Figure S1. PDA chromatograms of samples solubilized in DMSO with minimal heat versus heated extraction in dilute HCl. On the left, extraction of C.I. Pigment Red 60 (barium salt of C.I. Mordant Red 9), and on the right extraction of C.I. Pigment Green 12 component (iron complex of barium salt of C.I. Acid Green 1).

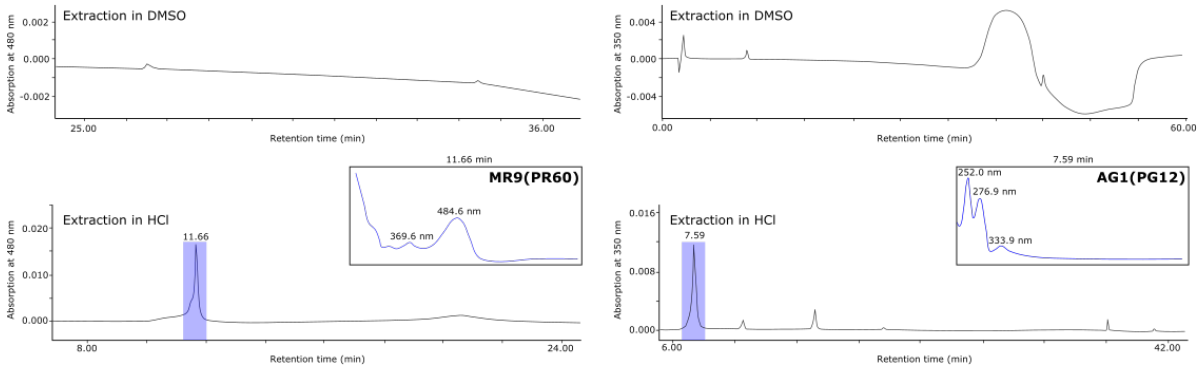


Figure S2. PDA spectra of major components and corresponding structures of four β-naphthol pigments.

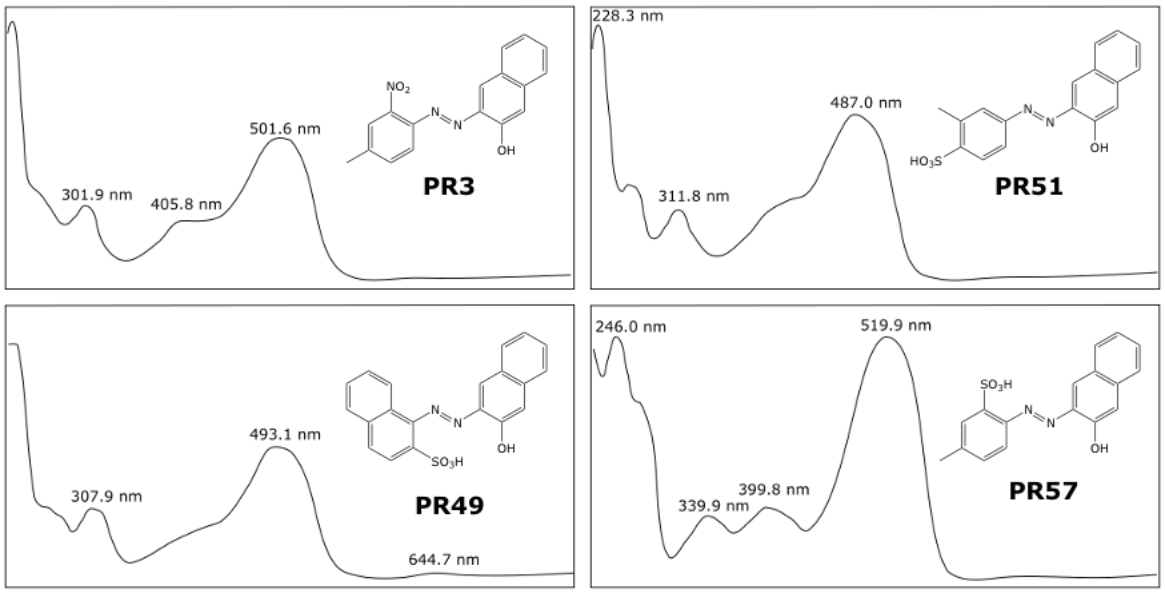


Table S1: gradient used UPLC-PDA analysis

Time (min)	Buffer A (v%)	Buffer B (v%)
0 – 1.50	95	5
1.50 – 45.50	5	95
45.50 – 50.50	5	95
50.50 – 52.50	95	5
52.50 – 57.50	95	5

Table S2: gradient used UPLC-PDA-HRMS analysis

Time (min)	Buffer A (v%)	Buffer B (v%)
0 – 1.50	95	5
1.50 – 5.00	80	20
5.00 – 7.00	80	20
7.00 – 40.00	40	60
40.00 – 45.00	40	60
45.00 – 55.00	5	95
55.00 – 60.00	5	95
60.00 – 62.00	95	5
62.00 – 67.00	95	5

Table S3. Sample naming convention.

General rules:

- Numbers are assigned to locate a sample paint-out and pigment wash from books with hundreds of samples. Counting proceeds from front to back (of a book), top to bottom, and left to right.
- A "plate" is a single sheet or panel containing several paint-outs or pigment washes. Books or charts with multiple plates have a roman numerals assigned to each plate.
- The sample position within a plate is specified by its coordinates, specified by the row, and the position in the row.
- The general sample name format is (source)(year)-(plate)-(position).

Sources:

Paint tubes (PT):

- Tubes arbitrarily numbered 1 through 176
- E.g. PT6

Wagner books (Wagner28 and Wagner38):

- Two editions, book specified by year of publication
- Plate specified by the number of the page proceeding it
- E.g. Wagner28-p448-1,4 is a sample found in the 1928 edition on the plate next to page 448 and is the fourth paint-out in the first row

Kittel book (Kittel):

- E.g. Kittel-VI-3,2 is a sample found on the sixth plate in the text and is the second paint-out in the third row

Kerdijk books (K):

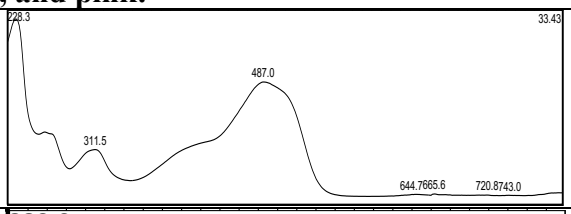
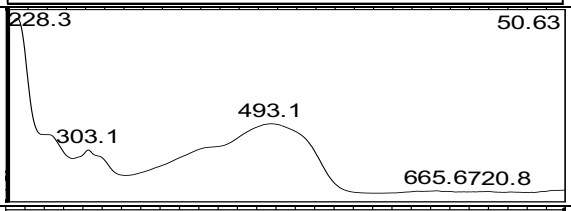
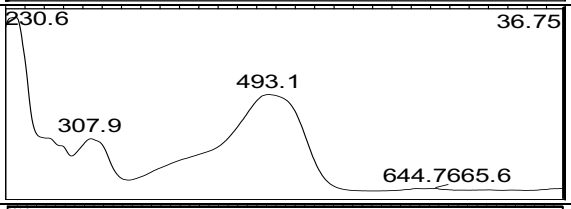
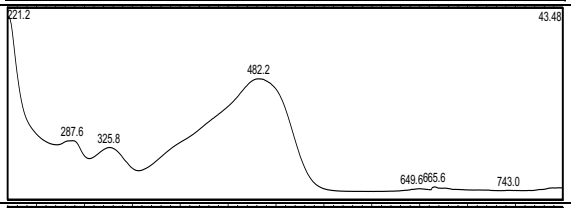
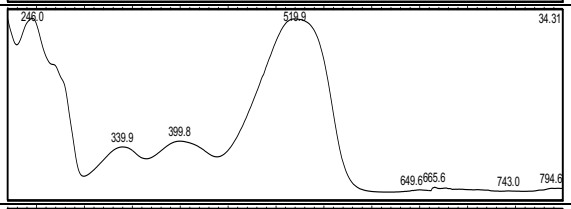
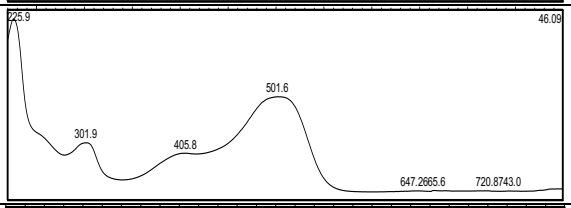
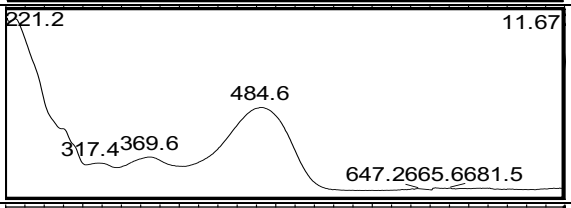
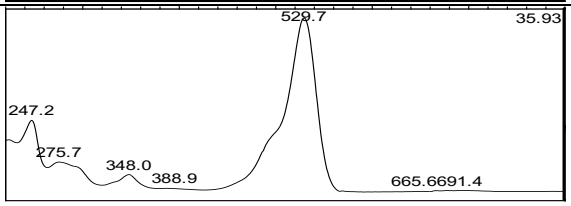
- Several editions, book specified by year of publication
- E.g. K50-IV-3,7 is a sample from the 1950 edition found on plate IV and is the seventh paint-out in row three

Color charts (C):

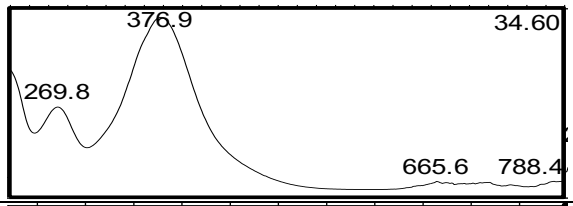
- Arbitrarily numbered 1 through 10
- Included numbers assigned to individual paint-outs in the color chart, if available, in parentheses
- E.g. C1-II-1,3(20) is a sample on the second plate of color chart 1 and is the third paint-out in row one, labelled in the chart as #20

Table S4. Table of raw PDA spectra (225 nm-800 nm) for SOPs identified

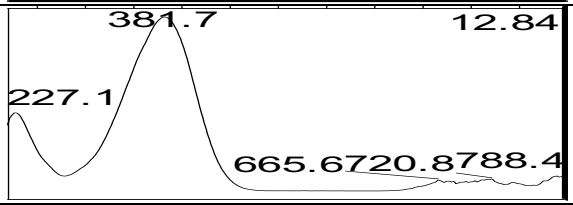
Red, orange, and pink:

PR51	
PR49	
PR49 component	
PO5	
PR57	
PR3	
MR9(PR60)	
BR1(PR81)	

MO1

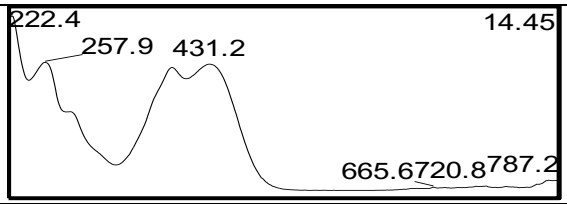


MO1 component (p-nitroaniline)

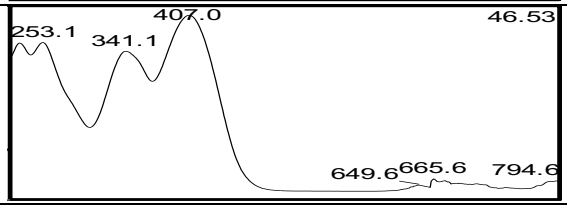


Yellow:

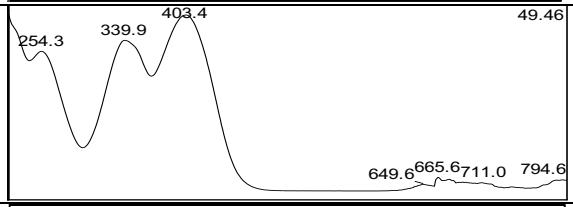
AY1



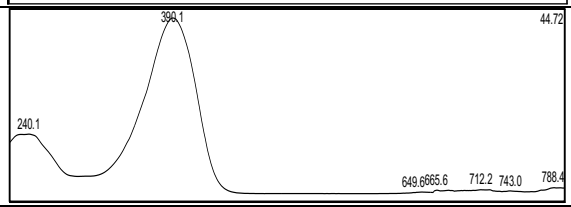
PY1



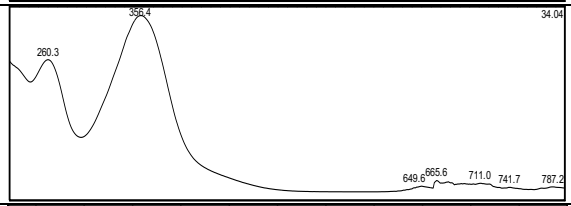
PY3



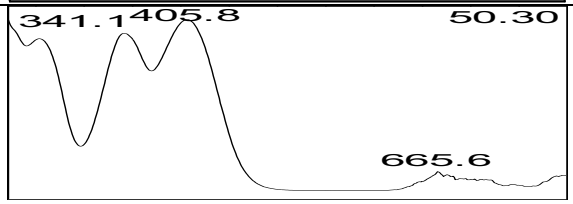
PY4

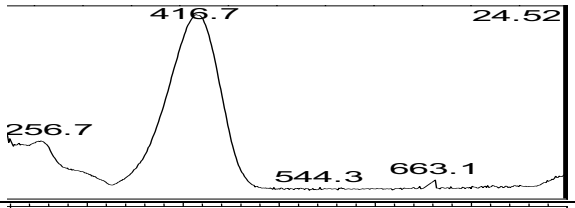
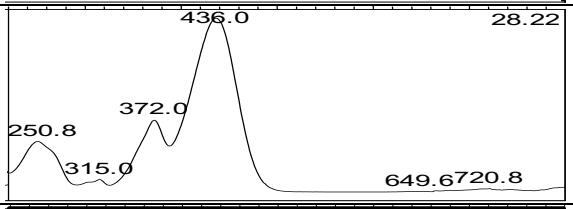
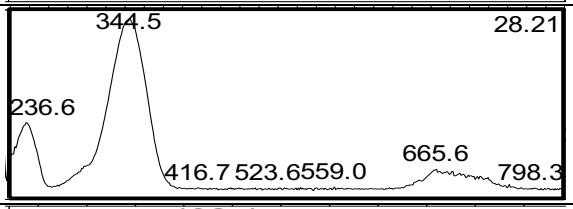
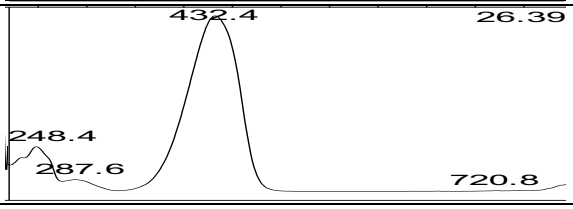


MY1

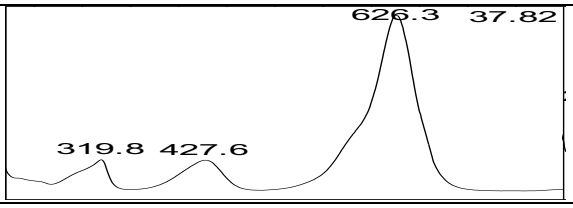
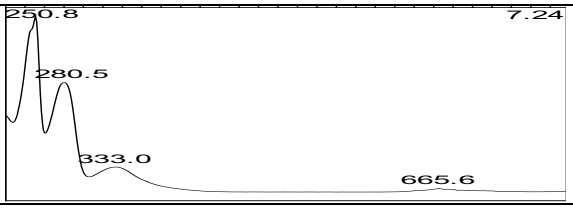


PY2



BY1(PY18)	
BY2	
BY21	
Indolenine yellow	

Green:

BG1(PG1)	
PG2 (mixture of PG1 and one of two yellows, indolenine yellow or BY21)	
AG1(PG12) component	

Blue and violet:

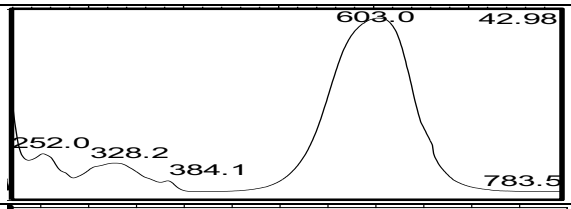
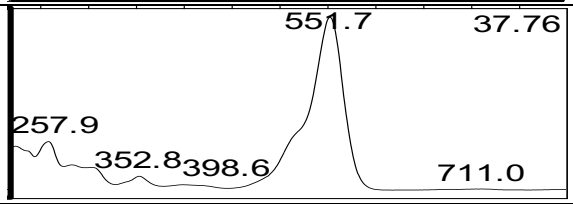
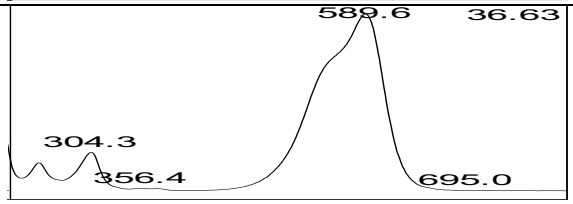
BB7(PB1)	
BV10(PV2)	
BV1(PV3)	

Table S5. Table of exact masses of colorants identified in select samples.

Sample number	Extraction	Mass	Ion	M	ID
Vermiljoen licht					
PT6	DMSO, HCl	341.06059	$[M-H]^-$	$C_{17}H_{14}N_2O_4S$	PR51
	DMSO, HCl	379.07441	$[M+H]^+$	$C_{20}H_{14}N_2O_4S$	PR49
	HCl	299.11754	$[M+H]^+$	$C_{20}H_{14}ON_2$	PR49-SO_3
Talensrood					
PT173	DMSO, HCl	308.10263	$[M+H]^+$	$C_{17}H_{13}N_3O$	PR3
Alizarine oranje					
C1-II-1,3(20)	DMSO	286.04733	$[M-H]^-$	$C_{13}H_9O_5N_3$	MO1
	DMSO	139.05020	$[M+H]^+$	$C_6H_6O_2N_2$	Nitroaniline
K32-IV-3,1	HCl	"	"	"	MO1
	HCl	"	"	"	Nitroaniline
K37-III-4,1	HCl	"	"	"	MO1
	HCl	"	"	"	Nitroaniline
K41-III-4,1	HCl	"	"	"	MO1
	HCl	"	"	"	Nitroaniline
K44-III-4,1	HCl	"	"	"	MO1
	HCl	"	"	"	Nitroaniline
K50-III-4,1	HCl	312.97770	$[M-H]^-$	$C_{10}H_6N_2O_8S$	AY1
	HCl	233.02049	$[M-H]^-$	$C_{10}H_6N_2O_5$	AY1-SO_3
	HCl	"	"	"	MO1
	HCl	"	"	"	Nitroaniline
Fanalgelb					
Kittel-I-1,1	HCl	255.09489	[M]+	$C_{15}H_{15}N_2S$	BY1-C_2H_6
	HCl	269.11057	[M]+	$C_{16}H_{17}N_2S$	BY1-CH_3
	HCl	283.12620	[M]+	$C_{17}H_{19}N_2S$	BY1
Wagner38-p608-6,3	HCl	"	"	"	BY1-C_2H_6
	HCl	"	"	"	BY1-CH_3
	HCl	"	"	"	BY1
Indischgeel imitatie					
K32-V-3,5	HCl	339.11011	$[M-H]^-$	$C_{17}H_{16}N_4O_4$	PY1
Fanalgelbgrun GG					
Wagner28-p400-8,4	DMSO	254.16514	$[M]^+$	$C_{16}H_{20}N_3$	BY2/3-CH_3
	DMSO	268.18093	$[M]^+$	$C_{17}H_{22}N_3$	BY2/3*
	DMSO	385.26378	$[M]^+$	$C_{27}H_{33}N_2$	BG1
Talens groen donker					
C6-I-1,9	DMSO	317.20192	$[M]^+$	$C_{22}H_{25}N_2$	BY21
	DMSO	357.23313	$[M]^+$	$C_{25}H_{29}N_2$	BG1-C_2H_5
	DMSO	"	"	"	BG1
C9-II-5,5	DMSO	331.21751	$[M]^+$	$C_{23}H_{27}N_2$	C.I. 48010
	DMSO	335.13147			
	DMSO	349.14725	$[M]^+$	$C_{22}H_{22}ClN_2$	BB1-CH_3
	DMSO	363.16302	$[M]^+$	$C_{23}H_{22}ClN_2$	BB1

K32-V-4,6	DMSO	“	“	“	C.I.48010
	DMSO	“	“	“	BB1-CH_3
	DMSO	“	“	“	BB1
	DMSO	“	“	“	BG1-C_2H_5
	DMSO	“	“	“	BG1
K37-IV-4,5	DMSO	“	“	“	C.I.48010
	DMSO	“	“	“	BG1-C_2H_5
	DMSO	“	“	“	BG1
K41-IV-4,3	DMSO	“	“	“	C.I.48010
	DMSO	“	“	“	BG1-C_2H_5
	DMSO	“	“	“	BG1
K42-IV-4,4	DMSO	“	“	“	BY1
	DMSO	“	“	“	C.I.48010
	DMSO	“	“	“	BY21
	DMSO	“	“	“	BG1-C_2H_5
	DMSO	“	“	“	BG1
K44-IV-4,5	DMSO	“	“	“	BY1
	DMSO	“	“	“	BY21
	DMSO	“	“	“	BG1-C_2H_5
	DMSO	“	“	“	BG1
Talens groen blauw					
K37-IV-4,6	DMSO	“	“	“	BB1-CH_3
	DMSO	“	“	“	BB1
	DMSO	391.19414	$[M]^+$	$C_{25}H_{28}N_2Cl$	BB5
	DMSO	478.32206	$[M]^+$	$C_{33}H_{40}N_3$	BB7
K32-V-4,7	DMSO	“	“	“	BB1-CH_3
	DMSO	“	“	“	BB1
	DMSO	“	“	“	BB5
	DMSO	“	“	“	BG1
	DMSO	“	“	“	BB7
C9-I-4,7	DMSO	“	“	“	BB1-CH_3
	DMSO	“	“	“	BB1
	DMSO	“	“	“	BB5
	DMSO	“	“	“	BB7
Fanalbremerblau					
Wagner28-p400-8,2	DMSO	“	“	“	BB1-CH_3
	DMSO	“	“	“	BB1
	DMSO	“	“	“	BB5
	DMSO	“	“	“	BG1
	DMSO	“	“	“	BB7

*isomers; were not distinguishable by MS/MS