PS: 5250/2013
ICS NO:71.100.70

PAKISTAN STANDARD

OXIDATION HAIR DYES LIQUID

PAKISTAN STANDARDS AND QUALITY CONTROL AUTHORITY,
STANDARDS DEVELOPMENT CENTRE,
PSQCA Complex Plot # ST-7/A, Block-3, Scheme No: 36, Gulistan-e- Johar,
Karachi.

PAKISTAN STANDARD SPECIFICATION FOR OXIDATION HAIR DYES LIQUID

0. FOREWORD

0.1 This Pakistan Standard was adopted by Pakistan Standards & Quality Control Authority on 20th March,2013 after the draft finalized by the Cosmetics & Toilet Goods Technical Committee had been approved by the Chemical National Standard Committee.

0.2 In general, hair dyes may be broadly classified as solid hair dyes and liquid hair dyes. The requirements pertaining to powder hair dyes are covered in PS: 4079-1998 Specification for Powder hair dyes.

Liquid hair dyes, however, may be further classified into the following types.

a- Oxidation hair dyes (liquid)
b- Lead salt based hair darkener.
c- Emulsion type hair dye and
d- Vegetable based hair dye

This Standard covers only liquid Oxidation hair dyes based on para-phenylenediamine (PPD).

0.3 Fixing of lower limit for dye content was considered essential in order to safeguard consumer's interest to enable him to get dye that would perform and is money's worth whereas upper limit is fixed to allow only a safe dye in the market as PPD is a known carcinogenic ingredient if used in concentration above 6 percent .

0.4 The requirements for active matter is the dye ready for use prepared after formulation with developer as per manufacturer's instruction is being prescribed with a procedure to calculate the same. The lower limit for this requirement shall take care of effectiveness of the dye, where as the upper limit shall ensure the safe concentration of PPD.

0.5 The marking would be mandatory for the manufactures to declare PPD content in dye ready for use, instruction for preparation of dye ready for use, besides warning, declaration and other relevant information and precaution expiry date is being prescribed as a regular requirement.

0.6 For the purpose of deciding whether a particular requirement of this standard is complied with the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with PS: 103, Rule for rounding off Numerical value. The number of significant places retained in the rounded of values should be the same as that of the specified value in this standard.

0.7 For preparation of this the assistance derived from IS: 8481-993 is acknowledged with thanks.

0.1 **SCOPE**

1.1 This standard prescribes the requirements and the methods of sampling and test for oxidation hair dyes, liquid.

2. **TYPES**

There are two types of dyes,

Type 1 – Black

Type 2 – Brown

3. **REQUIREMENTS**

3.1 **Description**

The oxidation hair dye (liquid) normally consists of two parts, namely (a) the dye (ary1 amine), and (b) the developer, which are supplied in separate containers.

3.2 **Ingredients**

Unless specified otherwise, all raw materials used in the manufacture of oxidation hair dye (liquid) shall conform to the requirements prescribed in the relevant Pakistan Standards where such standards exist.

3.3 **Dye**

The active ingredient is usually para-phenylenediamine (PPD) dispersed in a suitable surface active agent in an alkaline medium. The brown variant shall also contain other dye chemicals like ortho amino phenol, para amino phenols, etc. besides aryl amine. It may contain suitable modifiers such as resorcinol. The dye shall comply with the requirements given in Table 1 when tested according to the methods given in Annex A.

TABLE 1 REQUIREMENT FOR DYES
(Clause 3.3)

Sl. #	CHARACTERISTIC	REQUIREMENT		METHOD OF TEST
		Type 1 (Black)	Type 2 (Brown)	
(1)	(2)	(3)	(4)	(5)
i)	pH	9.0-11.0	9.0-11.0	A-2
ii)	Active matter as PPD content, percent by mass	2.5-4.0	1.0-2.0	A-3

3.4 **Developer**

The developer is an oxidizing agent, usually a dilute solution of hydrogen peroxide, free from any foreign matter and suitably stabilized. It shall comply with the requirements given in Table-2 when tested according to methods given in Annex A.

3.5 **Dye Ready for Use**

The dye ready for use is prepared after mixing the dye content and developer in the proportion recommended by the manufacturer in the leaflet which is enclosed in the container packing the dye and developer or may be printed on the carton itself, as the case may be. The active content (PPD) in dye ready for use may be calculated by the procedure given below. The lower limit of dye ready for use is being prescribed to check the effectiveness of the dye whereas the upper limit is being prescribed to check the concentration of PPD to ensure that the same remain within the safe limits.

TABLE 2 REQUIREMENTS FOR THE DEVELOPER
(Clause 3.4)

Sl. #	CHARACTERISTIC	REQUIREMENT	METHOD OF TEST (Ref to Annex A)
(1)	(2)	(3)	(4)
i)	pH	1.8 to 4	A-2
ii)	Assay (as H_2O_2), percent by mass (m/m)	2 to 12	A-4
iii)	Residue on evaporation, percent by mass (m/v), Max	0.2	A-5

TABLE 3 REQUIREMENTS FOR DYE READY FOR USE
(Clause 3.5)

Sl. #.	CHARACTERISTIC	REQUIREMENT		METHOD OF TEST
		Type 1 (Black)	Type 2 (Brown)	
(1)	(2)	(3)	(4)	(5)
i)	Calculated active matter (as PPD content) in the solution after recommended dilution with developer, percent by mass	1.25-2.0	0.5-1.0	Procedure for calculation as given note below

NOTE: - The procedure for calculation of PPD content in solution after recommended dilution with developer is as follows:

If PPD content in liquid hair dye is = x % and manufacturer recommends that 1 part of dye may be mixed with y parts of developer than PPD content in dye ready for use is:

$$= \frac{X}{y + 1}$$

4. PACKING AND MARKING

Ref. PS: ISO: 22715
Cosmetics – Packaging and Labelling

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4.1 CAUTION

Para-Phenylenediamine may cause skin irritation in certain cases, so a preliminary test according to the accompanying direction should first be made (see 4.4.1). The material should not be used for dyeing the eyelashes or eyebrows, as it use may cause blindness.

4.1.1 Each package shall contain instructions in English and local languages on the following lines for carrying out the test: "Para-phenlenediamine containing preparation may cause serious inflammation of the skin in some cases and so a preliminary test should always be carried out to determine whether or not special sensitivity exists. For carrying out the test, cleanse a small area of skin behind the ear or upon the inner surface of the forearm, using either soap and water or alcohol. Apply a small quantity of the hair dye as prepared for use to the area and allow it to dry. After 24 hours, wash the area gently with soap and water. If no irritation or inflammation is apparent, it may be assumed that no hypersensitivity to the dye exists. The test should, however, be carried out before each and every application. This preparation should on no account be used for dyeing eyebrows or eyelashes as severe inflammation of the eye or even blindness may result".

5. SAMPLING

5.1 Representative samples of the material shall be drawn as prescribed PS: 1720-1998.

5.2 Test for all characteristics shall be carried out on the composite sample.

5.3 The material shall be taken to have conformed to the specification if the composite sample passes all the tests.

A N N E X – A
(Clause 3.4 and 3.5)

METHODS OF TEST FOR HAIR DYES, LIQUID

A-1 QUALITY OF REAGENTS

Unless specified otherwise, pure chemicals and distilled water (see PS: 593) shall be employed in test.

Note: - *'Pure chemicals shall mean chemicals that do not contain impurities which affect the results of analysis.*

A-2 DETERMINATION OF pH

A-2.1 Apparatus

A pH meter preferably equipped with glass electrode.

A-2.2 Procedure

A-2.2.1 **For Dye**

Take 15 ml of the dye and determine its pH at 27 $\pm$ 2^0C using the pH meter.

A-2.2.2 **For Developer**

Take 15 ml of the developer and determine its pH at 27 $\pm$ 2^0C using the pH meter.

A-3 DETERMINATION OF ARYL AMINE CONTENT

A-3.0 Outline of the Method

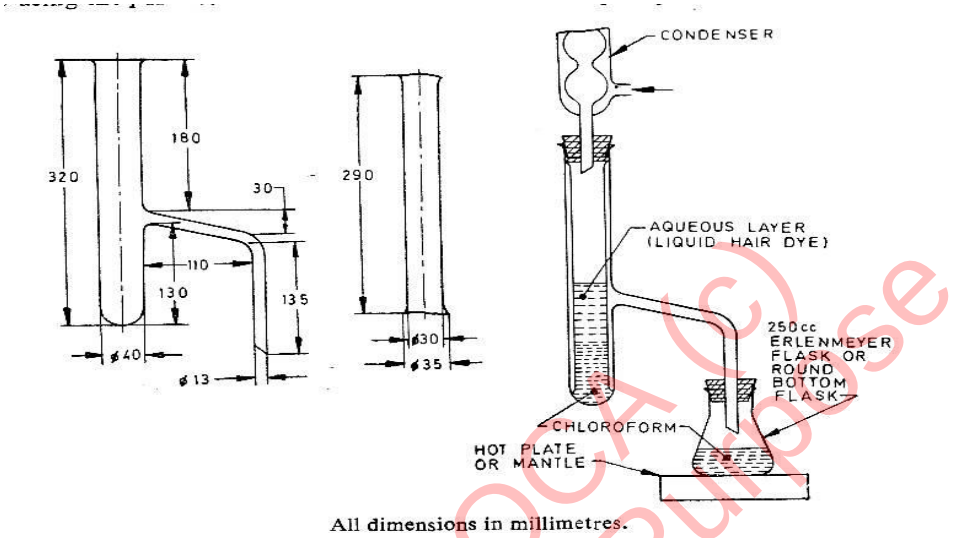
This method estimates the aryl amine as diacetyl derivative of aryl amine.

A-3.1 Apparatus

A-3.1.1. Continuous extraction apparatus as illustrated in Fig. 1

A-3.1.2. G 4 sintered glass crucible

A-3.1.3 **Beaker** 100 ml capacity



All dimensions in millimetres.

FIG. 1 CONTINUOUS EXTRACTION APPARATUS

A-3.2 **Reagents**

A-3.2.1 **Chloroform Laboratory Reagent Grade**

A-3.2.2 **Acetic Anhydride Ana1ytical Reagent Grade**

A-3.3 **Procedure**

A-3.3.1Transfer accurately weighed quantity (about 5 g) of liquid hair dye, so as to contain 0.1 to 0.3 g para-pheny1enediamine, to the inner tube of the continuous extractor, previously charged with chloroform. Take 60 ml of chloroform in the flask to completely extract the dye. About 5 hours extraction is sufficient. Remove the flask, and transfer chloroform extract to a 100 ml beaker, rinsing the flask with few small portions of chloroform. Evaporate chloroform to about 25 mL and add 1 mL of acetic anhydride slowly, with stirring. Let it stand for one hour and filter on a weighed G 4 sintered glass crucible. Wash the beaker and precipitate with three or four 5 mL portions of chloroform. Carefully remove last traces of precipitate from the beaker. Dry to constant mass at 120^0C and weigh the precipitate of diacety1 para-pheny1enediamine, C_6H_4 $(NHCOCH_3)_2$.

A-3.4 **Calculation:**

$$\text{Aryl amine content (as para-phenlenediamine)} = \frac{\text{m X 0.05626 X 100}}{\text{M}}$$

Where

m = mass in g of the precipitate, and

M = mass in g of the hair dye taken for extraction.

A- 4.0 **DETERMINATION OF HYDROGEN PEROXIDE**

A-4.1 **Reagents**

A-4.1.1**Dilute Sulphuric Acid**

A-4.1.2**Potassium Permanganate Solution**

N/10 freshly standardized

A-4.2 **Procedure**

A-4.21Weigh accurately about 10 g of the developer and dilute to 500 ml. Take 25 ml of the diluted solution in a conical flask, add 5 mL of sulphuric acid and titrate against potassium permanganate solution.

A-4.3 **Calculation:**

$$\text{Assay, percent (m/m)} = \frac{VN}{M} \times 34.02$$

Where

V= Volume of potassium permanganate solution required for titration,
N = normality of potassium permanganate solution, and
M = mass of developer taken to prepare 500 ml solution

A- 5 **DETERMINATION OF RESIDUE ON EVAPORATION**

A-5.1 **Procedure**

A-5.1.1Take 10 ml of the developer in platinum dish and evaporate on a water bath till the entire liquid volatilizes. Weigh till constant mass is obtained.

A-5.2 **Calculation:**

$$\text{Residue on evaporation, percent by mass (m/v)} = \frac{m}{V} \times 100$$

Where

m= mass in g of the residue, and
V= volume in ml of developer.

ALTERNATE

Annex B

[Clause 4.4, table 1, Sl No. (ii)]

ESTIMATION OF OXDIATION HAIR DYES COSMETIC FORMULATIONS

B-1 OUTLINE OF THE METHOD

Applicable to all cosmetic to all cosmetic formulations containing oxidative dyes. The method described a reverse phase gradient HPLC technique for the quantitative estimation of *o*-aminophenol, N, N, Bis-2-Hydroxyethyl-PPD sulphate, *p*-aminophenol and *p*-phenylinediamine.

B-2 REAGENTS

B-2.1 Mobile Phase

B-2.1.1 Mobile Phase (*A*)

a) Sorenesen buffer (buffer solution pH8) Add 440 ml of 0.1 hydrochloric acid and 2 g L- Ascorbic acid sodium slat to 560 ml of 0.1 M sodium tetra borate decahydrate solution, mix and filter through 0.45 mm filter (ensure that the final *p*H is 8).

b) Methanol HPLC grade Mix 600 ml of (a) and 400 ml (b) to give mobile phase (A)

B-2.1.2 Mobile Phase (*B*)

A 0.05 M acetic acid solution is adjusted to a pH of 5.9 with 10 percent ammonia solution and after through 0.45 mm filter (preserve at 4^0C when not in use to prevent bacterial growth).

B-2.2 *n*-Heptane

Above and make up to volume with the mobile phase (A) and mix corresponding to concentration of 1.0, 2.3`, 3.0, 4.0 and 5.0 mg/10 ml working standards.

B-3.2 Preparation of mixed Standard

Weigh about accurately about 4.0 g of the sample in a 100 ml beaker, dissolve in buffer solution (A), transfer quantitatively to a 100 ml volumetric flask and make up to volume with the same mobile phase and mix.

B-2.3 standard – Dye chemicals like *p*-phenylinediamine, N, N, Bis-2 hydroxyetheyl-PPD sulpahte, Resocinol, Aminophenols.

B-2.4 Column – Merck Lichrospher RP60 B (C8), 250 mm x 10 mm, 5 particle size.

B-2.5 **RP HPLC Conditions**

B-2.5.1 **Gradient Elution Condition:**

a) 0.25 percent A for 19 min

b) 25.80 percent A for 10 min

c) 80 percent A for 5 min

d) 85.95 percent A for 5 min

e) 95 percent A for 3 min

B-2.5.2 **Flow Rate- 1 ml/min**

B-2.5.3 **Column Temperature, 48^0C**

B-2.5.4 **VU Detection at 220 mm, 235 nm and 290 nm**

B-3 **PROCEDURE**

B-3.1 **Standard Solution**

Weigh accurately about 1.0 g of each of the 4 standards into separate 100 ml beaker. Dissolve in mobile phase (A) and dilute to 100 ml in standard volumetric flask with the same mobile phase and mix well (primary standard). Transfer to a series of 10 ml volumetric flasks 1.0, 2.0, 3.0m 4.0 and 5.0 ml of standards prepared.

B-3.4 **Extraction of Actives from the Sample**

Transfer 2 ml of solution from D-3.2 to a 50 or 100 ml separator funnel. Add. 20 ml *n*- Heptane, shake for 1 min and allow the liquid phases to separate. Inject the aqueous phase.

B-4 **CALCULATION**

Percent dyer content =

$$\frac{\text{Concentration of standard in µg x Sample area}}{100 \times \text{Standard area} \times \text{Weight of sample (g)}}$$

REFERENCES

- *Oxidation hair dye liquid. IS: 8481-2005*
- *Method of sampling cosmetic and Toilet Goods PS: 1720-1985*