

ORIGINAL ARTICLE

Non-oxidative hair dye products on the European market: What do they contain?

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Background: Hair dyeing is very common and may cause allergic contact dermatitis. Oxidative (often termed permanent or semi-permanent) hair dye products have constituted the focus of market surveys and toxicological risk assessments, while non-oxidative (semi-permanent, temporary or direct) products have not been assessed.**Objectives:** To identify the hair dye substances presently used in non-oxidative hair dye products in Europe.**Methods:** Ingredient label data on eligible products in 5 European countries were collected, and 289 different non-oxidative hair dye products were included in this study.**Results:** Up to 9 hair dye substances were present in each product. Sixty-eight individual hair dye substances were identified on the 289 product labels, and their occurrence ranged from 0.3% to 34%. There were differences concerning substances used and their number per product between products of different consistency and colour.**Conclusions:** The hair dye substances in non-oxidative hair dye products are different from those in oxidative hair dye products, and are currently not covered by patch test series. The toxicological and skin-sensitizing profile of the substances in non-oxidative hair dye products, as well as their concentrations, should be further investigated.**KEYWORDS**

consumer products, cosmetics, exposure analysis, hair dyes, ingredient label, market survey, non-permanent, temporary

1 | INTRODUCTION

Hair dyeing is very common even at a relatively young age, especially in females, and the frequency of hair dyeing is increasing in males.¹⁻³ It is also common at older ages to cover grey hair.⁴ Hair dyeing can be achieved either by the use of oxidative hair dye products (often referred to as permanent), or by the use of non-oxidative hair dye products (often referred to as temporary or direct dyes). Semi-permanent hair dye products are present in both groups. Oxidative hair dye products constitute 70% to 80% of the market in Europe.⁵ Many hair dye substances are allowed to be used in either oxidative

or non-oxidative hair dye products or in both types, and the use concentration is restricted for many substances.⁶

The terminology of hair dye products and substances varies considerably, and there is much overlap and inconsistency.^{7,8} In this study, we use the concepts oxidative and non-oxidative hair dye products, as in the Cosmetics Regulation. Terminology based on the expected durability of the colouring includes permanent (until hair grows out), semi-permanent (~ 24 washings), and temporary or direct (up to 8-12 washings). Oxidative hair dye products are composed of 2 components (dye precursors and an oxidizing substance, generally hydrogen peroxide), and their mechanism of action involves an in situ polymerization reaction in the hair shaft, forming large molecules that cannot leave the hair shaft. Non-oxidative hair dye products are

Yolanda S. Hedberg and Wolfgang Uter have shared first authorship.

TABLE 1 Manufacturers, brands and number of unique non-oxidative hair dye products per manufacturer (after elimination of duplicates, etc.), and countries where products were collected. Sampling was performed between July 2015 and May 2017

Manufacturer (n = 25)	Brand	Number of products (n = 289)	Country
Accent	Color 2 go, Schaum-Tönung	14	Germany
Basler	Basler Schaumtönung	6	Germany
Bleach London	Bleach London	9	UK
Glynt	Mangala	6	Germany
Goldwell	Elumen	25	Germany
Henkel/Schwarzkopf	Blonde, Brilliance, Live	16	Denmark, Germany, Switzerland, UK
Herb UK Ltd	Tints of nature	11	UK
Keralock	Inspiration, Night life	8	Germany
Knight & Wilson	Colour-freedom	7	UK
La Riché	Directions	36	Denmark, Germany, Sweden
L'Oréal/L'Oréal Paris	Colorista, Magic retouch	20	Denmark, Sweden, Switzerland, UK
L'Oréal/Matrix	Color graphics	5	Germany
Scott Cornwall	Colour restore	8	UK
StarGazer	Hair colour rinse	27	Denmark, Sweden
Tish & Snooky's	Manic panic	47	Sweden
Wella	Color fresh	24	Germany, Sweden
Nine others with <5 products		20	Denmark, Germany, Switzerland, UK

composed of 1 component (without an oxidizing substance), and do not stick firmly to the hair.

The risk of contact allergy associated with the use of oxidative hair dye products is very well known, and it is likewise known that a substantial proportion of hair dye substances are potent skin sensitizers.^{9,10} Efforts have been directed to update patch test series of hair cosmetics in order to better cover potentially important hap- tens.^{11,12} However, non-oxidative hair dye products have so far mostly been neglected both in terms of systematic patch testing and in terms of exposure analysis, risk assessment, and risk management.

The aim of the present study was to identify the hair dye sub- stances presently used in non-oxidative hair dye products on the basis of a European multicentre study. The results of this study are meant to serve as a starting point both for risk assessment and for drafting an experimental patch test series, to increase knowledge on the sensi- tization risk associated with these substances.

2 | METHODS

2.1 | Selection of products

Shops and hairdressing salons that were expected to sell non- oxidative hair dye products were visited in the following 5 cities in Europe: Copenhagen, Denmark; Davos, Switzerland; Erlangen, Ger- many; London, United Kingdom; and Stockholm, Sweden. Only non- oxidative hair dye products were included in the study. Inclusion cri- teria were as follows: statements on the package or container that the colour would be washed out after a maximum of 12 hair washes; and the products should not be 2-component products or contain hydro- gen peroxide, and should not be raw plant material products.

Hairdressing salons and shops selling consumer products (includ- ing small shops, grocery stores, and supermarkets) were visited; the type and number of sites visited varied between cities. Most products

were selected in drugstores (Matas) and alternative punk/goth shops in Copenhagen, drugstores (Müller) and supermarkets in Davos, hair- dressing salons in Erlangen, drugstores in London, and in shops branded as "alternative styles" (eg, rock, punk, and goth) in Stockholm.

2.2 | Information collected

Each product was photographed in the shop or salon. All hair dye sub- stances identified on the ingredient label, the name of the producer, the brand, the product, the colour and the shade, and whether or not the product was intended for professional use, were documented. The consistency of the products was divided into 3 categories (cream or liquid, foam or spray, and paste) on the basis of information on the product or its appearance. Products with the consistency "paste" were, in all cases, sold in hard jars with wide openings. Colours and shades were grouped into 11 colour categories, and products were assigned to these on the basis of product information or appearance on the photograph or website. The colour description by manufac- turers often differed significantly among brands and from that of oxidative hair dye products, and we therefore invented our own col- our categories. This market survey was conducted from July 2015 to May 2017.

All data were later checked independently by 2 of the authors (C.L. and Y.S.H.), on the basis of the photographs, and corrected if necessary. Data on 398 products were initially collected. However, data on 61 products were removed because they were duplicates or triplicates. Additionally, 48 products were removed for various rea- sons (31 with missing or incomplete photographs, 12 oxidative hair dye products, 1 conditioner, 3 with "may contain" or "+/-" on the ingredient label, and 1 with insufficient information), leaving, in total, 289 products that were assessed in this study.

The sample was treated as a European sample, and not by coun- try, because the sampling strategy, number of products and number remaining after omission of duplicates varied between centres.

TABLE 2 Hair dye substances in non-oxidative hair dye products according to ingredient labelling (289 investigated products). Substance identifiers^a (e.g. INCI name, CI number, and CAS no.) and frequency of occurrence in the product sample are shown. Sampling was performed from July 2015 to May 2017. Information on the occurrence in products categorized by consistency or colour, respectively, is available in Tables S1 to S14 in Appendix S1

INCI name or other common ingredients glossary name	CI number	CAS no.	Occurrence in this study, n (%)	Reported in other studies	
				Oxidative products (13-17)	Non-oxidative products (17)
Basic Blue 99	CI 56059	68123-13-7	97 (33.6)		X
HC Blue No. 15		74578-10-2	86 (29.8)		
Basic Red 51		77061-58-6	84 (29.1)	X	
Acid Violet 43	CI 60730	4430-18-6	80 (27.7)		X
Basic Violet 2	CI 42520	3248-91-7	66 (22.8)		
HC Yellow No. 4		59820-43-8	66 (22.8)		
Basic Orange 31		97404-02-9	63 (21.8)	X	
Basic Violet 16	CI 48013	6359-45-1	62 (21.5)		
Basic Red 76	CI 12245	68391-30-0	34 (11.8)		
Basic Brown 16	CI 12250	26381-41-9	33 (11.4)	X	X
Basic Brown 17	CI 12251	68391-32-2	29 (10.0)	X	X
Basic Yellow 57	CI 12719	68391-31-1	28 (9.7)		
Acid Blue 9	CI 42090	3844-45-9	23 (8.0)		
Acid Orange 7	CI 15510	633-96-5	22 (7.6)		X
Basic Yellow 87		68259-00-7	22 (7.6)	X	
HC Yellow No. 2		4926-55-0	22 (7.6)	X	
3-Nitro- <i>p</i> -hydroxyethylaminophenol		65235-31-6	21 (7.3)		
HC Blue No. 16		502453-61-4	21 (7.3)		
HC Blue No. 2		33229-34-4	19 (6.6)		
HC Red No. 3		2871-01-4	19 (6.6)	X	
4-Hydroxypropylamino-3-nitrophenol		92952-81-3	18 (6.2)	X	
Acid Yellow 3	CI 47005	95193-83-2	18 (6.2)		X
HC Red No. 10		95576-89-9	18 (6.2)		
HC Red No. 11		95576-92-4	18 (6.2)		
Basic Yellow 40		29556-33-0	17 (5.9)		
2-Amino-6-chloro-4-nitrophenol		6358-09-4	14 (4.8)	X	
HC Blue No. 12		132885-85-9/104516-93-0	12 (4.2)	X	
Hydroxyethyl-2-nitro- <i>p</i> -toluidine		100418-33-5	12 (4.2)	X	
<i>N,N'</i> -Bis(2-hydroxyethyl)-2-nitro- <i>p</i> -phenylenediamine		84041-77-0	9 (3.1)	X	
Titanium dioxide	CI 77891	13463-67-7	9 (3.1)		
Acid Black 1	CI 20470	1064-48-8	8 (2.8)		X
Iron oxide black ^b	CI 77499 ^b	Several	8 (2.8)		
Acid Red 52	CI 45100	3520-42-1	7 (2.4)	X	
Disperse Violet 1	CI 61100	128-95-0	7 (2.4)		
HC Yellow No. 13		10442-83-8	7 (2.4)		
Iron oxide red ^b	CI 77491 ^b	Several	6 (2.1)		
Iron oxide yellow ^b	CI 77492 ^b	51274-00-1	6 (2.1)		
HC Blue No. 11		23920-15-2	5 (1.7)		
4-Amino-3-nitrophenol		610-81-1	4 (1.4)	X	
Acid Red 33	CI 17200	3567-66-6	4 (1.4)		X
Basic Blue 9 ^c	CI 52015	61-73-4	4 (1.4)		
2-Hydroxyethyl picramic acid		99610-72-7	3 (1.0)		
Acid Red 18	CI 16255	2611-82-7	3 (1.0)		
Acid Yellow 23	CI 19140	1934-21-0	3 (1.0)		
Basic Green 4 ^c	CI 42000	569-64-2	3 (1.0)		

TABLE 2 (Continued)

INCI name or other common ingredients glossary name	CI number	CAS no.	Occurrence in this study, n (%)	Reported in other studies	
				Oxidative products (13-17)	Non-oxidative products (17)
Basic Blue 3 ^c		47367-75-9/33203-82-6	3 (1.0)		
Hydroxyanthraquinone-aminopropyl methyl morpholinium methosulfate		38866-20-5	3 (1.0)		
2,6-Diamino-3-([pyridin-3-yl]azo)pyridine		28365-08-4	2 (0.7)		
Acid Green 25	CI 61570	4403-90-1	2 (0.7)		
Acid Red 92	CI 45410	18472-87-2	2 (0.7)		
Basic Green 1 ^c	CI 42040	633-03-4	2 (0.7)		
Carmines ^b	CI 75470 ^b	1390-65-4	2 (0.7)		
Ferric ferrocyanide ^b	CI 77510 ^b	14038-43-8/12240-15-2/ 25869-00-5	2 (0.7)		
HC Blue No. 17		16517-75-2	2 (0.7)		
Lazurite ^b	CI 77007 ^b	12769-96-9/1302-83-6/ 57455-37-5	1 (0.3)		
2-Chloro-6-ethylamino-4-nitrophenol		131657-78-8	1 (0.3)		
Basic Blue 54 ^d		38901-83-6	1 (0.3)		
Basic Red 17 ^e			1 (0.3)		
Basic Violet 4 ^c	CI 42600	2390-59-2	1 (0.3)		
Basic Yellow 4 ^e			1 (0.3)		
Chromium oxide greens	CI 77288	1308-38-9	1 (0.3)		
Curry Red	CI 16035	25956-17-6	1 (0.3)		X
Disodium 6-hydroxy-5- ([4-sulphonatophenyl]azo) naphthalene-2-sulfonate ^b	CI 15985 ^b	2783-94-0	1 (0.3)		
Disperse Blue 377		4471-41-4/67674-26-4/ 67701-36-4	1 (0.3)		
HC Orange No. 1		54381-08-7	1 (0.3)		
HC Red No. 13		94158-13-1	1 (0.3)		
HC Violet No. 2		104226-19-9	1 (0.3)		
Pigment Red 57	CI 15850	5858-81-1	1 (0.3)		

Abbreviations: CAS, Chemical Abstracts Service; CI, colour index number; INCI, International Nomenclature of Cosmetic Ingredients.

^a Based on the European Commission database for information on cosmetic substances and ingredients (CosIng) and the Cosmetics Regulation.

^b When a CI number is also the INCI name, the substance name is given in the first column.

^c Prohibited in hair dye products (Cosmetics Regulation, Annex II).

^d Substance not identified in CosIng or the Cosmetics Regulation, but in PubChem <https://pubchem.ncbi.nlm.nih.gov/compound/147317#section=Top;PatentUS770821>.

^e Substance not identified in CosIng, the Cosmetics Regulation or elsewhere (labelling error?)

Furthermore, as duplicates were recorded “for professional use” by 1 centre, and “for non-professional use” in another, it was decided to not analyse the data in terms of perceived professional use.

2.3 | Statistical analysis and data presentation

To compare the number of dye substances per product in different categories, Kruskal-Wallis tests for non-parametric data were used (R statistical software, version 3.4.3; www.r-project.org). The level of significance was set at $P < .05$.

3 | RESULTS

In total, 289 non-oxidative hair dye products from 25 different manufacturers were included in this study comprising 5 European countries

(Table 1). In total, 68 different hair dye substances were identified on the labels of these 289 products. The individual substances were present in 0.3% to 34% of the products (Table 2). Between 1 and 9 hair dye substances were found per product.

Those products applied as foams or sprays contained a lower number of hair dye substances per product (median 3 [first quartile, 2 to third quartile, 4], $n = 36$) than those products applied as liquid or cream (3 [2-6], $n = 169$) and those applied as paste (4 [2-8], $n = 84$), with $P = .022$ for overall heterogeneity (Kruskal-Wallis test) (Figure 1A).

The most frequently used substances overall were Basic Blue 99, HC Blue No. 15, Basic Red 51, and Acid Violet 43, which were present in >25% of all assessed products (Table 2). They were more frequently present in the products characterized as liquid or cream, and paste (Tables S1 and S3 in Appendix S1). Metal-based pigments

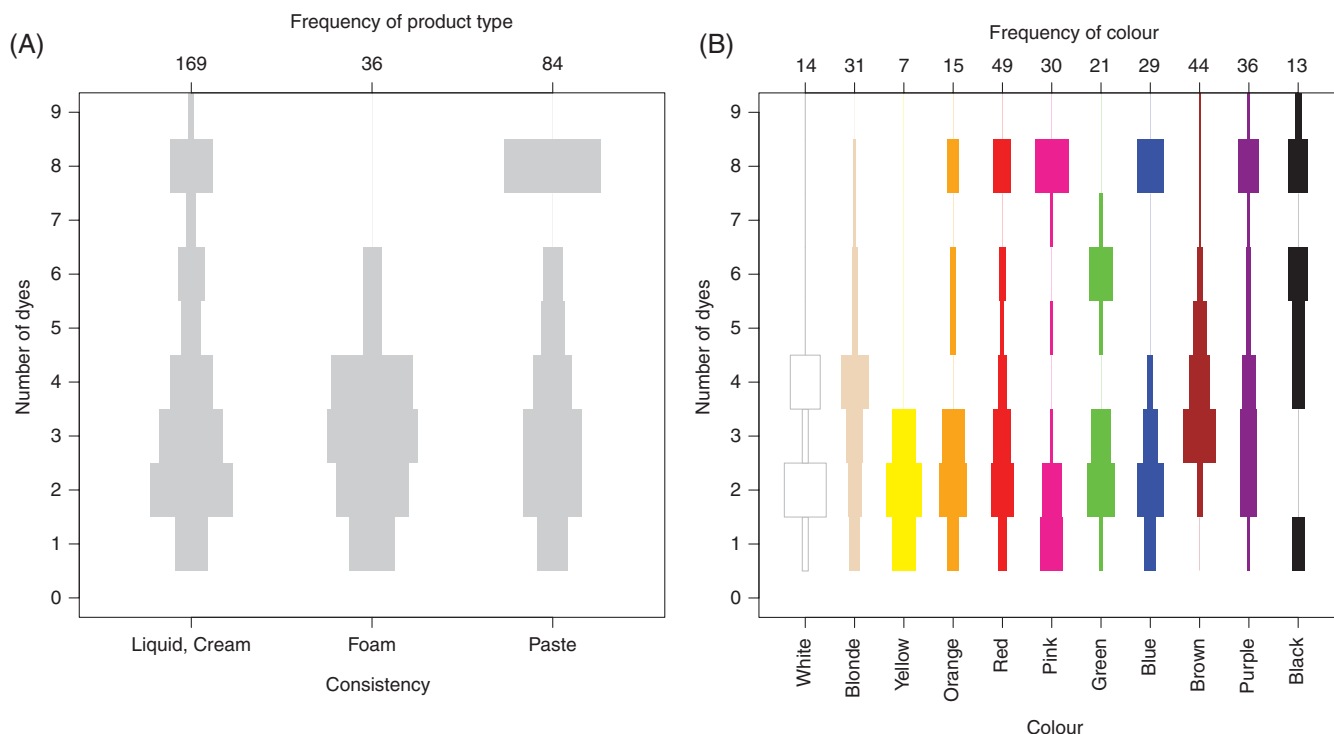


FIGURE 1 Number of hair dye substances per product on the labels of non-oxidative hair dye products ($n = 289$). (A), Applied as liquid or cream, as foam or spray, or as paste. (B), For different colours. The graphic is a modified violin plot in terms of a stacked bar plot, whereby the area of all vertically stacked horizontal bars corresponds to 100% in the category, that is, consistency and colour

($n = 7$) based on iron, titanium, aluminium or chromium were used to a greater extent in those products applied as foam or spray than in those applied as pastes, liquids, and creams (Tables S1-S3 in Appendix S1). The use of hair dye substances was also slightly different between those products applied as paste and those applied as liquids or creams and foams or sprays (Figure S1a in Appendix S1, Appendix S2).

Figure 1B shows the number of hair dye substances per product, with products stratified by 11 different colours. The number of dye substances was significantly heterogeneous ($P = .015$, Kruskal-Wallis test). White, yellow and blonde products had the lowest number of dyes per product, namely 2 (2-4; $n = 14$), 2 (1.5-2.5; $n = 7$), and 4 (2-4; $n = 31$), respectively. There were clear differences in the presence of hair dye substances among the different colours (Tables S4-S14 and Figure S1b in Appendix S1). For example, violet and blue hair dye substances were most common in white products, Basic Brown 17 was the most common substance in blonde products, Basic Red 51 was the most common substance in red and pink products, and HC Blue No. 15 was the most common substance in blue and green products. Brown, purple and black products were not dominated by single hair dye substances.

4 | DISCUSSION

This study found 68 hair dye substances in 289 different non-oxidative hair dye products. The 4 most frequently occurring substances (Basic Blue 99, HC Blue No. 15, Basic Red 51, and Acid Violet 43) were present in 28% to 34% of the products. This is a lower

frequency of occurrence than in oxidative hair dye products, in which the most frequent substances (resorcinol, *m*-aminophenol, toluene-2,5-diamine [sulfate], and *p*-phenylenediamine) were found in 50% to 89% of products.¹³⁻¹⁶ Studies within this area are often not directly comparable, owing to different selection criteria. Some have considered potent skin sensitizers only,^{13,15-17} whereas others have considered all hair dye substances^{8,14}; the present study was based on all hair dye substances in non-oxidative products. Both oxidative and non-oxidative hair dye products may contain potent sensitizers, but this issue was not covered in the present study.

Only 14 of the 68 hair dye substances in this study have been reported by earlier surveys on oxidative hair dye products (Table 2). Among the substances most frequently reported in oxidative hair dye products are HC Yellow No. 2, HC Red No. 3, 4-hydroxypropylamino-3-nitrophenol, 2-amino-6-chloro-4-nitrophenol, hydroxyethyl-2-nitro-*p*-toluidine, *N,N'*-bis(2-hydroxyethyl)-2-nitro-*p*-phenylenediamine, and 4-amino-3-nitrophenol.¹³⁻¹⁶ Only 1 of the 68 substances in the present study, 4-hydroxypropylamino-3-nitrophenol, has been reported to be used in a hair cosmetics patch test series by at least 1 department in different European countries.¹² Seven of the 68 substances found in the present study were also reported in a subset of 35 non-oxidative hair dye products in a study on hair dye products advertised as "natural".¹⁷ Acid Violet 43 was most frequently used in that sample (37%).

On the basis of these observations alone, it seems challenging to identify a set of relatively few relevant hair dye substances as candidates for an experimental patch test series for non-oxidative hair dye products, as compared with oxidative products. Despite some limited overlap, the hair dye substances found in non-oxidative hair dye

products differ from those found in oxidative hair dye products. This study provides a list of relevant hair dye substances that can be considered in future risk assessment and for the development of relevant patch test substances. Evidently, in addition to the exposure information provided by the present study, data on sensitization hazard and, where present, evidence for sensitization risk, and considerations regarding cross-reactivity, should also influence the decision on whether to include a substance in such a new patch test series.

One limitation of this study is that it relied on labelling information; that is, the content of hair dye substances was not verified and was not quantified by chemical analysis. It would not have been feasible, however, to perform chemical analysis of few or many hair dye substances in the hair dye products. The results from this study may serve as a basis for future developmental work with the aim of identifying and quantifying some target substances of interest in non-oxidative products. *p*-Phenylenediamine and toluene-2,5-diamine have been target substances for chemical analysis of oxidative hair dye products.^{8,18} One study found that these substances were incorrectly labelled on 13% of the products, which, however, were from several continents.¹⁸ In our study, 3 of 398 initially selected products used the terms “may contain” or “+/-”, which are not allowed for hair dye substances according to the Cosmetics Regulation. This was, however, a smaller fraction than found in other studies.^{14,15,18} Another limitation is that the selection of products might not have been representative. In addition, actual exposure and, thereby, sensitization risk at the population level will depend on the usage of the different products, implying that widely sold products will drive exposure significantly more than niche products. This aspect could not be taken into account in the present study. The usage and length of application may also vary among the investigated products. For example, products applied as sprays and foams, often advertised as “finishing/retouch” or “party colour”, are probably applied for shorter times than products with the other consistencies, but the exact usage by consumers is not possible to assess from the study data.

The major strength of this first study on the occurrence of hair dye substances in a large sample of non-oxidative hair dye products is that it has generated new knowledge concerning a largely neglected group of cosmetic products.

5 | CONCLUSIONS

Sixty-eight hair dye substances were found in 289 non-oxidative hair dye products on the European market. Up to 9 hair dye substances were present in each product, and their frequency of occurrence in the products ranged from 0.3% to 34% of all products. Some differences in the number of hair dye substances per product were found for products of different consistency and colour. The hair dye substances used in non-oxidative hair dye products differ from those used in oxidative hair dye products, despite some overlap, and they are currently not covered by patch test series. Further analyses should therefore be conducted to assess the toxicological and skin-sensitizing potential of the substances found in non-oxidative hair dye products, as well as their concentrations.

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Conflict of interest

W.U. has received travel reimbursement for presentations given to cosmetic associations from these, and an educational lecture fee from mixed dermatological sponsors. The other authors declare that they have no conflicts of interest.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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Appendix S1

Analysis by principal component analysis (PCA)

Matlab (version 2018a) was used for principal component analysis, with the 68 substances as input value for 289 products, divided into groups of either eleven colours or three consistencies. The first two principal components (describing 35% and 26% of the variance of the data, respectively) were plotted in order to determine any differences in substance use for the investigated groups.

Table S1. Hair dye substances in non-oxidative hair dye products of liquid or cream consistency (n=169)

Hair dye substance	Number	%
Acid Violet 43	48	28
Basic Blue 99	48	28
Basic Red 51	46	27
HC Blue No. 15	36	21
HC Yellow No. 4	32	19
Basic Brown 16	29	17
Basic Red 76	29	17
Basic Orange 31	28	17
Basic Violet 2	27	16
Basic Yellow 57	23	14
Acid Orange 7	21	12
HC Blue No. 16	21	12
Basic Brown 17	20	12
3-Nitro- <i>p</i> -Hydroxyethylaminophenol	17	10
Acid Yellow 3	17	10
Basic Violet 16	17	10
HC Blue No. 2	16	9
HC Red No. 10	16	9
HC Red No. 11	16	9
HC Yellow No. 2	14	8
2-Amino-6-chloro-4-nitrophenol	13	8
Basic Yellow 87	13	8
HC Red No. 3	12	7
HC Blue No. 12	11	7
4-Hydroxypropylamino-3-Nitrophenol	10	6
Hydroxyethyl-2-nitro- <i>p</i> -toluidine	9	5
Acid Black 1	8	5
Acid Blue 9	8	5
Acid Red 52	7	4
N,N'-Bis(2-Hydroxyethyl)-2-nitro- <i>p</i> -phenylenediamine	7	4
Disperse Violet 1	6	4
HC Yellow No. 13	6	4

Basic Yellow 40	5	3
2-Hydroxyethyl picramic acid	3	2
4-Amino-3-nitrophenol	3	2
Acid Red 33	3	2
Hydroxyanthraquinoneaminopropyl methyl morpholinium methosulfate	3	2
Acid red 18	3	2
2,6-Diamino-3-((pyridin-3-yl)azo)pyridine	2	1
Acid Red 92	2	1
Acid Green 25	1	0.6
Acid Yellow 23	1	0.6
HC Violet No. 2	1	0.6
Basic Red 17	1	0.6
Basic Yellow 4	1	0.6
Disperse Blue 377	1	0.6
HC Orange No. 1	1	0.6

Table S2. Hair dye substances in non-oxidative hair dye products applied as foams or sprays (n=36)

Hair dye substance	Number	%
Basic Brown 17	9	25
Titanium dioxide	9	25
Iron oxide black	8	22
HC Red No. 3	7	19
Basic Blue 99	6	17
Iron oxide red	6	17
Iron oxide yellow	6	17
HC Blue No. 11	5	14
3-Nitro- <i>p</i> -Hydroxyethylaminophenol	4	11
Basic Brown 16	4	11
Basic Red 76	4	11
Basic Yellow 57	4	11
Acid Violet 43	3	8
Basic Violet 2	3	8
Hydroxyethyl-2-nitro- <i>p</i> -toluidine	3	8
HC Blue No. 17	2	6
HC Red No. 10	2	6
HC Red No. 11	2	6
HC Yellow No. 2	2	6
Carmines	2	6
Ferric ferrocyanide	2	6
Lazurite	1	3
2-Amino-6-chloro-4-nitrophenol	1	3
2-Chloro-6-ethylamino-4-nitrophenol	1	3
4-Amino-3-nitrophenol	1	3
4-Hydroxypropylamino-3-nitrophenol	1	3
Acid Blue 9	1	3

Acid Red 33	1	3
Basic Red 51	1	3
Pigment Red 57	1	3
Curry Red	1	3
Disperse Violet 1	1	3
HC Blue No. 15	1	3
HC Blue No. 12	1	3
HC Red No. 13	1	3
HC Yellow No. 13	1	3
Chromium oxide greens	1	3

Table S3. Hair dye substances in non-oxidative hair dye products with a paste consistency (n=84)

Hair dye substance	Number	%
HC Blue No. 15	49	58
Basic Violet 16	45	54
Basic Blue 99	43	51
Basic Red 51	37	44
Basic Violet 2	36	43
Basic Orange 31	35	42
HC Yellow No. 4	34	40
Acid Violet 43	29	35
Acid Blue 9	14	17
Basic Yellow 40	12	14
Basic Yellow 87	9	11
4-Hydroxypropylamino-3-nitrophenol	7	8
HC Yellow No. 2	6	7
Basic Blue 9	4	5
HC Blue No. 2	3	4
Basic Green 4	3	4
Basic Blue 3	3	4
Acid Yellow 23	2	2
N,N'-Bis(2-hydroxyethyl)-2-nitro- <i>p</i> -phenylenediamine	2	2
Basic Green 1	2	2
Acid Green 25	1	1
Acid Orange 7	1	1
Acid Yellow 3	1	1
Basic Red 76	1	1
Basic Yellow 57	1	1
Basic Blue 54	1	1
Basic Violet 4	1	1
Disodium 6-hydroxy-5-[(4-sulphonatophenyl)azo]naphthalene-2-sulphonate	1	1

Table S4. Hair dye substances in white non-oxidative hair dye products (n=14)

Hair dye substance	Number	%
Acid Violet 43	6	43
Basic Blue 99	6	43
Acid Blue 9	4	29
Basic Red 76	4	29
Disperse Violet 1	4	29
HC Yellow No. 4	3	21
HC Blue No. 15	2	14
HC Blue No. 2	2	14
HC Blue No. 16	2	14
Basic Violet 16	1	7
Basic Violet 2	1	7
Basic Yellow 87	1	7
Basic Blue 9	1	7
Disperse Blue 377	1	7

Table S5. Hair dye substances in blonde non-oxidative hair dye products (n=31)

Hair dye substance	Number	%
Basic Brown 17	15	48
Basic Blue 99	9	29
Basic Brown 16	9	29
Basic Red 76	9	29
Basic Yellow 57	8	26
Acid Violet 43	7	23
HC Red No. 10	5	16
HC Red No. 11	5	16
Hydroxyethyl-2-nitro- <i>p</i> -toluidine	5	16
HC Blue No. 16	4	13
2-Hydroxyethyl picramic acid	3	10
HC Blue No. 11	3	10
HC Red No. 3	3	10
HC Yellow No. 13	3	10
2-Amino-6-chloro-4-nitrophenol	2	6
Acid Orange 7	2	6
Acid Yellow 3	2	6
Titanium dioxide	2	6
Disperse Violet 1	2	6
HC Blue No. 2	2	6
HC Yellow No. 4	2	6
Iron oxide black	2	6
Iron oxide red	2	6
Iron oxide yellow	2	6
HC Blue No. 17	1	3

Table S6. Hair dye substances in yellow non-oxidative hair dye products (n=7)

Hair dye substance	Number	%
HC Yellow No. 4	3	43
Acid Orange 7	2	29
Basic Yellow 87	2	29
Acid Green 25	1	14
Acid Yellow 23	1	14
Acid Yellow 3	1	14
Basic Orange 31	1	14
Basic Yellow 40	1	14
Basic Yellow 57	1	14
Disodium 6-hydroxy-5-[(4-sulphonatophenyl)azo]naphthalene-2-sulphonate	1	14

Table S7. Hair dye substances in orange non-oxidative hair dye products (n=15)

Hair dye substance	Number	%
Basic Orange 31	11	73
Basic Red 51	5	33
Basic Yellow 87	5	33
Basic Violet 16	4	27
Basic Violet 2	4	27
HC Yellow No. 4	4	27
Acid Orange 7	2	13
Acid Violet 43	2	13
Basic Blue 99	2	13
Basic Yellow 40	2	13
HC Blue No. 15	2	13
HC Yellow No. 2	2	13
4-Hydroxypropylamino-3-nitrophenol	1	7
Acid Red 33	1	7
Acid Red 52	1	7
Acid Yellow 3	1	7
Basic Red 76	1	7
Acid Red 92	1	7

Table S8. Hair dye substances in red non-oxidative hair dye products (n=49)

Hair dye substance	Number	%
Basic Red 51	27	55
Basic Orange 31	19	39
Basic Violet 16	15	31
Basic Violet 2	14	29
Basic Blue 99	13	27
HC Yellow No. 4	13	27
4-Hydroxypropylamino-3-nitrophenol	11	22
3-Nitro- <i>p</i> -hydroxyethylaminophenol	10	20
Acid Violet 43	9	18
HC Blue No. 15	9	18
Basic Yellow 87	7	14
2-Amino-6-chloro-4-nitrophenol	5	10
Basic Red 76	5	10
Basic Yellow 57	5	10
HC Red No. 3	4	8
HC Yellow No. 2	4	8
4-Amino-3-nitrophenol	3	6
HC Red No. 10	3	6
HC Red No. 11	3	6
Basic Brown 16	2	4
Basic Yellow 40	2	4
N,N'-Bis(2-hydroxyethyl)-2-nitro- <i>p</i> -phenylenediamine	2	4
Acid red 18	2	4
2-Chloro-6-ethylamino-4-nitrophenol	1	2
Acid Orange 7	1	2
Acid Red 52	1	2
Curry Red	1	2
HC Blue No. 12	1	2
Hydroxyethyl-2-nitro- <i>p</i> -toluidine	1	2
Basic Red 17	1	2
HC Orange No. 1	1	2

Table S9. Hair dye substances in pink non-oxidative hair dye products (n=30)

Pink	Number	%
Basic Red 51	20	67
Basic Violet 2	16	53
Basic Violet 16	15	50
HC Blue No. 15	15	50
Basic Blue 99	13	43
Basic Orange 31	12	40
HC Yellow No. 4	12	40
Acid Violet 43	11	37
Acid Red 52	2	7
2-Amino-6-chloro-4-nitrophenol	1	3
3-Nitro- <i>p</i> -hydroxyethylaminophenol	1	3
4-Hydroxypropylamino-3-nitrophenol	1	3
Acid Blue 9	1	3
Acid Red 33	1	3
Basic Red 76	1	3
Basic Yellow 57	1	3
Titanium dioxide	1	3
Disperse Violet 1	1	3
HC Blue No. 16	1	3
HC Red No. 10	1	3
HC Red No. 11	1	3
HC Yellow No. 2	1	3
Hydroxyanthraquinoneaminopropyl methyl morpholinium methosulfate	1	3
Basic Green 4	1	3
Acid Red 92	1	3
Carmines	1	3

Table S10. Hair dye substances in green non-oxidative hair dye products (n=21)

Hair dye substance	Number	%
HC Blue No. 15	14	67
Acid Blue 9	13	62
Basic Yellow 40	12	57
HC Yellow No. 4	8	38
Basic Blue 99	7	33
HC Yellow No. 2	7	33
Basic Yellow 87	3	14
Acid Yellow 3	2	10
Basic Blue 3	2	10
Acid Black 1	1	5
Acid Green 25	1	5
Acid Yellow 23	1	5
Basic Yellow 57	1	5
Titanium dioxide	1	5
Basic Blue 9	1	5
Basic Green 4	1	5
Basic Yellow 4	1	5
Basic Green 1	1	5
Chromium oxide greens	1	5

Table S11. Hair dye substances in blue non-oxidative hair dye products (n=29)

Hair dye substance	Number	%
HC Blue No. 15	21	72
Basic Blue 99	14	48
Basic Red 51	14	48
Acid Violet 43	13	45
Basic Violet 2	10	34
Basic Orange 31	9	31
Basic Violet 16	9	31
HC Yellow No. 4	9	31
Basic Yellow 87	2	7
HC Blue No. 2	2	7
HC Blue No. 16	2	7
Basic Blue 9	2	7
Acid Black 1	1	3
Acid Blue 9	1	3
Basic Yellow 57	1	3
Titanium dioxide	1	3
Basic Blue 54	1	3
Basic Violet 4	1	3
Basic Blue 3	1	3
Basic Green 1	1	3
Ferric ferrocyanide	1	3
Lazurite	1	3

Table S12. Hair dye substances in brown non-oxidative hair dye products (n=44)

Hair dye substance	Number	%
Acid Violet 43	15	34
Basic Brown 16	14	32
Acid Orange 7	11	25
Basic Blue 99	11	25
Acid Yellow 3	10	23
Basic Brown 17	10	23
HC Blue No. 2	7	16
HC Blue No. 12	7	16
3-Nitro- <i>p</i> -hydroxyethylaminophenol	6	14
Basic Red 76	6	14
Basic Yellow 57	6	14
HC Blue No. 16	6	14
2-Amino-6-chloro-4-nitrophenol	5	11
HC Red No. 3	5	11
HC Yellow No. 2	5	11
Hydroxyethyl-2-nitro- <i>p</i> -toluidine	5	11
Acid Black 1	4	9
HC Red No. 10	4	9
HC Red No. 11	4	9
Iron oxide black	4	9
Iron oxide red	4	9
Iron oxide yellow	4	9
HC Yellow No. 13	3	7
HC Yellow No. 4	3	7
N,N'-Bis(2-hydroxyethyl)-2-nitro- <i>p</i> -phenylenediamine	3	7
4-Hydroxypropylamino-3-nitrophenol	2	5
Titanium dioxide	2	5
HC Blue No. 15	2	5
HC Blue No. 11	2	5
2,6-Diamino-3-((pyridin-3-yl)azo)pyridine	1	2
4-Amino-3-nitrophenol	1	2
Acid Red 33	1	2
Acid Red 52	1	2
Acid Yellow 23	1	2
Basic Red 51	1	2
Basic Yellow 87	1	2
HC Blue No. 17	1	2

Table S13. Hair dye substances in purple non-oxidative hair dye products (n=36)

Hair dye substance	Number	%
Basic Violet 2	20	56
HC Blue No. 15	18	50
Basic Blue 99	16	44
Basic Violet 16	16	44
Basic Red 51	14	39
Acid Violet 43	11	31
Basic Orange 31	10	28
HC Red No. 3	7	19
HC Yellow No. 4	7	19
3-Nitro- <i>p</i> -hydroxyethylaminophenol	4	11
Basic Red 76	4	11
Acid Blue 9	3	8
HC Blue No. 2	3	8
HC Blue No. 16	3	8
HC Red No. 10	3	8
HC Red No. 11	3	8
N,N'-Bis(2-hydroxyethyl)-2-nitro- <i>p</i> -phenylenediamine	3	8
4-Hydroxypropylamino-3-nitrophenol	2	6
Acid Orange 7	2	6
Acid Red 52	2	6
Basic Brown 16	2	6
Titanium dioxide	2	6
HC Blue No. 12	2	6
HC Yellow No. 2	2	6
Hydroxyanthraquinoneaminopropyl methyl morpholinium methosulfate	2	6
Basic Brown 17	1	3
Basic Yellow 57	1	3
Pigment Red 57	1	3
HC Violet No. 2	1	3
Basic Green 4	1	3
Acid red 18	1	3
Carmines	1	3
Ferric ferrocyanide	1	3
HC Red No. 13	1	3

Table S14. Hair dye substances in black non-oxidative hair dye products (n=13)

Black	Number	%
Acid Violet 43	6	46
Basic Blue 99	6	46
Basic Brown 16	6	46
Basic Red 76	4	31
Basic Yellow 57	4	31
Basic Brown 17	3	23
Basic Red 51	3	23
HC Blue No. 15	3	23
HC Blue No. 2	3	23
HC Blue No. 16	3	23
Acid Black 1	2	15
Acid Orange 7	2	15
Acid Yellow 3	2	15
Basic Violet 16	2	15
HC Blue No. 12	2	15
HC Red No. 10	2	15
HC Red No. 11	2	15
HC Yellow No. 4	2	15
Iron oxide black	2	15
2-Amino-6-chloro-4-nitrophenol	1	8
2,6-Diamino-3-((pyridin-3-yl)azo)pyridine	1	8
4-Hydroxypropylamino-3-nitrophenol	1	8
Acid Blue 9	1	8
Acid Red 33	1	8
Basic Orange 31	1	8
Basic Violet 2	1	8
Basic Yellow 87	1	8
HC Yellow No. 13	1	8
HC Yellow No. 2	1	8
Hydroxyethyl-2-nitro- <i>p</i> -toluidine	1	8
N,N'-Bis(2-hydroxyethyl)-2-nitro- <i>p</i> -phenylenediamine	1	8

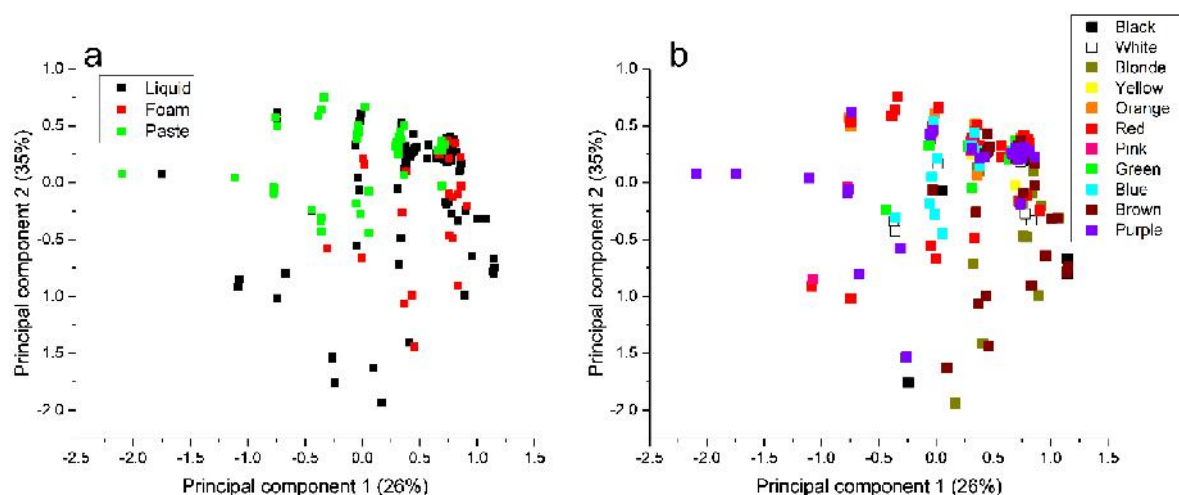


Figure S1. The first two principal components (describing in total 35% of the variance of the data) of the occurrence of 68 hair dye substances in 289 non-oxidative hair dye products are shown for a) different consistencies – liquid/cream, foam/spray, and paste, and b) eleven different colours. A separation of data points in the graphs indicates a different pattern in the occurrence of hair dye substances, i.e. which hair dye substances were used in the products belonging to the category of interest.