Texas Commission on Environmental Quality Response to Public Comments Received on the January 25, 2011 Proposed Amorphous Silica Development Support Document

The public comment period for the January 2011 Proposed Development Support Document (DSD) for silica, amorphous and other non-crystalline forms (amorphous silica) ended in April 2011. The Synthetic Amorphous Silica and Silicate Industry Association ("SASSI") submitted comments on April 29, 2011. The Toxicology Division (TD) of the Texas Commission on Environmental Quality (TCEQ) appreciates the effort put forth by SASSI to provide technical comments on the proposed DSD for amorphous silica. The goal of the TCEQ is to protect human health and welfare based on the most scientifically-defensible approaches possible (as documented in the DSD), and evaluation of these comments furthered that goal. A summary of comments from each organization is provided below, followed by TCEQ responses. The full comments are provided in Appendices A. Comments on issues that suggest changes in the DSD are addressed whereas comments agreeing with TCEQ's approach are not. TCEQ responses indicate what changes, if any, were made to the DSD in response to the comment.

Comments from the Synthetic Amorphous Silica and Silicate Industry Association (SASSI)

A. Executive Summary

Comment:

In its Executive Summary, SASSI stated that, unlike crystalline silica, synthetic amorphous silica (SAS) is a GRAS and widely used in commerce without adverse health effects. SASSA believes that the real target of TCEQ review is crystalline silica. It further stated that the naturally occurring forms of amorphous silica such as diatomaceous earth, in calcined and uncalcined forms, have different physical, chemical and toxicological profiles than SAS.

TCEQ Response:

The DSD was not revised based on this comment. The TD does appreciate ACC's comments. While the TD acknowledges that the naturally occurring forms of amorphous silica have different physical, chemical and toxicological profiles than SAS, there are no relevant toxicity data available for naturally occurring forms of amorphous. Thus, the acute and chronic ReVs and ESLs developed for SAS are used for all forms of amorphous and non-crystalline silica. The TD, however, may develop separate toxicity factors for non-SAS forms of amorphous silica if available studies for non-SAS forms become available.

B. List of Recommendations

Comment No. 1 (DSD Cover Page):

SASSI indicated that since the detection limits for crystalline silica have improved, the proposed DSD for amorphous silica uses a limit of containing < 1% crystalline silica may not be appropriate. SASSI recommended that a limit of 0.1 % instead of 1% be used because crystalline

is a carcinogen. It further stated that the limit of 0.1% would match the OSHA reportable concentration limits for carcinogens.

TCEQ Response:

The purpose of a limit containing < 1% crystalline silica is to minimize potential effects which may cause by crystalline silica contained in naturally occurring forms of amorphous silica. While the TD acknowledges that the limit of 0.1% would match the OSHA reportable concentration limits for carcinogens, the limit, however, is not relevant to the detection limits for crystalline silica contained in amorphous silica. As indicated in the 2009 DSD for crystalline forms of silica, the acute and chronic toxicity values developed for amorphous silica are 2 and 7 times, respectively, higher than those for crystalline silica, the limit of "containing < 1% crystalline" for the characterization of amorphous silica has been removed. Since SAS does not contain measurable levels of crystalline silica (e.g., < 0.01%) and since naturally occurring forms of amorphous silica usually contains up to 8 % of crystalline silica, the proposed toxicity values are expected to be protective for amorphous silica containing crystalline silica. The proposed DSD for amorphous silica was developed for all forms of amorphous and non-crystalline silica. However, if amorphous silica contains high percentage of crystalline (e.g., > 14 %), the toxicity values for crystalline silica must also be met.

Comment No. 2 (CAS Registry Numbers):

SASSI indicated that CAS No. 7631-86-9 (synthetic amorphous silica) is missing from the list of amorphous silica in the proposed DSD.

TCEQ Response:

The CAS No. 7631-86-9 (synthetic amorphous silica) has been added to the DSD accordingly.

Comment No. 3:

SASSI indicated that natural forms of amorphous silica may contain impurities, particularly crystalline silica. It is essential to distinguish carefully between crystalline silica and non-crystalline or amorphous silica forms.

TCEQ Response:

As described in Chapter 2 of the proposed DSD, naturally occurring forms of amorphous silica such as uncalcined diatomaceous earth usually contains certain amounts of crystalline silica, sometimes up to 8 %. Certain industrial processes such as manufacture of elemental silicon and silicon alloys produce silica fume and fused silica as by-products may contain impurities, particularly crystalline silica. The TD agrees with SASSI that it is essential to distinguish between crystalline silica and amorphous silica. The TD has developed ReVs and ESLs for crystalline forms of silica in a separate DSD in 2009.

Comment No. 4:

SASSI indicated that according to European EINECS, SAS includes pyrogenic, precipitated and gel forms, while silica fume is assigned to a separate form of amorphous silica.

TCEQ Response:

The TD agrees with SASSI's comment and has revised the DSD by stating that amorphous silica includes SAS, and non-SAS forms of amorphous silica such as diatomaceous earth, and fumed and fused silica.

Comment No. 5 (Page 3: Table 3: CAS Numbers):

SASSI commented that it is inappropriate to list SAS with other forms of amorphous silica. The physical-chemical properties, toxicology and ecotoxicology could be significantly different between an SAS and other forms of silica.

TCEQ Response:

The TD agrees with SASSI's comment and has revised the Table 3 of the DSD accordingly.

Comment No. 6 (Page 3: Table 3: Log K_{ow}):

SASSI suggested that the TD reference ECETOC JACC No.51, 2006 Report for missing data on the dissolution kinetics (Log K_{ow}) of SAS.

TCEQ Response:

After reviewing the ECETOC (2006) report, the TD was unable to locate such data. Thus, the DSD was not revised based on this comment.

Comment No. 7 (Page 4: Line 8):

SASSI indicated that industrial by-products of amorphous silica include fused silica and silica fume. However, neither fused silica or silica fume are of commercial relevance.

TCEQ Response:

The TD acknowledges SASSI's comments. The aforementioned comments have been described in Chapter 2 Major Sources or Uses.

Comment No. 8 (Page 4: Line 9 and 10):

SASSI indicated that there seems to be confusion between fused silica, silica fume and amorphous fumed (pyrogenic) silica in regards to major sources and uses.

TCEQ Response:

The TD appreciates SASSI's comments. The aforementioned comments have been clarified in Chapter 2 Major Sources or Uses.

Comment No. 9 (Chapter 3: Acute Evaluation):

SASSI indicated that a reference to ECETOC JACC No. 51 Report is missing and should be cited.

TCEQ Response:

The TD appreciates SASSI's comments. The reference (ECETOC 2006) has been reviewed and cited in Chapter 3.

Comment No. 10 (Chapter 3: Line 28):

SASSI commented that there is no scientific justification for applying toxicity factors which are developed for crystalline silica to amorphous silica containing crystalline silica greater than 1%.

TCEQ Response:

The TD agrees with SASSI's comments. Please see Response to Comment No. 2.

Comment No. 11 (Page 5: Line 2):

SASSI commented that the scientific rationale for using the same toxicity factors for all forms of non-crystalline silica with a < 1 wt% crystalline level should be explained. SASSI further commented that the use of a common toxicity factor for SAS is justified but not for the other (non-SAS) forms of amorphous silica.

TCEQ Response:

The TD appreciates SASSI's comments. As indicated in the Response to Comment No. 2 and 10, the proposed DSD for amorphous silica will be used for all forms of amorphous silica. The limit of "containing < 1% crystalline silica" has been deleted.

Comment No. 12 (Page 5: Line 31):

SASSI further commented that the use of a common toxicity factor for SAS is justified but not for the other (non-SAS) forms of amorphous silica.

TCEQ Response:

As indicated in Section 3.1 and 4.1.2 of the proposed DSD, because no studies of non-SAS amorphous silica were available, the developed acute and chronic ReVs and ESLs for SAS will be used for all forms of amorphous and non-crystalline silica. The TD, however, may develop separate chronic toxicity factors for non-SAS forms of amorphous silica if available studies for non-SAS forms become available.

Comment No. 13 (Page 7: Line 26):

SASSI indicated that the DSD should identify Zeofree 80 as being precipitated silica.

TCEQ Response:

Precipitated silica has been added after Zeofree 80 accordingly.

Comment No. 14 (Page 10: Section 3.1.3):

SASSI indicated that Aerosil 200 is pyrogenic silica, Aerosil R974 is a surface treated (hydrophobic) pyrogenic silica, and Sipernat 22S is precipitated silica.

TCEQ Response:

The DSD has been revised accordingly (see Section 3.1.2.3).

Comment No. 15 (Page 10: Line 8):

SASSI indicated that Aerosil 200 is pyrogenic silica, Aerosil R974 is a surface treated (hydrophobic) pyrogenic silica, and Sipernat 22S is precipitated silica.

TCEQ Response:

The DSD has been revised accordingly (see Section 3.1.2.3).

Comment No. 16 (Page 11: Section 3.1.6.2 Default Dosimetry Adjustments from Animal-to-Human Exposure):

SASSI commented that SAS is a nanostructure material consisting of primary particles < 100 nm. These primary particles do not exist in isolated, unbound form but form during the production process aggregates and agglomerates of sizes well above 100 nm. At working places only small fractions of the SAS particle size distribution is respirable. It further commented that the real particle size of SAS must be considered when develops toxicity values.

TCEQ Response:

The DSD was not revised based on this comment. The TD does appreciate ACC's comments. Since amorphous silica is a solid granule and the key studies used to develop acute ReV and ESL were conducted in rats, the deposition fraction of silica in the target respiratory region was modeled. The MMAD of Zeofree 80 amorphous silica used in the Warheit et al. (1995) study ranged from 2.4-3.4 μm. The MMAD and other parameters were then used in the MPDD model to calculate a Regional Deposition Dose Ratio (RDDR). The calculated RDDR was then used to dosimetrically adjust from an animal POD identified from the key study to human POD (see Section 3.1.6.2 for details). Thus, the TD did consider the real particle size of silica used in the key study when develops toxicity values. The toxicity factors developed in this proposed DSD will apply to all non-crystalline silica particles less than or equal to the median cut point for the thoracic region of 10 μm (PM_{10}), i.e., 50% thoracic particulate matter (TPM) fraction collected. The TPM fraction consists of those particles that are hazardous when deposited anywhere within the lung airways and the gas-exchange region (see Section 3.1.1 and 4.1.1).

Comment No. 17 (Page 13: Section 3.1.7.2 Uncertainty Factors):

SASSI commented that the assessment factors from ECETOC TR 110 - Guidance on Assessment Factors to Derive a DNEL, October 2010, would be appropriate to use in the MOA evaluation. SASSI commented that as stated in its Guidance on Assessment Factors to Derive a DNEL (ECETOC TR 110, 2010), no additional interspecies extrapolation (UF_A) is needed due to the higher respiratory rate of rodents that leads to a greater respiratory tract burden. SASSI commented that a UF_A of 1 instead of 3 would be appropriate to use in the MOA evaluation.

TCEQ Response:

The TD appreciates ACC's comments. While ECETOC (2010) indicates that no additional UF_A is needed due to the higher respiratory rate of rodents that leads to a greater respiratory tract burden, since default dosimetric adjustments using the RDDR were conducted to account for toxicokinetic differences but not toxicodynamic differences, a UF_A of 3 is conservatively applied. Therefore, the DSD was not revised based on this comment.

Comment No. 18 (Section 4.2 Carcinogenic Potential):

SASSI commented that based on the ECETOC JACC No.51, 2006 report, SAS are not mutagenic. There is no indication of any carcinogenic effects of SAS by inhalation exposure.

TCEQ Response:

The TD agrees with SASSI that SAS are not mutagenic and there is no indication of any carcinogenic effects of SAS in animal inhalation studies and very little epidemiological evidence in workers employed in the manufacture of SAS. The TD has added the reference of the ECETOC JACC No.51, 2006 report (ECETOC 2006) to Section 4.2 of the DSD accordingly.

APPENDIX 1

Synthetic Amorphous Silica and Silicate Industry Association (SASSI)

Comments Regarding the TCEQ Development Support Document for Amorphous Silica

April 29, 2011

Comments from the

Synthetic Amorphous Silica and Silicate Industry Association
To
Texas Commission on Environmental Quality

The Synthetic Amorphous Silica and Silicate Industry Association (SASSI) is a nonprofit organization incorporated in the District of Columbia as a 501(c)(6) entity on July 18, 2007 by eight founding members. Key tenets of SASSI's mission focus on furthering the scientific based knowledge and understanding of synthetic amorphous silica and silicate health and safety data within the industry, monitoring the regulation of synthetic amorphous silica and silicate by government, educating the public and government on the views of the industry, and consulting and cooperating with officials and agencies on matters having an industry-wide significance.

Consistent with our mission, the members of SASSI would like to take this opportunity to submit comments on the TCEQ Development Support Document (Proposed, January 25, 2011) "Silica, Amorphous and Other Non-Crystalline Forms (Containing < 1% Crystalline Silica) CAS Registry Numbers: 60676-86-0 (fused), 69012-64-2 (silica fume), 61790-53-2 (uncalcined diatomaceous earth), 112945-52-5 (Fumed synthetic amorphous silica or pyrogenic colloidal silica), 112926-00-8 (precipitated silica and silica gel).

A. Executive Summary: Historically we have encountered frequent confusion over the differentiation of synthetic amorphous silica products, which have very low toxicity profiles, and crystalline silica, which we believe is the real target of your review even though it is stated that it is not. Synthetic amorphous silicas are GRAS and have wide use in food, pharmaceutical, and consumer products as opposed to crystalline silicas which can cause serious lung injury. The chemical formulas for the two types of substances are identical, but the structure of amorphous silicas allows them to be widely used in commerce without adverse health effects, unlike the crystalline forms. Also, the naturally occurring forms of amorphous silica such as diatomaceous earth, in calcined and uncalcined forms, have different physical, chemical and toxicological profiles than synthetic amorphous silicas.

B. List of Recommendations:

1. Development Support Document Cover Page:
   (Containing <1% Crystalline Silica): Since the detection limits for crystalline silica have improved, it may be more appropriate to use 0.1% as the limit instead of 1%, since crystalline silica is a carcinogen a limit of 0.1% would match the OSHA reportable concentration limits for carcinogens.
2. CAS Registry Numbers: There is a generic CAS number for Silica - SiO2 (including both non-crystalline and crystalline forms), CAS No. 7631-86-9 which is missing from the list.
3. Attention to Differentiating Polymorphs: As the polymorphs of silica differ in their hazards to human health, it is essential to distinguish carefully between crystalline silica and non-crystalline or amorphous silica forms. Natural forms of amorphous silica like diatomaceous earth, especially flux-calcined diatomaceous earth, and amorphous silica fume (a by-product of silicon (Si) metal and ferrosilicon alloy manufacturing) may contain impurities, particularly crystalline silica. Any "Read-across" comparison between different amorphous forms such as diatomaceous earths, precipitated silicas and pryogenic silicas would need to be validated.
4. In reference to European EINECS, the definition of Synthetic Amorphous Silica includes pyrogenic, precipitated and gel forms: under EINECS No. 231-545-4, while silica fume is assigned to a separate EINECS No. 273-761-1.
5. Page 3: Table 3: CAS Registry Numbers: It is inappropriate to list Synthetic Amorphous Silicas (SAS) with other amorphous forms including naturally occurring and calcined materials. The physical-chemical properties, toxicology and ecotoxicology could be significantly different between an SAS and other forms of silica.
6. Page 3: Table 3: Log Kow: For missing data on the dissolution kinetics of SAS, please reference ECETOC JACC No.51, 2006. original literature citation. F.Roelofs, W.Vogelsberger. 2004 J. Phys. Chem. 8, 2004, 108 (31), pp 11308-11316, etc.
7. Page 4: Line 8: Industrial by-products of amorphous silica include fused silica and silica fume. Neither fused silica or silica fume are of commercial relevance.
8. Page 4: Lines 9 and 10: There seems to be confusion between fused silica, silica fume and amorphous fumed (pyrogenic) silica in regards to major sources and uses.
9. Chapter 3: Acute Evaluation: A reference to ECETOC JACC No. 51 is missing and should be cited.
10. Chapter 3: Line 28: The scientific justification for the > 1 wt% is missing. The current detection limit for crystalline is at least 0.3 wt%.
11. Page 5: Line 2: The scientific rationale for using the same toxicity factors for all forms of non-crystalline silica with a < 1 wt% crystalline level should be explained; the use of a common toxicity factor for SAS is justified but not for the other (non-SAS) forms of amorphous silica.

12. Page 5: Line 31: The document should identify Zeofree 80 as being a precipitated silica.
13. Page 7: Line 26: Aerosil 200 is pyrogenic silica, Aerosil R974 is a surface treated (hydrophobic) pyrogenic silica, and Sipernat 22S is a precipitated silica.
14. Page 10: Section 3.1.3: Mode of Action Analysis: All the studies referenced in Chapter 3 are based on SAS; there is no relevant data given for silica fume, fused silica, or diatomaceous earth.
15. Page 10: Line 8: The clearance of SAS from the lungs by dissolution should be considered. Please refer to the JACC No 51 report and an article by W.Koch, W. Stöber. 2001, Inhalation Toxicology, 13: 129-148. A simple pulmonary retention model accounting for dissolution and macrophage-mediated removal of deposited polydisperse particles
16. Page 11: Section 3.1.6.2: Default Dosimetry Adjustments from Animal-to-Human Exposure: The real particle size of SAS must be considered. According to ISO TC 229 (TS 80004-2 and DTS 80004-4) SAS is a nanostructured material. I.e. a material consisting of primary particles < 100 nm. These primary particles do not exist in isolated, unbound form but form during the production process aggregates and agglomerates of sizes well above 100 nm. At working places only small fractions of the SAS particle size distribution is respirable. This fraction is responsible for effects seen in animal tests. It has to be noted that according to OECD Guideline requirements of Animal Inhalation tests, the respirable fraction is enriched by artificially destroying the coarse particle fractions. High shearing forces are necessary to break up SAS particle aggregates and agglomerates to create respirable or smaller sized particles. Therefore, for example in Germany, an OEL related to inhalable dust is defined, and here in the US NIOSH has also proposed a separate REL (Recommended Exposure Limit) for respirable forms of amorphous silica.
17. Page 13: Section 3.1.7.2 Uncertainty Factors: The assessment factors from ECETOC TR 110 - Guidance on Assessment Factors to Derive a DNEL, October 2010, would be appropriate to use in the MOA evaluation.
18. Page 24: Section 4.2 Carcinogenic Potential: Based on the ECETOC JACC No.51, 2006 report, SAS are not mutagenic. There is no indication of any carcinogenic effects of SAS by inhalation exposure (literature).

We appreciate your consideration of our comments and concerns. We are open to meeting with you and discussing any opportunity to assist TCEQ in completing a comprehensive and accurate review of synthetic amorphous silicas. Please contact me to determine how we can support your efforts.

Sincerely yours,

David A. Pavlich

Association Manager
Synthetic Amorphous Silica and Silicate Industry

SASSI Member Companies:

- J.M. Huber Corporation
- Evonik Degussa Corporation
- Wacker Chemical Corp.
- Cabot Corporation
- Rhodia Inc.
- PPG Industries, Inc.
- PQ Corp.
- W.R. Grace & Co.

SASSI Website: www.sassiassociation.org