GLASS BEADS FOR USE IN PAVEMENT MARKING PAINTS

1. SCOPE

a) This specification applies to glass beads used with pavement marking paints, to increase the retroreflectivity of pavement markings, thereby improving the safety performance of pavement markings.

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

c) APAS certification to this specification, shall only be claimed by APAS participating manufacturers and suppliers (listed in APAS Document AP-D152) that demonstrate conformance to the requirements documented in this specification, when assessed by the APAS.

2. BACKGROUND

a) APAS Document AP-D001 should be read to obtain a broad overview of how APAS operates.

b) APAS Document AP-D123 should be read to obtain an overview of restricted ingredients in APAS certified products.

c) APAS Document AP-D152 should be read to obtain the current list of APAS participating manufacturers and suppliers.

d) APAS Document AP-D177 should be read to obtain an overview of how to participate in APAS.

e) APAS Document AP-D192 should be read to obtain an overview of the APAS product certification system.

f) This specification originally came about at the request of some state road authorities; concerned about the level of heavy metal contamination in some glass beads and, the potential impact on the environment should heavy metals escape from the glass matrix to the environment.

3. DEFINITIONS & ACRONYMS

3.1 General terms

Campaign Run – a continuous production run of one type of glass beads.

Lot – a sub-sample of a Campaign Run, where the glass beads are made from known soda lime glass cullet feed stock at essentially the same time, by essentially the same processes and essentially under the same system of control, is defined as;

➢ 20 metric tonnes (maximum) for glass beads manufactured by Direct Melt process.

➢ 10 metric tonnes (maximum) for glass beads manufactured by non Direct Melt processes.

Heavy metals – elements as nominated in Table 1. For the purposes of this specification, “heavy metals” are antimony, arsenic, cadmium, hexavalent chromium (Cr(VI)), lead and mercury.

Retroreflectivity – a measure of the light visible to the driver compared to the light entering the pavement marking. Read Note 1 for further explanation.

Note 1: The popular definition of the night time visibility of a pavement marking is defined as its retroreflectivity; a measurement of the efficiency of the pavement 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 retro-reflected light is usually a function of the surface applied glass beads; which are a component part of the pavement marking.

3.2 Acronyms

APAS Australian Paint Approval Scheme
AS Australian Standard
AS/NZS Australian Standard/New Zealand Standard
CSIRO Commonwealth Scientific and Industrial Research Organisation
IAF International Accreditation Forum
ICPMS Inductively Coupled Plasma Mass Spectrometry
IEC International Electrotechnical Commission
ILAC International Laboratory Accreditation Cooperation
ISO International Organisation for Standardization
JAS-ANZ Joint Accreditation Society – Australia & New Zealand
mm millimetres
NATA National Association of Testing Authorities
XRF X-ray Fluorescence
µm micrometres

4. DESCRIPTION & GUIDE FOR USERS

4.1 General product description

a) Pavement marking materials require the addition of glass beads to provide increased retroreflectivity performance compared to the un-beaded marking. Glass beads are available in different types; specified in AS/NZS 2009.

b) Glass beads are normally applied, either hand-strewed or by an automatic drop on mechanism, onto the wet pavement marking immediately after the pavement marking has been applied.
GLASS BEADS FOR USE IN PAVEMENT MARKING PAINTS

4.2 Technical basis of specification

This specification is based on AS/NZS 2009 with the addition of heavy metals content restrictions as well as retroreflectivity testing and performance requirements for Type B-HR and Type C-HR glass beads.

4.3. Sub-classes

a) This specification is divided into the following subclasses as described in AS/NZS 2009;
   i). 0042/1 – Type B beads
   ii). 0042/2 – Type C beads
   iii). 0042/3 – Type D beads
   iv). 0042/4 – Type E beads

b) Type B, Type C and Type D beads may be available in two grades;
   i). Standard grade and,
   ii). HR or high retroreflectivity grade.

5. REFERENCED DOCUMENTS

This specification makes reference to the following documents;
- AP-D200 Application form for glass bead certification
- AS 1199 Sampling procedures for inspection by attributes.
- AS/NZS 1580 Paints and related materials – Methods of test
- AS/NZS 2009 Glass beads for pavement marking materials
- ISO 9001 Quality management systems - Requirements
- ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories

ISO, AS or AS/NZS documents and standards may be downloaded from various national standards bodies' websites. In Australia, these documents and standards may be sourced from the Standards Australia partner website https://www.techstreet.com

All APAS Documents may be downloaded from the APAS website at http://www.apas.gov.au

6. COMPOSITIONAL REQUIREMENTS

6.1 General

Type B, Type C and Type D glass beads shall be made from soda lime glass cullet conforming to reference 4 MATERIALS OF MANUFACTURE in AS/NZS 2009.

Type E glass beads have no specific composition requirements.

6.2 Heavy metal content

a) The heavy metals content in the glass beads shall not be greater than that specified in Table 1.
b) As the preferred test method for heavy metals is ICPMS (refer to Appendix A, clause A3), previous measures for Cadmium Oxide and Chrome 6+ have been changed to Cadmium and Total Chromium respectively, due to limitations of the ICPMS test method.
c) The use of the XRF method is allowable provided that the XRF method is validated against ICPMS or, a certified glass matrix reference standard is used for measurement validation. Refer to clause A4.

7. PRODUCT CERTIFICATION REQUIREMENTS

7.1 General

a) The application for product certification shall conform to the relevant requirements of APAS Document AP-D192.
b) APAS Document AP-D200 shall be supplied in lieu of APAS Document AP-D139.
c) Interim certification (once only) of glass beads shall be granted for a period of 12 months; having demonstrated conformance to all the requirements of this specification.
d) Full certification (renewable) of glass beads shall be granted for a period, having demonstrated on-going conformance to all the requirements of this specification;
   i) 12 months for organisations who have not finalised ISO/IEC 17025 accreditation or not ISO/IEC 17025 accredited for all glass beads test methods defined in clause B4 f).
   ii) 24 months for organisations who are ISO/IEC 17025 accredited for all glass beads test methods defined in clause B4 f).
b) Glass beads shall conform to the compositional requirements (clause 6) and applicable performance requirements (Table 1) of this specification throughout the certification period.
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7.2 Technical

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, but not the compositional limitations, then a request may be made to APAS for a variation. This variation request shall be treated Commercial-in-Confidence by APAS, who shall decide on the validity of the variation request. In making this decision, APAS officers may consult with industry experts.

7.3 Safety & environmental

The product Safety Data Sheet (SDS) 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 beads manufacturer or supplier encounters test failures, the quality assurance system (conforming to ISO 9001) shall describe the process for handling non-conforming results. This shall include re-testing, isolation, rework or disposal, as appropriate.
b) Records of non-conformities shall be kept.

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 conformance to this specification.
b) Sampling is a key aspect to ensure results are representative of deliveries and the method of sampling is defined in clause A2.

A2. Sampling

a) Sampling shall be carried out in accordance with Appendix A, Method 1 or Method 2 of AS/NZS 2009. The sampling method shall be stated.
b) Samples shall be taken at the time of manufacture or upon delivery of glass beads product, but prior to the glass beads product being applied onto pavement markings. Samples shall be taken for all APAS certified grades of glass beads.
c) Frequency of sampling shall be not less than once per Lot. Samples will be generated as representative composites of the Campaign Run.

A3. Testing via ICPMS

A3.1 General

a) Testing to the method detailed shall be carried out by a laboratory accredited to ISO/IEC 17025 with this method included in their Scope of Accreditation.
b) ISO/IEC 17025 accreditation shall be provided by an organisation accredited by an ILAC Mutual Recognition Arrangement signatory and having a scope of accreditation covering ISO/IEC 17025 requirements. In Australia, NATA provides ISO/IEC 17025 accreditation. A list of international ILAC accreditation bodies can be found on the ISO website.
c) Due to the specific nature of the test 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 provided that the laboratory is accredited to ISO/IEC 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 total 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 clause A4.

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 SDS 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 clause A4.

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. De-ionised water, 18M ohm-cm or better

A3.4 Apparatus

a) The following equipment is required:
b) Sample milling equipment, zirconium mill
c) Microwave digester
d) Teflon microwave vessels
e) 10mL polypropylene tubes with lids
GLASS BEADS FOR USE IN PAVEMENT MARKING PAINTS

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, 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 labelled 10mL tube, rinse vessel thoroughly with de-ionised water and add to the tube. Make tube volume up to the 10mL mark with de-ionised 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

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 per gram 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, where the testing authority is ISO/IEC 17025 accredited to conduct a non-ICPMS method, the testing authority shall establish and document a process that demonstrates method validity against ICPMS. The method shall be assessed by APAS for approval prior to the non-ICPMS methodology being implemented.

c) For non-ICPMS methodology, where the testing authority is not ISO/IEC 17025 accredited to conduct a non-ICPMS method, testing for heavy metals content of glass beads against ICPMS shall occur every 3 months.

APPENDIX B

MANUFACTURE & TESTING CONTROLS

B1. Scope

a) This Appendix details the controls imposed on glass beads manufacture and testing 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 beads manufacturers in a similar manner to paint manufacturers.

B2. Principle

a) Confidence in glass beads quality and conformance to this specification can be demonstrated by conforming to the requirements of clause B3.

B3. Requirements for the manufacture and testing of glass beads

a) A local glass beads manufacturer is defined as having its manufacturing plant located in Australia. The manufacturer may sell its glass beads direct to end-user customers or use a local distributor.

b) An overseas glass beads manufacturer is defined as having its manufacturing plant located outside of Australia. The manufacturer may sell its glass beads direct to end-user customers, to pavement marking suppliers or, use a local distributor.

c) Manufacturers, pavement marking suppliers and local distributors shall operate under a quality management system, externally assessed as conforming to ISO 9001, by an entity accredited to do so by a member of the IAF. JAS-ANZ is the IAF member for Australia and New Zealand.
GLASS BEADS FOR USE IN PAVEMENT MARKING PAINTS

d) Manufacturers shall operate their own or use an external test laboratory to verify product conformity. Tests results shall be provided by a laboratory that fulfils ISO/IEC 17025, and its accredited for the relevant scope of testing by an accreditation body that fulfils the requirements of AS ISO/IEC 17011 and is a signatory of the ILAC MRA.

e) Manufacturers shall demonstrate confidence in their technical controls by conducting random sampling and testing of their production output as follows:
  
i) Sampling, which shall be conducted at least once per Lot, shall be in accordance with Appendix A, Method 1 or Method 2 of AS/NZS 2009 or, any alternative method which maintains the intent of, and when tested, is shown to be equivalent to AS/NZS 2009. If an alternative method is used, it is the responsibility of the manufacturer to demonstrate that any alternative method is equivalent to, or exceeds, the requirements of AS/NZS 2009. Any alternative sampling method shall be submitted to and assessed by APAS for approval prior to the sampling method being implemented. The sampling method shall be specified.
  
ii) Testing, which shall be conducted at least once per lot, shall be in accordance to clause B3 f). Testing shall be carried out by an authority agreed to by APAS.

f) Pavement marking suppliers and local distributors, who shall source glass beads only from manufacturers who conform to clause B3 d), shall either have the glass beads manufacturer undertake sampling and testing of glass beads or conduct its own sampling and testing. Sampling shall occur in accordance to clause B3 e). Testing shall occur in accordance to clause B3 g).

g) Mandatory tests (AS/NZS 2009 reference is noted in brackets) to be conducted for every Lot of glass beads sampled are:
  - Foreign matter (5.2)
  - Optical quality (5.3)
  - Size (5.4)
  - Shape (5.5)
  - Colour (5.6)
  - Water resistance (5.7)
  - Flow properties (5.8) – whenever a moisture proof coating is claimed to be present.
  - Adhesion coating (5.9) – whenever an adhesion coating is claimed to be present.
  - Refractive index (5.10)
  - Heavy metals (5.11); refer to clause 6.2 and clause A4.
  - Retroreflectivity (Appendix M) - for all HR grades of glass beads; refer to Table 1.

h) Records of all test results shall be kept for every Lot of glass beads tested. Numerical values shall be reported where the conclusion of a test method produces a numerical result.

i) Records of test results shall be made available to APAS officers for certification/re-certification applications to this specification or upon request to do so by the APAS.

j) Traceable retained samples of test samples, of sufficient quantity to re-do all tests specified in clause B3 f), shall be kept for a minimum period of 24 months.

APPENDIX C
MODIFIED RETROREFLECTIVITY TEST

C1. Scope

a) This Appendix details the method used to assess the retroreflectivity of Type B-HR and Type C-HR glass beads (assessment of Type D-HR beads is referenced in AS/NZS 2009 Appendix M). It is based on a modification of the AS/NZS 2009 Appendix M method as developed by the South Australian Department of Planning, Transport and Infrastructure.

C2. Modifications to the Procedure

a) In addition to the requirements of Table 1 of this specification, Type B-HR beads (sub-class 0042/1) shall also be tested to Appendix M of AS/NZS 2009 with the following modifications:
   
i) M4 APPARATUS (a) The draw down paint applicator shall be capable of casting a 100 mm wide application of 200 - 250 µm dry film thickness of paint.
   
ii) M4 APPARATUS (h) Reference paint material - GTL-104-14B shall be replaced with a white water-borne pavement marking paint conforming to the testing and performance requirements listed under reference 6.1 Laboratory testing of AS 4049.3 with the following modifications; reference 6.1.4 Application properties is excluded, reference 6.1.8 Specular gloss shall not exceed 5 gloss units and, reference 6.1.9 Luminance factor shall be 88.5% +/- 2.5%.
   
iii) M5 PROCEDURE (b) Weigh 24 ± 0.5 grams of Type B-HR beads. Record the mass of beads.
   
iv) M5 PROCEDURE (e) Set the blade of the draw down applicator to apply the paint so that a uniform dry film thickness of 200 - 250 µm is achieved.
   
vi) M5 PROCEDURE (f) The required dry film thickness shall be 200 - 250 µm over a minimum length of 600 mm on the test panel.

b) In addition to the requirements of Table 1 of this specification, Type C-HR beads (sub-class 0042/2) shall
GLASS BEADS FOR USE IN PAVEMENT MARKING PAINTS

also be tested to Appendix M of AS/NZS 2009 with the following modifications;

i). M4 APPARATUS (a) The draw down paint applicator shall be capable of casting a 100 mm wide application of 200 - 250 µm dry film thickness of paint.

ii). M4 APPARATUS (h) Reference paint material - GTL-104-14B shall be replaced with a white water-borne pavement marking paint conforming to the testing and performance requirements listed under reference 6.1 Laboratory testing of AS 4049.3 with the following modifications; reference 6.1.4 Application properties is excluded, reference 6.1.8 Specular gloss shall not exceed 5 gloss units and, reference 6.1.9 Luminance factor shall be 88.5% +/- 2.5%.

iii). M5 Procedure (b) Weigh 27 ± 0.5 grams of Type C-HR beads. Record the mass of beads.

iv). M5 PROCEDURE (e) Set the blade of the draw down applicator to apply the paint so that a uniform dry film thickness of 200 - 250 µm is achieved.

v). M5 PROCEDURE (f) The required dry film thickness shall be 200 - 250 µm over a minimum length of 600 mm on the test panels.

c) In addition to the requirements of Table 1 of this specification, Type D-HR beads (sub-class 0042/3) shall be tested as per Appendix M of AS/NZS 2009 with the following modification;

i) M4 APPARATUS (h) Reference paint material - GTL-104-14B shall be replaced with a white water-borne pavement marking paint conforming to the testing and performance requirements listed under reference 6.1 Laboratory testing of AS 4049.3 with the following modifications; reference 6.1.4 Application properties is excluded, reference 6.1.8 Specular gloss shall not exceed 5 gloss units and, reference 6.1.9 Luminance factor shall be 88.5% +/- 2.5%.

Note 6: At the time of writing this specification, no data was available to document a procedure allowing for retroreflectivity testing of HR grade glass beads using a white thermoplastic material in lieu of a white water-borne pavement marking paint.

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### 8. TABLE 1 – TESTING AND PERFORMANCE REQUIREMENTS

<table>
<thead>
<tr>
<th>TEST</th>
<th>METHOD</th>
<th>REQUIREMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 General requirements</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PROPERTIES stated at references 5.2 to 5.11 inclusive of AS/NZS 2009</td>
<td>AS/NZS 2009 references 5.2 to 5.11 inclusive</td>
<td>All PROPERTIES shall conform to their stated requirements.</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>AS/NZS 2009, Appendix I</td>
<td>Type E beads shall have a refractive index of not less than 1.9</td>
</tr>
<tr>
<td>Retroreflectivity</td>
<td>AP-S0042, Appendix C</td>
<td>Type B-HR &amp; Type C-HR beads shall have a minimum retroreflectivity of 450 mcd/lux/m² Type D-HR beads are documented at Appendix M of AS/NZS 2009</td>
</tr>
<tr>
<td>8.2 Heavy metal requirements</td>
<td></td>
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</tr>
<tr>
<td>Antimony (Sb)</td>
<td>AP-S0042, Appendix A</td>
<td>Not greater than 50ppm for each element.</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td></td>
<td></td>
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<tr>
<td>Lead (Pb)</td>
<td></td>
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<tr>
<td>Cadmium (Cd)</td>
<td>AP-S0042, Appendix A</td>
<td>Not greater than 10ppm for each element.</td>
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<tr>
<td>Mercury (Hg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromium (Cr₆⁺)</td>
<td></td>
<td>If Total Chromium is greater than 10ppm, specific testing for hexavalent Chromium Cr₆⁺ should be undertaken via colorimetric method or other test method agreed to by APAS.</td>
</tr>
</tbody>
</table>