GLASS BEADS FOR USE IN PAVEMENT MARKING PAINTS

1. SCOPE

   a) This specification applies to glass beads used in water based pavement marking paints to increase their retroreflectivity and thereby, their safety.

   b) APAS is a registered trademark owned by CSIRO and protected under applicable laws. Use of the trademark or the general scheme is prohibited unless prior approval in writing is obtained from CSIRO via the APAS Secretariat.

   c) APAS approval to this specification may be gained by a manufacturer or importer, by compliance with the requirements detailed in this specification and those in document D192 "The APAS Product Approval System".

2. BACKGROUND

   a) APAS Document D001 should be read to obtain a broad overview of the Australian Paint Approval Scheme (APAS).

   b) This specification came about at the request of some state road authorities concerned about the level of heavy metal contamination in some glass beads and its potential impact on the environment should they escape from the glass matrix and enter the environment.

   c) Glass beads may be manufactured either locally (Australasia) or overseas. Manufacturer controls are described in Appendix B below.

   d) This version now includes references to new sub classes of beads available in the market but not fully covered by AS2009:2006 or the previous APAS AP-VS0042

3. DEFINITIONS & ACRONYMS

   3.1 General terms

   Campaign Run – a continuous production run of one type of glass bead. Typically, Campaign Runs are of the order of 100 tonnes or more.

   Heavy metal – elements as nominated in Table 1 below. For the purposes of this specification, the "heavy metals" of note include metalloids such as lead, arsenic and antimony; transition metals such as mercury, cadmium and chromium.

   Overseas – bead manufacturers based overseas are those NOT located in either Australia or New Zealand.

   Retroreflectivity – a measure of the light visible to the driver compared to the light entering the pavement marking. See also Note 1 below.

   Note 1: The popular definition of night time visibility of pavement markings is defined as retroreflectivity of the markings. This is a measurement of the efficiency of the marking to return light in the general direction from which it is generated. It is simply a measure of the light visible to the driver compared to the light entering the pavement marking. The majority of the retroreflective light is usually a function of the surface applied glass beads which form part of the marking.

3.2 Acronyms

   APAS Australian Paint Approval Scheme
   CSIRO Commonwealth Scientific and Industrial Research Organisation
   ICPMS Inductively Coupled Plasma Mass Spectrometry
   ILAC International Laboratory Accreditation Cooperation www.ilac.org
   NATA National Association of Testing Authorities
   XRF X-ray Fluorescence

4. DESCRIPTION & GUIDE FOR USERS

4.1 General product description

   a) Pavement marking materials require the addition of glass beads to provide retroreflectivity. These beads may be of different types as specified in AS/NZS 2009 and are normally applied either hand strewn or by an automatic drop-on mechanism onto the wet pavement marking shortly after it has been applied.

   b) Depending on the source of glass beads, their chemical composition may vary greatly with respect to ingredients such as heavy metals.

   c) Some end users may choose to implement a policy of environmental awareness in their product selection. Through this policy they may require the minimisation of any real or potential environmental impact arising from the use of glass beads.

   d) The purpose of this specification is to facilitate for the end user, the use of glass beads with low levels of potentially hazardous elements or compounds.

4.2 Technical basis of specification

   This specification is based on AS/NZS 2009 with the addition of restriction on the heavy metal content and other compounds in the glass beads.
GLASS BEADS FOR USE IN PAVEMENT MARKING PAINTS

4.3. Sub-classes

a) This specification is divided into the following sub-classes as described in AS/NZS 2009;
   i). 0042/1 – Drop On (Type B) beads
   ii). 0042/2 – Intermix (Type C) beads
   iii). 0042/3 – Large (Type D) beads
   iv). 0042/4 – High refractive index (Type E) beads

b) Each bead of type i), ii) or iii) above may be available in two grades;
   i). Standard grade
   ii). HR or high retroreflectivity grade

5. REFERENCED DOCUMENTS

This specification makes reference to the following documents;

- ISO 9001 Quality management systems - Requirements
- ISO 17025 General requirements for the competence of testing and calibration laboratories
- AS/NZS 1580 Paints and related materials – methods of test
- AS/NZS 2009 Glass beads for pavement marking materials

ISO and AS or AS/NZS Documents and Standards may be downloaded from various national standards bodies web sites; in Australia at;
http://www.sai-global.com.au

- APAS Document AP-D001 How APAS Operates
- AP-D139 Application form for product certification
- AP-D192 The APAS product certification system

All APAS Documents may be downloaded from the APAS web site located at;
http://www.apas.gov.au

6. COMPOSITIONAL REQUIREMENTS

6.1 General

All glass beads shall be made from minimum 99% soda lime glass as defined in clause 4 of AS/NZS2009 except for 0042/4.

6.2 Heavy metal content

a) The amount of heavy metals in the beads shall not be greater than that specified in Table 1 (8.2) below.

b) As the preferred test method for heavy metals is ICPMS (refer section A.3.5.2) below, the previous measures for Cadmium Oxide and Chrome 6+ has been changed to Cadmium and Total Chromium respectively due to limitations of the ICPMS test method.

c) The use of XRF method is allowable provided that the XRF method is validated against ICPMS and validation data is provided to APAS together with the original submission for bead certification. Refer A4 below.

7. PRODUCT CERTIFICATION REQUIREMENTS

7.1 General

a) The product and its application shall comply with all requirements of APAS Document D192 during the application process and the life of the certification with the following exceptions;

b) The application form AP-D139 need not be supplied as it relates to paint products. Certifications will be granted for a (renewable) period of 12 months maximum.

7.2 Technical

a) The product shall comply with all requirements detailed in Table 1 (section 8) below during the APAS certification period.

b) For the purposes of product certification applications, compliance with Table 1 below including AS/NZS2009 shall be demonstrated.

c) For the purposes of on-going product certification during the life of the certification, continuing compliance with the requirements of Appendix B below shall be demonstrated.

d) Technical innovation – where a manufacturer of glass beads believes a new technical innovation will allow their beads to pass the performance requirements specified in Table 1 below but not the compositional, coating/s and/or additive/s limitations then a request may be made to APAS for a variation. This variation request shall be treated Commercial-in-Confidence by APAS officers who shall endeavour to decide on the validity of the variation request. In making this decision, APAS officers may consult with various industry experts including a ballot of the industry (once approval by the applicant is given).
7.3 Safety & environmental

a) The manufacturer's Material Safety Data Sheet (MSDS) must be studied closely prior to using the product and complied with during use of the product.

7.4 Test failure procedure

a) Where the glass bead manufacturer or importer encounters test failures, the manufacturer's or importer's quality assurance system (ISO 9001) shall describe the process for handling such non-complying results. This shall include re-testing, isolation and rework or disposal, as appropriate.
b) Records of such non-conformities shall be kept.

c) Due to the specific nature of the test below and the likely frequency of testing, it may not be possible to locate an accredited laboratory. In such cases, if the method is not included in the Scope of Accreditation the laboratory may still undertake the test below provided that the laboratory is accredited to ISO 17025 for other tests in the same field of activity i.e. Chemical Testing.

A3.2 Principle

a) A representative sample of glass beads is milled to a fine particle size (<5µm), followed by complete dissolution in an acid mixture.
b) Analysis for lead, antimony, arsenic, mercury, cadmium and chromium is then carried out using ICPMS or equivalent analytical techniques capable of measuring parts per million levels of the elements in question.
c) Method equivalence for non-ICPMS testing shall be demonstrated by means described in A4 below.

APPENDIX A

SAMPLING & TESTING FOR HEAVY METALS

A1. Scope

a) This method details the accepted method for the analysis of glass beads for the purposes of compliance with AP-S0042.
b) Sampling is a key aspect to ensure results are representative of deliveries and the method of sampling is defined in A2 below.

A2. Sampling

a) Sampling and sample preparation shall be carried out in accordance with the Appendix A Method 2 of AS/NZS 2009 by a facility accredited to ISO 17025 for that method.
b) Samples may be taken from a consignment on delivery or from pavement marking plant as appropriate.
c) Frequency of sampling shall be not less than once per 20MT manufactured. Samples will be generated as representative composites of the Campaign Run.

A3. Testing via ICPMS

A3.1 General

a) Testing to the method detailed below shall be carried out by a laboratory accredited to ISO 17025 with this method included in their Scope of Accreditation.
b) ISO 17025 accreditation shall be provided by an organisation accredited by an ILAC Mutual Recognition Arrangement (MRA) signatory and having a scope of accreditation covering ISO 17025 requirements. Within Australia NATA is such an accredited organisation. Outside Australia, NATA has a Mutual Recognition Agreement (MRA) with other competent accreditation bodies. [Examples can be found on NATA’s web site – see Mutual Recognition Agreement (http://www.nata.asn.au)].

c) Due to the specific nature of the test below and the likely frequency of testing, it may not be possible to locate an accredited laboratory. In such cases, if the method is not included in the Scope of Accreditation the laboratory may still undertake the test below provided that the laboratory is accredited to ISO 17025 for other tests in the same field of activity i.e. Chemical Testing.

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c) Method equivalence for non-ICPMS testing shall be demonstrated by means described in A4 below.

Note 2 These are analytical test procedures and must be conducted following recognised analytical principles.

Note 3 Dangerous chemical agents are used in this process and must be handled and used in accordance with the MSDS and the required laboratory standards.

Note 4 The analysis is to be carried using recognised reference materials traceable to international standards. Repeatability needs to be demonstrated as part of the analysis process. See A4 below.

A3.3 Reagents

The following reagents are required:

a) Analytical grade concentrated nitric acid
b) Analytical grade 40% hydrofluoric acid
c) Analytical grade concentrated hydrochloric acid
d) Deionised water, 18M ohm-cm or better

A3.4 Apparatus

The following equipment is required:

a) Sample milling equipment, zirconium mill
b) Microwave digester
c) Teflon microwave vessels
d) 10mL polypropylene tubes with lids
e) 5mL polypropylene tubes with lids
f) Tube racks
g) Fume cupboard
h) Adjustable pipettes: 5mL, 1mL, 0.5mL
i) Balance, readable and accurate to 0.0001g
j) ICPMS or equivalent instrumentation

A3.5 Procedure

A3.5.1 Sample Digestion

a) The zirconium mill must be ‘flushed’ of any previous samples. 10 to 20 grams of clean dry sand is milled and discarded and then the process repeated.
b) 10 to 20 grams of glass beads are split from the composite sample obtained as in Clause A1 above, and are placed into the mill and...
ground to finer than 5µm. This material is discarded and the process repeated. On the second repeat with the sample, the ground material is kept and transferred from the mill to a clean, labeled container and sealed for subsequent analysis.

c) Weigh out approximately 200mg of sample into a microwave vessel recording the weight to 4 decimal places. Prepare a duplicate and record sample mass as m1 and m2 for the first and duplicate masses of the sample.

d) In a fume cupboard add 2mL nitric acid, 1mL hydrochloric acid and 1mL hydrofluoric acid to each vessel containing the previously weighed sample.

e) Place the lids on the vessels then place the vessels into the microwave digester.

f) Digest the samples until no glass beads remain. Once the digestion is completed, carefully remove the vessels from the microwave and allow to cool.

g) Transfer total contents of microwave vessel to a labeled 10mL tube, rinse vessel thoroughly with deionised water and add to the tube. Make tube volume up to the 10mL mark with deionised water.

Note 5: Clean vessels between each digestion with 2mL nitric acid and 1mL hydrochloric acid, digested for an appropriate period.

A3.5.2 Analysis

a) Carry out an analysis of the digestion sample for lead, antimony, arsenic, mercury, cadmium and chromium using ICPMS or equivalent analytical techniques capable of measuring parts per million levels of the elements in question. Samples may require dilution in order to produce results of an appropriate order of magnitude.

A3.5.3 Reporting

a) Results shall be reported as the average of the duplicates and as ppm of each metal/g of glass beads.

b) The report shall include the details of the person who carried out the sampling and the sampling details.

A4 Method validation

a) For ICPMS methodology, method validation shall be demonstrated using certified reference materials.

b) For non-ICPMS methodology the testing authority shall establish and document a process that demonstrates method validity against ICPMS. This shall be submitted to APAS for prior approval. Frequency of this validation shall initially not be greater than 6 months.

c) Where three (3) consecutive equivalent validation results are obtained, the frequency of validation may be adjusted to annual checks.

APPENDIX B

MANUFACTURER CONTROLS

B1. Scope

a) This Appendix details the controls imposed on manufacturers of glass beads necessary to impart confidence in APAS certification of such products.

b) The process is necessary as APAS does not undertake assessments of capability of glass bead manufacturers in a similar manner to paint manufacturers.

B2. Principle

a) Confidence in bead quality and compliance with this specification can be achieved by the following methods;
   i). Local manufacturing plant conforming to the requirements of B3 below
   ii). Overseas manufacturing plant conforming to the requirements of B4 below

B3. Local (Australasian) bead manufacturers

a) The manufacturing plant shall be situated in either Australia or New Zealand.

b) The manufacturing plant shall operate under a quality management system externally assessed as complying with ISO 9001 by an authority accredited by JAS-ANZ for such assessments.

c) The manufacturing plant shall either operate its own or use an external laboratory accredited as complying with ISO 17025 by an authority accredited by JAS-ANZ for such assessments to verify compliance with requirements for the purposes of product certification.

d) The manufacturing plant shall comply with B6 below.

e) The bead manufacturer shall generate confidence in its technical controls by conducting random sampling and testing of its own production output. Rules for this sampling and testing are as follows;
   i). Random sampling and testing for general properties (shall be conducted on nominal 1 tonne lots as a minimum. Any variation to this nominal batch size shall be submitted with justification to APAS for prior approval.
   ii). Sampling shall be conducted in accordance with Appendix A of AS/NZS 2009. The sampling method shall be specified.
   iii). The proposed program of routine testing shall be submitted to APAS for prior approval
   iv). Records of test results shall be kept.

f) Reporting – at least once per calendar quarter a summary report of testing shall be issued to APAS by the testing agency.

g) The report shall be kept Commercial-in-Confidence by APAS and shall contain the
GLASS BEADS FOR USE IN PAVEMENT MARKING PAINTS

following information for each APAS certified glass bead type;
  i). The period covered by the data
  ii). Total production of each bead type over the reporting period
  iii). The total number of (1 tonne) lots tested during the period
  iv). The percentage of lots passed wholly within specification (Table 1 below)
  v). Full details of all tests that failed to meet specification or were concession passed where the lot was released anyway to the market.

d) Where a Does Not Conform result is verified eg by retesting, the importer or agent shall advise APAS of disposition action taken. Refer B6g) below.

B4. Overseas bead manufacturers

a) The manufacturing plant shall be situated in a country other than Australia or New Zealand and;
  i). Shall operate under a quality management system externally assessed as complying with ISO 9001 by an authority accredited by ILAC for such assessments, and
  ii). Shall either operate its own or use an external laboratory accredited to ISO 17025 by an authority accredited by ILAC for such assessments to verify compliance with requirements for the purposes of product certification.

b) Manufacturers complying with B4a) shall also comply with B6 below.

c) Manufacturers not complying with B4a) may delegate compliance responsibility to the local importer/agent in Australasia under B5 & B6 compliance requirements.

B5. Local importer of overseas manufactured beads

a) Local importers of overseas manufactured glass bead shall generate confidence in the technical properties of their imported product by having random sampling and testing conducted on received product. Rules for this sampling and testing are as follows;
  i). Random sampling and testing shall be conducted by a NATA accredited laboratory or an independent authority approved by APAS for the task. Refer Note 6 below.
  ii). Random sampling and testing shall be conducted on nominal 1 tonne shipment lots as a maximum for each bead type shipment received.
  iii). Sampling shall be conducted in accordance with Appendix A of AS/NZS 2009. The sampling method shall be specified.

b) The independent testing and reporting shall be carried out at the importer's or local agent's expense.

c) The report shall be kept Commercial-in-Confidence by APAS and contain the following information;
  i). The period covered by the data
  ii). The shipment quantity by bead type
  iii). The total number of (1 tonne) lots sampled and tested per bead type for the shipment
  iv). The percentage of lots passed wholly within specification (ie complying with B6a above)
  v). Full details of all tests that failed to meet technical requirements.

B6. Testing requirements

a) Mandatory testing parameters (as defined in AS/NZS 2009) to be tested for each lot sampled are;
   • Optical quality; including shape, surface crazing and air inclusions (5.3)
   • Size or gradation to specification (5.4)
   • Percentage rounds (5.5)
   • Water resistance or flow properties (5.7)
   • Adhesion coating (5.9)
   • Colour
   • Refractive index (0042/4 Type E beads only) (5.10)
   • Retroreflectivity testing for all HR nominated grades

b) Records of test results shall be kept.

c) Traceable retained samples of test samples shall be kept for a minimum period of 12 months.

de) Reporting – a summary report of testing on each lot tested shall be issued to APAS by the testing agency. The report shall comply with either B3g or B5c as appropriate.

e) Where one or more tests indicate a failure to comply with technical requirements, resampling and retesting shall be carried to verify or negate the original result/s.

f) Where a Does Not Conform result is verified, the manufacturer shall advise APAS of disposition action.

g) Disposition action may be one of the following;
   i). Concessional approval. Justification for such a decision shall be provided to APAS
   ii). Quarantining the shipment or part thereof until resolution with the manufacturer is achieved
   iii). Isolating distribution to non APAS linemarking markets
   iv). Dumping

Note 6: Acceptable sampling authorities are;

➢ SGS Australia Pty. Ltd.
  16/33 Maddox St Alexandria NSW 2015
  Dr David Stone
  T +61 2 8594 0451; E david.stone@sgs.com
APPENDIX C

MODIFIED RETROREFLECTIVITY TEST

C1. Scope
a) This Appendix details the method used to assess the retroreflectivity of 0042/1 Type B-HR glass beads. It is based on a modification of the AS2009 Appendix M method as developed by the Department of Planning, Transport and Infrastructure (SA).

C2. Modifications to the Procedure
a) In addition to Table 1 requirement below, 0042/1 Type B-HR beads shall also be tested to Appendix M of AS 2009 but with the following modifications:
   i). Section M4 Apparatus Clause a) Dry film thickness of paint will be 200 -250 µm
   ii). Section M5 Procedure Clause b) Weigh 24 ± 0.5 grams of beads
   iii). Section M5 Procedure Clause e) Wet Film thickness of paint will be 375 ± 25 µm

8. TABLE 1 – PERFORMANCE PROPERTIES

<table>
<thead>
<tr>
<th>TEST</th>
<th>AS/NZS 1580 METHOD</th>
<th>REQUIREMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 General requirements</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AS/NZS 2009</td>
<td>Various as nominated in the standard</td>
<td>Shall comply with all requirements. Where values are arrived at by the test method, these values shall be reported.</td>
</tr>
<tr>
<td>Retroreflectivity</td>
<td>Appendix C</td>
<td>0042/1 only. Minimum 450 mcd/m²/lx Where values are arrived at by the test method, these values shall be reported.</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>AS/NZS 2009 Appendix I</td>
<td>0042/4 only shall have a refractive index of not less than 1.9</td>
</tr>
<tr>
<td>8.2 Heavy metal requirements</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>Appendix A</td>
<td>Not greater than 50ppm each element</td>
</tr>
<tr>
<td>Antimony (Sb)</td>
<td>Appendix A</td>
<td>Not greater than 10ppm each entity. (If total Cr is &gt;10ppm specific testing for Cr⁶⁺ should be undertaken via colourimetry or other APAS approved method)</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>Appendix A</td>
<td>Not greater than 10ppm each entity. (If total Cr is &gt;10ppm specific testing for Cr⁶⁺ should be undertaken via colourimetry or other APAS approved method)</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>Appendix A</td>
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</tr>
<tr>
<td>Total Chromium</td>
<td>Appendix A</td>
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