BEST PRACTICE GUIDANCE DOCUMENT

EN71-3 Compliance Testing Procedures and Methodology for Artists Colours and Writing Instruments

Version 1, February 2024

Table of Contents

Overview

This document is intended to be used as a key reference for manufacturers and testing laboratories when testing artists' colours or writing instruments products to the harmonised standard EN 71-3:2019 + A1:2021 (Standard for migration of certain elements), in order to confirm compliance with the EU's Toy Safety Directive (EU Directive 2009/48/EC). The document has been developed jointly by the European Artists Colours Association (EuACA) and the European Writing Instruments Manufacturers Association (EWIMA), with the support and assistance of Toy Industries of Europe (TIE), and Deutscher Verband der Spielwarenindustrie e.V. (DVSI), as well as the participation of accredited testing laboratory partners, who run such testing for these sectors. This document is the result of discussions between the above organisations on the acknowledged issue of inconsistent results to EN71-3 testing for certain toy materials, especially for aqueous based paints, inks and writing material from across the sector, and the need to minimise this problem.

Any comments or questions on this document may be addressed to secretariat@cepe.org.

Introduction

The testing of different solid and liquid products supplied for children's use to the EN 71-3 standard can on occasion lead to considerable inconsistencies between results from different laboratories and with regard to repeatability. Although this standard stipulates clear procedures and analytical methodologies, there are certain nuances in individual laboratories' test protocols and test sample preparation that can lead to different results being obtained on nominally the same sample. There are also known issues relating to raw material quality and residual element content that can also contribute to this issue. This level of inconsistency has, for certain constituents, led to products failing compliance with the Toy Safety Directive from a first analysis, but then being confirmed as compliant when tested a second time. Please see Annex A for some examples illustrating these inconsistencies – a total of 50 examples were shared by members of EWIMA, EuACA and TIE (surveyed Spring-Summer 2022). Such situations result in additional costs and wasted resource, and general concerns as to the validity when it comes to certifying products as meeting the specific requirements set out in EN71-3.

These best practice recommendations, which are applicable to both manufacturers and to the testing of their products, arise from in-depth technical discussions between the different organisations mentioned in the overview. They are an attempt to reach a common set of agreed guidelines to minimise inconsistent test results and, thus, have been developed with the aim to provide greater assurance to manufacturers and test laboratories (and ultimately to the authorities enforcing and checking compliance) that the products supplied to the market are safe for their intended use.

Sample Preparation

Section 7.2 of EN71-3 covers this topic in some detail, however it is important to point out some of the nuances to sample preparation which can have a major impact on test results. One of the important issues to testing to this Standard is to ensure the homogeneity of the sample that is prepared and submitted for analysis. Working with small samples of e.g. artists paints, waxy crayons, or the ink from writing instruments, presents several challenges to ensure that the sample obtained is truly representative of the product under test. Obtaining a sample can be done in many different ways (scraping the surface of a solid material, pipetting liquid products etc.), and any processing of the sample to try and achieve a better homogeneity may lead to an unintended detrimental change to the sample itself.

Examples of key parameters and issues include:

- mechanical / high-shear sampling techniques have been known to cause a change in state (e.g. breakdown of the product matrix) leading to higher reported values.

- waxy or oily samples also present challenges, as the surfaces of these may not be easily wetted by the acidic migration media or the solvent-extraction of wax or oil incomplete due to the nature of the wax/oil.
- precise pH adjustment is important, especially in situations where the products under test contain substances that have an effect on pH e.g. those that react with acids.
- Problems associated with the filtration of liquid aqueous samples after pH adjustment.

Specific Recommendations when preparing…

a) Liquid Products

Several key issues need to be highlighted when considering the testing of liquid products. The EN 71-3 standard includes the simple instruction 'mix the laboratory sample' in Table 3 under section 7.2.2. It is important to note that higher / incorrect values have been observed when samples are dried to a residue, comminuted (reduced to fine particles or fragments) and then subsequently redissolved / redispersed before testing. Thus, this procedure should not be followed – liquid products should be tested in the same state as that in which they are supplied to the market and should not undergo any physical alterations. Liquid products that are going to be applied to a toy and then dried / cured (paints, varnishes etc.) should be similarly prepared to simulate the process – the test sample has to represent the final form of the product that will be present in its end-function on / in the toy supplied to the market.

A second issue to note is the importance of monitoring the compatibility / solubility of the liquid product in the testing media. It has been demonstrated that the solubility of some products (e.g. inks in writing instruments) in the migration media (aqueous hydrochloric acid) can influence the results to testing to EN 71-3. It is important to identify when this issue may be a factor affecting the consistency of the results, and to address this accordingly.

Thirdly, as mentioned above, the use of high-shear mechanical sampling techniques should be avoided as far as possible, as this can lead to a breakdown of the product's matrix or individual components (such as aluminised pigments or pigments containing Aluminium within their molecular structure) within the product, thus leading to an unrepresentative high value when running migration testing.

Finally, it is important to consider whether the sample being tested is solvent- or oil-based, or if it is an aqueous liquid product. There are specific issues with the preparation and testing according to the nature of the liquid product, and different approaches need to be taken (compatibility of an oil-based product with test media, adjustment of the pH of aqueous samples etc.). We recommend that the testing laboratory carefully checks whether the test procedure they intend to use may have an influence on the results due to the specific matrix / nature of the sample under test.

b) Waxy Products

First it should be noted that dewaxing steps should obviously not be applied to products for which no oily or waxy surface is present. Several waxy product types such as wax crayons pose a particular challenge for testing to EN 71-3. Consistent and efficient removal of the waxy matrix parts (to ensure subsequent compatibility with analytical testing media) needs careful consideration, as there are different waxes and oils used in the preparation of these products. It is understood that there is no 'universal' solvent that can be used to dewax all products currently on the market in a consistent manner.
n-Heptane (which is described in the standard) is a commonly used solvent and can successfully remove some types of waxes from certain materials however doesn't exhaustively extract from the matrix. In addition, the protocol for performing the dewaxing step has not been standardised – extraction times vary, for example.

A separate paper on this topic was presented within the related task-group of CEN/TC52/WG5 responsible for the EN 71-3 standard[1]. Also take note of Annex H section H11 of EN 71-3. There is also an intention to eliminate the dewaxing step from EN 71-3 testing protocols in a future revision of the standard (expected end 2024).

c) Dry films of Coatings, Inks, Varnishes etc.

Scraping off dried paint, coating, ink and varnish films depends on the nature of the substrate. EN 71-3 comprehensively covers this topic in table 3 – note especially the recommendations relating to the use of solvents and plastic materials, to avoid contamination from the base material. The use of solvent sampling is commonly used for heavy metals only when removing from metallic substrates. It should be noted that solvent sampling may influence the results to soluble organotin analysis. Each deviation from standard procedure should be checked and validated by the testing laboratory – any deviation to the standard needs to be reported. It should be noted that the use of solvent is only intended to verify inconclusive results after scraping.

pH Adjustment of the test sample

Once the test sample has been prepared it is important for the pH to be adjusted in accordance with EN 71-3 prior to the migration testing step. Failure to do this can have an impact on the subsequent migration testing and results. This is clearly documented and explained in section 8.2 and in 8.3.1.2 (after finalizing the migration) of the Standard and in Annex H, section H10. Note that the current 5-fold step procedure (revision 3) has been specifically optimised to minimise variability and should be followed very precisely during testing. pH value changes may be observed before or after migration for paper materials, so accurate pH adjustment is necessary.

[1] *CEN/TC52/WG5/TG2/N0493 (not publicly available)*

Filtration of the test sample

Filtration / separation procedures can be very challenging when considering aqueous liquid products (e.g. fingerpaints), especially after pH adjustment. The main issue is that these products can contain very fine particles (resulting from the use of fine pigments, fillers or glitters, for example) which interfere with the EN71-3 test protocol and can lead to erroneous results. Filtration is normally carried out in two steps – first the test sample is subjected to high speed centrifugation, then it is filtered through different filters according to the nature of the sample (0,45 µm, 0,2 µm and 0,02 µm are often referenced). 0,02 µm filtration is used in the case of samples containing Copper (based on e.g. Pigment Blue 15:3). Solid Phase Extraction (SPE) techniques and instruments are often utilised, although it is of course important to ensure that this does not remove the element(s) under test (Mercury, for example, would probably be retained in the SPE filtration system). It would be helpful for the test laboratories to be aware of which types of pigments and extenders are present in the sample in order to apply the most appropriate filtration techniques.

Best Practice Recommendations:

1. *Any concerns over the sampling technique should be discussed between the manufacturer of the product under test and the test laboratory, preferably at the outset before proceeding with the analysis*
2. *The sampling technique used should be referenced / reported in detail by the test laboratory in the final test report to confirm the procedure that was followed*
3. *Testing of liquid products should be carried out strictly on their supplied form when possible – they should not be dried and then redissolved prior to testing as this may affect results. Products should be tested in the correct form (liquid or dried film) that they will be present in the final toy article.*
4. *The test protocol should be discussed in detail between manufacturer and test laboratory when there may be concerns over the solubility / compatibility of liquid products in the testing media.*
5. *Waxy products and their treatment require particular attention – it is important to ensure that the dewaxing step is exhaustive and successfully completed before proceeding with testing (note that this step will be removed from the Standard in a future revision).*
6. *Alternative dewaxing solvents should be identified and referenced by the test laboratory if n-heptane is not appropriate*
7. *The pH adjustment to samples should be done carefully and with precision, and in accordance with EN 71-3, to adjust for situations where e. g. chemical (acid-consuming) reactions may take place due to test protocol.*
8. *It would be beneficial if manufacturers were able to share compositional details about their products (under Non-Disclosure Agreements) so that appropriate methods for sample preparation are followed, especially with regard to filtration.*

Specific Recommendations when testing for…

i) Aluminium

Pigments based on or containing Aluminium are particularly sensitive to production processes, for artists' colours and writing instrument products, especially when these involve the use of equipment that imparts high-shear forces to the product (such as stirring, dispersing or tablet preparation). This also holds true for the sample preparation of such materials.
Addition of sensitive components (e. g. ultramarine blue pigment) should be done as far as possible towards the end of the production process, and under low shear conditions. Likewise sample preparation including dewaxing steps should be carried out without using high-shear techniques, where possible.

Best Practice Recommendation:

9. *Avoid the use of high-shear stirring equipment in both the production and test sample preparation, when the product contains sensitive components that are based on aluminium, such as ultramarine blue pigment.*
10. *Formulators to select the most appropriate pigment grades – some grades are specifically designed (coated) to avoid releasing aluminium.*

ii) Barium

Non-compliance due to high barium content has been studied in some detail. The main cause of such issues has been traced to the quality of the "Lithopone" (C.I. Pigment White 5, mix of Barium Sulphate with Zinc Sulphide) which is used as an alternative to Titanium dioxide. Mixing procedures need to be carefully controlled, and as for aluminium, the use of high-shear forces on the product during production and sampling should be avoided. Barium Sulphate alone does not appear to lead to major problems with free Barium content

Best Practice Recommendation:

11. *Manufacturers should carefully control & monitor barium migration (as a quality criteria) and mixing procedures, especially if using lithopone.*

iii) Chromium VI

This element species is known to be a very challenging component to monitor, control and ensure compliance (especially in fingerpaints) due to its complex physico-chemical behaviour and a high degree of uncertainty arising from the analytical test method, combined with the very stringent requirements set in EN 71-3. Considerable variability has been observed relating

to the matrix of the product under test, so this needs to be taken into account. The presence of Chromium-based complex dyes in the product under test is particularly difficulty to manage and needs careful consideration. Note especially the comments in the Standard on this topic (section 9.3 and Annex H section H7, solution stability).

Best Practice Recommendation:

12. *Pay particular attention to the overall composition of the product when testing for Chromium (VI), especially when chromium-based dyes are present. Consider possible matrix influences on the test results and the possibility of conversion to Chromium (III) or the interconversion from Chromium (III) to Chromium (VI), which means, Chromium (VI) is generated under certain conditions.*

iv) Copper

Many issues with EN 71-3 compliance relating to copper content have been traced back to the quality of the copper-based pigments used, and to the finished product manufacturing process employed. It is well-known that certain pigments (e.g. Pigment Blue 15:3, Pigment Green 7) can have higher than anticipated residual copper contents, and the quality of such pigments therefore needs to be carefully controlled by manufacturers. In addition, copper-based pigment structures can be sensitive to high-shear forces, so these need to be avoided during production and test sample preparation.
It must be also pointed out, that the proper filtration of the final migration solution is crucial. Copper-based pigments often present very small particle diameters and due to this, they may be analysed as colloidal particles (without migration), which result in significant higher results for Copper – see the above section on filtration for further details.

Best Practice Recommendation:

13. *Manufacturers should monitor the copper content in certain pigments that they use and avoid applying high-shear forces during product manufacture and sample preparation.*
14. *Test labs should check the filtration step for the presence of colloidal particles.*

v) Lead

A common cause of non-compliance due to high lead content is the choice of source for the chalk / calcium carbonate or comparable filler. It is well-known that in certain locations the natural lead content of the chalk is considerable higher than expected, and higher than the average for chalk supply. This can then translate to a fail when testing under EN 71-3.

Best Practice Recommendation:

15. *If lead content exceeds the permitted level, then manufacturers should check the quality of their chalk / calcium carbonate or comparable filler as this is a common reason for high lead migration*

vi) Zinc

Inconsistent results from the testing of products containing the filler zinc sulphide are common. This is believed to be due to the high solubility of this material in aqueous hydrochloric acid. Great care should be taken with the sampling protocol when testing for Zinc. For example, removing paint from die-cast models can result in zinc contaminating the paint sample

Best Practice Recommendation:

16. *Care should be taken when testing for Zinc, as Zinc Sulphide may be present in the test sample (from e.g. lithopone use, or in glow pigments). The pH adjustment step has an important impact on Zinc testing.*

Concluding Remarks

Inconsistencies observed during the testing of artists' colours and writing instruments products to the harmonised standard EN 71-3 (specific migration testing for certain elements) are likely to be caused by one or more likely a combination of factors that have been described in detail in this document. These include: product formulation; raw material quality; the product manufacturing process; sampling procedure; sample preparation; pH adjustment; dewaxing and a differences in the testing regime used for liquid products.

It is hoped that, by following the above recommendations, manufacturers and their partner testing laboratories will be able to identify the cause of any inconsistencies encountered and thus take appropriate action to ensure the validity of test results which thus confirm compliance with the Toy Safety Directive.

Acknowledgements

Our thanks go to the following technical experts and their organizations for assisting with the preparation of this document:

Alexander Breunig, Senior Consultant, Deutscher Verband der Spielwarenindustrie e.V.
Dr. Claudia Nickl, Chemical consumer protection, product safety, environmental protection, and standardisation, EWIMA
Dominique Billeret, Senior Technical Advisor, TIE
Anke Kramer, Head of Chemical Analysis, Ostthüringische Materialprüfgesellschaft für Textil und Kunststoffe mbH
Eric To, Global Restricted Substances Testing Services (RSTS), SGS Hong Kong Limited

Annex A – Selected Examples of EN71-3 Inconsistencies

Selected examples on EN71-3 inconsistencies - information from members of EuACA, EWIMA & TIE, Aug 2022

Product	Product group (select)	Colour shade (select)	Intended use (select)	Physical appearance (select)	Deviating analyte (select)	Test method (select)	Test result 1 (mg/kg) (fill in)	Test done by	Test result 2 (mg/kg) (fill in)	Test done by	Test result 3 (mg/kg) (fill in)	Test done by
2	Water colour tablets	blue	hand painting	solid	Al	EN71-3	3180	Not specified	>5000	Not specified	790	Institute A
3	Oil crayons	dark red	drawing	solid	Al	EN71-3	234	Institute D	<50	Institute E		
4	Oil crayons	blue	drawing	solid	Al	EN71-3	8442	Institute D	3200	Institute B	145	Institute E
7	Coatings	blue	coating	scraped-off	Al	EN71-3	13974	Not specified	1450	Not specified		
8	Wax crayons	White	colouring	solid	Ba	EN71-3	2274	Institute G	341	Institute F		
9	Wax crayons	White	colouring	solid	Ba	EN71-3	1709	Institute G	172	Institute F		
12	Coloured pencil leads	blue	drawing	solid	Cr-VI	EN71-3	0,15	Institute A	<0.02	Institute E	<0.02	Institute E
13	Poster paint	white	brush painting	liquid	Cr-VI	EN71-3	0,2	Not specified	<0.004	Not specified		
16	Fibre pen ink	red	colouring	liquid	Cr-VI	EN71-3	0,007	Institute D	<0,0025	Institute B	< 0,005	Institute E
18	Coloured pencil leads	white	colouring	scraped-off	Cr-VI	EN71-3	0,095	Institute E	<0,002	Institute D		
24	Fibre pen ink	black	drawing	liquid	Cu	EN71-3	112	Institute D	<5	Institute D		
25	Poster paint	dark green	brush painting	liquid	Cu	EN71-3	514	Institute D	<5	Institute D		
26	Fibre pen ink	light blue	drawing	liquid	Cu	EN71-3	390	Not specified	11	Institute B		
27	Fibre pen ink	green	drawing	liquid	Cu	EN71-3	210	Not specified	10	Institute B		
37	Fibre pen ink	light green	colouring	liquid	Pb	EN71-3	1	Not specified	<0.05	Not specified	<0.05	Institute A
38	Poster paint	white	brush painting	liquid	Pb	EN71-3	0,65	Institute F	0,28	Institute F		
39	Oil crayons	dark red	drawing	solid	Pb	EN71-3	1,6	Institute D	<0,5	Institute E		
40	Wax crayons	brown	colouring	solid	Pb	EN71-3	3,1 ppm	Institute D	Compliant<2ppn	Institute E	3,2	Institute F
43	Wax crayons	light blue	drawing	solid	Zn	EN71-3	822	Institute D	280	Institute B	317	Institute E
45	Coloured pencil leads	blue	colouring	solid	Zn	EN71-3	2556	Not specified	5700	Institute B	4950	Institute D
47	Wax crayons	White	colouring	solid	Zn	EN71-3	1441	Institute G	36	Institute F		
49	Wax crayons	pink	colouring	solid	Zn	EN71-3	4958	Institute D	141	Institute E		