

p-Phenylenediamine and other hair dye sensitizers in Spain

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Summary

Background. Oxidative hair dyes are important skin sensitizers, causing contact allergy and dermatitis in hairdressers and consumers.

Objectives. To study the prevalence of hair dye substances, categorized as potent skin sensitizers, in consumer-available oxidative hair dye products on the market of a southern European country and to compare it with that in Sweden.

Methods. Ingredient labels of 105 oxidative hair dye products from 19 brands were studied, and the prevalence and use pattern of hair dye substances, categorized as potent skin sensitizers, was assessed. Network diagrams were used to display results.

Results. According to the labelling, all 105 products contained hair dye substances categorized as potent skin sensitizers. A total of 25 different hair dye substances categorized as potent skin sensitizers were identified. Eighty-seven per cent of the products contained at least four such substances. Either *p*-phenylenediamine, toluene-2,5-diamine or toluene-2,5-diamine sulfate was present in 103 products.

Conclusions. Hair dye substances categorized as potent skin sensitizers were used in all studied hair dye products on the Spanish market. The prevalence of *p*-phenylenediamine was higher in the present study than in a similar study in Sweden. More than 20 potent sensitizers were identified in each country. Not only *p*-phenylenediamine should be used to diagnose allergy to hair dyes.

Key words: allergic contact dermatitis; consumer product safety; cosmetics; exposure analysis; hair dye; market survey; patch test; *p*-phenylenediamine; risk assessment; toluene-2,5-diamine.

Oxidative hair dyes are important skin sensitizers, causing contact allergy and dermatitis in hairdressers and consumers (1, 2). The use of hair dye products has increased considerably over the last decade, and the oxidative hair dyes have a share of approximately 80% of the total hair dye market in the EU and United States (3, 4). The results from a recent study,

which estimated the hair dye exposure of hairdressing apprentices as compared with a matched sample from the general population in Denmark, indicate an increase in exposure to hair dyes and hair dye allergy in young people (5). *p*-Phenylenediamine (PPD) has been the allergen of major concern in scientific reporting and diagnostic patch testing for hair dye contact allergy, in some cases even being used as a synonym for hair dye allergy (6). However, a large number of hair dye substances are currently allowed, and recent studies have concluded that several of them are potent skin sensitizers (7, 8).

On the basis of these sources of information, we recently studied the ingredient labels of 122 consumer-available oxidative hair dye products on the Swedish market (9). It was concluded that hair dye substances categorized as

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potent skin sensitizers were very common in the products, with the vast majority of products containing four or more skin-sensitizing hair dye substances. PPD was found in only 16% of the products, none of them from any of the leading hair dye producers. Ten other hair dye substances categorized as potent skin sensitizers were more frequently found than PPD. Whether this picture is specific for Sweden or Scandinavia is not known. Thyssen et al. found that PPD allergy was significantly more prevalent among patients patch tested in central and southern European centres than in Scandinavian centres (10). This raised the question of whether there are regional differences in Europe regarding the composition of oxidative hair dyes.

The present aim was to study the prevalence of hair dye substances, categorized as potent skin sensitizers, in consumer-available oxidative hair dye products on the market of a southern European country, and to compare the main findings with results from Sweden.

Materials and Methods

Of many possible locations in southern Europe, Barcelona in Spain was chosen. There is a wide range of stores in Barcelona selling consumer-available hair dye products. Barcelona is a large and densely populated city, with a marked city centre and good communications, suitable for a survey of products on the market. A Spanish-speaking person who was very familiar with Barcelona was engaged to assist in collecting the materials.

Selection of products

In April 2010, stores in Barcelona expected to sell consumer-available hair dye products were visited. In a first step, approximately 30 different department stores, shopping malls, hypermarkets, supermarkets and cosmetic stores were visited; large shopping streets were walked (e.g. Passeig de Gràcia and Rambla Catalunya), and it was noted which hair dye products were sold. In addition, with the help of the Spanish-speaking assistant, shop personnel were asked which hair dye brands they considered to be common on the Spanish market and where they were primarily sold. On the basis of these sources of information, 111 consumer-available oxidative hair dye products from 19 different brands were purchased (Table 1). One shop, which specialized in hairdressing products, sold products from the professional series of some of the leading hair dye companies, both to consumers and to hairdressers. These products were, by definition, consumer-available, and were thus included in the study. The ingredient labelling of one brand, Fanola (Pettenon

Table 1. Hair dye products included in a study of the prevalence of hair dye substances, categorized as potent skin sensitizers, in oxidative hair dye products on the Spanish market

Company	Brand	No. of products	PPD or TDA(S)
Eugeneperma	Colorcrem	6	PPD
Garnier	Belle Color	6	PPD
Garnier	Herbabrillo	6	TDA
Garnier	Nutrisse Crema	6	PPD, TDA
Lanofil	Crema Gel Colorante Permanente	6	PPD
Les Cosmétiques	Capilar	6	PPD
Llongueras	Color Advance	6	PPD
Phergal	Naturtint	6	PPD
L'Oréal Paris	Casting crème gloss	6	TDA
L'Oréal Paris	Excel 10'	5	PPD, TDA
L'Oréal Paris	Excellence Creme	6	PPD
L'Oréal Paris	Récital Préférence	5	PPD, TDA
L'Oréal Paris	Majirel	6	TDA
Professionnel			
Schwarzkopf	Brillance	6	TDAS
Schwarzkopf	Palette	5	TDAS
Schwarzkopf	Igora Royal	6	TDAS
Professional			
Wella	Kolestint	6	TDAS
Wella Professionals	Koleston Perfect	6	TDAS
Total number of hair dye products in the study		105	

PPD, *p*-phenylenediamine; TDA, toluene-2,5-diamine; TDAS, toluene-2,5-diamine sulfate. Market survey in Barcelona, Spain in April 2010.

Cosmetics S.p.A.), did not comply with the requirements of the European Cosmetics Directive (11). The term 'may contain' and the symbol (+/–) preceded the declaration of hair dye substances on the ingredient labels, and all Fanola products declared the exact same list of hair dye substances. This symbol is restricted to the declaration of colouring agents listed in annex IV to the Cosmetics Directive, and should not be used for hair dye substances. The six Fanola products were excluded from the study, leaving 105 products for further examination.

A systematic selection of products to be purchased from each hair dye brand was applied, including the darkest blonde shade available, one 'regular' light brown shade, one 'regular' dark brown shade, one 'regular' black shade, and two further shades with different colours (red, blue, purple, etc.). If any of these shades was not available, a shade close to this was chosen. If there was no similar shade available, it was not replaced by any other shade. The ingredient labels of the purchased products were photographed to document them. This selection was a slight modification of the selection applied in a previous study (9). The purpose was to include as many brands as possible in the study and obtain a general picture of the frequency of use of various hair dye substances.

Identification of target hair dyes and assessment of products

In a previous study (9), a list of hair dyes categorized as potent skin sensitizers was made on the basis of assessments performed by Søstet et al. (7) and the European Commission's Scientific Committee on Consumer Products (SCCP) (8, 12) on the skin-sensitizing properties of hair dye substances. The list contained all hair dye substances categorized as strong/moderate skin sensitizers by Søstet et al. and/or as strong or extreme skin sensitizers by the SCCP. In the present study, these substances are jointly referred to as target hair dyes or hair dye substances categorized as potent skin sensitizers. The list comprised 179 different hair dye substances, 68 of which were already prohibited by the Cosmetics Directive (11) at the time of the previous study (August to October 2008). At the time of purchase of products for the present study, 18 additional target hair dyes had been prohibited. They were included in the list of target hair dyes in the present study, as it was considered that they could be present in hair dye products on the market. In 2009, the SCCP was replaced by the Scientific Committee on Consumer Safety (SCCS). The opinions of the SCCS published in 2009–2010 concerning hair dye substances were studied (13). None of the opinions provided any new information that would require a revision of the original list of target hair dyes.

Target hair dyes identified on the ingredient labels were recorded in Microsoft Excel™, and their prevalence was calculated. The prevalence and pattern of concomitant use were further examined with the use of PAJEK, a freely available program for analysis and visualization of networks (available at: <http://pajek.imfm.si/doku.php>). No chemical analyses were performed in the present study.

A group of products intended for professional use ($n = 18$) were compared with the total results in order to identify any substantial differences in composition.

Results

The results of the study are shown in Tables 1 and 2 and Figs. 1 and 2.

A total of 25 different hair dye substances categorized as potent skin sensitizers were identified on the labels of 105 consumer-available hair dye products on the Spanish market in Barcelona (Table 2). The most frequent was resorcinol (81%), followed by *m*-aminophenol (76%). PPD was the third most frequently identified hair dye, being found on the labels of 50% of the products. Toluene-2,5-diamine (TDA) or toluene-2,5-diamine sulfate (TDAS) was found in 49%. Altogether, either PPD, TDA or TDAS was found in 99% of the products (all except two); they

Table 2. Hair dye substances categorized as potent skin sensitizers (9), identified on the labels of 105 oxidative hair dye products on the Spanish market, April 2010

INCI name	CAS no.	Products containing substance (%)
Resorcinol	108-46-3	81
<i>m</i> -Aminophenol	591-27-5	76
<i>p</i> -Phenylenediamine	106-50-3	50
4-Amino-2-hydroxytoluene	2835-95-2	35
2-Methylresorcinol	608-25-3	33
<i>p</i> -Aminophenol	123-30-8	32
2,4-Diaminophenoxyethanol.HCl	66422-95-5	30
Toluene-2,5-diamine sulfate	615-50-9	26
Toluene-2,5-diamine	95-70-5	23
<i>N,N</i> -Bis(2-hydroxyethyl)- <i>p</i> -phenylenediamine sulfate	54381-16-7	18
2-Methyl-5-hydroxyethylaminophenol	55302-96-0	15
Phenyl methyl pyrazolone	89-25-8	15
2-Amino-3-hydroxypyridine	16867-03-1	13
1-Naphthol	90-15-3	13
4-Chlororesorcinol	95-88-5	11
Hydroxybenzomorpholine	26021-57-8	10
4-Amino- <i>m</i> -cresol	2835-99-6	9
2-Amino-6-chloro-4-nitrophenol	6358-09-04	6
1-Hydroxyethyl-4,5-diaminopyrazole sulfate	155601-30-2	6
6-Hydroxyindole	2380-86-1	6
Hydroxypropyl bis(<i>N</i> -hydroxyethyl- <i>p</i> -phenylenediamine).HCl	128729-28-2	4
5-Amino-6-chloro- <i>o</i> -cresol	84540-50-1	3
4-Amino-3-nitrophenol	610-81-1	3
2,7-Naphthalenediol	582-17-2	2
1,3-Bis-(2,4-diaminophenoxy)propane.HCl	74918-21-1	1

were never combined in a product (Fig. 1). The substance used was primarily associated with the producer. Products from Spanish companies (Lanofil, Llongueras, and Phergal) were all declared to contain PPD, whereas products from the internationally represented companies Schwarzkopf and Wella were declared to contain TDAS, and L'Oréal and Garnier had a more diverse pattern, using primarily PPD in some brands and TDA in others (Table 1).

All 105 products examined were declared to contain hair dye substances categorized as potent skin sensitizers, and the number of these substances in a single product ranged between two and 10. The average product contained five potent sensitizers (mean 5.2, median 5), and 87% of the products contained four or more (Fig. 2).

Of 25 potent skin sensitizers identified on the Spanish market in the present study, 24 were also identified in Sweden (Fig. 1). The frequency of PPD was higher in

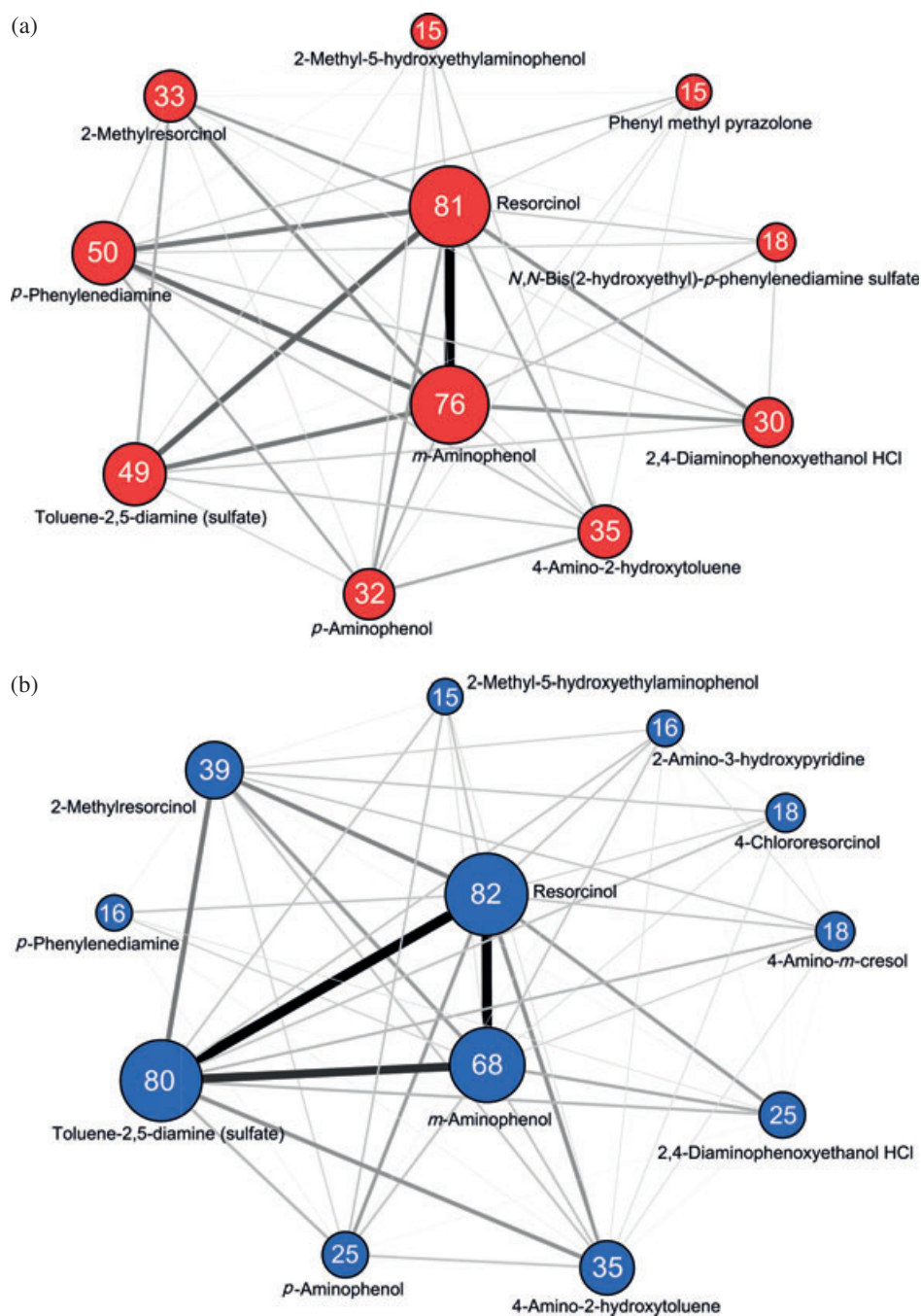


Fig. 1. Network diagram showing hair dye substances, categorized as potent skin sensitizers, identified on the labels of $\geq 15\%$ of examined oxidative hair dye products on the Spanish and Swedish markets. Circles show the prevalence of substances (%). Lines show the concomitant use of substances in products. Thicker and darker lines indicate a higher frequency of concomitant use of substances in products. (a) Hair dye substances in 105 products in Spain in April 2010. (b) Hair dye substances in 122 products in Sweden between August and October 2008.

Spain (50% of the products) than was found in the study in Sweden (16%). PPD and TDA/TDAS were more evenly distributed in the present study than in the Swedish study, where TDA/TDAS was declared on the labels of 80% of

the products. Six hair dye brands (produced by three international companies) were examined in both Spain and Sweden. A comparison showed that, in some cases, the same brands were declared to contain PPD in Spain

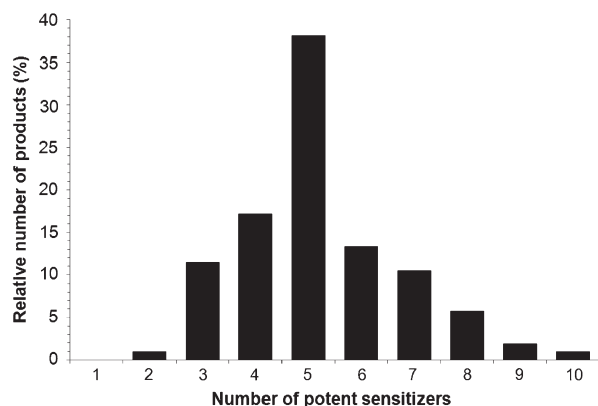


Fig. 2. Number of identified hair dye substances, categorized as potent skin sensitizers, in 105 oxidative hair dye products on the Spanish market in April 2010.

and TDA/TDAS in Sweden. This was the case even when ingredient labels of the same shades were compared.

The products intended for professional use were all declared to contain TDA/TDAS; otherwise, the same major ingredients were present as in the total picture.

Discussion

Our findings imply that hair dye substances, categorized as potent skin sensitizers, are very common in consumer-available hair dye products sold in Barcelona in Spain, a large southern European city. Every examined product was declared to contain target hair dyes, and nearly 90% of the products contained four or more, according to their ingredient labels.

The results largely correspond with those of a similar study in Sweden; the major hair dye ingredients were, to a large extent, the same in both countries. One noteworthy difference was the higher frequency of PPD in Spain than in the study in Sweden. The same brand and shade were in some cases declared to contain PPD in Spain but declared to contain TDA/TDAS in Sweden; however, chemical analysis was not performed to verify the content. These outcomes indicate that there may be regional differences in allergen exposure associated with the use of

hair dyes, which is much in line with a recent multicentre study by Thyssen et al. (10). The authors found that PPD allergy was significantly more prevalent among patients patch tested in central and southern European centres than among those tested in Scandinavian centres.

A number of potent skin sensitizers other than PPD were also frequently declared. Thus, hair dye allergy may be underdiagnosed in dermatitis patients tested with the baseline series. In two retrospective analyses of patients patch tested with PPD and TDA simultaneously, 14% and 17% of those reacting to TDA tested negative for PPD (14, 15). Consequently, the hair dye allergy in these patients would have been missed by the baseline series. In a cross-reactivity study with PPD, TDA and *p*-aminophenol in guinea pigs, cross-reactivity was recorded (16). However, the results clearly indicate that testing also with TDA and *p*-aminophenol would detect more cases of hair dye allergy than testing merely with PPD.

In the Cosmetics Directive, there are restrictions regarding use concentrations for the most frequently identified hair dye substances in the present study, except for *p*-aminophenol. *p*-Aminophenol was common in the products, and a significant increase in *p*-aminophenol allergy has been reported among dermatitis patients (17, 18). It should be stressed that the current limits on and use concentrations of PPD, TDA and several other hair dye substances are insufficient for protection of consumers and hairdressers against skin sensitization and contact dermatitis.

It is concluded that all products examined in the present study were declared to contain hair dye substances categorized as potent skin sensitizers. The products generally contained several potent skin sensitizers. Once again, we wish to express our concern regarding the risk that cases of hair dye allergy may be missed by patch testing with the current baseline series containing PPD only.

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