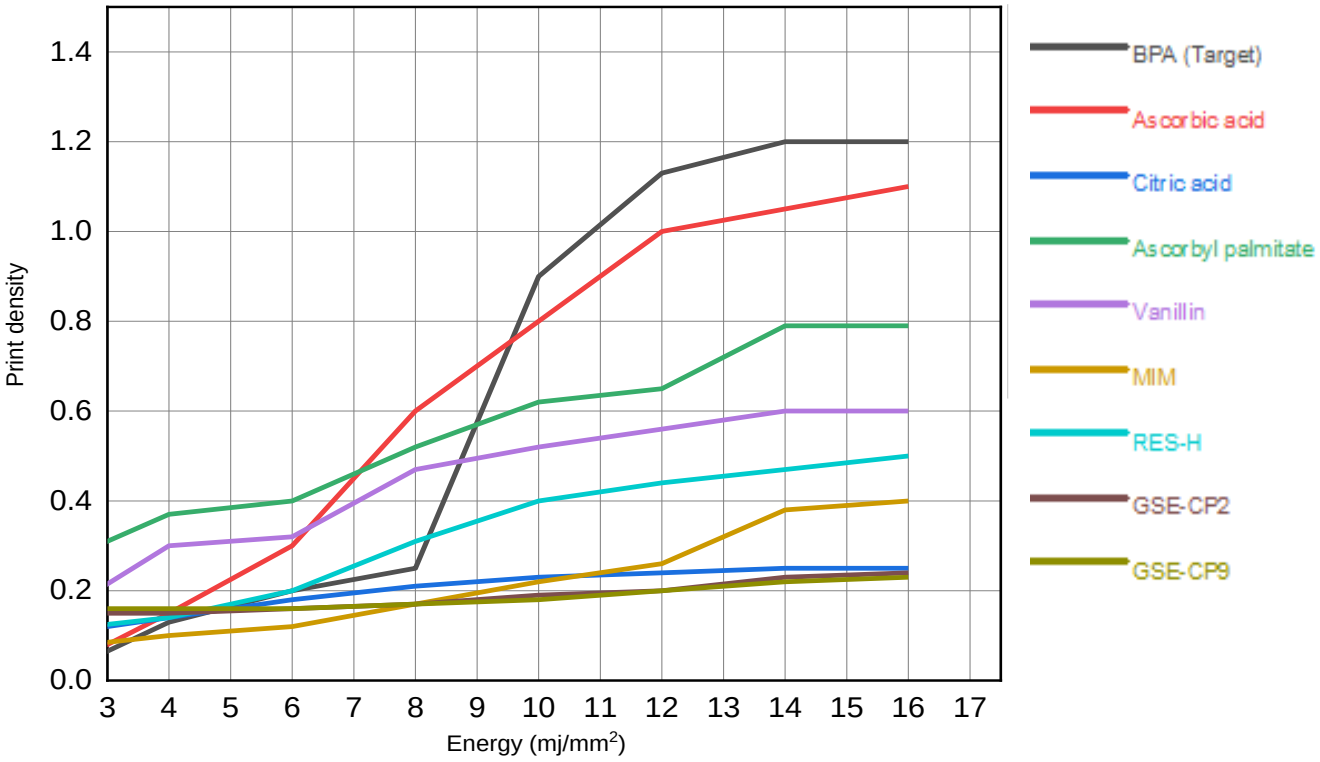


Figure 83. Thermal Printing Test: Variation of print density of green developer-based thermal papers with applied energy

4.9.1 Organic carboxylic acids-based thermal paper

Thermal paper was produced by applying dispersions containing ODB-2, PVA as well as ascorbic acid, salicylic acid, citric acid, and ascorbyl palmitate as developer on a pre-coated paper. The weight ratio between the developer and the colour former in the final coating formulation was 3.3:1. The developer and the colour former mixed very well without any visible reaction. Citric acid dissolved easily in dispersion because of its high-water solubility. Therefore, 15% aqueous citric acid solution was used without further additives. On the application of the coating, the measured whiteness of the dried paper produced with ascorbic acid was 88% under UV light. While the unprinted ascorbyl palmitate-coated paper was off-white with a whiteness of 78%, the unprinted citric acid-coated paper was greenish-grey in appearance with a whiteness of 79%.

A maximum print density of 1.1 was achieved with ascorbic acid paper on printing with the thermal printer. This value was lower than the reference value of 1.20 obtained from BPA-coated thermal paper. Evaluation of the shelf life of the colour formed showed that the colour was not stable. On exposure to humidity of 90% RH at 40^{o}C for 24h, 75% of the colour faded away. After 7 days, the print density was less than 10% of the original value. Exposure to oil such as lanolin, ethanol solvent, and water for 20min led to about 80% reduction in the colour density.

Figure 84. Thermal Printing Test: Ascorbyl-palmitate based thermal paper showing the print density.

In comparison, ascorbyl palmitate and citric acid produced maximum print densities of 0.79 and 0.25, respectively. In addition, the printout of citric acid paper was not legible enough, and the background colour caused a very poor contrast between the printed and unprinted paper. Therefore, citric acid may not be suitable as a developer. On the other hand, the print of ascorbyl palmitate-coated paper was solid, legible, and relatively stable. (**Figure 84**).

4.9.2 Monomeric phenols-based thermal paper

Vanillin, vanillic acid, isovanillin, and isovanillic were used as developers to prepare thermal paper. To prepare a vanillin-based thermal paper, a 30% aqueous vanillin suspension with 8% of polyvinyl alcohol and suspension of ODB-2 was mixed. An increased viscosity was observed after grinding. Vanillin mixed thoroughly well with the colour former in the dispersion without premature colour formation. The weight ratio between vanillin and ODB-2 in the prepared dispersion was 2.3:1. The finished suspension was applied as explained in 4.9.1. On drying of the coat, the sweet vanillin scent could be perceived. On printing, a maximum print density of 0.6 was achieved. The vanillin scent was also evident in printing. This suggested a partial sublimation of vanillin. A closer look at the printed image under a microscope revealed a heterogeneous pattern different from a standard thermal paper which appeared with a full surface (**Figure 85**).

Figure 85. Microscopic image of a vanillin-based thermal paper

The stability of the vanillin-based thermal paper was studied. The printed paper was stored in an air-conditioned room at 23°C, 50% RH for 24 hours, and then the print density was measured again. After 24h storage, the optical print density was 0.4 (down from 0.6). After 24h storage under humid conditions (40°C and 90% RH), the printout faded and unrecognizable. This poor durability cast doubt on the suitability of vanillin as a developer in thermal paper. Vanillin derivatives such as vanillic acid, isovanillin, and isovanillic acid did not show any thermal reaction within the settings of the thermal printer.

4.9.3 Tannin-based thermal paper

Commercially obtained tannin samples (Tanal 02, Tanex 20, Tanal 40, and tannin) described in section 4.2.1 were used as a developer to prepare thermal papers. The addition of tannins to the coating formulation resulted in the immediate thickening of the mixture. Further processing of the coating colour under such circumstances was impossible. All tannin samples (Tanal 02, Tanex 20, Tanal 40, and tannin) showed this behaviour. The coating formulation prepared from ODB-2, PVA and water tagged F1 and developer was applied to the paper separately to circumvent this problem. Firstly, the coating formulation was spread on the paper then the developer was added. The individual coatings were allowed to dry before adding the next. However, this procedure may not be suitable for technical applications in production, but it allowed for lab-based evaluation of the samples. Test sheets were prepared as described in **Table** 37.

Table 37. Design and optical density of tannin-based thermal papers

S/N	Sample	Optical density (print)	Optical density (heat)	Observation
1	**F1** + Tanal 02	0.66	0.96	strong adhesion
2	**F1** + Tanex 20	0.07	0.53	no printout
3	**F1** + Tanal 40	0.55	0.95	strong adhesion
4	**F1** + 2 x Tanal 40	0.66	0.97	strong adhesion
5	2 x **F1** + Tanal 40	0.69	0.95	strong adhesion
6	Tanal 40 + **F1**	0.37	0.61	-
7	**F1** + tannin	0.64	0.92	grey

For samples 1 to 3 and 7, **F1** was first applied without a developer, and then the corresponding tannin solution was added. In sample 4, **F1** was first applied without a developer, and then double the amount of Tanal 40 was added. In sample 5, twice the amount of **F1** was applied and then the Tanal 40. Samples 4 and 5 were prepared to observe the effect of more tannin and coating mixture on the optical density. In sample 6, the tannin sample was applied first, and **F1** was added to complete the formulation. After obtaining the maximum possible optical print density with all the samples, the papers were subjected to a flame treatment to see if external heat could improve the density of the colour formed (**Figure 86).** An open flame was used to generate heat. The printed paper was carefully held over the flame for a short time and density was measure again. With the flame test, optical densities were increased, suggesting that the reaction of colorant and tannin under the thermal printer was not completed. The thermal printing energy may not be sufficient to complete the reaction. Application of external heat with higher energy could trigger a further reaction. However, the optical densities of all thermal papers obtained from tannin-based sheets were lower than the reference value (1.20).

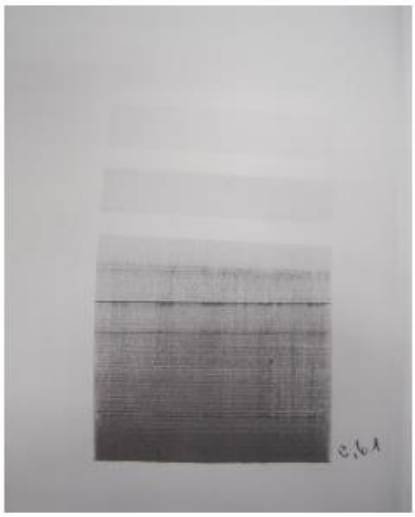


Figure 86. Thermal Printing Test: Tanal 40-based thermal paper after flame application.

Furthermore, the tannin-coated sheets were not thoroughly smooth. On printing, the sheets of Tanal 02 and Tanal 40 stuck to the thermal header and mainly were pulled out by hand. More so, the printouts were mostly not readable. The sticking of the tannin-coated sheets to the thermal head could be attributed to the reaction of

tannin with some other components of the coating mixture, possibly with PVA. Therefore, some chemical additives may be needed to ease this problem.

Of all methanol-purified tannin extracts, only mimosa extract (MIM) showed a reaction in thermal paper. MIM was added to the dispersion in its uncrushed form, and it dissolved quite well. The finished coating of MIM, colour former, and PVA appeared light brown. On printing, the maximum optical print density of 0.40 was recorded (**Figure 87**). The background of MIM-coated paper could limit its application.

Figure 87. Thermal Printing Test: Mimosa extract (MIM)-based thermal paper.

4.9.4 Phenol-amine complex-based thermal paper

The print of paper coated with resorcinol-amine complex (RES-H) is shown below (**Figure 88**).

Figure 88. Thermal Printing Test: Resorcinol-amine complex (RES-H)-based thermal paper showing the print density.

After storage in the laboratory, RES-H powder drifted from its off-white colour to a shade of green & blue with some large lumps. When the lumps were crushed, they turned slightly yellow on the inside. Preparation of dispersion with RES-H was relatively easy. However, some samples of large particle size remained in the mixture. RES-H coated paper was grey/brown when dried. On printing, a maximum optical print density of 0.50 was achieved.

4.9.5 Phenol-glyoxal polymer-based thermal paper

Most of the polymers were too hard and difficult to ground into small particle sizes. Only PHCP2, GSE-CP2, and GSE-CP9 were successfully ground to reduced particle size manageable for the application of the phenol-glyoxal polymers. The particle sizes of the other ground polymers were too large and remained unchanged after several hours of grinding. Small particle size enhances the interaction between the polymer and leuco dye due to increased surface area. The ground polymers were included as developers in the coating formulation for the thermal paper. The coating colour appeared brown. Only GSE-CP2 and GSE-CP9-coated papers gave a colour reaction when heated in the thermal printer. The maximum print density was 0.24 and 0.23, respectively. The thermal reaction of PHCP2 was too weak to be considered. The grape seed extract-glyoxal polymer-based-thermal papers are shown in **Figure 89**.

Figure 89. Thermal Printing Test: Grapeseed extract (GSE)-based thermal paper (a) GSE-CP2, and (b) GSE-CP9 showing the print density.

5 Conclusions and recommendations

The potential of several bio-based substances such as ascorbic acid, salicylic acid, ascorbyl palmitate, citric acid, tannin, vanillin, vanillic acid, and their derivatives, to effectively replace BPA as a developer in thermal paper was investigated. Phenolic resins produced and characterised from glyoxal, and methanol extracts of vegetable tannin and tannin-model compounds were also assessed for their colour-forming potential in a leuco dye-based system. In addition, phenol-amine complexes aimed at mitigating the premature colour formation associated with phenols were synthesised using HMDA and tannins as phenol. FTIR and DSC characterized the phenol resins and amine complexes. The condensed summary of the performance evaluation of these substances in the thermal paper is presented in **Table 38.**

Preliminary evaluation of the colour-forming potential of the studied compounds through acetone and dispersion tests confirmed that most of these substances, including vanillin, ascorbic acid, ascorbyl palmitate, citric acid, salicylic acid, and tannin compounds, can participate in a proton-transfer-reaction with ODB-2 to produce the characteristic black colour. These interactions were examined through spectroscopic analysis. The reduction or total disappearance of the lactone ring of ODB-2 was confirmed by FTIR, while a shift in the signal of the central carbon of the leuco dye was ascertained with NMR.

In a three-component system containing ODB-2 and tetradecanol, lignin-derived monomers such as vanillin and vanillic acid showed their ability to interact with the leuco dye at different temperature ranges. These thermochromic mixtures showed distinct lightness at a temperature above the melting point of the co-solvent while forming a deep colouration at a lower temperature. Furthermore, a melt-darkened state was observed in the presence of a higher concentration of the developer and leuco dye. The vanillin and vanillic acid performance showed their potential for utilisation in thermochromic systems.

One of the essential steps in preparing thermal paper is the addition of dispersion of the developer, dye, and other additives on a base paper resulting in the heat-sensitive layer. Dispersions used for thermal paper are expected to be homogenous and colourless to achieve a marketable thermal paper of high quality. Ascorbic acid, ascorbyl palmitate, vanillin, vanillic acid, isovanillic acid, isovanillin,

resorcinol-amine complex, and phloroglucinol-glyoxal polymer produced fine dispersion for effective coating with no premature colour reaction. These compounds were easy to be pulverised into the small particle size required for a coating application. Unlike other organic carboxylic acids, dispersions containing salicylic acid as developer produced a black colour, signifying a premature reaction with ODB-2 before the coating is applied. Citric acid dispersion was also slightly grey in appearance. The dispersion of tannin compounds such as Tanal 40, Tanal 02, and Tanex 20 was difficult to produce. They became viscous on mixing with PVA in ODB-2 suspension. To circumvent this problem, coating application with tannin compounds was done stepwise. First, the formulation containing ODB-2 and PVA was spread on the base paper before the tannin was introduced. This process produced a good thermal paper with a fine coat but would need modification to be less complex and amenable to industrial process technology. Other studied substances like phenol-glyoxal polymers and phenol-amine complexes produced coloured dispersion, mostly brownish. The dispersion of grape seed extract polymer was greyish. Some of the polymers were hard and difficult to crush into fine particle size. Some large-sized particles of the polymer were observed in the coat. Several of these bio-based compounds were applied as a developer in thermal paper through the application of the coating formulation. Their qualitative properties were monitored by the measurement of the print density of the thermal papers.

Organic carboxylic acids such as ascorbic acid, ascorbyl palmitate, and citric showed very good amenability as a developer in thermal paper with print densities of 1.1, 0.79, and 0.25, respectively. The print from ascorbic and ascorbyl palmitate-coated papers was solid and legible. However, citric-acid coated paper, which appeared greenish-grey with a whiteness value of 79% in the unprinted state, had low print legibility. The relatively low whiteness caused a poor contrast between the printed and unprinted paper. Furthermore, the ascorbic acid-coated thermal paper was unstable with a very low resistance to moisture and solvent, confirmed by a 90% reduction in colour density within 7 days. Thermal paper produced from ascorbyl palmitate, however, showed higher resistance to oil and solvent. This may be attributed to the long alkyl chain group's presence in the developer's matrix. Therefore, of the studied organic carboxylic acids, ascorbyl palmitate and ascorbic acid can be

recommended for use as developers in thermal paper. These compounds are commercially available and pose little or no threat to human health.

Of vanillin and related compounds, only vanillin-coated paper had a good outcome. The print, however, had low stability in humidity and faded almost completely when exposed to the humidity of 90% RH for 24 hours. Also, on printing, the paper gave off a characteristic sweet scent that suggested the phenol substance's sublimation. This is one of the problems associated with the use of vanillin as a developer in thermal paper. Vanillic acid, isovanillin, and isovanillic acid did not produce a thermal reaction worthy of industrial consideration.

Using the stepwise process explained earlier, all studied tannin compounds produced fine coats and prints of varying qualities. The optical densities of thermal paper coated with Tanal 02, Tanex 20, Tanal 40, and tannin were 0.66, 0.07, 0.55, and 0.64, respectively. The low print density of the Tanex 20 paper may be attributed to the low phenolic content of the developer compared to the other tannin compounds. Methanol extract of mimosa tannin gave a low print density of 0.40, while other extracts from mimosa-sulphite and grape seed showed a weak thermal reaction on printing. An attempt was made to see if an increase in the optical density of tannin-based paper can be achieved by doubling the amount of either the developer or the ODB-2 dispersion in the coating formulation. When Tanal 40 was doubled, the optical density increased to 0.66, while the optical density was 0.69 when ODB-2 was doubled. A 30% improvement in the optical print density of papers coated with the tannin compounds was achieved when the papers were further subjected to a flame test. The print density of thermal paper coated with Tanal 02, Tanex 20, Tanal 40, and tannin increased to 0.96, 0.53, 0.95, and 0.92, respectively. This showed that the applied temperature might not be sufficient to achieve an optimum print density with the tannin compounds. A higher applied printing temperature, unsuitable for energy-efficient technical application, would be required to achieve a deeper coloration and higher print density.

The use of various commercially available tannins as a developer in thermal paper comes with some merits and limitations. The optical densities of the prints were low compared to BPA thermal paper with a standard print density of 1.2. Print from Tanex 20 paper was not legible. In addition, thermal papers from Tanal 02 and Tanal

40 adhered strongly to the printer's thermal head on printing. This may be attributed to the interaction of these compounds with the PVA binder. The introduction of an additive may limit such interaction. Further fractionation to isolate the phenolic compounds may be needed to achieve better results with vegetable tannin extracts such as mimosa, mimosa sulphite, and grape seed extract.

Nonetheless, tannin is a high molecular weight polymer with little or no known toxicity. In addition, high molecular weight compounds such as tannin are associated with very low dermal migration potential. This may help to overcome the skin-penetration and bioaccumulation problem associated with the use of BPA, BPS, and similar compounds.

Amine complexes produced from the reaction of resorcinol and HMDA showed a melting property like BPA. The complex was used to produce a fine dispersion and coat for thermal paper. The thermal paper made from this coat gave an optical print density of 0.50. The use of resorcinol-amine complex might help to ease the fading problem associated with BPA-based paper. However, this compound was observed to be prone to air oxidation and could also lead to colour deformation over time. Other phenol-amine complexes did not produce colour, possibly due to high thermal stability, which required higher printing energy. The only visible colour observed with complexes of mimosa extract, mimosa sulphite extract and grape seed extract were the inherent brown colours evident in the dispersion. This property made their papers brownish in appearance and therefore limited their applicability.

Furthermore, some phenol-glyoxal polymers showed promising potential as a developer in a thermal paper while most did not. No thermal reaction was observed with the polymers of mimosa extract and mimosa sulphite extract. The phloroglucinol-glyoxal polymer showed a very weak thermal reaction which is not useful for quantitative evaluation. The thermal paper produced from the polymer of grape seed extract gave a print density of 0.24. The weak or lack of thermal reaction may be attributed to the high thermal stability of the polymers. A higher temperature may be needed to initiate the colour reaction, but this may not be applicable under the prevailing industrial process. However, phenolic polymers in thermal paper are highly recommended because these polymers are easy to synthesise with commercially available compounds. They have a high molecular weight which might enhance their

low dermal migration potential. Their high thermal stability could be an advantage. It ensures that prints are only produced at end-use temperature. However, more work still to be done to improve the properties of these polymers with a bid to ensure their suitability as a developer in thermal paper.

In general, this study has shown the functionality and amenability of a large catalogue of promising bio-based compounds that have good and acceptable properties to be used as a sustainable, healthy, and environmentally friendly replacement for BPA in heat-sensitive materials like thermal paper. These substances can be used either in pure form, modified form, or building blocks for higher valued chemicals. Organic carboxylic acids and their esters, such as ascorbic acid and ascorbyl palmitate, are developer candidates because of their functional properties, commercial availability, and little or no known toxicity to man. Purified vegetable tannin can be used as a source of phenol to produce bio-based resins of high molecular weight and good thermal properties suitable for application in thermal paper. Commercially available variants of tannin such as Tanal 02, Tanex 20, and Tanal 40 are recommended because of their high molecular weight and potential to produce a print of high optical density at higher application temperatures. These recommended substances may be used singly or in combination with other developers in a colour-forming dispersion to enhance the quality of the output image or print. It also helps to reduce the amount of BPA needed in the coating dispersion.

There is still an array of bio-based compounds open for further study of their colour-developing potential. Bio-based phenol resins, urea-urethane-based resins, sugar-based copolymers, cellulosic compounds, and lignin-derived compounds are few examples. A deeper look into the various synthesis and modification routes available in literature could lead to new ideas for the discovery of bio-based and environmentally friendly developers for heat-sensitive materials, like thermal paper.

Table 38**.** Performance evaluation of green developers in thermal paper

Substance	Function as a developer in thermal paper?	Merit	Demerit
Ascorbic acid	Yes	• Produced fine dispersion for coating with no premature reaction. • Produced solid and legible print. • Commercially available	• Low oil and moisture resistance of print.
Ascorbyl palmitate	Yes	• Produced fine dispersion for coating with no premature reaction. • Produced solid and legible print. • Commercially available	• Expensive compared to BPA, BPS, and other alternatives.
Citric acid	Yes	• Produced fine dispersion for coating. • Commercially available	• Low print legibility. • Low contrast of printed and unprinted paper due to background colour.
Salicylic acid	No	• Commercially available	• Premature colour formation.
Vanillin	Yes	• Produced fine dispersion for coating with no premature reaction. • Commercially available	• Gradual sublimation of print. • Paper produced vanillin scent • Low oil and moisture resistance
Vanillic acid	No	• Produced fine dispersion for coating with no premature reaction. • Commercially available	• No thermal reaction.

Substance	Function as a developer in thermal paper?	Merit	Demerit
Isovanillic acid	No	• Produced fine dispersion for coating with no premature reaction. • Commercially available	• No thermal reaction.
Isovanillin	No	• Produced fine dispersion for coating with no premature reaction. • Commercially available	• No thermal reaction.
Tannin	Yes	• High molecular weight polymer with little or no dermal migration potential • Commercially available	• Produced dispersion of high viscosity. • Required an unconventional two-step process for application. • Required temperature unsuitable for technical application. • Strong adhesion to thermal head • High background colour (grey)
Tanal 02	Yes	• High molecular weight polymer with little or no dermal migration potential • Commercially available	• Produced dispersion of high viscosity. • Required an unconventional two-step process for application. • Required temperature unsuitable for technical application. • Strong adhesion to thermal head

Substance	Function as a developer in thermal paper?	Merit	Demerit
Tanex 20	No	• High molecular weight polymer with little or no dermal migration potential • Commercially available	• Produced dispersion of high viscosity. • Required an unconventional two-step process for application. • Required temperature unsuitable for technical application. • Strong adhesion to thermal head • Print not readable
Tanal 40	Yes	• High molecular weight polymer with little or no dermal migration potential • Commercially available	• Produced dispersion of high viscosity. • Required an unconventional two-step process for application. • Required temperature unsuitable for technical application. • Strong adhesion to thermal head
Mimosa extract	Yes	• Commercially available	• Low print density. • Low print stability • High background colour (brown) • Required further fractionation to isolate the phenolic compounds
Mimosa sulphite extract	No	• Commercially available	• Weak thermal reaction. • Required further fractionation to isolate the phenolic compounds.

Substance	Function as a developer in thermal paper?	Merit	Demerit
Grape seed extract	No	• Commercially available	• Weak thermal reaction • Required further fractionation to isolate the phenolic compounds
Resorcinol-amine complex	Yes	• Produced dispersion for coating with no premature reaction. • Melting property like BPA • Easy to synthesise.	• Substance prone to air oxidation • High background colour (grey/brown)
Mimosa extract-amine complex	No	• Easy to synthesise.	• Produced coloured dispersion unsuitable for application • No thermal reaction.
Mimosa sulphite-amine complex	No	• Easy to synthesise.	• Produced coloured dispersion unsuitable for application • No thermal reaction.
Grape seed extract-amine complex	No	• Easy to synthesise.	• Produced coloured dispersion unsuitable for application • No thermal reaction.
Mimosa extract-glyoxal polymer	No	• Easy to synthesise. • High molecular weight • Low dermal migration potential • High thermal stability	• Produced coloured dispersion unsuitable for application • No thermal reaction. • No melting temperature

Substance	Function as a developer in thermal paper?	Merit	Demerit
Mimosa sulphite extract-glyoxal polymer	No	• Easy to synthesise. • High molecular weight • Low dermal migration potential • High thermal stability	• Produced coloured dispersion unsuitable for application. • No thermal reaction. • No melting temperature
Grape seed extract-glyoxal polymer	Yes	• Easy to synthesise. • High molecular weight • Low dermal migration potential • High thermal stability	• High background colour (grey/brown) • Weak thermal reaction
Phloroglucinol-glyoxal polymer	No	• Produced fine dispersion for coating with no premature reaction. • Easy to synthesise. • High molecular weight • Low dermal migration potential	• Weak thermal reaction
Tannic acid-glyoxal polymer	No	• Easy to synthesise. • High molecular weight • Low dermal migration potential • High thermal stability	• Difficult to mill into small particle size. • Produced heterogeneous dispersion unsuitable for application. • No thermal reaction. • No melting temperature

6 Literature

[1] Keizaburo, Y., Yoshimitsu, T., Kiyoharu, H., Akihiro, Y. (**1994)**. *Color-developing compositions and their use.* United States Patent No. 5,376,615.

[2] Thayer, K.A., Taylor, K.W., Garantziotis, S., Schurman, S.H., Kissling, G.E., Hunt, D., Herbert, B., Church, R., Jankowich, R., Churchwell, M.I., Scheri, R.C., Birnbaum, L.S., Bucher, J.R. (**2016)**. *Bisphenol A, Bisphenol S, and 4-Hydroxyphenyl 4-Isoprooxyphenylsulfone (BPSIP) in urine and blood of cashiers*. *Environmental Health Perspectives*, 124(4):437-444.

[3] Jan, D.B., Marcus, M.H.M.M. (**2000)**. *The 500 Dalton rule for the skin penetration of chemical compounds and drugs*. *Experimental Dermatology*, 9:165-169.

[4] Bjornsdotter, M.K., Jonker, W., Legradi, J., Kool, J., Ballesteros-Gomez, A. (**2017)**. *Bisphenol A alternatives in thermal paper from the Netherlands, Spain, Sweden and Norway. Screening and potential toxicity*. *Science of the Total Environment*, 601-602:210-221.

[5] Vandenberg, L.N., Hauser, R., Marcus, M., Olea, N., Welshons, W.V. (**2007)**. *Human exposure to bisphenol A (BPA)*. *Reproductive Toxicology*, 24(2):139-77.

[6] Agence nationale de sécurité sanitaire de l'alimentation de l'environnement et du travail (ANSES). (**2014)**. *France's proposal on the restriction of bisphenol A use in thermal paper*. Retrieved from *https://www.anses.fr/en/content/frances-proposal-restriction-bisphenol-use-thermal-paper-prepared-anses-submitted-public*. Accessed last on 04 September, 2019.

[7] Wu, L.-H., Zhang, X.-M., Wang, F., Gao, C.-J., Chen, D., Palumbo, J.R., Guo, Y., Zeng, E.Y. (**2018)**. *Occurrence of bisphenol S in the environment and implications for human exposure: A short review*. *Science of the Total Environment*, 615:87-98.

[8] van Es, D.S. (**2014)**. *Analysis of alternatives for BPA in thermal paper*. Wageningen UR Food & Biobased Research Wageningen. Report No. 1515. 12 December 2014. Retrieved from *www.wur.nl*.

[9] Scholl, T., Jabs, G., Richartz, A. (**1990)**. *Hydroxycarboxylic acid/unsaturated aromatic hydrocarbon resin useful as recording material*. United States Patent No. 4,929,710.

[10] Bodmer, J.R. (**1979)**. *Method of preparing zinc-modified phenolaldehyde novolak resins and use as a color-developing agent*. United States Patent No. 4,165,103.

[11] García, D.E., Glasser, W.G., Pizzi, A., Paczkowski, S.P., Laborie, M.-P. (**2016)**. *Modification of condensed tannins: from polyphenol chemistry to materials engineering*. *New Journal of Chemistry*, 40(1):36-49.

[12] Tutty, G.C. (**1982)**. *Color developable composition*. United States Patent No. 4,339,275.

[13] Arbenz, A., Avérous, L. (**2015)**. *Chemical modification of tannins to elaborate aromatic biobased macromolecular architectures*. *Green Chemistry*, 17(5):2626-2646.

[14] Shirmohammadli, Y., Efhamisisi, D., Pizzi, A. (**2018)**. *Tannins as a sustainable raw material for green chemistry: A review*. *Industrial Crops and Products*, 126:316-332.

[15] Choi, K.-H., Kwon, H.-J., An, B.-K. (**2018)**. *Synthesis and developing properties of functional phenolic polymers for ecofriendly thermal papers*. *Industrial & Engineering Chemistry Research*, 57(2):540-547.

[16] Jang, Y.-I., An, B.-K. (**2015)**. *Hyperbranched polyester copolymers for thermal printing papers: The effects of alkyl chain units in the polymer backbone on developing capability*. *Polymer*, 78:193-201.

[17] Huneke, A.A. (**2015)**. *Entwickler für thermochrome Schichten auf Basis nachwachsender Rohstoffe*. Master of Science Holzwirtschaft, Master Thesis. Department of Biologie, Fakultät für Mathematik, Informatik und Naturwissenschaften, Universität Hamburg, Hamburg. 04 August, 2015.

[18] Diener, R., McCall, B., Gimm, J.A. (**2009)**. *The Secret of Smart Paper*. *Journal of Chemical Education*, 86(4).

[19] Chang, J.C.H., Dimitriou, T. (**1984)**. *Pressure-sensitive record system*. United States Patent No. 4,448,445.

[20] Kay, D.J., Patel, R.R. (**1979)**. *Pressure-sensitive record material containing urea-formaldehyde resin pigment*. United States Patent No. 4,166,644.

[21] Bayless, R.G., Springs, Y., Striley, D.J. (**1971)**. *Pressure-sensitive record sheet and coating composition*. United States Patent No. 3,576,660.

[22] Brown, G.T., Clark, D.B. (**1972)**. *Pressure-sensitive record material*. United States Patent No. 3,697.323.

[23] de Kruif, C.G., Weinbreck, F., de Vries, R. (**2004)**. *Complex coacervation of proteins and anionic polysaccharides*. *Current Opinion in Colloid & Interface Science*, 9(5):340-349.

[24] Chai, G.-Y., Krantz, W.B. (**1994)**. *Formation and characterization of polyamide membranes via interfacial polymerization*. *Journal of Membrane Science*, 93(2):175-192.

[25] Ohara, Y. (**1982)**. *Reproducing a color image on a photosensitive material in response to an element-sequential color signal*. United States Patent No. 4,346,401.

[26] Morita, K. (**2017)**. *Thermal recording material*. United States Patent No. 9,834,022 B2.

[27] Marginean, B.L.S., Cuch, S.R., Whittaker, C.A., Patel, M.C. (**1995)**. *Aqueous coating composition for thermal imaging film*. United States Patent No. 5,424,182.

[28] Clark, B.L. (**1957)**. *Heat-sensitive copying paper*. United States Patent No. 2,813,043.

[29] Baum, H.H. (**1970)**. *Thermo-responsive record sheet*. United States Patent No. 3,539,375.

[30] Chakar, F.S., Fisher, M.R. (**2014)**. *Thermally-responsive record material*. United States Patent No. 8,916,496 B2.

[31] Kawaguchi, T., Hanada, K., Torii, K., Umezu, M., Kamita, T. (**2004)**. *Thermal recording media*. United States Patent No. 2004/0180152 A1.

[32] Lassen, C., Mikkelsen, S.H., Brandt, U.K. (**2011)**. *Migration of bisphenol-A from cash register receipts and baby dummies*. Danish Ministry of the Environment - Environmental Protection Agency Denmark. Report No. 110 2011. Retrieved from: *https://substitution-bp.ineris.fr/sites/substitution-bp/files/documents/migration_of_bisphenol_a_from_cash_register_receipts_and_baby_dummies_0.pdf*.

[33] Haider, S. (**2017)**. *Look Ahead: How to spot future profits in the world of chemicals*. Retrieved from *https://marketplace.chemsec.org/articles/best-practices-in-chemicals-management/how-to-spot-future-profits-in-the-world-of-chemicals/*. Accessed last on 01 January, 2019.

[34] ReportsnReports. (**2018)**. *Thermal paper market outlook, revenue, insights, statistics and 2025 global forecast report*. Retrieved from *https://www.prnewswire.com/news-releases/thermal-paper-market-outlook-revenue-insights-statistics-and-2025-global-forecast-report-837320000.html*. Accessed last on 12 December, 2019.

[35] PGPaper. (**2018)**. *Thermal paper - in hot demand!* Retrieved from *https://www.pgpaper.com/thermal-paper-market/*. Accessed last on 20 December, 2019.

[36] Grandview Research. (**2017)**. *Thermal paper market analysis by technology (direct thermal, thermal transfer), by application (pos, lottery & gaming, tags & label), by region (north america, europe, asia pacific, central & south america), and segment forecasts, 2018 - 2025*. Retrieved from *https://www.grandviewresearch.com/*. Accessed last on 10 June, 2020.

[37] Fact.MR. (**2019)**. *Thermal papers market expansion to be persistent during 2018-2028*. Retrieved from *https://www.factmr.com/connectus/sample?flag=S&rep_id=2487*. Accessed last on 15 June, 2019.

[38] Diener, L., McCall, B., Gimm, J.A. (**2010)**. *Thermal paper exposed: the secret of "smart" paper*. *Science Scope*, 34(4).

[39] Mazur, D., Cassie, C., Forstall, F., Bryan, N., Klir, M., Bernstein, M., Shields, L. (**2007)**. *Certain lightweight thermal paper from china, germany, and korea*. U.S. International Trade Commission. Report No. 701-TA-451 and 731-TA-1126-1128. November 2007. Retrieved from *www.usitc.gov*.

[40] Bradbury, R. (**1996)**. *Thermal printing.* In: chemistry and technology of printing and imaging systems. (P. Bergthaller RB, R. S. Gairns, P. Gregory, P. A. Hunt, T. S. Jewitt und R. W. Kenyon., editor). Springer; Netherlands.

[41] Cheon, K., Filosa, M.P., Marshall, J.L. (**2006)**. *Dyes and use thereof in imaging members and methods*. United States Patent No. 7,008,759 B2.

[42] Takayama, S., Gotanda, T., Sekiguchi, Y., Sano, K. (**2012)**. *Image erasing apparatus and image forming apparatus*. Patent No. US 8,284.220 B2.

[43] Hida, Y. (**1983)**. *Thermosensitive recording materials*. United States Patent No. 4,401.72.

[44] Brockett, B.W., Miller, R.E., Hinkle, M.L. (**1973)**. *Record material*. United States Patent No. 3,723,156.

[45] Chakar, F., Warner, J.C., Whitfield, J.R., Lugus, L.W.M., Banerjee, D. (**2015)**. *Thermal recording materials*. United States Patent No. 9.126,451 B2.

[46] Stimac, J.T. (**2003)**. *Thermal & carbonless papers: A fundamental understanding for latent friction ridge development*. *Journal of Forensic Identification*, 53(2):185-197.

[47] Minami, T., Nagai, T., Hamada, K., Sekine, A. (**1998)**. *Reversible multi-color thermal recording medum*. United States Patent No. 5,710,094.

[48] Diamond, A. (**2002)**. *Handbook of Imaging Materials*.(2nd Edition ed). CRC Press, Boca Raton.

[49] Amazon. *Thermal Printer*. Retrieved from *https://www.amazon.de/Thermal-printer-Elektronik-Foto/s?k=Thermal+printer&rh=n%3A562066*. Accessed last on 14 January, 2021.

[50] Gregory, P. (**2002)**. *Functional Dyes.* In: Industrial Dyes. (Hunger K, editor). Wiley-VCH Verlag GmbH & Co. KGaA.

[51] Saito, T. (**1983)**. *Two-dimensional thermal head*. Patent No. 4,401,881.

[52] Takeno, S., Shimizu, T., Saito, T. (**1987)**. *Thermal print head*. United States Patent No. 4,680,593.

[53] Nassau, K. (**2001)**. *The physics and chemistry of color: The fifteen causes of color*.(2nd Edition ed). Wiley-VCH, Weinheim.

[54] Mathammal, R., Jayamani, N., Geetha, N. (**2013)**. *Molecular structure, NMR, HOMO, LUMO, and vibrational analysis of o-anisic acid and anisic acid based on DFT calculations*. *Journal of Spectroscopy*, 2013:18.

[55] Tsuneda, T., Singh, R.K., Nakata, A. (**2016)**. *Relationship between orbital energy gaps and excitation energies for long-chain systems*. *Journal of Computational Chemistry*, 37(16):1451-1462.

[56] Hunger, K., Gregory, P., Miederer, P., Berneth, P., Heid, C., Mennicke, W. (**2002)**. *Important Chemical Chromophores of Dye Classes.* In: Industrial Dyes: Chemistry, Properties, Applications. (Hunger K, editor).

[57] Hunger, K., Hamprecht, R., Miederer, P., Heid, C., Engel, A., Kunde, K., Mennicke, W., Griffiths, J. (**2002)**. *Dye classes for principal applications*. *Industrial Dyes*:113-338.

[58] Kim, S.-H., Lee, E.-M. (**2016)**. *Dye, Functional.* In: Encyclopedia of Color Science and Technology. (Luo R, editor). Springer Berlin Heidelberg; Berlin, Heidelberg.

[59] Ishige, S., Kato, H., Saeki, K., Kiritami, M. (**1978)**. *Recording method comprising reacting cellulose fiber with a basic color former*. United States Patent No. 4,070,508.

[60] Hojo, M., Ueda, T., Inoue, A., Tokita, S. (**2009)**. *Interaction of a practical fluoran-based black color former with possible color developers, various acids and magnesium ions, in acetonitrile*. *Journal of Molecular Liquids*, 148(2-3):109-113.

[61] Kulčar, R., Friškovec, M., Gunde, M.K., Knešaurek, N. (**2011)**. *Dynamic colorimetric properties of mixed thermochromic printing inks*. *Coloration Technology*, 127(6):411-417.

[62] Okada, K. (**1996)**. *X-ray crystal structure analysis and atomic charges of color former and developer: 2. Color formers*. *Journal of Molecular Structure*, 380:235 247.

[63] Yamamoto, S., Furuya, H., Tsutsui, K., Ueno, S., Sato, K. (**2008)**. *In situ observation of thermochromic behavior of binary mixtures of phenolic long-chain molecules and fluoran dye for rewritable paper application*. *Crystal Growth & Design*, 8(7):2256 - 2263.

[64] Campbell, D.J., Bosma, W.B., Bannon, S.J., Gunter, M.M., Hammar, M.K. (**2012)**. *Demonstration of thermodynamics and kinetics using frixion erasable pens*. *Journal of Chemical Education*, 89(4):526-528.

[65] Mizuguchi, J., Sato, K. (**2009)**. *A redetermination of 2-(6-diethyl-amino-3-diethyl-iminio-3H-xanthen-9-yl)benzoate-ethyl gallate (1/1) at room temperature*. *Acta Crystallographica Section E*, E65(Pt 4):o701–o702.

[66] Hinckley, D.A., Seybold, P.G. (**1988)**. *A spectroscopic/thermodynamic study of the rhodamine B lactone ⇌ zwitterion equilibrium*. *Spectrochimica Acta Part A: Molecular Spectroscopy*, 44(10):1053-1059.

[67] Markuszewski, R., Diehl, H. (**1980)**. *The infrared spectra and structures of the three solid forms of fluorescein and related compounds*. *Talanta*, 27(11, Supplement 2):937-946.

[68] Okada, K. (**1997)**. *X-ray crystal structure analysis and atomic charges of color former and developer 3. Color formers*. *Journal of Molecular Structure*, 406:29–43.

[69] Hajzeri, M., Bašnec, K., Bele, M., Gunde, M.K. (**2015)**. *Influence of developer on structural, optical and thermal properties of a benzofluoran-based thermochromic composite*. *Dyes and Pigments*, 113:754-762.

[70] Azizian, F., Field, A.J., Heron, B.M., Kilner, C. (**2012)**. *Intrinsically thermochromic fluorans*. *Chemical Communications*, 48(5):750-752.

[71] Masahiko Inouye, K.T., and Teijiro Kitao. (**1992)**. *New thermo-response dyes: Coloration by the claisen rearrangement and intramolecular acid- base reaction*. *Angew Chem Inl Ed Engl*, 31(2).

[72] James, T.H., Mees, C.E.K. (**1977)**. *The theory of the photographic process*. Macmillan, New York.

[73] Kosche, H. (**1982)**. *Heat-sensitive recording or copying material*. United States Patent No. 4,324,420.

[74] Ikeda, K., Yanagihara, N., Iwakura, K. (**1989)**. *Heat-sensitive recording material*. United States Patent No. 4,839,332.

[75] Yamato, N., Satake, T. (**1983)**. *Heat-sensitive recording sheet*. United States Patent No. 4,399,188.

[76] Masafumi, T., Hiromi, F., Masaru, S., Kyoji, T. (**2000)**. *Reversible thermosensitive coloring composition and reversible thermosensitive recording medium using the same.* United States Patent No. 6,063,173.

[77] Nishimura, T., Ohmuta-shi, F. (**1996)**. *Sulfonated phenol (salt) containing color-developing agents and color-developing sheets*. European Patent No. 0714785 A1.

[78] Seitz, M.E.A. (**1985)**. *Color developers for pressure-sensitive or heat-sensitive recording papers*. United States Patent No. 4,531,139.

[79] Kadota, Y., Ikeda, T. (**2008)**. *Thermosensitive recording material*. United States Patent No. 7.425,522.

[80] Satake, T., Takano, T., Hayasaka, H., Uehori, Y., Nagai, T. (**1985)**. *Thermal recording sheet*. United States Patent No. 5,470,816.

[81] Minami, T., Nagai, T., Hamada, K., Sekine, A. (**1998)**. *Reversible multi-colour thermal recording medium*. United States Patent No. 5,710,094.

[82] Matsumoto, S., Takeshima, S., Satoh, S., Kabashima, K. (**2010)**. *The crystal structure of two new developers for high-performance thermo-sensitive paper: H-bonded network in urea–urethane derivatives*. *Dyes and Pigments*, 85(3):139-142.

[83] Naito, K. (**1998)**. *Rewritable color recording media consisting of leuco dye and biphenyl developer with a long alkyl chain*. *Journal of Materials Chemistry*, 8(6):1379–1384.

[84] Ono, Y. (**2012)**. *Thermochromic coloring color-memory composition and thermochromc coloring color-memory microcapsule pigment containing the same*. United States Patent No. 8,222,183 B2.

[85] Fujita, K., Ono, Y. (**1999)**. *Reversible thermochromic compositions*. United States Patent No. 5,919,404.

[86] Naito, K. (**1999)**. *Rewritable thermal recording medium*. United States Patent No. 5,869,420.

[87] Horn, M. (**2018)**. *Heat sensitive recording material*. United States Patent No. 2018/0079243 A1.

[88] Shimizu, G., Hayashi, Y. (**1988)**. *Thermochromic composition*. United States Patent No. 4,717,710.

[89] Satake, T., Minami, T., Nagai, T., Fujimura, F. (**1989)**. *Heat-sensitive recording material*. United States Patent No. 4,849,396.

[90] Takeshi, N., Sato, K. (**1990)**. *Heat-sensitive transfer materials*. United States Patent No. 4,892,858.

[91] Lawton, W.R., Nashua, N.H. (**1964)**. *Heat senstive sheets*. United States Patent No. 3,149,992.

[92] Lawton, W.R. (**1978)**. *Heat sensitive recording composition containing a complexed phenolics and a spiropyran or leuco lactone*. United States Patent No. 4,097,288.

[93] Lawton, W.R. (**1978)**. *Heat-sensitive coating composition with 4-aromatic and hydroxy substituted piperdine derivative and cyclic polyketo compound*. United States Patent No. 4,111,703.

[94] Katsen, B.J., Brinkworth, R.T., Kay, D.J., Riester, A.J. (**1985)**. *Heat sensitive recording papers*. United States Patent No. 4,500,354.

[95] Green, B.K. (**1950)**. *Pressure sensitive recording material*. United States Patent No. 2,505,470.

[96] Green, B.K. (**1952)**. *Process of making pressure sensitive record material*. United States Patent No. 2,618,573.

[97] Shackle, D.R., Chaloner-Gill, B. (**2001)**. *Developer for use with carbonless copy paper and photo imaging systems*. United States Patent No. 6,242,167 B1.

[98] Eckardt, M., Simat, T.J. (**2017)**. *Bisphenol A and alternatives in thermal paper receipts - a German market analysis from 2015 to 2017*. *Chemosphere*, 186:1016-1025.

[99] Russo, G., Barbato, F., Grumetto, L. (**2017)**. *Monitoring of bisphenol A and bisphenol S in thermal paper receipts from the Italian market and estimated transdermal human intake: A pilot study*. *Science of the Total Environment*, 599-600:68-75.

[100] Takahashi, H., Tsurugaya, M., Matsuda, T. (**2007)**. *Developer for recording materials*. United States Patent No. 2007/0099130 A1.

[101] Fisher, M.R., Chakar, F.S., Defrenne, Y. (**2014)**. *Thermally-responsive record material*. United States Patent No. 8,916,497 B2.

[102] Suga, M., Okamoto, N., Kato, A., Takashi, D., Yoshihide, K. (**2011)**. *Developer mixture for thermal recording materals and thermal recording materials*. United State Patent No. 8,062,993 B2.

[103] Futaki, K., Kohmura, I., Haino, K. (**1974)**. *Heat sensitive composition and thermal recording sheet containing the same*. United States Patent No. 3,846,153.

[104] Rong-Chang, L., Emerson, K.C., Kelli, J.B. (**1989)**. *Developer composition comprising phenol resins and vinylic or acrylic resin*. United States Patent No. 4,853,364.

[105] Miller, R.E., Phillips, P.S. (**1972)**. *Pressure sensitive record material*. United States Patent No. 3,672,935.

[106] Bhatt, J.C., Daoshen, B., Kuang-Chou, C., Feng, Y.D. (**2003)**. *Imaging medium incorporating a polymeric developer for leuco dye*. United States Patent No. 2003/0050191 A1.

[107] Keizaburo, Y., Yoshimitsu, T., Makoto, A., Akihiro, Y. (**1991)**. *Salicylic acid copolymers and their metal salts, production process thereof. Color-developing agents comprising metal salts of the copolymers, and color-developing sheets employing the agents*. United States Patent No. 5,023,366.

[108] Yuyama, Y., Motosugi, T., Honda, Y., Ichikawa, A. (**1987)**. *Thermosensitive recording adhesive sheet*. United States Patent No. 4,711,874.

[109] Kato, H., Yasuhiro, O. (**1980)**. *Recording Sheet*. United States Patent No. 4,234,212.

[110] Makitalo, J., Mattila, E., Pylvas, A. (**2005)**. *Heat-sensitive recording material*. United States Patent No. 2005/0148467 A1.

[111] Taylor., J.P. (**2005)**. *Mixture of colour developers*. United States Patent No. 2005/0255998A1.

[112] Endo, K., Fujita, I., Kobayashi, N. (**1991)**. *Structure analysis of a colouring and decoloring unsymmetrical fluoran dye by carbon-13 nuclear magnetic resonance method*. *Analytical Sciences*, 7.

[113] Tang, H., MacLaren, D.C., White, M.A. (**2010)**. *New insights concerning the mechanism of reversible thermochromic mixtures*. *Canadian Journal of Chemistry*, 88(11):1063-1070.

[114] MacLaren, D.C., White, M.A. (**2003)**. *Dye–developer interactions in the crystal violet lactone–lauryl gallate binary system: implications for thermochromism*. *Journal of Materials Chemistry*, 13(7):1695-1700.

[115] Bourque, A.N. (**2014)**. *Investigations of reversible thermochromism in three-component systems*. Doctor of Philosophy, Doctoral Thesis. Dalhousie University, Halifax, Nova Scotia. March 2014.

[116] Takayama, S., Fujioka, S., Okuyama, T., Nishizawa, H., Miyamoto, H., Sugiuchi, M. (**1998)**. *Reversible thermal recording medium*. United States Patent No. 5,849,651.

[117] MacLaren, D.C., White, M.A. (**2003)**. *Competition between dye–developer and solvent–developer interactions in a reversible thermochromic system*. *Journal of Materials Chemistry*, 13(7):1701-1704.

[118] Bašnec, K., Hajzeri, M., Klanjšek Gunde, M. (**2016)**. *Thermal and colour properties of leuco dye-based thermochromic composite with dodecanol solvent*. *Journal of Thermal Analysis and Calorimetry*, 127(1):55-61.

[119] Panák, O., Držková, M., Kaplanová, M. (**2015)**. *Insight into the evaluation of colour changes of leuco dye based thermochromic systems as a function of temperature*. *Dyes and Pigments*, 120:279-287.

[120] Yuan, Y., Zhang, N., Tao, W., Cao, X., He, Y. (**2014)**. *Fatty acids as phase change materials: a review*. *Renewable and Sustainable Energy Reviews*, 29:482-498.

[121] Kahwaji, S., Johnson, M.B., Kheirabadi, A.C., Groulx, D., White, M.A. (**2017)**. *Fatty acids and related phase change materials for reliable thermal energy storage at moderate temperatures*. *Solar Energy Materials and Solar Cells*, 167:109-120.

[122] Sato, A., Aida, Y., Shimizu, I. (**1976)**. *Pressure sensitive record material, employing diaryl alkane solvents*. United States Patent No. 3,936,566.

[123] Nakashima, A., Shibahashi, Y. (**1996)**. *Thermochromic color-memory composition*. United States Patent No. 5,558,699.

[124] Jacobson., J.M., Michael Bove, J. (**2000)**. *Bistable, Thermochromic Recording Method For Rendering Color and Gray Scale*. Patent No. 6,022,648.

[125] Naito, K., Takayama, S., Sasaki, T. (**2000)**. *Rewritable thermal recording medium and recording method*. Patent No. 6,010,808.

[126] Kazuo Yamane, M.N. (**1999)**. *Thermosensitive Reversible Recording Material*. Patent No. 5,928,988.

[127] Panák, O., Držková, M., Kailová, N., Syrový, T. (**2018)**. *Colorimetric analysis of thermochromic samples in different forms employing a digital camera*. *Measurement*, 127:554-564.

[128] Oh, W., Angupillai, S., Muthukumar, P., So, H.-S., Son, Y. (**2016)**. *Synthesis of novel tert-butyl substituted fluorans and an investigation of their thermochromic behavior*. *Dyes and Pigments*, 128:235-245.

[129] Raditoiu, A., Raditoiu, V., Nicolae, C.A., Raduly, M.F., Amariutei, V., Wagner, L.E. (**2016)**. *Optical and structural dynamical behavior of Crystal Violet Lactone – Phenolphthalein binary thermochromic systems*. *Dyes and Pigments*, 134:69-76.

[130] Zhu, C.F., Wu, A.B. (**2005)**. *Studies on the synthesis and thermochromic properties of crystal violet lactone and its reversible thermochromic complexes*. *Thermochimica Acta*, 425(1-2):7-12.

[131] Gunde, M.K., Friskovec, M., Kulcar, R., Hauptman, N., Kaplanova, M., Panak, O., Vesel, A. (**2011)**. *Functional properties of the leuco dye-based thermochromic printing inks*. Proceedings of the 63rd Annual TAGA Technical Conference, Pittsburgh, Pennsylvania, U.S.A. March 6–9, 2011.

[132] Seeboth, A., Klukowska, A., Ruhmann, R., Lötzsch, D. (**2007)**. *Thermochromic polymer materials*. *Chinese Journal of Polymer Science*, 25(2):123-125.

[133] White, M.A., LeBlanc, M. (**1999)**. *Thermochromism in commercial products*. *Journal of Chemical Education*, 76(9).

[134] Friend, C.M., Thorpe, C. (**2003)**. *Smart consumer goods*. Proceedings of the European workshop on smart structures in engineering and technology (Culshaw B, editor), Giens, France. 13 March, 2003.

[135] Jonas, A., Rubner, I., Oetken, M. (**2018)**. *Magische acetondämpfe*. *Chemkon*, 25(7):293-297.

[136] Burkinshaw, S.M., Griffiths, J., Towns, A.D. (**1998)**. *Reversibly thermochromic systems based on pH-sensitive spirolactone-derived functional dyes*. *Journal of Materials Chemistry*, 8:2677-2683.

[137] Bourque, A.N., White, M.A. (**2015)**. *Control of thermochromic behaviour in crystal violet lactone (CVL)/alkyl gallate/alcohol ternary mixtures*. *Canadian Journal of Chemistry*, 93(1):22-31.

[138] Hirata, S., Vacha, M., Watanabe, T. (**2010)**. *Investigation of quenching mechanism in thermoreversible fluorescent recording materials of fluorescence using thermochromic fluorescence resonance energy transfer*. *Japanese Journal of Applied Physics*, 49(5):052501.

[139] Hong, T. (**2007)**. *Use of Ink-jet combinatorial techniques to investigate thermochromic materials*. Master of Science, Master Thesis. Dalhousie University, Halifax, Nova Scotia. December 2007.

[140] Ibata, K., Orriishi, K., Otsuka, T., Saito, S. (**1992)**. *On the mechanism of the development and fixation of leuco-dye in thermal printing.* Paper presented at the IS&T's eigth international congress on advances in non-impact printing technologies, Williamsburg, Virginia. October 25-30, 2012.

[141] MacLaren, D.C., White, M.A. (**2005)**. *Design rules for reversible thermochromic mixtures*. *Journal of Materials Science*, 40:669-676.

[142] Ohashi, T., Gontani, S., Miyanaga, K., Kurata, T., Akatani, Y., Matsumoto, S. (**2017)**. *A novel black crystalline composite based on a fluoran dye and a bisphenol S derivative for high performance thermal papers*. *Dyes and Pigments*, 142:198-200.

[143] Takahashi, Y., Shirai, A., Segawa, T., Takahashi, T., Sakakibara, K. (**2002)**. *Why does a color-developing phenomenon occur on thermal paper comprising of a fluoran dye and a color developer molecule? Bulletin of the Chemical Society of Japan*, 75:2225–2231.

[144] Yanagita, M., Kanda, S., Tokita, S. (**1999)**. *The relationship between the steric hindrance and absorption spectrum of fluoran dyes. Part II*. *Molecular Crystals and Liquid Crystals Science and Technology Section A Molecular Crystals and Liquid Crystals*, 327(1):53-56.

[145] Tsutsui, K., Yamaguchi, T., Sato, K. (**1994)**. *Thermochromic properties of mixture systems of octadecylphosphonic acid and fluoran dye. Japanese Journal of Applied Physics*, 33(10):5925-5928.

[146] MacLaren, D.C. (**2003)**. *Investigation of reversible thermochromic mixtures*. Doctor of Philosophy, Doctoral Thesis. Dalhousie University, Halifax, Nova Scotia. July 2003.

[147] Luthern, J., Peredes, A. (**2003)**. *Determination of the stoichiometry of a thermochromic color complex via the method of continuous variation*. *Journal of Materials Science Letters*, 22:881-884.

[148] Rihs, G., Weis, C.D. (**1991)**. *Interaction of colorformers and coreactants. Part I. First crystal structures of the colorforming species composed of crystal violet lactone and metal*. *Dyes and Pigments*, 15(2):107-127.

[149] Rihs, G., Weis, C.D. (**1991)**. *Interaction of colorformers and coreactants: Part II. crystal structure of a xanthene type colorformer and cadmium iodide*. *Dyes and Pigments*, 15(3):165-173.

[150] Okada, K. (**1996)**. *X-ray crystal structure analyses and atomic charges of color former and developer. I. Color developers*. *Journal of Molecular Structure*, 380:223 - 233.

[151] Okada, K. (**1999)**. *X-ray crystal structure analysis and atomic charges of color former and developer 5. Colored formers*. *Journal of Molecular Structure*:35–51.

[152] Okada, K. (**1999)**. *X-ray crystal structure analysis and atomic charges of color former and developer 4. colored formers*. *Journal of Molecular Structure*:161–179.

[153] Takaoka, K., Maeda, S., Miura, H., Endo, K., Chong, D.P. (**1998)**. *Theoretical valence XPS and UV-visible absorption spectra of four leuco dyes using MO calculations*. *Bulletin of the Chemical Society of Japan*, 71(4):807-816.

[154] Horiguchi, T., Koshiba, Y., Ueda, Y., Origuchi, C., Tsutsui, K. (**2008)**. *Reversible coloring/decoloring reaction of leuco dye controlled by long-chain molecule*. *Thin Solid Films*, 516(9):2591-2594.

[155] Sekiguchi, Y., Takayama, S., Gotanda, T., Sano, K. (**2007)**. *Molecular structures of the colouring species of a leuco dye with phenolic colour developers*. *Chemistry Letters*, 36(8):1010-1011.

[156] Shima, H., Sato, K., Mizuguchi, J. (**2010)**. *Stabilization mechanism of a black leuco-developer system and its tinctorial strength as viewed from the crystal structure*. *Journal of Imaging Science and Technology*, 54(2):20502-1-20502-4.

[157] Kawasaki, K., Sakakibara, K. (**2007)**. *Hydrogen bond donor ability α_2^H is a good index for finding an appropriate color developer for the molecular design of functional thermal paper*. *Bulletin of the Chemical Society of Japan*, 80(2):358-364.

[158] Hojo, M., Ueda, T., Yamasaki, M., Inoue, A., Tokita, S., Yanagita, M. (**2002)**. *^{1}H and ^{13}C NMR detection of the carbocations or zwitterions from rhodamine b base, a fluoran-based black color former, tritylbenzoate, and methoxy-substituted trityl chlorides in the presence of alkali metal or alkaline earth metal perchlorates in acetonitrile solution. Bulletin of the Chemical Society of Japan*, 75:1569–1576.

[159] Yanagita, M., Aoki, I., Tokita, S. (**1997)**. *^{13}CNMR and electronic absorption spectroscopic studies on the equilibrum between the colorless lactone and the colored forms of flouran based black color former*. *Bulletin of the Chemical Society of Japan*, 70:2757-2763.

[160] Rosenthal, I., Peretz, P. (**1979)**. *Thermochromic and hyperchromic effects in rhodamine B solutions*. *The Journal of Physical Chemistry*, 83(3).

[161] Bailin, P.D., Byrne, M., Lewis, S., Liroff, R. (**2008)**. *Public awareness drives market for safer alternatives: Bisphenol A market analysis report.* Retrieved from *http://www.iehn.org/publications.reports.bpa.php*. Accessed last on 10 December, 2016.

[162] Geens, T., Goeyens, L., Covaci, A. (**2011)**. *Are potential sources for human exposure to bisphenol-A overlooked? International Journal of Hygiene and Environmental Health*, 214(5):339-47.

[163] Tsai, W.-T. (**2006)**. *Human health risk on environmental exposure to bisphenol-A: a review*. *Journal of Environmental Science and Health, Part C*, 24(2):225-255.

[164] Metz, C.M. (**2016)**. *Bisphenol A: Understanding the controversy*. *Workplace Health & Safety*, 64(1):28-36.

[165] Rochester, J.R. (**2013)**. *Bisphenol A and human health: a review of the literature*. *Reproductive Toxicology*, 42:132-55.

[166] Andra, S.S., Kalyvas, H., Andrianou, X.D., Charisiadis, P., Christophi, C.A., Makris, K.C. (**2015)**. *Preliminary evidence of the association between monochlorinated bisphenol A exposure and type II diabetes mellitus: A pilot study*. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*, 50(3):243-59.

[167] Bjornsdotter, M.K., de Boer, J., Ballesteros-Gomez, A. (**2017)**. *Bisphenol A and replacements in thermal paper: A review*. *Chemosphere*, 182:691-706.

[168] Jalal, N., Surendranath, A.R., Pathak, J.L., Yu, S., Chung, C.Y. (**2018)**. *Bisphenol A (BPA) the mighty and the mutagenic*. *Toxicology Reports*, 5:76-84.

[169] Kuiper, G.G.J.M., Lemmen, J.G., Carlsson, B., Corton, J.C., Safe, S.H., van der Saag, P.T., van der Burg, B., Gustafsson, J.-A.k. (**1998)**. *Interaction of Estrogenic Chemicals and Phytoestrogens with Estrogen Receptor β*. *Endocrinology*, 139(10):4252-4263.

[170] Diamanti-Kandarakis, E., Bourguignon, J.-P., Giudice, L.C., Hauser, R., Prins, G.S., Soto, A.M., Zoeller, R.T., Gore, A.C. (**2009)**. *Endocrine-disrupting chemicals: An endocrine society scientific statement*. *Endocrine Reviews*, 30(4):293-342.

[171] European Food Safety Authority (EFSA). (**2015)**. *Scientific opinion on the risks to public health related to the presence of bisphenol a (bpa) in foodstuffs*. *EFSA Journal*, 13(1).

[172] Bae, B., Jeong, J.H., Lee, S.J. (**2002)**. *The quantification and characterization of endocrine disruptor bisphenol-A leaching from epoxy resin*. *Water Science and Technology*, 46(11-12):381-387.

[173] Geens, T., Aerts, D., Berthot, C., Bourguignon, J.P., Goeyens, L., Lecomte, P., Maghuin-Rogister, G., Pironnet, A.M., Pussemier, L., Scippo, M.L., Van Loco, J., Covaci, A. (**2012)**. *A review of dietary and non-dietary exposure to bisphenol-A*. *Food and Chemical Toxicology*, 50(10):3725-40.

[174] Cunha, S.C., Almeida, C., Mendes, E., Fernandes, J.O. (**2011)**. *Simultaneous determination of bisphenol A and bisphenol B in beverages and powdered infant formula by dispersive liquid–liquid micro-extraction and heart-cutting multidimensional gas chromatography-mass spectrometry*. *Food Additives & Contaminants: Part A*, 28(4):513-526.

[175] Cao, X.-L., Corriveau, J., Popovic, S. (**2009)**. *Levels of bisphenol a in canned soft drink products in canadian markets*. *Journal of Agricultural and Food Chemistry*, 57(4):1307-1311.

[176] Sajiki, J., Miyamoto, F., Fukata, H., Mori, C., Yonekubo, J., Hayakawa, K. (**2007)**. *Bisphenol A (BPA) and its source in foods in Japanese markets*. *Food Additives & Contaminants*, 24(1):103-112.

[177] Goodson, A., Robin, H., Summerfield, W., Cooper, I. (**2004)**. *Migration of bisphenol A from can coatings—effects of damage, storage conditions and heating*. *Food Additives & Contaminants*, 21(10):1015-1026.

[178] Castle, L., Jickells, S.M., Gilbert, J., Harrison, N. (**1990)**. *Migration testing of plastics and microwave-active materials for high-temperature food-use applications*. *Food Additives & Contaminants*, 7(6):779-796.

[179] Carwile, J.L., Ye, X., Zhou, X., Calafat, A.M., Michels, K.B. (**2011)**. *Canned soup consumption and urinary bisphenol a: A randomized crossover trial*. *Journal of the American Medical Association (JAMA)*, 306(20):2218-2220.

[180] Braun, J.M., Kalkbrenner, A.E., Calafat, A.M., Bernert, J.T., Ye, X., Silva, M.J., Barr, D.B., Sathyanarayana, S., Lanphear, B.P. (**2011)**. *Variability and predictors of urinary*

bisphenol a concentrations during pregnancy. *Environmental Health Perspectives*, 119(1):131-137.

[181] Rudel, R.A., Gray, J.M., Engel, C.L., Rawsthorne, T.W., Dodson, R.E., Ackerman, J.M., Rizzo, J., Nudelman, J.L., Brody, J.G. (**2011)**. *Food packaging and bisphenol a and bis(2-ethyhexyl) phthalate exposure: Findings from a dietary intervention*. *Environmental Health Perspectives*, 119(7):914-920.

[182] Chapin, R.E., Adams, J., Boekelheide, K., Gray Jr, L.E., Hayward, S.W., Lees, P.S.J., McIntyre, B.S., Portier, K.M., Schnorr, T.M., Selevan, S.G., Vandenbergh, J.G., Woskie, S.R. (**2008)**. *NTP-CERHR expert panel report on the reproductive and developmental toxicity of bisphenol A*. *Birth Defects Research Part B: Developmental and Reproductive Toxicology*, 83(3):157-395.

[183] Plastics Europe. (**2007)**. *Applications of Bisphenol A*. Retrieved from *http://bisphenol-a-europe.org/what-is-bpa/*. Accessed last on 01 June, 2019.

[184] Liao, C., Liu, F., Guo, Y., Moon, H.B., Nakata, H., Wu, Q., Kannan, K. (**2012)**. *Occurrence of eight bisphenol analogues in indoor dust from the United States and several Asian countries: implications for human exposure*. *Environmental Science & Technology*, 46(16):9138-45.

[185] Fleisch, A.F., Sheffield, P.E., Chinn, C., Edelstein, B.L., Landrigan, P.J. (**2010)**. *Bisphenol A and related compounds in dental materials*. *Pediatrics*, 126(4):760-768.

[186] Ballesteros-Gómez, A., Ruiz, F.-J., Rubio, S., Pérez-Bendito, D. (**2007)**. *Determination of bisphenols A and F and their diglycidyl ethers in wastewater and river water by coacervative extraction and liquid chromatography–fluorimetry*. *Analytica Chimica Acta*, 603(1):51-59.

[187] Goldinger, D.M., Demierre, A.L., Zoller, O., Rupp, H., Reinhard, H., Magnin, R., Becker, T.W., Bourqui-Pittet, M. (**2015)**. *Endocrine activity of alternatives to BPA found in thermal paper in Switzerland*. *Regulatory Toxicology and Pharmacology*, 71(3):453-462.

[188] Fan, R.F., Zeng, B.Y., Liu, X.S., Chen, C., Zhuang, Q.W., Wang, Y.J., Hu, M.L., Lv, Y.S., Li, J.N., Zhou, Y.X., Lin, Z.Y.W. (**2015)**. *Levels of bisphenol-A in different paper products in Guangzhou, China, and assessment of human exposure via dermal contact*. *Environmental Science-Processes & Impacts*, 17(3):667-673.

[189] Babu, S., Uppu, S.N., Martin, B., Agu, O.A., Uppu, R.M. (**2015)**. *Unusually high levels of bisphenol A (BPA) in thermal paper cash register receipts (CRs): development and application of a robust LC-UV method to quantify BPA in CRs*. *Toxicology Mechanisms and Methods*, 25(5):410-416.

[190] Biedermann, S., Tschudin, P., Grob, K. (**2010)**. *Transfer of bisphenol A from thermal printer paper to the skin*. *Analytical and Bioanalytical Chemistry*, 398(1):571-6.

[191] Mendum, T., Stoler, E., VanBenschoten, H., Warner, J.C. (**2011)**. *Concentration of bisphenol A in thermal paper*. *Green Chemistry Letters and Reviews*, 4(1):81-86.

[192] Liao, C.Y., Kannan, K. (**2011)**. *Widespread occurrence of bisphenol a in paper and paper products: Implications for human exposure*. *Environmental Science & Technology*, 45(21):9372-9379.

[193] Geens, T., Goeyens, L., Kannan, K., Neels, H., Covaci, A. (**2012)**. *Levels of bisphenol-A in thermal paper receipts from Belgium and estimation of human exposure*. *Science of the Total Environment*, 435:30-33.

[194] Rocha, B.A., Azevedo, L.F., Gallimberti, M., Campiglia, A.D., Barbosa, F. (**2015)**. *High levels of bisphenol a and bisphenol s in brazilian thermal paper receipts and estimation of daily exposure*. *Journal of Toxicology and Environmental Health-Part a-Current Issues*, 78(18):1181-1188.

[195] United States Environmental Protection Agency (USEPA). (**2015)**. *Bisphenol a alternatives in thermal paper*. United States Environmental Protection Agency. Report No. Retrieved from *https://www.epa.gov/sites/production/files/2014-05/documents/bpa_final.pdf*.

[196] Panos Zarogiannis, P.F. (**2003)**. *Interim risk reduction strategy and analysis of advantages and drawbacks for bisphenol-A (Stage 4 Report)*. Department for Environment, Food and Rural Affairs (DEFRA). Report No. August 2003. Retrieved from *www.rpaltd.co.uk*.

[197] Lise, M., Helweg, C., Charlotte, H.P., Allan, W., Skak, C. (**2004)**. *Evaluation of alternatives for compounds under risk assessment in the EU, bisphenol A*. Danish Environmental Protection Agency Denmark. Report No. 901 2004. Retrieved from *https://www2.mst.dk/udgiv/publications/2004/87-7614-181-0/html/kap01_eng.htm*.

[198] Zalko, D., Jacques, C., Duplan, H., Bruel, S., Perdu, E. (**2011)**. *Viable skin efficiently absorbs and metabolizes bisphenol A*. *Chemosphere*, 82(3):424-30.

[199] Demierre, A.L., Peter, R., Oberli, A., Bourqui-Pittet, M. (**2012)**. *Dermal penetration of bisphenol A in human skin contributes marginally to total exposure*. *Toxicology Letters*, 213(3):305-8.

[200] Mielke, H., Partosch, F., Gundert-Remy, U. (**2011)**. *The contribution of dermal exposure to the internal exposure of bisphenol A in man*. *Toxicology Letters*, 204(2-3):190-8.

[201] Zhang, Y.Y., Cheng, M.Q., Wu, L., Zhang, G., Wang, Z.Z. (**2016)**. *Bisphenol A induces spermatocyte apoptosis in rare minnow Gobiocypris rarus*. *Aquatic Toxicology*, 179:18-26.

[202] Hauser, R., Sokol, R. (**2008)**. *Science linking environmental contaminant exposures with fertility and reproductive health impacts in the adult male*. *Fertility and Sterility*, 89(2, Supplement):e59-e65.

[203] Soto, A.M., Vandenberg, L.N., Maffini, M.V., Sonnenschein, C. (**2008)**. *Does breast cancer start in the womb? Basic & Clinical Pharmacology & Toxicology*, 102(2):125-133.

[204] Lang, I.A., Galloway, T.S., Scarlett, A., Henley, W.E., Depledge, M., Wallace, R.B., Melzer, D. (**2008)**. *Association of urinary bisphenol a concentration with medical disorders and laboratory abnormalities in adults. Journal of the American Medical Association (JAMA)*, 300(11):1303-1310.

[205] Bhandari, R., Xiao, J., Shankar, A. (**2013)**. *Urinary bisphenol a and obesity in US children*. *American Journal of Epidemiology*, 177(11):1263-1270.

[206] Ishido, M., Masuo, Y., Kunimoto, M., Oka, S., Morita, M. (**2004)**. *Bisphenol A causes hyperactivity in the rat concomitantly with impairment of tyrosine hydroxylase immunoreactivity*. *Journal of Neuroscience Research*, 76(3):423-433.

[207] Liu, X., Miao, M., Zhou, Z., Gao, E., Chen, J., Wang, J., Sun, F., Yuan, W., Li, D.-K. (**2015)**. *Exposure to bisphenol-A and reproductive hormones among male adults*. *Environmental Toxicology and Pharmacology*, 39(2):934-941.

[208] Inagaki, T., Smith, N.L., Sherva, K.M., Ramakrishnan, S. (**2016)**. *Cross-generational effects of parental low dose BPA exposure on the gonadotropin-releasing hormone3 system and larval behavior in medaka (Oryzias latipes)*. *Neurotoxicology*, 57:163-173.

[209] Melzer, D., Rice, N.E., Lewis, C., Henley, W.E., Galloway, T.S. (**2010)**. *Association of urinary bisphenol-A concentration with heart disease: Evidence from NHANES 2003/06*. *Plos One*, 5(1):e8673.

[210] Ehrlich, S., Williams, P.L., Missmer, S.A., Flaws, J.A., Ye, X., Calafat, A.M., Petrozza, J.C., Wright, D., Hauser, R. (**2012)**. *Urinary bisphenol A concentrations and early reproductive health outcomes among women undergoing IVF*. *Human Reproduction*, 27(12):3583-3592.

[211] Fujimoto, V.Y., Kim, D., vom Saal, F.S., Lamb, J.D., Taylor, J.A., Bloom, M.S. (**2011)**. *Serum unconjugated bisphenol A concentrations in women may adversely influence oocyte quality during in vitro fertilization*. *Fertility and Sterility*, 95(5):1816-1819.

[212] Cantonwine, D., Meeker, J.D., Hu, H., Sánchez, B.N., Lamadrid-Figueroa, H., Mercado-García, A., Fortenberry, G.Z., Calafat, A.M., Téllez-Rojo, M.M. (**2010)**. *Bisphenol a exposure in Mexico City and risk of prematurity: a pilot nested case control study*. *Environmental Health*, 9(1):62.

[213] Wolff, M.S., Britton, J.A., Boguski, L., Hochman, S., Maloney, N., Serra, N., Liu, Z., Berkowitz, G., Larson, S., Forman, J. (**2008)**. *Environmental exposures and puberty in inner-city girls*. *Environmental Research*, 107(3):393-400.

[214] Braun, J.M., Yolton, K., Dietrich, K.N., Hornung, R., Ye, X., Calafat, A.M., Lanphear, B.P. (**2009)**. *Prenatal bisphenol-A exposure and early childhood behavior*. *Environmental Health Perspectives*, 117(12):1945-1952.

[215] Zhao, H., Bi, Y., Ma, L., Zhao, L., Wang, T., Zhang, L., Tao, B., Sun, L., Zhao, Y., Wang, W., Li, X., Xu, M., Chen, J., Ning, G., Liu, J. (**2012)**. *The effects of bisphenol A (BPA) exposure on fat mass and serum leptin concentrations have no impact on bone mineral densities in non-obese premenopausal women*. *Clinical Biochemistry*, 45(18):1602-1606.

[216] Shankar, A., Teppala, S., Sabanayagam, C. (**2012)**. *Urinary bisphenol a levels and measures of obesity: results from the national health and nutrition examination survey 2003-2008*. *ISRN Endocrinol*, 2012:965243.

[217] Manfo, F., Jubendradass, R., Nantia, E., Moundipa, P., Mathur, P. (**2014)**. *Adverse effects of bisphenol-A on male reproductive function.* In: Reviews of Environmental Contamination and Toxicology Volume 228. (Whitacre DM, editor). Springer International Publishing; Cham.

[218] Karnam, S.S., Ghosh, R.C., Mondal, S., Mondal, M. (**2015)**. *Evaluation of subacute bisphenol - A toxicity on male reproductive system*. *Vet World*, 8(6):738-44.

[219] Bhandari, R.K. (**2016)**. *Medaka as a model for studying environmentally induced epigenetic transgenerational inheritance of phenotypes*. *Environmental Epigenetics*, 2(1):dvv010.

[220] Vandenberg, L.N., Ehrlich, S., Belcher, S.M., Ben-Jonathan, N., Dolinoy, D.C., Hugo, E.R., Hunt, P.A., Newbold, R.R., Rubin, B.S., Saili, K.S., Soto, A.M., Wang, H.-S., vom Saal, F.S. (**2014)**. *Low dose effects of bisphenol A*. *Endocrine Disruptors*, 1(1):e26490.

[221] vom Saal, F.S., Hughes, C. (**2005)**. *An extensive new literature concerning low-dose effects of bisphenol A shows the need for a new risk assessment*. *Environmental Health Perspectives*, 113(8):926-33.

[222] Wang, Z., Liu, H., Liu, S. (**2017)**. *Low-dose bisphenol a exposure: A seemingly instigating carcinogenic effect on breast cancer*. *Advanced Science (Weinh)*, 4(2):1600248.

[223] Kasper-Sonnenberg, M., Wittsiepe, J., Koch, H.M., Fromme, H., Wilhelm, M. (**2012)**. *Determination of bisphenol a in urine from mother-child pairs-results from the duisburg birth cohort study, Germany*. *Journal of Toxicology and Environmental Health*, 75(8-10):429-37.

[224] Robledo, C., Peck, J.D., Stoner, J.A., Carabin, H., Cowan, L., Koch, H.M., Goodman, J.R. (**2013)**. *Is bisphenol-A exposure during pregnancy associated with blood glucose levels or diagnosis of gestational diabetes? Journal of Toxicology and Environmental Health*, 76(14):865-73.

[225] Vandenberg, L.N., Maffini, M.V., Sonnenschein, C., Rubin, B.S., Soto, A.M. (**2009)**. *Bisphenol-A and the great divide: a review of controversies in the field of endocrine disruption*. *Endocrine Reviews*, 30(1):75-95.

[226] Tyl, R.W., Myers, C.B., Marr, M.C., Sloan, C.S., Castillo, N.P., Veselica, M.M., Seely, J.C., Dimond, S.S., Van Miller, J.P., Shiotsuka, R.N., Beyer, D., Hentges, S.G., Waechter, J.M., Jr. (**2008)**. *Two-generation reproductive toxicity study of dietary bisphenol a in cd-1 (swiss) mice*. *Toxicological Sciences*, 104(2):362-384.

[227] Sekizawa, J. (**2008)**. *Low-dose effects of bisphenol A: a serious threat to human health? The Journal of Toxicological Sciences*, 33(4):389-403.

[228] Myers, J.P., Saal, F.S.v., Akingbemi, B.T., Arizono, K., Belcher, S., Colborn, T., Chahoud, I., Crain, D.A., Farabollini, F., Guillette, L.J., Hassold, T., Ho, S.-m., Hunt, P.A., Iguchi, T., Jobling, S., Kanno, J., Laufer, H., Marcus, M., McLachlan, J.A., Nadal, A., Oehlmann, J., Olea, N., Palanza, P., Parmigiani, S., Rubin, B.S., Schoenfelder, G., Sonnenschein, C., Soto, A.M., Talsness, C.E., Taylor, J.A., Vandenberg, L.N., Vandenbergh, J.G., Vogel, S., Watson, C.S., Welshons, W.V., Zoeller, R.T. (**2009)**. *Why public health*

agencies cannot depend on good laboratory practices as a criterion for selecting data: The case of bisphenol a. *Environmental Health Perspectives*, 117(3):309-315.

[229] Wikipedia. *BPA controversy*. Retrieved from *https://en.wikipedia.org/wiki/BPA_controversy*. Accessed last on 04 September, 2019.

[230] European Food Safety Authority (EFSA). (**2008)**. *Bisphenol A*. Retrieved from *https://www.efsa.europa.eu/en/topics/topic/bisphenol*. Accessed last on 04 September, 2019.

[231] Egan, L. (**2010)**. *Canada declares BPA toxic, sets stage for more bans*. Retrieved from *https://www.reuters.com/article/us-bpa/canada-declares-bpa-toxic-sets-stage-for-more-bans-idUSTRE69D4MT20101014*. Accessed last on 04 Sept, 2019.

[232] Institut National de la Santé Et de la Recherche Médicale (INSERM). (**2010)**. *Bisphénol A effets sur la reproduction: Rapport préliminaire*. INSERM, Paris. Report No. 02 June, 2010. Retrieved from *https://solidarites-sante.gouv.fr/IMG/pdf/rapport_preliminaire_sur_les_perturbateurs_endocriniens_relatif_aux_effets_du_bisphenol_A_sur_la_reproduction.pdf*.

[233] Musu, T., Balué, A., Maria, P.M. (**2019)**. *Trade Union actions to phase out BPA*. Paper presented at the substitution workshop on alternatives to BPA in thermal paper, Brussels, Belgium. 26th of March, 2019.

[234] The Government of the Hong Kong Special Administrative Region. (**2017)**. *Health risks of thermal paper containing Bisphenol A*. Retrieved from *https://www.info.gov.hk/gia/general/201711/08/P2017110800531.htm*. Accessed last on 04 September, 2019.

[235] Barraza, L. (**2013)**. *A new approach for regulating bisphenol-A for the protection of the public's health*. *Journal of law, medicine & ethics*, 41(1):9-12.

[236] European Commission. (**2011a).** *Amending directive 2002/72/EC as regards the restriction of use of Bisphenol A in plastic infant feeding bottles.* Commission directive 2011/8/EU. *Official Journal of the European Union,* Brussels, 28 January 2011.

[237] European Commission. (**2013).** *Union guidance on regulation (eu) no 10/2011 on plastic materials and articles intended to come into contact with food as regards information in the supply chain. European Commission,* Brussels. 28 November, 2013.

[238] European Commission. (**2011b).** *Amending regulation (EU) no 10/2011 as regards the restriction of use of bisphenol a in plastic infant feeding bottles. Official Journal of the European Union,* Brussels, 01 April, 2011.

[239] Umweltbundesamtes. (**2012)**. *Substance monograph on bisphenol A (BPA) - reference and human biomonitoring (HBM) values for BPA in urine. Opinion of the human biomonitoring commission of the German Federal Environment Agency (UBA)*. *Bundesgesundheitsblatt Gesundheitsforschung Gesundheitsschutz*, 55(9):1215-31.

[240] Chemical Watch. (**2011)**. *France votes to ban BPA in food contact materials*. Retrieved from *https://chemicalwatch.com/8667/france-votes-to-ban-bpa-in-food-contact-materials*. Accessed last on 04 September, 2019.

[241] Stern, S. (**2013)**. *A local law to reduce exposure to bisphenol a in Suffolk County ("The Safer Sales Slip Act").* Retrieved from *https://www.scnylegislature.us/DocumentCenter/View/4506/2013-Local-Laws-PDF*. Accessed last on 08, August, 2019.

[242] European Food Safety Authority (EFSA). (**2014)**. *Draft scientific opinion on the risks to public health related to the presence of bisphenol A (BPA) in foodstuffs*. *EFSA Journal*.

[243] Registration Evaluation Authorisation and Restriction of Chemicals (REACH). (**2016)**. *REACH Regulation Annex XVII*. Retrieved from *https://echa.europa.eu/substances-restricted-under-reach/-/dislist/details/0b0236e18155ec2b*. Accessed last on 13 November, 2020.

[244] Umweltbundesamt. (**2018)**. *EU identifies Bisphenol A as a substance of very high concern*. Retrieved from *https://www.umweltbundesamt.de/en/press/pressinformation/eu-identifies-bisphenol-a-as-a-substance-of-very*. Accessed last on 13 November, 2020.

[245] Institut national de l'environnement industriel et des risques (INERIS). (**2018)**. *BPA free and no phenols added products certification*. Retrieved from *https://prestations.ineris.fr/fr/certification/bpa-free-and-no-phenols-added-products-certification*. Accessed last on 14 January, 2020.

[246] vom Saal, F.S., Akingbemi, B.T., Belcher, S.M., Birnbaum, L.S., Crain, D.A., Eriksen, M., Farabollini, F., Guillette, L.J., Jr., Hauser, R., Heindel, J.J., Ho, S.M., Hunt, P.A., Iguchi, T., Jobling, S., Kanno, J., Keri, R.A., Knudsen, K.E., Laufer, H., LeBlanc, G.A., Marcus, M., McLachlan, J.A., Myers, J.P., Nadal, A., Newbold, R.R., Olea, N., Prins, G.S., Richter, C.A., Rubin, B.S., Sonnenschein, C., Soto, A.M., Talsness, C.E., Vandenbergh, J.G., Vandenberg, L.N., Walser-Kuntz, D.R., Watson, C.S., Welshons, W.V., Wetherill, Y., Zoeller, R.T. (**2007)**. *Chapel Hill bisphenol A expert panel consensus statement: integration of mechanisms, effects in animals and potential to impact human health at current levels of exposure*. *Reproductive Toxicology*, 24(2):131-8.

[247] Boudalia, S., Oudir, M. (**2016)**. *Bisphenol-A: Legislation in industrials countries and in Algeria*. *Research Journal of Environmental Toxicology*, 10(3):189-192.

[248] Cioci, M. (**2015)**. *Reducing use of BPA and BPS thermal receipt paper in the hospitality sector. BPA in thermal receipt project: Whitepaper #2*. Minnesota Pollution Control Agency. Report No. p-p2s10-14. Retrieved from *https://www.pca.state.mn.us/sites/default/files/p-p2s10-14.pdf*.

[249] Minnesota Legislature. (**2009).** *Bisphenol-a in certain children's products. The Revisor of Statutes, State of Minnesota,* Minnesota, May 7, 2009.

[250] Safeguards. (**2019)**. *US state of Illinois bans BPA in thermal paper*. Retrieved from *https://www.sgs.com/en/news/2019/09/safeguards-12519-us-state-of-illinois-bans-bpa-in-thermal-paper*. Accessed last on 14.01.2020.

[251] Chemical Watch. (**2017)**. *Switzerland bans the use of BPA and BPS in thermal paper*. Retrieved from *https://chemicalwatch.com/register/result?o=77769&layout=main&productID=1*. Accessed last on 01 January, 2019.

[252] Federal Public Service (FPS) Economy and Health. (**2019)**. *Supply chain substitution workshop on alternatives to bisphenol A in thermal paper*. Retrieved from *https://www.health.belgium.be/en/supply-chain-substitution-workshop-alternatives-bisphenol-thermal-paper*. Accessed last on 14.01.2020.

[253] van de Poel, I., Robaey, Z. (**2017)**. *Safe-by-Design: from safety to responsibility*. *NanoEthics*, 11(3):297-306.

[254] Margerit, A. (**2019)**. *FRANCE: New national strategy on endocrine disruptors*. Retrieved from *http://lynxee.consulting/en/france-new-national-strategy-on-endocrine-disruptors-2/*. Accessed last on 14 January, 2020.

[255] United States Environmental Protection Agency (USEPA). (**2012)**. *Draft assessment of BPA thermal paper alternatives*. Retrieved from *http://www.epa.gov/dfe/pubs/projects/bpa/aa-for-bpa-fullversion.pdf*. Accessed last on 15 December, 2019.

[256] European Chemicals Agency (ECHA). (**2017)**. *Use of Bisphenol A and its alternatives in thermal paper in the EU 2014-16*. European Chemicals Agency Helsinki, Finland. Report No. 15 December 2017. Retrieved from *echa.europa.eu*.

[257] European Chemicals Agency (ECHA). (**2018)**. *Market Survey: Use of bisphenol A and its alternatives in thermal paper in the EU from 2014 to 2017*. European Chemicals Agency Helsinki, Finland, May 2018: Agency EC. Report No. May 2018. Retrieved from *https://echa.europa.eu/documents/10162/22863068/bpa_entry_en.pdf/6b1d66d4-6a1d-c1c4-e628-4a8a768f274a*.

[258] Kemikalieinspektionen. (**2012)**. *Bisfenol A i kassakvitton– rapport från ett regeringsuppdrag*. Kemikalieinspektionen. Report No. 4/12. June 2012. Retrieved from *www.kemikalieinspektionen.se*.

[259] Liao, C., Liu, F., Kannan, K. (**2012)**. *Bisphenol s, a new bisphenol analogue, in paper products and currency bills and its association with bisphenol a residues*. *Environmental Science & Technology*, 46(12):6515-22.

[260] Molina-Molina, J.M., Jiménez-Díaz, I., Fernández, M.F., Rodriguez-Carrillo, A., Peinado, F.M., Mustieles, V., Barouki, R., Piccoli, C., Olea, N., Freire, C. (**2019)**. *Determination of bisphenol A and bisphenol S concentrations and assessment of estrogen- and anti-androgen-like activities in thermal paper receipts from Brazil, France, and Spain*. *Environmental Research*, 170:406-415.

[261] Rochester, J.R., Bolden, A.L. (**2015)**. *Bisphenol S and F: A systematic review and comparison of the hormonal activity of bisphenol a substitutes*. *Environmental Health Perspectives*, 123(7):643-650.

[262] Wang, W.F., Ndungu, A.W., Wang, J. (**2016)**. *Monitoring of endocrine-disrupting compounds in surface water and sediments of the three gorges reservoir region, china*. *Archives of Environmental Contamination and Toxicology*, 71(4):509-517.

[263] Pivnenko, K., Pedersen, G.A., Eriksson, E., Astrup, T.F. (**2015)**. *Bisphenol A and its structural analogues in household waste paper*. *Waste Manag*, 44:39-47.

[264] Viñas, R., Watson Cheryl, S. (**2013)**. *Bisphenol S disrupts estradiol-induced nongenomic signaling in a rat pituitary cell line: Effects on cell functions*. *Environmental Health Perspectives*, 121(3):352-358.

[265] Danzl, E., Sei, K., Soda, S., Ike, M., Fujita, M. (**2009)**. *Biodegradation of bisphenol a, bisphenol f and bisphenol s in seawater*. *International Journal of Environmental Research and Public Health*, 6(4):1472-1484.

[266] Kabashima, K., Kobayashi, H., Iwaya, T. (**2009)**. *Compound for colour-producing composition, and recording material*. United States Patent No. 7,635,662 B2.

[267] Kawakami, H., Nozaki, C., Iwakura, K. (**1995)**. *Thermal recording material*. Patent No. 5,464,804.

[268] Yutaka, S., Toshimitsu, N., Shigetoshi, H. (**1992)**. *Heat sensitive recording material*. United States Patent No. 5,079,211.

[269] DanishEPA. (**2014)**. *Alternative technologies and substances to bisphenol A (BPA) in thermal paper receipts*. The Danish Environmental Protection Agency Copenhagen. Report No. Retrieved from *http://www.mst.dk/*.

[270] Kinch, C.D., Ibhazehiebo, K., Jeong, J.H., Habibi, H.R., Kurrasch, D.M. (**2015)**. *Low-dose exposure to bisphenol A and replacement bisphenol S induces precocious hypothalamic neurogenesis in embryonic zebrafish*. *Proceedings of the National Academy of Sciences of the United States of America*, 112(5):1475-80.

[271] Ohta, Y. (**1989)**. *Simple organic acids.* In: natural products of woody plants. (Rowe JW, editor). Springer Berlin Heidelberg; Berlin, Heidelberg.

[272] Kumar, H., Alén, R. (**2015)**. *Recovery of aliphatic low-molecular-mass carboxylic acids from hardwood kraft black liquor*. *Separation and Purification Technology*, 142:293-298.

[273] Kumar, N., Pruthi, V. (**2014)**. *Potential applications of ferulic acid from natural sources*. *Biotechnology Reports*, 4:86-93.

[274] Becerra Siabato, D.V., Petersen, N. (**2016)**. *Wärmeempfindliches Aufzeichnungsmaterial mit Salicylsäure-Derivat als mit einem Farbstoffvorläufer reaktionsfähiger (Farb-)Entwickler*. International Patent Patent No. WO 2016/016084 AI.

[275] Gore, M.P., Jayprakash, B., Vladek, P.K. (**2005)**. *Metal salt activators for use in leuco dye compositions*. United States Patent No. 6,890,614 B2.

[276] APPVION. (**2014)**. *Appvion launches first thermal receipt paper made using vitamin c in time for the 2014 holiday shopping season*. Retrieved from *http://www.appvion.com/mobile/Documents/Historical%20News/Appvion_Alpha_Free_national_release.pdf*. Accessed last on 13 November, 2020.

[277] Jeffrey, N., Richard, H.E., Robert, M.O.B., Kevin, R., Howard, K., Mark, S.V.M., Lan, D. (**2016)**. *Developer for thermally responsive record materials*. United States Patent No. 9,475,328 B2.

[278] Yoshikawa, T., Yagi, T., Shinohara, S., Fukunaga, T., Nakasaka, Y., Tago, T., Masuda, T. (**2013)**. *Production of phenols from lignin via depolymerization and catalytic cracking*. *Fuel Processing Technology*, 108:69-75.

[279] Fernández-Rodríguez, J., Erdocia, X., Sánchez, C., González Alriols, M., Labidi, J. (**2017)**. *Lignin depolymerization for phenolic monomers production by sustainable processes*. *Journal of Energy Chemistry*.

[280] Barta, K., Warner, G.R., Beach, E.S., Anastas, P.T. (**2014)**. *Depolymerization of organosolv lignin to aromatic compounds over Cu-doped porous metal oxides*. *Green Chemistry*, 16(1):191-196.

[281] Wang, H., Tucker, M., Ji, Y. (**2013)**. *Recent development in chemical depolymerization of lignin: A review*. *Journal of Applied Chemistry*, 2013:9.

[282] Roberts, V.M., Stein, V., Reiner, T., Lemonidou , A., Li, X., Lercher, J.A. (**2011)**. *Towards quantitative catalytic lignin depolymerization*. *Chemistry – A European Journal*, 17(21):5939-5948.

[283] Faustino, H., Gil, N., Baptista, C., Duarte, A.P. (**2010)**. *Antioxidant activity of lignin phenolic compounds extracted from kraft and sulphite black liquors*. *Molecules*, 15(12):9308-22.

[284] Fache, M., Viola, A., Auvergne, R., Boutevin, B., Caillol, S. (**2015)**. *Biobased epoxy thermosets from vanillin-derived oligomers*. *European Polymer Journal*, 68:526-535.

[285] Laird, K. (**2014)**. *Lignin-derived compound to replace potentially harmful Bisphenol-A in plastics*. Retrieved from *https://www.plasticstoday.com/content/lignin-derived-compound-replace-potentially-harmful-bisphenol-plastics/82706564820207*. Accessed last on 13 November, 2020.

[286] Nicastro, K.H., Kloxin, C.J., Epps, T.H. (**2018)**. *Potential lignin-derived alternatives to bisphenol a in diamine-hardened epoxy resins*. *ACS Sustainable Chemistry & Engineering*, 6(11):14812-14819.

[287] Peng, Y., Nicastro, K.H., Epps, T.H., Wu, C. (**2018)**. *Evaluation of estrogenic activity of novel bisphenol a alternatives, four bioinspired bisguaiacol f specimens, by in vitro assays*. *Journal of Agricultural and Food Chemistry*, 66(44):11775-11783.

[288] Zuñiga, C., Lligadas, G., Ronda, J.C., Galià, M., Cádiz, V. (**2017)**. *Chapter 23 - polybenzoxazine materials from renewable diphenolic acid.* In: Advanced and Emerging

Polybenzoxazine Science and Technology. (Ishida H, Froimowicz P, editor). Elsevier; Amsterdam.

[289] Chowdhury, A., Sarkar, S., Chowdhury, A., Bardhan, S., Mandal, P., Chowdhury, M. (**2016)**. *Tea waste management: A case study from west bengal, india*. *Indian Journal of Science and Technology*, 9(42).

[290] Janissen, B., Huynh, T. (**2018)**. *Chemical composition and value-adding applications of coffee industry by-products: A review*. *Resources, Conservation and Recycling*, 128:110-117.

[291] Yilmaz, Y., Toledo, R.T. (**2004)**. *Major flavonoids in grape seeds and skins: Antioxidant capacity of catechin, epicatechin, and gallic acid*. *Journal of Agricultural and Food Chemistry*, 52(2):255-260.

[292] Bianchi, S. (**2017)**. *Extraction and characterization of bark tannins from domestic softwood species*. Doctoral degree, Doctoral Thesis. Biology Faculty of Mathematics, Informatics and Natural Sciences (MIN), University of Hamburg, Hamburg. 13 January, 2017.

[293] Tutty, G.C. (**1981)**. *Image wise developable system*. United States Patent No. 4,295,662.

[294] Itabashi, Y., Hayashi, T., Igarashi, A. (**1990)**. *Heat-sensitive recording material*. United States Patent No. 4,923,844.

[295] Duval, A., Averous, L. (**2016)**. *Characterization and physicochemical properties of condensed tannins from acacia catechu*. *J Agric Food Chem*, 64(8):1751-60.

[296] Gaugler, M., Grigsby, W.J. (**2009)**. *Thermal degradation of condensed tannins from radiata pine bark*. *Journal of Wood Chemistry and Technology*, 29(4):305-321.

[297] Suzuki, K., Kimura, Y., Sumikawa, N. (**2004)**. *Developers for thermal recording materials and thermal recording materials*. European Patent Patent No. 1 393 923 A1.

[298] Mamoru, S., Kaori, S., Takashi, O., Takashi, D. (**2004)**. *Developer for thermal recording material and thermal recording materials*. United States Patent Patent No. 2004/0241598 A1.

[299] Mamoru, S., Kaori, S., Yoshihide, K., Naomi, S. (**2006)**. *Developers for thermal recording materals and thermal recording materials*. United State Patent Patent No. 7,141,359 B2.

[300] Brinkman, K.M., John, L.S., David, R.H. (**1991)**. *Alkyl salicylate developer resin for carbonless copy paper and imaging use*. Patent No. 5,017,546.

[301] Liang, R.-C., Kintz, K.A., Joseph, G.O.C., Paul, C.A. (**1991)**. *Vinyl developer resins*. United States Patent No. 5,008,237.

[302] Gao, C., Yan, D. (**2004)**. *Hyperbranched polymers: from synthesis to applications*. *Progress in Polymer Science*, 29(3):183-275.

[303] Pizzi, A. (**2006)**. *Recent developments in eco-efficient bio-based adhesives for wood bonding: opportunities and issues*. *Journal of Adhesion Science and Technology*, 20(8):829-846.

[304] Tondi, G. (**2017)**. *Tannin-based copolymer resins: Synthesis and characterization by solid state ^{13}C NMR and FT-IR spectroscopy*. *Polymers (Basel)*, 9(6).

[305] Kosche, H. (**1980)**. *Pressure-sensitive recording or copying material*. United States Patent No. 4,210,345.

[306] Riou, C.R., Jean, F.F. (**1985)**. *Thermographic recording compositions*. United States Patent No. 4,536,219.

[307] Michael, H. (**2019)**. *BLUE4EST -An alternative thermal printing media*. Paper presented at the substitution workshop on alternatives to BPA in thermal paper, Brussels, Belgium. 26 March, 2019.

[308] Paint & Coatings Industry Magazine (PCIMAG). (**2017)**. *BPA-free thermal paper coating technology named 2017 ICIS innovation award finalist*. Retrieved from *https://www.pcimag.com/articles/103830-bpa-free-thermal-paper-coating-technology-named-2017-icis-innovation-award-finalist*. Accessed last on 13 November, 2020.

[309] Luthern, J., Peredes, A. (**2000)**. *Determination of the stoichiometry of a thermochromic color complex via Job's method*. *Journal of Materials Science Letters*, 19:185-188.

[310] Lawton, W.R. (**1978)**. *Heat sensitive recording compostion containing a complexed phenolics and a spropyran or leuco lactone*. United States Patent No. 4,097,288.

[311] Panák, O., Držková, M., Svoboda, R., Klanjšek Gunde, M. (**2016)**. *Combined colorimetric and thermal analyses of reversible thermochromic composites using crystal violet lactone as a colour former*. *Journal of Thermal Analysis and Calorimetry*, 127(1):633-640.

[312] Bianchi, S., Kroslakova, I., Janzon, R., Mayer, I., Saake, B., Pichelin, F. (**2015)**. *Characterization of condensed tannins and carbohydrates in hot water bark extracts of European softwood species*. *Phytochemistry*, 120:53-61.

[313] Melone, F., Saladino, R., Lange, H., Crestini, C. (**2013)**. *Tannin structural elucidation and quantitative ^{31}P NMR analysis. 2. Hydrolyzable tannins and proanthocyanidins*. *Journal of Agricultural and Food Chemistry*, 61(39):9316-24.

[314] Melone, F., Saladino, R., Lange, H., Crestini, C. (**2013)**. *Tannin structural elucidation and quantitative ^{31}P NMR analysis. 1. Model compounds*. *Journal of Agricultural and Food Chemistry*, 61(39):9307-15.

[315] EasyRGB. *Convert color data into different standards and color spaces*. Retrieved from *https://www.easyrgb.com/en/convert.php#inputFORM*. Accessed last on 15 December, 2020.

[316] Lewis, L.M., Indig, G.L. (**2000)**. *Solvent effects on the spectroscopic properties of triarylmethane dyes*. *Dyes and Pigments*, 46:145-154.

[317] Sancho, M.I., Almandoz, M.C., Blanco, S.E., Castro, E.A. (**2011)**. *Spectroscopic study of solvent effects on the electronic absorption spectra of flavone and 7-hydroxyflavone in neat and binary solvent mixtures*. *International Journal of Molecular Sciences*, 12(12):8895-912.

[318] Behera, P.K., Xess, A., Sahu, S. (**2014)**. *Solvent effects on the electronic spectra of some heterocyclic azo dyes*. *Bulletin of the Korean Chemical Society*, 35(2):610-616.

[319] Patel, R.G., Patel, M.P., Patel, R.G. (**2005)**. *3,6-Disubtituted fluorans containing 4(3H)-quinazolinon-3-yl, diethyl amino groups and their application in reversible thermochromic materials*. *Dyes and Pigments*, 66(1):7-13.

[320] Carla S. Oliveira, K.P.B., Mauricio S. Baptista, Guilherme L. Indig. (**2002)**. *Solvent and concentration effects on the visible spectra of tripara-dialkylamino-substituted triarylmethane dyes in liquid solutions*. *Spectrochimica Acta Part A*, 58:2971-2982.

[321] Sekiguchi, Y., Takayama, S., Gotanda, T., Sano, K. (**2006)**. *Importance of solvent polarity in the equilibrium reaction of leuco dye and developer*. *Chemistry Letters*, 35(4):458-459.

[322] Muthyala, R., Lan, X. (**2002)**. *The chemistry of leuco triarylmethanes.* In: Chemistry and Applications of Leuco Dyes. (Muthyala R, editor). Springer US; Boston, MA.

[323] Sachin, P., Manish, P., Ranjan, P. (**2007)**. *Synthesis and characterization of heterocyclic substituted fluoran compounds*. *Journal of the Serbian Chemical Society*, 72(11):1039–1044.

[324] Orndorff, W.R., Gibbs, R.C., Shapiro, C.V. (**1928)**. *The absorption spectra of fluorescein, fluoran and some related compounds*. *Journal of the American Chemical Society*, 50(3):819-828.

[325] Aghili, Y. (**2013)**. *Study of chromogenic zwitterionic chromophores*. Master in Chemistry, Master Thesis. Chemistry, Carleton University, Ottawa, Ontario. August 2013.

[326] Bellamy, L.J. (**1975)**. *Esters and Lactones.* In: The infra-red spectra of complex molecules. (Bellamy LJ, editor). Springer Netherlands; Dordrecht.

[327] Zhu, X., Liu, Y., Dong, N., Li, Z. (**2017)**. *Fabrication and characterization of reversible thermochromic wood veneers*. *Sci Rep*, 7(1):16933.

[328] Raditoiu, V., Raditoiu, A., Wagner, L., Amariutei, V., Nicolae, C.A. (**2013)**. *Thermochromic systems based on complexes of some triarylmethane dyes*. *Rev CHIM (Bucharest)*, 64(2).

[329] Fletcher, I.J., Zink, R. (**2002)**. *Synthesis and properties of phthalide-type color Formers.* In: Chemistry and Applications of Leuco Dyes. (Muthyala R, editor). Springer US; Boston, MA.

[330] Panák, O., Držková, M., Kaplanová, M., Novak, U., Klanjšek Gunde, M. (**2017)**. *The relation between colour and structural changes in thermochromic systems comprising crystal violet lactone, bisphenol A, and tetradecanol*. *Dyes and Pigments*, 136:382-389.

[331] Missio, A.L., Tischer, B., dos Santos, P.S.B., Codevilla, C., de Menezes, C.R., Barin, J.S., Haselein, C.R., Labidi, J., Gatto, D.A., Petutschnigg, A., Tondi, G. (**2017)**. *Analytical characterization of purified mimosa (Acacia mearnsii) industrial tannin extract: Single and sequential fractionation*. *Separation and Purification Technology*, 186:218-225.

[332] Kamanashis, D., Md, Y., Nasir, U.M., Md, S.I., Nayma, M. (**2014)**. *Evaluation of antioxidant and cytotoxic activity of methanolic extract of Mimosa pudica leaves*. *The Pharma Innovation - Journal*, 3(4).

[333] Moncao, N.B., Araujo, B.Q., Silva Jdo, N., Lima, D.J., Ferreira, P.M., Airoldi, F.P., Pessoa, C., Cito, A.M. (**2015)**. *Assessing chemical constituents of Mimosa caesalpiniifolia stem bark: possible bioactive components accountable for the cytotoxic effect of M. caesalpiniifolia on human tumour cell lines*. *Molecules*, 20(3):4204-24.

[334] Poudel, P.R., Tamura, H., Kataoka, I., Mochioka, R. (**2008)**. *Phenolic compounds and antioxidant activities of skins and seeds of five wild grapes and two hybrids native to Japan*. *Journal of Food Composition and Analysis*, 21(8):622-625.

[335] Rababah, T.M., Ereifej, K.I., Al-Mahasneh, M.A., Ismaeal, K., Hidar, A.-G., Yang, W. (**2008)**. *Total phenolics, antioxidant activities, and anthocyanins of different grape seed cultivars grown in jordan*. *International Journal of Food Properties*, 11(2):472-479.

[336] Scott, R., De Palma, D., Vinogradov, S. (**1968)**. *Proton-transfer complexes. I. Preferential solvation of p-nitrophenol-amine complexes in nonaqueous-solvent mixtures*. *The Journal of Physical Chemistry*, 72(9):3192-3201.

[337] Barry, J.E., Finkelstein, M., Hutchins, G.A., Ross, S.D. (**1983)**. *Hydrogen bonded complexes IV: Urea-phenol complexes*. *Tetrahedron*, 39(13):2151-2156.

[338] Utas, J. (**2006)**. *Hydrogen bonded phenols as models for redoxactive tyrosines in enzymes*. Doctoral Degree, Doctoral Thesis. Organic Chemistry, Arrhenius Laboratory, Stockholm University, Sweden. May 2006.

[339] Kavitha, C., Prabu, N.P.S., Mohan, M.L.N.M. (**2014)**. *Birefringence study in hydrogen bonded complexes*. *Molecular Crystals and Liquid Crystals*, 592(1):163-180.

[340] Santiago-Medina, F.-J., Pizzi, A., Basso, M., Delmotte, L., Celzard, A. (**2017)**. *Polycondensation resins by flavonoid tannins reaction with amines*. *Polymers*, 9(12):37.

[341] Ramires, E.C., Megiatto, J.D., Gardrat, C., Castellan, A., Frollini, E. (**2010)**. *Biobased composites from glyoxal–phenolic resins and sisal fibers*. *Bioresource Technology*, 101(6):1998-2006.

[342] Jang, Y.I., Choi, W.H., An, B.K. (**2013)**. *Hyperbranched poly(aryl ester)s as developer materials for thermal printing system*. *Bulletin of the Korean Chemical Society*, 34(4):1225-1231.

7 Appendix

Table A1. Description of samples

S/N	Sample code	Sample description
1.	VI	Mixture of 3.75 X 10-5 mol of ODB-2 and 1g of tetradecanol.
2.	VII	Mixture of vanillin and ODB-2 in ratio 1:9 with ca. 1g tetradecanol.
3.	VIII	Mixture of vanillin and ODB-2 in ratio 1:4 with ca. 1g tetradecanol.
4.	VIV	Mixture of vanillin and ODB-2 in ratio 1:2.3 with ca. 1g tetradecanol.
5.	VV	Mixture of vanillin and ODB-2 in ratio 1:1.5 with ca. 1g tetradecanol.
6.	VVI	Mixture of vanillin and ODB-2 in ratio 1:1 with ca. 1g tetradecanol.
7.	VVII	Mixture of vanillin and ODB-2 in ratio 1.5:1 with ca. 1g tetradecanol.
8.	VVIII	Mixture of vanillin and ODB-2 in ratio 2.3:1 with ca. 1g tetradecanol.
9.	VIX	Mixture of vanillin and ODB-2 in ratio 4:1 with ca. 1g tetradecanol.
10.	VX	Mixture of vanillin and ODB-2 in ratio 9:1 with ca. 1g tetradecanol.
11.	VXI	Mixture of 3.75 X 10-5 mol of vanillin and 1g of tetradecanol.
12.	VAI	Mixture of 3.75 X 10-5 mol of ODB-2 and 1g of tetradecanol.
13.	VAII	Mixture of vanillic acid and ODB-2 in ratio 1:9 with ca. 1g tetradecanol.
14.	VAIII	Mixture of vanillic acid and ODB-2 in ratio 1:4 with ca. 1g tetradecanol.
15.	VAIV	Mixture of vanillic acid and ODB-2 in ratio 1:2.3 with ca. 1g tetradecanol.
16.	VAV	Mixture of vanillic acid and ODB-2 in ratio 1:1.5 with ca. 1g tetradecanol.
17.	VAVI	Mixture of vanillic acid and ODB-2 in ratio 1:1 with ca. 1g tetradecanol.
18.	VAVII	Mixture of vanillic acid and ODB-2 in ratio 1.5:1 with ca. 1g tetradecanol.
19.	VAVIII	Mixture of vanillic acid and ODB-2 in ratio 2.3:1 with ca. 1g tetradecanol.
20.	VAIX	Mixture of vanillic acid and ODB-2 in ratio 4:1 with ca. 1g tetradecanol.
21.	VAX	Mixture of v vanillic acid and ODB-2 in ratio 9:1 with ca. 1g tetradecanol.
22.	VAXI	Mixture of 3.75 X 10-5 mol of vanillic acid and 1g of tetradecanol.
23.	VAI_5	Mixture of 15 x 10^{-5}mol of vanillic acid and 1g of tetradecanol.
24.	$VAII_5$	Mixture of vanillic acid and ODB-2 in ratio 5:9 with ca. 1g tetradecanol.
25.	$VAIII_5$	Mixture of vanillic acid and ODB-2 in ratio 5:4 with ca. 1g tetradecanol.
26.	$VAIV_5$	Mixture of vanillic acid and ODB-2 in ratio 5:2.3 with ca. 1g tetradecanol.
27.	VAV_5	Mixture of vanillic acid and ODB-2 in ratio 5:1.5 with ca. 1g tetradecanol.
28.	$VAVI_5$	Mixture of vanillic acid and ODB-2 in ratio 5:1 with ca. 1g tetradecanol.
29.	$VAVII_5$	Mixture of vanillic acid and ODB-2 in ratio 7.5:1 with ca. 1g tetradecanol.
30.	MIM	Methanol fraction of mimosa extract
31.	MIM-S	Methanol fraction of mimosa sulphite extract

	Sample code	Sample description
32.	GSE	Methanol fraction of grape seed extract
33.	MIM_R	Raw mimosa extract
34.	$MIM\text{-}S_R$	Raw mimosa sulphite extract
35.	GSE_R	Raw grape seed extract
36.	MIM-H	Mimosa-amine complex produced from MIM and HMDA
37.	MIM-S-H	Mimosa sulphite-amine complex produced from MIM-S and HMDA
38.	GSE-H	Grape seed extract-amine complex produced from GSE and HMDA
39.	RES-H	Resorcinol-amine complex produced from resorcinol and HMDA
40.	PH-H	Phloroglucinol-amine complex produced from phloroglucinol and HMDA
41.	CAT-H	Catechin-amine complex produced from catechin and HMDA
42.	MIM-CP2	Polymer produced from MIM and glyoxal (10ml, 40%) at pH 2
43.	MIM-CP7	Polymer produced from MIM and glyoxal (10ml, 40%) at pH 7
44.	MIM-CP9	Polymer produced from MIM and glyoxal (10ml, 40%) at pH 9
45.	MIM-S-CP2	Polymer produced from MIM-S and glyoxal (10ml, 40%) at pH 2
46.	MIM-S-CP7	Polymer produced from MIM-S and glyoxal (10ml, 40%) at pH 7
47.	MIM-S-CP9	Polymer produced from MIM-S and glyoxal (10ml, 40%) at pH 9
48.	GSE-CP2	Polymer produced from GSE and glyoxal (10ml, 40%) at pH 2
49.	GSE-CP7	Polymer produced from GSE and glyoxal (10ml, 40%) at pH 7
50.	GSE-CP9	Polymer produced from GSE and glyoxal (10ml, 40%) at pH 9
51.	TA-CP2	Polymer produced from tannic acid and glyoxal (10ml, 40%) at pH 2
52.	TA-CP7	Polymer produced from tannic acid and glyoxal (10ml, 40%) at pH 7
53.	TA-CP9	Polymer produced from tannic acid and glyoxal (10ml, 40%) at pH 9
54.	PH-CP2	Polymer produced from phloroglucinol and glyoxal (10ml, 40%) at pH 2
55.	PH-CP7	Polymer produced from phloroglucinol and glyoxal (10ml, 40%) at pH 7
56.	PH-CP9	Polymer produced from phloroglucinol and glyoxal (10ml, 40%) at pH 9
57.	PH-CP2-12	Polymer produced from phloroglucinol and glyoxal (12ml, 40%) at pH 2
58.	PH-CP2-25	Polymer produced from phloroglucinol and glyoxal (25ml, 40%) at pH 2
59.	PH-CP2-40	Polymer produced from phloroglucinol and glyoxal (40ml, 40%) at pH 2
60.	$RES\text{-}H_{0.5}$	Mixture of RES-H and ODB-2 in the ratio 0.5:1
61.	$RES\text{-}H_1$	Mixture of RES-H and ODB-2 in the ratio 1:1
62.	$RES\text{-}H_{1.5}$	Mixture of RES-H and ODB-2 in the ratio 1.5:1
63.	$RES\text{-}H_2$	Mixture of RES-H and ODB-2 in the ratio 2:1
64.	$RES\text{-}H_4$	Mixture of RES-H and ODB-2 in the ratio 4:1
65.	$RES\text{-}H_8$	Mixture of RES-H and ODB-2 in the ratio 8:1

	Sample code	Sample description
66.	MIM-CP2$_{0.5}$	Mixture of MIM-CP2 and ODB-2 in the ratio 0.5:1
67.	MIM-CP2$_{1}$	Mixture of MIM-CP2 and ODB-2 in the ratio 1:1
68.	MIM-CP2$_{1.5}$	Mixture of MIM-CP2 and ODB-2 in the ratio 1.5:1
69.	MIM-CP2$_{2}$	Mixture of MIM-CP2 and ODB-2 in the ratio 2:1
70.	MIM-CP2$_{4}$	Mixture of MIM-CP2 and ODB-2 in the ratio 4:1
71.	MIM-CP2$_{8}$	Mixture of MIM-CP2 and ODB-2 in the ratio 8:1
72.	MIM S-CP2$_{0.5}$	Mixture of MIM S-CP2 and ODB-2 in the ratio 0.5:1
73.	MIM S-CP2$_{1}$	Mixture of MIM S-CP2 and ODB-2 in the ratio 1:1
74.	MIM S-CP2$_{1.5}$	Mixture of MIM S-CP2 and ODB-2 in the ratio 1.5:1
75.	MIM S-CP2$_{2}$	Mixture of MIM S-CP2 and ODB-2 in the ratio 2:1
76.	MIM S-CP2$_{4}$	Mixture of MIM S-CP2 and ODB-2 in the ratio 4:1
77.	MIM S-CP2$_{8}$	Mixture of MIM S-CP2 and ODB-2 in the ratio 8:1
78.	GSE-CP2$_{0.5}$	Mixture of GSE-CP2 and ODB-2 in the ratio 0.5:1
79.	GSE -CP2$_{1}$	Mixture of GSE-CP2 and ODB-2 in the ratio 1:1
80.	GSE-CP2$_{1.5}$	Mixture of GSE-CP2 and ODB-2 in the ratio 1.5:1
81.	GSE-CP2$_{2}$	Mixture of GSE-CP2 and ODB-2 in the ratio 2:1
82.	GSE-CP2$_{4}$	Mixture of GSE-CP2 and ODB-2 in the ratio 4:1
83.	GSE-CP2$_{8}$	Mixture of GSE-CP2 and ODB-2 in the ratio 8:1
84.	GSE-CP9$_{0.5}$	Mixture of GSE-CP9 and ODB-2 in the ratio 0.5:1
85.	GSE-CP9$_{1}$	Mixture of GSE-CP9 and ODB-2 in the ratio 1:1
86.	GSE-CP9$_{1.5}$	Mixture of GSE-CP9 and ODB-2 in the ratio 1.5:1
87.	GSE-CP9$_{2}$	Mixture of GSE-CP9 and ODB-2 in the ratio 2:1
88.	GSE-CP9$_{4}$	Mixture of GSE-CP9 and ODB-2 in the ratio 4:1
89.	GSE-CP9$_{8}$	Mixture of GSE-CP9 and ODB-2 in the ratio 8:1
90.	PH-CP2-12$_{0.5}$	Mixture of PH-CP2-12 and ODB-2 in the ratio 0.5:1
91.	PH-CP2-12$_{1}$	Mixture of PH-CP2-12 and ODB-2 in the ratio 1:1
92.	PH-CP2-12$_{1.5}$	Mixture of PH-CP2-12 and ODB-2 in the ratio 1.5:1
93.	PH-CP2-12$_{2}$	Mixture of PH-CP2-12 and ODB-2 in the ratio 2:1
94.	PH-CP2-12$_{4}$	Mixture of PH-CP2-12 and ODB-2 in the ratio 4:1
95.	PH-CP2-12$_{8}$	Mixture of PH-CP2-12 and ODB-2 in the ratio 8:1
96.	PH-CP2-40$_{0.5}$	Mixture of PH-CP2-40 and ODB-2 in the ratio 0.5:1
97.	PH-CP2-40$_{1}$	Mixture of PH-CP2-40 and ODB-2 in the ratio 1:1
98.	PH-CP2-40$_{1.5}$	Mixture of PH-CP2-40 and ODB-2 in the ratio 1.5:1
99.	PH-CP2-40$_{2}$	Mixture of PH-CP2-40 and ODB-2 in the ratio 2:1

	Sample code	Sample description
100.	PH-CP2-40$_4$	Mixture of PH-CP2-40 and ODB-2 in the ratio 4:1
101.	PH-CP2-40$_8$	Mixture of PH-CP2-40 and ODB-2 in the ratio 8:1
102.	PH-CP2$_{0.5}$	Mixture of PH-CP2 and ODB-2 in the ratio 0.5:1
103.	PH-CP2$_1$	Mixture of PH-CP2 and ODB-2 in the ratio 1:1
104.	PH-CP2$_{1.5}$	Mixture of PH-CP2 and ODB-2 in the ratio 1.5:1
105.	PH-CP2$_2$	Mixture of PH-CP2 and ODB-2 in the ratio 2:1
106.	PH-CP2$_4$	Mixture of PH-CP2 and ODB-2 in the ratio 4:1
107.	PH-CP2$_8$	Mixture of PH-CP2 and ODB-2 in the ratio 8:1
108.	VV1	Mixture of vanillin and vanillic acid in mol ratio 1:1 with ODB-2 (0.05g), tetradecanol (5g), and PVA (2.5g)
109.	VV2	Mixture of vanillin and vanillic acid in mol ratio 2:1 with ODB-2 (0.05g), tetradecanol (5g), and PVA (2.5g)
110.	VV3	Mixture of vanillin and vanillic acid in mol ratio 3:1 with ODB-2 (0.05g), tetradecanol (5g), and PVA (2.5g)
111.	VV4	Mixture of vanillin and vanillic acid in mol ratio 4:1 with ODB-2 (0.05g), tetradecanol (5g), and PVA (2.5g)
112.	VV5	Mixture of vanillin and vanillic acid in mol ratio 5:1 with ODB-2 (0.05g) and tetradecanol (5g)
113.	VV6	Mixture of vanillin and vanillic acid in mol ratio 1:2 with ODB-2 (0.05g), tetradecanol (5g), and PVA (2.5g)
114.	VV7	Mixture of vanillin and vanillic acid in mol ratio 1:3 with ODB-2 (0.05g), tetradecanol (5g), and PVA (2.5g)
115.	VV8	Mixture of vanillin and vanillic acid in mol ratio 1:4 with ODB-2 (0.05g), tetradecanol (5g), and PVA (2.5g)
116.	VV9	Mixture of vanillin and vanillic acid in mol ratio 1:5 with ODB-2 (0.05g), tetradecanol (5g), and PVA (2.5g)
117.	RES-H-VA1	Mixture of 90% RES-H and 10% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
118.	RES-H-VA2	Mixture of 80% RES-H and 20% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
119.	RES-H-VA3	Mixture of 70% RES-H and 30% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
120.	RES-H-VA4	Mixture of 60% RES-H and 40% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
121.	RES-H-VA5	Mixture of 50% RES-H and 50% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
122.	RES-H-VA6	Mixture of 10% RES-H and 90% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
123.	RES-H-VA7	Mixture of 20% RES-H and 80% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)

	Sample code	Sample description
124.	RES-H-VA8	Mixture of 30% RES-H and 70% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
125.	RES-H-VA9	Mixture of 40% RES-H and 60% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
126.	RES-H-V1	Mixture of 90% RES-H and 10% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
127.	RES-H-V2	Mixture of 80% RES-H and 20% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
128.	RES-H-V3	Mixture of 70% RES-H and 30% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
129.	RES-H-V4	Mixture of 60% RES-H and 40% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
130.	RES-H-V5	Mixture of 50% RES-H and 50% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
131.	RES-H-V6	Mixture of 10% RES-H and 90% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
132.	RES-H-V7	Mixture of 20% RES-H and 80% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
133.	RES-H-V8	Mixture of 30% RES-H and 70% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
134.	RES-H-V9	Mixture of 40% RES-H and 60% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
135.	RES-H-TA1	Mixture of 90% RES-H and 10% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
136.	RES-H-TA2	Mixture of 80% RES-H and 20% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
137.	RES-H-TA3	Mixture of 70% RES-H and 30% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
138.	RES-H-TA4	Mixture of 60% RES-H and 40% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
139.	RES-H-TA5	Mixture of 50% RES-H and 50% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
140.	RES-H-TA6	Mixture of 10% RES-H and 90% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
141.	RES-H-TA7	Mixture of 20% RES-H and 80% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
142.	RES-H-TA8	Mixture of 30% RES-H and 70% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
143.	RES-H-TA9	Mixture of 40% RES-H and 60% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
144.	RES-H-CA1	Mixture of 90% RES-H and 10% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)

	Sample code	Sample description
145.	RES-H-CA2	Mixture of 80% RES-H and 20% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
146.	RES-H-CA3	Mixture of 70% RES-H and 30% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
147.	RES-H-CA4	Mixture of 60% RES-H and 40% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
148.	RES-H-CA5	Mixture of 50% RES-H and 50% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
149.	RES-H-CA6	Mixture of 10% RES-H and 90% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
150.	RES-H-CA7	Mixture of 20% RES-H and 80% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
151.	RES-H-CA8	Mixture of 30% RES-H and 70% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
152.	RES-H-CA9	Mixture of 40% RES-H and 60% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
153.	RES-H-AS1	Mixture of 90% RES-H and 10% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
154.	RES-H-AS2	Mixture of 80% RES-H and 20% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
155.	RES-H-AS3	Mixture of 70% RES-H and 30% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
156.	RES-H-AS4	Mixture of 60% RES-H and 40% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
157.	RES-H-AS5	Mixture of 50% RES-H and 50% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
158.	RES-H-AS6	Mixture of 10% RES-H and 90% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
159.	RES-H-AS7	Mixture of 20% RES-H and 80% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
160.	RES-H-AS8	Mixture of 30% RES-H and 70% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
161.	RES-H-AS9	Mixture of 40% RES-H and 60% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
162.	RES-H-SLY1	Mixture of 90% RES-H and 10% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
163.	RES-H-SLY2	Mixture of 80% RES-H and 20% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
164.	RES-H-SLY3	Mixture of 70% RES-H and 30% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
165.	RES-H-SLY4	Mixture of 60% RES-H and 40% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)

	Sample code	Sample description
166.	RES-H-SLY5	Mixture of 50% RES-H and 50% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
167.	RES-H-SLY6	Mixture of 10% RES-H and 90% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
168.	RES-H-SLY7	Mixture of 20% RES-H and 80% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
169.	RES-H-SLY8	Mixture of 30% RES-H and 70% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
170.	RES-H-SLY9	Mixture of 40% RES-H and 60% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
171.	PHCP2-VA1	Mixture of 90% PHCP2 and 10% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
172.	PHCP2-VA2	Mixture of 80% PHCP2 and 20% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
173.	PHCP2-VA3	Mixture of 70% PHCP2 and 30% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
174.	PHCP2-VA4	Mixture of 60% PHCP2 and 40% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
175.	PHCP2-VA5	Mixture of 50% PHCP2 and 50% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
176.	PHCP2-VA6	Mixture of 10% PHCP2 and 90% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
177.	PHCP2-VA7	Mixture of 20% PHCP2 and 80% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
178.	PHCP2-VA8	Mixture of 30% PHCP2 and 70% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
179.	PHCP2-VA9	Mixture of 40% PHCP2 and 60% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
180.	PHCP2-V1	Mixture of 90% PHCP2 and 10% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
181.	PHCP2-V2	Mixture of 80% PHCP2 and 20% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
182.	PHCP2-V3	Mixture of 70% PHCP2 and 30% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
183.	PHCP2-V4	Mixture of 60% PHCP2 and 40% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
184.	PHCP2-V5	Mixture of 50% PHCP2 and 50% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
185.	PHCP2-V6	Mixture of 10% PHCP2 and 90% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
186.	PHCP2-V7	Mixture of 20% PHCP2 and 80% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)

	Sample code	Sample description
187.	PHCP2-V8	Mixture of 30% PHCP2 and 70% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
188.	PHCP2-V9	Mixture of 40% PHCP2 and 60% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
189.	PHCP2-TA1	Mixture of 90% PHCP2 and 10% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
190.	PHCP2-TA2	Mixture of 80% PHCP2 and 20% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
191.	PHCP2-TA3	Mixture of 70% PHCP2 and 30% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
192.	PHCP2-TA4	Mixture of 60% PHCP2 and 40% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
193.	PHCP2-TA5	Mixture of 50% PHCP2 and 50% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
194.	PHCP2-TA6	Mixture of 10% PHCP2 and 90% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
195.	PHCP2-TA7	Mixture of 20% PHCP2 and 80% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
196.	PHCP2-TA8	Mixture of 30% PHCP2 and 70% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
197.	PHCP2-TA9	Mixture of 40% PHCP2 and 60% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
198.	PHCP2-CA1	Mixture of 90% PHCP2 and 10% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
199.	PHCP2-CA2	Mixture of 80% PHCP2 and 20% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
200.	PHCP2-CA3	Mixture of 70% PHCP2 and 30% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
201.	PHCP2-CA4	Mixture of 60% PHCP2 and 40% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
202.	PHCP2-CA5	Mixture of 50% PHCP2 and 50% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
203.	PHCP2-CA6	Mixture of 10% PHCP2 and 90% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
204.	PHCP2-CA7	Mixture of 20% PHCP2 and 80% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
205.	PHCP2-CA8	Mixture of 30% PHCP2 and 70% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
206.	PHCP2-CA9	Mixture of 40% PHCP2 and 60% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
207.	PHCP2-AS1	Mixture of 90% PHCP2 and 10% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)

	Sample code	Sample description
208.	PHCP2-AS2	Mixture of 80% PHCP2 and 20% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
209.	PHCP2-AS3	Mixture of 70% PHCP2 and 30% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
210.	PHCP2-AS4	Mixture of 60% PHCP2 and 40% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
211.	PHCP2-AS5	Mixture of 50% PHCP2 and 50% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
212.	PHCP2-AS6	Mixture of 10% PHCP2 and 90% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
213.	PHCP2-AS7	Mixture of 20% PHCP2 and 80% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
214.	PHCP2-AS8	Mixture of 30% PHCP2 and 70% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
215.	PHCP2-AS9	Mixture of 40% PHCP2 and 60% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
216.	PHCP2-SLY1	Mixture of 90% PHCP2 and 10% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
217.	PHCP2-SLY2	Mixture of 80% PHCP2 and 20% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
218.	PHCP2-SLY3	Mixture of 70% PHCP2 and 30% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
219.	PHCP2-SLY4	Mixture of 60% PHCP2 and 40% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
220.	PHCP2-SLY5	Mixture of 50% PHCP2 and 50% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
221.	PHCP2-SLY6	Mixture of 10% PHCP2 and 90% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
222.	PHCP2-SLY7	Mixture of 20% PHCP2 and 80% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
223.	PHCP2-SLY8	Mixture of 30% PHCP2 and 70% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
224.	PHCP2-SLY9	Mixture of 40% PHCP2 and 60% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
225.	MIM-CP2-VA1	Mixture of 90% MIM-CP2 and 10% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
226.	MIM-CP2-VA2	Mixture of 80% MIM-CP2 and 20% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
227.	MIM-CP2-VA3	Mixture of 70% MIM-CP2 and 30% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
228.	MIM-CP2-VA4	Mixture of 60% MIM-CP2 and 40% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)

	Sample code	Sample description
229.	MIM-CP2-VA5	Mixture of 50% MIM-CP2 and 50% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
230.	MIM-CP2-VA6	Mixture of 10% MIM-CP2 and 90% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
231.	MIM-CP2-VA7	Mixture of 20% MIM-CP2 and 80% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
232.	MIM-CP2-VA8	Mixture of 30% MIM-CP2 and 70% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
233.	MIM-CP2-VA9	Mixture of 40% MIM-CP2 and 60% vanillic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
234.	MIM-CP2-V1	Mixture of 90% MIM-CP2 and 10% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
235.	MIM-CP2-V2	Mixture of 80% MIM-CP2 and 20% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
236.	MIM-CP2-V3	Mixture of 70% MIM-CP2 and 30% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
237.	MIM-CP2-V4	Mixture of 60% MIM-CP2 and 40% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
238.	MIM-CP2-V5	Mixture of 50% MIM-CP2 and 50% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
239.	MIM-CP2-V6	Mixture of 10% MIM-CP2 and 90% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
240.	MIM-CP2-V7	Mixture of 20% MIM-CP2 and 80% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
241.	MIM-CP2-V8	Mixture of 30% MIM-CP2 and 70% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
242.	MIM-CP2-V9	Mixture of 40% MIM-CP2 and 60% vanillin (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
243.	MIM-CP2-TA1	Mixture of 90% MIM-CP2 and 10% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
244.	MIM-CP2-TA2	Mixture of 80% MIM-CP2 and 20% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
245.	MIM-CP2-TA3	Mixture of 70% MIM-CP2 and 30% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
246.	MIM-CP2-TA4	Mixture of 60% MIM-CP2 and 40% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
247.	MIM-CP2-TA5	Mixture of 50% MIM-CP2 and 50% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
248.	MIM-CP2-TA6	Mixture of 10% MIM-CP2 and 90% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
249.	MIM-CP2-TA7	Mixture of 20% MIM-CP2 and 80% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)

	Sample code	Sample description
250.	MIM-CP2-TA8	Mixture of 30% MIM-CP2 and 70% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
251.	MIM-CP2-TA9	Mixture of 40% MIM-CP2 and 60% tannic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
252.	MIM-CP2-CA1	Mixture of 90% MIM-CP2 and 10% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
253.	MIM-CP2-CA2	Mixture of 80% MIM-CP2 and 20% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
254.	MIM-CP2-CA3	Mixture of 70% MIM-CP2 and 30% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
255.	MIM-CP2-CA4	Mixture of 60% MIM-CP2 and 40% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
256.	MIM-CP2-CA5	Mixture of 50% MIM-CP2 and 50% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
257.	MIM-CP2-CA6	Mixture of 10% MIM-CP2 and 90% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
258.	MIM-CP2-CA7	Mixture of 20% MIM-CP2 and 80% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
259.	MIM-CP2-CA8	Mixture of 30% MIM-CP2 and 70% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
260.	MIM-CP2-CA9	Mixture of 40% MIM-CP2 and 60% citric acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
261.	MIM-CP2-AS1	Mixture of 90% MIM-CP2and 10% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
262.	MIM-CP2-AS2	Mixture of 80% MIM-CP2 and 20% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
263.	MIM-CP2-AS3	Mixture of 70% MIM-CP2 and 30% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
264.	MIM-CP2-AS4	Mixture of 60% MIM-CP2 and 40% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
265.	MIM-CP2-AS5	Mixture of 50% MIM-CP2 and 50% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
266.	MIM-CP2-AS6	Mixture of 10% MIM-CP2 and 90% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
267.	MIM-CP2-AS7	Mixture of 20% MIM-CP2 and 80% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
268.	MIM-CP2-AS8	Mixture of 30% MIM-CP2 and 70% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
269.	MIM-CP2-AS9	Mixture of 40% MIM-CP2 and 60% ascorbic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
270.	MIM-CP2-SLY1	Mixture of 90% MIM-CP2 and 10% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)

	Sample code	Sample description
271.	MIM-CP2-SLY2	Mixture of 80% MIM-CP2 and 20% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
272.	MIM-CP2-SLY3	Mixture of 70% MIM-CP2 and 30% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
273.	MIM-CP2-SLY4	Mixture of 60% MIM-CP2 and 40% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
274.	MIM-CP2-SLY5	Mixture of 50% MIM-CP2 and 50% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
275.	MIM-CP2-SLY6	Mixture of 10% MIM-CP2 and 90% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
276.	MIM-CP2-SLY7	Mixture of 20% MIM-CP2 and 80% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
277.	MIM-CP2-SLY8	Mixture of 30% MIM-CP2 and 70% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)
278.	MIM-CP2-SLY9	Mixture of 40% MIM-CP2 and 60% salicylic acid (g/g) with ODB-2 (0.05g), tetradecanol (5g) and PVA (2.5g)

Table A2. Colour densities of colour forming mixtures of RES-H and ODB-2 in different ratios over the course of 10 days.

Day	RES-$H_{0.5}$	RES-H_1	RES-$H_{1.5}$	RES-H_2	RES-H_4	RES-H_8
1.	1.70	1.75	1.84	1.85	1.88	2.18
2.	1.70	1.75	1.84	1.85	1.88	2.18
3.	1.70	1.75	1.84	1.85	1.88	2.16
4.	1.70	1.75	1.84	1.85	1.88	2.16
5.	1.70	1.75	1.84	1.85	1.88	2.15
6.	1.70	1.75	1.84	1.58	1.88	2.15
7.	1.70	1.75	1.60	1.58	1.88	2.13
8.	1.54	1.75	1.60	1.58	1.88	2.13
9.	1.54	1.59	1.59	1.58	1.74	1.93
10.	1.51	1.59	1.59	1.58	1.74	1.93

Table A3. Colour densities of colour forming mixtures of MIM-CP2 and ODB-2 in different ratios over the course of 10 days.

Day	MIM-$CP2_{0.5}$	MIM-$CP2_1$	MIM-$CP2_{1.5}$	MIM-$CP2_2$	MIM-$CP2_4$	MIM-$CP2_8$
1.	0.58	0.58	0.58	0.59	0.62	0.66
2.	0.58	0.58	0.58	0.58	0.59	0.64
3.	0.58	0.54	0.58	0.58	0.55	0.61
4.	0.58	0.54	0.51	0.57	0.55	0.60
5.	0.55	0.54	0.51	0.57	0.55	0.55
6.	0.55	0.44	0.49	0.57	0.52	0.55
7.	0.50	0.44	0.49	0.56	0.52	0.55
8.	0.40	0.41	0.47	0.56	0.52	0.55
9.	0.40	0.36	0.47	0.54	0.43	0.55
10.	0.40	0.36	0.47	0.54	0.43	0.52

Table A4. Colour densities of colour forming mixtures of MIM S-CP2 and ODB-2 in different ratios over the course of 10 days.

Day	MIM S-CP2$_{0.5}$	MIM S-CP2$_{1}$	MIM S-CP2$_{1.5}$	MIM S-CP2$_{2}$	MIM S-CP2$_{4}$	MIM S-CP2$_{8}$
1.	0.48	0.48	0.48	0.49	0.52	0.56
2.	0.46	0.48	0.48	0.48	0.52	0.54
3.	0.46	0.44	0.48	0.43	0.52	0.51
4.	0.46	0.44	0.41	0.43	0.52	0.50
5.	0.45	0.44	0.41	0.43	0.51	0.40
6.	0.42	0.43	0.40	0.41	0.50	0.40
7.	0.42	0.43	0.40	0.41	0.41	0.40
8.	0.42	0.43	0.37	0.38	0.41	0.40
9.	0.40	0.36	0.37	0.38	0.39	0.36
10.	0.40	0.36	0.37	0.35	0.39	0.32

Table A5. Colour densities of colour forming mixtures of GSE-CP2 and ODB-2 in different ratios over the course of 10 days.

Day	GSE-CP2$_{0.5}$	GSE-CP2$_{1}$	GSE-CP2$_{1.5}$	GSE-CP2$_{2}$	GSE-CP2$_{4}$	GSE-CP2$_{8}$
1.	0.68	0.66	0.68	0.69	0.72	0.76
2.	0.60	0.66	0.68	0.69	0.72	0.76
3.	0.60	0.56	0.68	0.69	0.72	0.76
4.	0.60	0.56	0.58	0.59	0.70	0.76
5.	0.48	0.56	0.58	0.59	0.70	0.65
6.	0.47	0.56	0.58	0.59	0.70	0.55
7.	0.42	0.43	0.39	0.49	0.49	0.54
8.	0.41	0.43	0.39	0.38	0.49	0.54
9.	0.40	0.41	0.37	0.37	0.35	0.50
10.	0.40	0.36	0.37	0.35	0.35	0.50

.

Table A6. Colour densities of colour forming mixtures of GSE-CP9 and ODB-2 in different ratios over the course of 10 days.

Day	GSE-CP9$_{0.5}$	GSE-CP9$_{1}$	GSE-CP9$_{1.5}$	GSE-CP9$_{2}$	GSE-CP9$_{4}$	GSE-CP9$_{8}$
1.	0.61	0.61	0.61	0.63	0.69	0.72
2.	0.56	0.59	0.58	0.61	0.62	0.70
3.	0.56	0.59	0.56	0.61	0.62	0.70
4.	0.56	0.59	0.48	0.61	0.60	0.70
5.	0.49	0.56	0.48	0.61	0.60	0.70
6.	0.48	0.42	0.48	0.41	0.44	0.61
7.	0.47	0.42	0.36	0.41	0.44	0.61
8.	0.42	0.42	0.36	0.33	0.44	0.45
9.	0.41	0.40	0.36	0.33	0.43	0.45
10.	0.40	0.36	0.36	0.30	0.38	0.45

Table A7. Colour densities of colour forming mixtures of PH-CP2-12 and ODB-2 in different ratios over the course of 10 days.

Day	PH-CP2-12$_{0.5}$	PH-CP2-12$_{1}$	PH-CP2-12$_{1.5}$	PH-CP2-12$_{2}$	PH-CP2-12$_{4}$	PH-CP2-12$_{8}$
1.	1.28	1.28	1.31	1.41	1.48	1.92
2.	1.28	1.21	1.27	1.41	1.47	1.87
3.	1.28	1.21	1.27	1.41	1.47	1.85
4.	1.28	1.21	1.27	1.31	1.47	1.50
5.	1.16	1.20	1.27	1.31	1.35	1.47
6.	1.16	1.18	1.14	1.31	1.34	1.42
7.	1.16	1.16	1.04	1.29	1.19	1.42
8.	1.02	1.16	1.03	1.29	1.19	1.42
9.	1.02	1.16	1.00	1.18	1.19	1.42
10.	1.02	1.06	1.00	1.18	1.16	1.42

Table A8. Colour densities of colour forming mixtures of PH-CP2-40 and ODB-2 in different ratios over the course of 10 days.

Day	PH-CP2-40$_{0.5}$	PH-CP2-40$_{1}$	PH-CP2-40$_{1.5}$	PH-CP2-40$_{2}$	PH-CP2-40$_{4}$	PH-CP2-40$_{8}$
1.	1.32	1.32	1.39	1.42	1.49	1.86
2.	1.30	1.31	1.37	1.40	1.48	1.77
3.	1.30	1.31	1.37	1.40	1.48	1.77
4.	1.30	1.31	1.37	1.40	1.48	1.77
5.	1.20	1.23	1.37	1.39	1.37	1.77
6.	1.20	1.22	1.27	1.39	1.37	1.52
7.	1.20	1.22	1.15	1.37	1.35	1.32
8.	1.17	1.19	1.09	1.37	1.29	1.32
9.	1.06	1.19	1.08	1.18	1.29	1.22
10.	1.06	1.19	1.08	1.18	1.16	1.22

Table A9. Colour densities of colour forming mixtures of PH-CP2 and ODB-2 in different ratios over the course of 10 days.

Day	PH-CP2$_{0.5}$	PH-CP2$_{1}$	PH-CP2$_{1.5}$	PH-CP2$_{2}$	PH-CP2$_{4}$	PH-CP2$_{8}$
1.	1.38	1.38	1.41	1.51	1.58	2.25
2.	1.38	1.31	1.40	1.51	1.57	2.16
3.	1.38	1.31	1.39	1.51	1.57	2.07
4.	1.20	1.30	1.39	1.51	1.57	2.05
5.	1.18	1.28	1.39	1.51	1.50	2.04
6.	1.16	1.26	1.29	1.47	1.50	1.93
7.	1.16	1.26	1.17	1.37	1.28	1.91
8.	1.16	1.26	1.14	1.37	1.19	1.85
9.	1.06	1.06	1.10	1.16	1.19	1.68
10.	1.06	1.06	1.10	1.15	1.17	1.66

Table A10. ^{13}C NMR Chemical Shifts of ODB-2 in $CDCl_3$

Carbon number	ODB-2 in CDCl3	Δ∂ (ascorbic acid)	Δ∂ (vanillin)	Δ∂ (salicylic acid)	Δ∂ (resorcinol)	Δ∂ (ascorbyl palmitate)	Δ∂ (citric acid)
1	127.00	0.28	0.43	3.79	3.03	2.18	0.07
2	104.55	10.57	-0.09	6.36	2.69	9,61	3.67
3	153.08	0,17	-5.27	-1.22	-3.49	18.47	-0.08
4	97.46	0.46	0.1	10.9	5.29	15.4	7.09
5	117.39	2.07	1.33	1.36	1.5	1.43	1.25
6	128.75	0.09	0.82	-2.06	1.84	10.23	-0.06
7	135.83	0.38	0.09	7.98	5.9	15.23	-0.16
8	114.93	2.59	-0.45	-2.4	0.29	2.15	-0.04
9	84.12	78.04	68.71	85.41	11.8	12.89	13.31
11	117.42	1.39	-2.48	-1.65	-0.56	1.88	-0.03
12	152.94	-1.24	-1.06	8.84	3.93	15.19	-0.05
13	147.91	0.01	2.07	6.65	9.6	8.59	-0.09
14	119.20	1.23	-0.02	-0.18	0.68	-0.2	0.1
15	149.94	0.08	-5.25	-1.6	-1.28	12.23	-0.04
16	123.80	1.45	1.01	2.89	5.18	5.86	-0.09
17	121.08	3.07	-0.28	7.97	-0.44	-0.09	-0.07
18	134.26	0.11	0.36	2.57	2.81	8.67	0.32
19	129.40	0.02	0	4.51	5.73	9.88	-0.14
20	124.80	0.3	2.09	0.47	4.59	5.22	0.05
21	144.69	-0.17	2.49	2.74	11.21	9.52	0.06
22	108.33	-2.39	-0,03	11.76	8.12	7,32	8.6
23	108.33	0.84	0.6	9.93	7.53	7.32	8.54
24	129.06	0.04	-0.47	6.75	2.23	4.16	0.03
25	121.9	3.35	1.93	6.77	6.02	5.18	5.88
26	134.84	0.46	0.07	2.31	4.49	13.94	0.03
27	169.49	-0.2	0.26	4.31	3.42	4.22	-0.06

Δ∂ = Difference in the chemical shift of ODB-2 in $CDCl_3$ and coloured species formed from reaction with developer