Australian Government

National Measurement Institute

Opinion concerning "mesoporous zinc oxide powder" described in United States Patent US 2010/0310871 A1

Nanometrology Section
Bradfield Road, West Lindfield NSW 2070
nano@measurement.gov.au

measurement.gov.au

For:	Friends of the Earth Australia
	Dr Gregory Crocetti
	312 Smith Street
	COLLINGWOOD VIC 3066
	gregory.crocetti@foe.org.au
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For further information contact: Dr Jan Herrmann, (02) 8467 3784

This report is wholly the work of the National Measurement Institute.
In generating this report there was no consultation with NICNAS, ISO
or any Patent offices (including USPTO, IPA and WIPO).

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1. Introduction

This report provides an opinion on whether or not the "mesoporous zinc oxide powder" described in the United States Patent US 2010/0310871 A1 ("the Patent") is

(1) a nanomaterial as defined by the International Organization for Standardization (ISO) and

(2) an industrial nanomaterial as defined in the Australian Government National Industrial Chemicals Notification and Assessment Scheme (NICNAS) document "Guidance on New Chemical Requirements for Notification of Industrial Nanomaterials".

The opinion provided is based on document review only. The mesoporous zinc oxide powder described in the Patent was not physically examined or measured by the National Measurement Institute.

2. Patent US 2010/0310871 A1

Note that the numbers in brackets after quotations refer to the Patent section numbers.

The Patent, titled "Mesoporous Zinc Oxide Powder and Method for Production Thereof", describes a *"powder consisting of mesoporous zinc oxide aggregates and a method of manufacturing the same, for use in visibly-transparent compositions that provide broad-spectrum photoprotection when applied to a substrate."* (0002)

The Patent states that *"... zinc oxide (ZnO) blocks ultraviolet (UV) radiation at wavelengths from 290 nm up to about 375 nm"* and that the *"...use of zinc oxide has been limited primarily due to an undesirable whitening effect on the substrate to which a zinc oxide-containing product was applied."* (0003)

The whitening on a substrate, such as the skin, after the application of a product containing dispersed ZnO powder is attributed in the Patent to the scattering of light from the ZnO particles in a backwards direction. The Patent states that two important factors that influence this scattering, and hence the whitening, are the ZnO particle size and the refractive index of the particles relative to the matrix in which the particles are dispersed.

The Patent states that increasing the transparency and reducing the whitening to the desired levels by reducing the ZnO particle sizes typically requires reducing the particle sizes to the nanoscale, namely less than about 100 nm. The Patent states that this is not desirable for various reasons and that there is a need for *"... transparency to be achieved using a dispersion of zinc oxide powders that are not predominantly comprised of nano-sized*

particles." (0011). The Patent describes a mesoporous zinc oxide powder, and methods for its production, that reduces light scattering and hence increases transparency by reducing the difference in the refractive index across the particle-matrix interface.

The mesoporous zinc oxide powder described in the Patent consists of "*discrete unattached aggregates*" (0043) of strongly bonded "*primary zinc oxide crystallites*" (0042). The average size of the primary zinc oxide crystallites ranges from 5 nm to about 50 nm (0054), while the average aggregate sizes range from 0.1 to 100 μm, with 0.2 to 10 μm being preferable (0052). Each aggregate is highly porous with pores that range in size from about 2 nm to about 100 nm (0048). These pores are classified as "open pores" that connect through and open onto a surface of the aggregate or "closed pores" that are sealed from fluid ingress from the aggregate surface.

The Patent states that the refractive index of each aggregate particle is equal to the volume-weighted average of the refractive index of the air-filled closed pores, the liquid-filled open pores, and the ZnO crystallites when the mesoporous powder is dispersed in a liquid carrier (0058). Increasing the volume of the open mesopores reduces the difference between the refractive indices of the aggregate and of the carrier phase of the dispersion. This reduction decreases the light scattering, resulting in a decrease in whiteness and an increase in transparency of the dispersion.

3. ISO definitions of a nanomaterial

Current ISO definitions of a nanomaterial and related terms are contained in the following published documents;

1. ISO Technical Specification 80004-1:2010 "Nanotechnologies — Vocabulary — Part 1: Core terms", hereafter referred to as "ISO 80004-1".

Note that in general a technical specification is a normative document representing the technical consensus within an ISO committee, in this case ISO Technical Committee 229 – Nanotechnologies.

2. ISO Technical Specification 27687:2008 "Nanotechnologies — Terminology and definitions for nano-objects — Nanoparticle, nanofibre and nanoplate" hereafter referred to as "ISO 27687".

3. ISO Technical Specification 80004-4:2011 "Nanotechnologies — Vocabulary — Part 4: Nanostructured materials" hereafter referred to as "ISO 80004-4".

The following relevant terms and definitions are taken from the documents above. The numbering is identical to the original documents.

3.1 ISO 80004-1

2.1

nanoscale

size range from approximately 1 nm to 100 nm

2.4

nanomaterial

material with any external dimension in the nanoscale (2.1) or having internal structure or surface structure in the nanoscale

NOTE 1 This generic term is inclusive of nano-object (2.5) and nanostructured material (2.7).

NOTE 2 See also engineered nanomaterial (2.8), manufactured nanomaterial (2.9) and incidental nanomaterial (2.10).

2.5

nano-object

material with one, two or three external dimensions in the nanoscale (2.1)

2.6

nanostructure

composition of inter-related constituent parts, in which one or more of those parts is a nanoscale (2.1) region

NOTE A region is defined by a boundary representing a discontinuity in properties.

2.7

nanostructured material

material having internal nanostructure (2.6) or surface nanostructure

NOTE This definition does not exclude the possibility for a nano-object (2.5) to have internal structure or surface structure. If external dimension(s) are in the nanoscale, the term nano-object is recommended.

3.2 ISO 27687

3.1

particle

minute piece of matter with defined physical boundaries

NOTE 1 A physical boundary can also be described as an interface.

NOTE 2 A particle can move as a unit.

NOTE 3 This general particle definition applies to nano-objects.

3.3

aggregate

particle comprising strongly bonded or fused particles where the resulting external surface area may be significantly smaller than the sum of calculated surface areas of the individual components

NOTE 1 The forces holding an aggregate together are strong forces, for example covalent bonds, or those resulting from sintering or complex physical entanglement.

NOTE 2 Aggregates are also termed secondary particles and the original source particles are termed primary particles.

4.1

nanoparticle

nano-object with all three external dimensions at the nanoscale

3.3 ISO 80004-4

The Introduction to ISO 80004-4 states that;

"A material should not be classified as nanostructured based solely on its crystalline properties (three-dimensional arrangements of atoms or molecules forming a crystallite, short range order of atoms in amorphous or quasi-amorphous phases, grain boundaries, intragranular interfaces, dislocations, etc.). In contrast, materials with a grain size distribution having a significant fraction of grains in the nanoscale (nanocrystalline), voids and pores in the nanoscale, or precipitations in the nanoscale (i.e. nano-objects in a solid matrix) are sufficient features for materials to be classified as "nanostructured" (see ISO/TS 80004-1:2010, 2.4, nanomaterial)."

2.13

nanopore

cavity with at least one dimension in the nanoscale (2.1), which may contain a gas or liquid

NOTE 1 The shape and content of the cavity can vary. The concept of nanopore overlaps with micropore (pore with width of about 2 nm or less), mesopore (pore with width between approximately 2 nm and 50 nm), and macropore (pore with width greater than about 50 nm). See ISO 15901-3:2007.

NOTE 2 When nanopores are appropriately interconnected they may allow for transport through the material (permeability).

3.1

nanostructured powder

powder comprising nanostructured agglomerates (3.1.2), or nanostructured aggregates (3.1.1), or other particles of nanostructured material (2.11)

NOTE The term "powder" is used in the sense of an assembly of discrete particles, usually less than 1 mm in size (see ISO 3252:1999, definition 1001).

3.1.1

nanostructured aggregate

aggregate (2.7) formed from nano-objects (2.2)

NOTE By definition, aggregates cannot easily release nano-objects.

4. NICNAS working definition of an industrial nanomaterial

The following NICNAS working definition of an industrial nanomaterial and associated notes are taken from the document "Guidance on New Chemical Requirements for Notification of Industrial Nanomaterials" available on the Nanotechnology page of the NICNAS website[1].

"... industrial materials intentionally produced, manufactured or engineered to have unique properties or specific composition at the nanoscale, that is a size range typically between 1 nm and 100 nm, and is either a nano-object (i.e. that is confined in one, two, or three dimensions at the nanoscale) or is nanostructured (i.e. having an internal or surface structure at the nanoscale)"

[Notes to the working definition:

- intentionally produced, manufactured or engineered materials are distinct from accidentally produced materials
- 'unique properties' refers to chemical and/or physical properties that are different because of its nanoscale features as compared to the same material without nanoscale features, and result in unique phenomena (e.g. increased strength, chemical reactivity or conductivity) that enable novel applications.
- aggregates and agglomerates are considered to be nanostructured substances
- where a material includes 10% or more number of particles that meet the above definition (size, unique properties, intentionally produced) NICNAS will consider this to be a nanomaterial.]

[1] http://www.nicnas.gov.au/Current_Issues/Nanotechnology.asp; last accessed on 20 June 2012.

5. Discussion

The Patent describes a mesoporous zinc oxide powder consisting of aggregate particles each comprising bonded zinc oxide crystallites. The crystallites are strongly bound together in an open structure so that each aggregate ZnO particle is highly porous with a significant fraction of both open and closed pores. The aggregate particles have a size in the range from 0.1 to 100 µm, and are not in the nanoscale. However, the primary ZnO crystallites (5 to 50 nm) and the pores (2 to 100 nm) are both in the nanoscale.

ISO 80004-1, Sections 2.1, 2.4, 2.6, 2.7, states that a "nanomaterial" is a material having internal structure in the nanoscale and that a nanomaterial is inclusive of a nanostructured material, that is, a material having an internal composition of inter-related constituent parts, in which one or more of those parts is a nanoscale region.

It is clear that both the aggregated primary ZnO nanoscale crystallites and the network of nanoscale pores are internal structures in the nanoscale and hence that the mesoporous zinc oxide described in the Patent is a nanostructured material and hence a nanomaterial.

This is further supported by the introduction to 80004-4, which states explicitly that *"... materials with a grain size distribution having a significant fraction of grains in the nanoscale (nanocrystalline), voids and pores in the nanoscale, or precipitations in the nanoscale (i.e. nano-objects in a solid matrix) are sufficient features for materials to be classified as "nanostructured"".*

The NICNAS working definition of an "industrial nanomaterial" is essentially the same as the ISO definition of a "nanomaterial", except that "intention" and "unique properties" are added. Certainly, the mesoporous zinc oxide powder described in the Patent is intentionally produced. It also has physical properties that are different because of its nanostructure, in particular a refractive index that significantly reduces whitening and increases transparency, enabling novel applications.

The NICNAS working definition, in its fourth note, also specifies that materials with a number fraction of at least 10 % of particles that meet the definition's criteria (size, unique properties, intentionally produced) is considered a nanomaterial. The Patent explicitly states that "***Each*** *aggregate comprises a plurality of zinc oxide crystallites having an average crystallite size in the range of 5 nm to about 50 nm and a high level of internal porosity.*" (0054, underlining and bold emphasis added by NMI). Therefore, the material described in the Patent meets the minimum number fraction criterion of the NICNAS working definition.

It follows that the zinc oxide powder described in the Patent is an industrial nanomaterial according to the NICNAS working definition.

6. Conclusion

It is the opinion of the National Measurement Institute (NMI) that the "mesoporous zinc oxide powder" described in Patent US 2010/0310871 A1 is a "nanomaterial" according to International Organization for Standardization (ISO) Technical Specifications, and an "industrial nanomaterial" as defined in the Australian Government National Industrial Chemicals Notification and Assessment Scheme (NICNAS) document "Guidance on New Chemical Requirements for Notification of Industrial Nanomaterials".
