DRAFT IN WIDE CIRCULATION

DOCUMENT DESPATCH ADVICE

REF:	DATE
PCD 12/T	21 -4-2011

TECHNICAL COMMITTEE: PLASTIC SECTIONAL COMMITTEE, PCD 12

All members of:

i) Plastic Sectional Committee, PCD 12;
ii) Members of Petroleum, Coal and Related Products Division Council, PCDC; and
iii) All others interested.

Dear Sir/Madam,

Please find enclosed the following documents:

Doc: No.	**Title**
PCD 12 (2583)C	Draft Amendment No. 3 to IS 9873(Part 3):1999/ ISO 8124-3:1997 Safety requirements for toys Part 3 Migration of certain elements. *(First Revision)*

Kindly examine this draft amendment and forward your views stating any difficulty which you are likely to experience in your business or profession, if they are finally adopted as amendments.

Last date for comments is : 20 June 2011

Comments if any, may please be made in the format as given overleaf and mailed to the undersigned at the above address. This document is also hosted on BIS website www.bis.org.in.

Thanking you,

Yours faithfully,

Dr (Mrs.) Vijay Malik
Sc.'F'&Head (PCD)

Encl: As above.

FORMAT FOR SENDING COMMENTS ON BIS DOCUMENTS

(Please use A4 size sheet of paper only and type within fields indicated. Comments on each clauses/sub-clauses/table/fig. etc be started on a fresh box. Information in Column 4 should include reasons for the comments and suggestions for modified wording of the clauses when the existing text is found not acceptable. Adherence to this format facilitates Secretariat's work)

Doc. No.: _____ TITLE: _____

LAST DATE OF COMMENTS: _____

NAME OF THE COMMENTATOR/ORGANIZATION: _____

Sl. No.	Clause/Sub-clause/ para/table/fig. No. commented	Commentator/ Organization/ Abbreviation	Type of Comments (General/Editorial/ Technical)	Justification	Proposed change

Doc:PCD 12(2583) C

Draft AMENDMENT NO 3
TO
IS 9873(Part 3):1999/ ISO 8124-3:1997 SAFETY REQUIREMENTS FOR TOYS
PART 3 MIGRATION OF CERTAIN ELEMENTS
(First Revision)

(First cover page- Designation of the standard)

Replace IS 9873(Part 3):1999/ ISO 8124-3:1997 with IS 9873(Part 3):1999 and wherever it exists.

(National foreword, first para)

Replace existing with the following:

This Indian Standard (Part 3) (first revision) is a modified adoption of International Standard "ISO 8124-3:1997, Safety requirements for toys, Part 3 Migration of certain elements" was adopted by the Bureau of Indian Standards on the recommendation of Plastics Sectional Committee and approval of the Petroleum, Coal and Related Products Division Council.

Phthalates are used as plasticizers (softening agents) in the manufacture of soft vinyl (also known as polyvinyl chloride [PVC]), which in turn is used in toys and child care articles. Phthalates do not bind to the soft vinyl, but are present as mobile components of the vinyl. However, the mere presence of phthalates in soft vinyl does not in itself equate to a health risk. It is the amount of phthalates that leach out of soft vinyl and are absorbed into the body that can be harmful. Although exposure to phthalates in soft vinyl through dermal contact or inhalation is negligible, phthalates may leach out of soft vinyl during periods of sustained mouthing action (sucking and chewing, but not licking) and enter the body through the saliva. Once in the body, some phthalates have the potential to cause adverse effects on reproduction and development. It is for this reason that a need was felt to specify the safe limits of Phthalates in toys.

(*National Foreword, last paragraph*) – Insert the following new paragraph at the end:

"Maximum permissible limits for six types of Phthalates along with the test method is given in National Annex B."

(*Page 22*) – Insert the following National Annex at the end of the standard:

NATIONAL ANNEX B
(*National Foreword*)

B-1 When tested in accordance with the method given at B-2, the toy shall not show the presence of Phthalates beyond the limits given as under:

Scope	Requirement
Vinyl in toys or childcare article	≤ 0.1% of i) Bis (2-ethylhexyl) phthalate (DEHP) ii) Dibutyl phthalate (DBP) or iii) Benzyl butyl phthalate (BBP)

Vinyl in any part of the toy or childcare article that can be placed in mouth of a child under 4 years of age.	≤ 0.1% of i) Di-"isononyl" phthalate (DINP) ii) Di-"isodecyl" phthalate (DIDP) or iii) Di-n-octyl phthalate (DNOP)

B-2 Method of Test for determination of Phthalates in Toys

B-2-1 Principle

The method is used for quantitative determination of the following six phthalates in toys made of Poly Vinyl Chloride.

i) Bis (2-ethylhexyl) phthalate (DEHP)
ii) Dibutyl phthalate (DBP)
iii) Benzyl butyl phthalate (BBP)
iv) Di-"isononyl" phthalate (DINP)
v) Di-"isodecyl" phthalate (DIDP)
vi) Di-n-octyl phthalate (DNOP)

The method involves extraction of these phthalates using dichloromethane and quantification of individual phthalates through Gas Chromatography - Mass Spectrometric technique.

B-2.2 Apparatus

B-2.2.1 Gas Chromatograph with Mass Spectrometer (GC-MS) with all required accessories including syringes, analytical columns with appropriate data system. The suggested operative parameters for GC-MS are as given below, but can be changed, provided standardization is done.

B-2.2.1.1 GC conditions

Column: 30m X 0.25mm x 0.25 μm
Inlet Temperature: 280^0C
Injection Volume: 1 μL
Carrier Gas Flow: Helium at 1mL/min
Injection Mode: Splitless, pulse injection at 35 psi for 0.6min
Oven Program; 50^0C for 2 min, to 280^0C at 30 ^{0}C/min, to 310^0C at 15^0C/min and hold for 3.33 min, for a total run time of 15 min
Washing Solvent: Hexane

B-2.2.1.2 MS conditions

Filament Delay: 5 min
Ion Trap Temp: 220^0C
Manifold Temp: 50^0C
Transfer Line Temp: 280^0C

B-2.2.2 Soxhlet Assembly comprising of Soxhlet Apparatus, Round Bottom Flask of suitable capacity (say 150ml, 250 ml or 500 ml), Thimble, Water Cooled Condenser, Heating Mantle.

B-2.2.3 Balance capable of weighing accurately upto 0.1 mg.

B-2.2.4 Volumetric Flasks of suitable capacities

B-2.3 Reagents

B-2.3.1 Certified Reference Material of following six phthalates

Compound	CAS No.
Bis (2-ethylhexyl)phthalate (DEHP)	117-81-7
Dibutyl Phthalate (DBP)	84-74-2
Benzyl butyl phthalate (BBP)	85-68-7
Di-n-octyl phthalate (DNOP)	117-84-0
Di-isononyl phthalate (DINP)	28553-12-0
Di-isodecyl phthalate (DIDP)	26761-40-0

B-2.3.2 Dichloromethane (Spectroscopy Grade or higher)

B-2.3.3 Hexane (Spectroscopy Grade or higher)

B-2.3.4 Internal Standard: Benzyl Benzoate (CAS No. 120-51-4)

B-2.4 Procedure:

A-4.1 Preparation of standard solutions –

a) High Concentration Stock Solution (S1) - Weigh accurately 0.1 g each of DEHP, DBP, BBP, DNOP and 0.4 g each of DINP & DIDP (accurately upto 0.1 mg) individually in separate 100 ml volumetric flasks. Add Hexane to the mark to make 1000 µg/ml concentration stock solution for DEHP, DBP, BBP & DNOP and 4000 µg/ml concentration stock solution for DINP & DIDP.

b) Middle Concentration Stock Solution (S2) - Add 1 ml each of DEHP, DBP, DBP, DNOP, DINP & DIDP to a 10 ml volumetric flask. Add Hexane to the mark to make the Middle Concentration Stock Solution (S2) containing 100 µg/ml each of DEHP, DBP, BBP, & DNOP and 400 µg/ml each of DINP & DIDP.

c) Internal Standard (IS)– Weigh accurately 0.1 g of Benzyl Benzoate (BB) in a 100 ml volumetric flask and make up the volume with Hexane to make stock solution of 1000 µg/ml concentration of Benzyl Benzoate. Add 1000 µl of the stock solution to a 10 ml volumetric flask to make Benzyl Benzoate Internal Standard (IS) of 100 µg/ml for use in preparation of calibration curve. Add 500 µl of the stock solution to another 10 ml volumetric flask to make 50 µg/ml concentration of Benzyl Benzoate for use in sample testing.

B-2.4.2 Preparation of calibration curves – Prepare calibration curves using standard solutions ranging from 0.5 to 5 µg/ml (or any other suitable range). A suggested plan for preparing the calibration curve is given under Table 1.

Table 1

Calibration solution	Volume (in µl) of S2	Volume (in µl) of Internal Standard of 100 µg/ml conc.	Final Volume (ml)	Concentration (µg/ml)	
				DEHP, DBP, DBP & DNOP	DINP, DIDP
Level 1	50	100	10	0.5	2
Level 2	100	100	10	1	4
Level 3	200	100	10	2	8

Level 4	300	100	10	3	12
Level 5	400	100	10	4	16
Level 6	500	100	10	5	20

Note: Each calibration Standard to have an internal standard concentration of 1 µg/ml.

B-2.4.3 Sample preparation

i) Select only PVC part of the toys by removing metal parts, ornaments, cloths, hair etc. if present with the toy
ii) Cut or chop or grind the PVC part of the toy sample to fine pieces/powder. Particle size upto 0.5mm is desirable
iii) In case, the grind/cut material is required to be stored, it may be stored preferably in non-plastic material, preferably glass material

B-2.4.3 Extraction & Estimation

i) Place 0.5g to 1 g of material accurately weighed in a paper thimble.
ii) Place the thimble into the Soxhlet Apparatus.
iii) Add dichloromethane to the round bottom flask upto 80% minimum of its full capacity;
iv) Start Soxhlet extraction for about 2 hrs ensuring uniform rate of extraction. A rate of 10 cycles/hr is considered suitable for this purpose.
v) On completion of the extraction, the extract be allowed to cool down to room temperature
vi) Remove the solvent from the extract by using suitable evaporator (rotary, turbo etc.) under suitable conditions depending upon the evaporator.
vii) Dissolve the residue with Hexane and transfer the solution to a 10ml volumetric flask by repeatedly rinsing the flask with Hexane for ensuring complete transfer.
viii) Make up the volume upto the mark (10ml) with Hexane.
ix) Combine 100 µl* of the solution with 20 µl of internal standard (BB, 50 µg/ml) and 880 µl of hexane in a GC-MS vial. Mix thoroughly and analyse with GC-MS

**** Note: Depending on the phthalate content in toy samples, a different dilution ratio may be necessary to bring the concentration levels within the calibration range.***

B-2.4.4 Illustrative Chromatograms – A typical Total Ion Chromatogram for the six phthalates is shown below. As could be seen, four phthalates, namely DBP, BBP, DEHP and DNOP appear as sharp single peaks whereas the remaining two phthalates, namely DINP and DIDP appear as hump (or finger peaks).

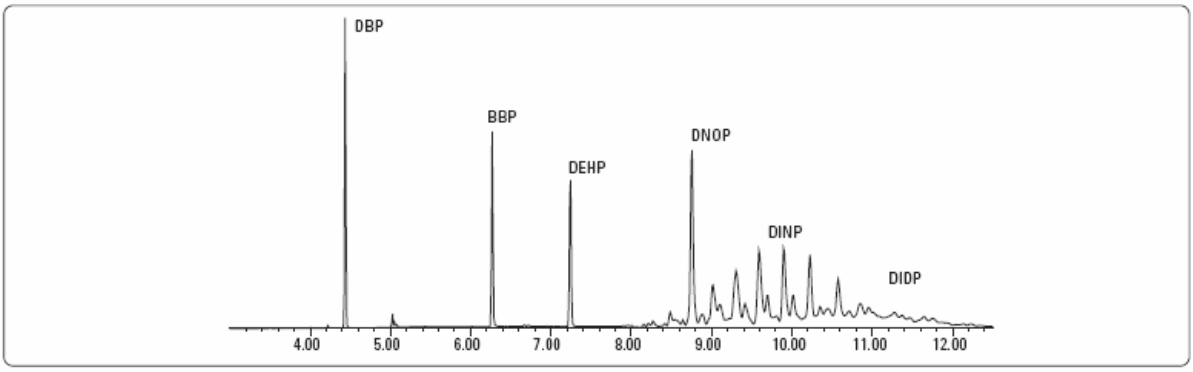

Fig.1 Typical Total Ion chromatogram for DEHP, DBP, BBP, DINP, DIDP & DNOP

The finger peaks could appear in the Total Ion Chromatograms for DINP and DIDP due to possibilities of number of isomers. It is recommended to use area summation integration technique for quantitation of these phthalates. Typical Extracted Ion Chromatogram for these two phthalates are given below for guidance:

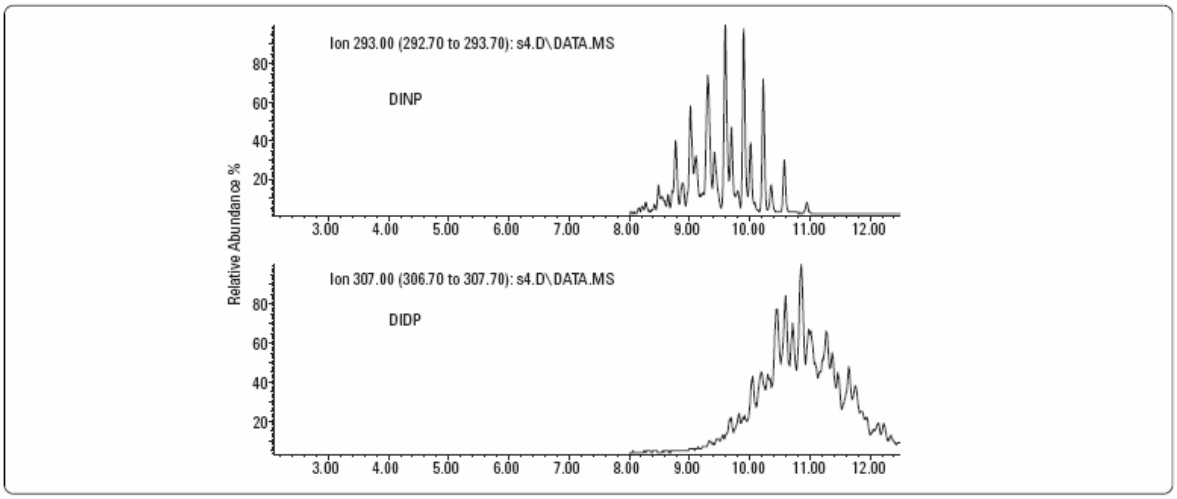

Fig.1 Typical Extracted Ion chromatogram for DINP & DIDP

B-2.5 Results

B-2.5.1 Qualitative Analysis - Identification of phthalates present in the toy samples be done by comparing the retention time of sample peaks with peaks of standard compounds which shall be run with the same equipment under similar conditions. Typical quantitation ions for the six phthalates are given under Table 2. Each ion produced from the same compound must have maximum intensity at the same scan or plus/minus one scan.

Table 2

Phthalate	Characteristic ions (m/z)			
	Target ion (m/z)	Qualification ion 1 (m/z)	Qualification ion 2 (m/z)	Qualification ion 3 (m/z)
DBP	149	150	223	205
BBP	149	91	206	238
DEHP	149	167	279	150
DNOP	279	149	150	261
DINP	293	149	127	167
DIDP	307	149	141	150

B-2.5.2 Quantitative analysis

Calculate the concentration of phthalate in sample using the following formula:

$$\text{Phthalate content (\%wt)} = \frac{A \times V}{W} \times F \times (1 \times 10^{-6}) \times 100\%$$

Where:

V - Final volume of extract
A - Concentration in extract (µg/mL)
W - Weight of sample (g)
F - Dilution factor