Fraunhofer Institut
Verfahrenstechnik
und Verpackung

Environmental Assessment to FCN No. 716

(including confidential information)

ColorMatrix Group Inc. Food Contact Notification

All information on the food contact substance "titanium nitride with a particle size < 20 nm" ("nanoscalic titanium nitride") highlighted in grey in this environmental assessment for FCN 716 is regarded as confidential.

1. Date: May 2, 2007

2. Name of Applicant/Notifier: ColorMatrix Group Inc.

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4. Description of the proposed action

a) Requested action

The action requested in this notification is to establish clearance of the food contact substance (FCS) titanium nitride with an average particle size of < 20 nm (in the following referred to as "nanoscalic titanium nitride"). The food contact substance is intended to be incorporated into polyethylene terephthalate (PET) at a use level not to exceed 20 ppm (w/w). The finished food contact articles (bottles) are intended for direct contact with food types I through VI, under conditions of use D through G as described in Tables 1 and 2 on FDA's website: http://www.cfsan.fda.gov/~rdb/opa-fcn3.html.

b) Need of action

The need for the requested notification of the food contact substance titanium nitride with an average particle size of < 20 nm is based upon the significantly improved technical properties of PET bottles containing nanoscalic titanium nitride. A detailed description of the intended technical effect of the use of nanoscalic titanium nitride in polyethylene terephthalate (PET) is included in section 5 "Intended technical effect" of this document (please refer to page 3).

c) Locations of use and disposals

The Notifier ColorMatrix Group Inc. does not intend to produce finished food packagings using the FCS nanoscalic titanium nitride. The FCS is being produced outside the US. As there will be no manufacturing of the FCS in the USA, no occupational exposure of environmental release as a result of the production of the FCS will occur in the USA. The titanium nitride with a particle size < 20 nm will be used as a dispersion in [redacted]. ColorMatrix Group Inc. sells this dispersion to PET resin manufacturers who directly add this dispersion during polymerisation when producing PET. Therefore it is anticipated that the use and disposal patterns of the PET bottles produced with the FCS "nanoscalic TiN" will be the same as those for conventional PET bottles.

Consequently, PET bottles containing nanoscalic titanium nitride will be utilized in patterns corresponding to the national population density and will be widely distributed across the United States. It is warranted to expect that the disposal of PET containing nanoscalic TiN will occur nationwide with the material being land disposed, combusted, or recycled. According to the U.S. Environmental Protection Agency's 2005 update regarding municipal solid waste in the United States, 54.3 % of municipal waste generally was land disposed, 13.6 % was combusted, and 32.1 % was recovered for recycling and composting[1].

The types of environments present at and adjacent to these disposal locations are the same as for the disposal of other food-contact materials in current use (including conventional PET). Consequently, there are no special circumstances

[1] U.S. Environmental Protection Agency, Office of Solid Waste (5306P): Municipal Solid Waste in the United States: 2005 Facts and Figures, EPA530-R-06-011, October 2006, Washington D.C.

regarding the environment surrounding either the use or disposal of PET bottles containing nanoscalic titanium nitride.

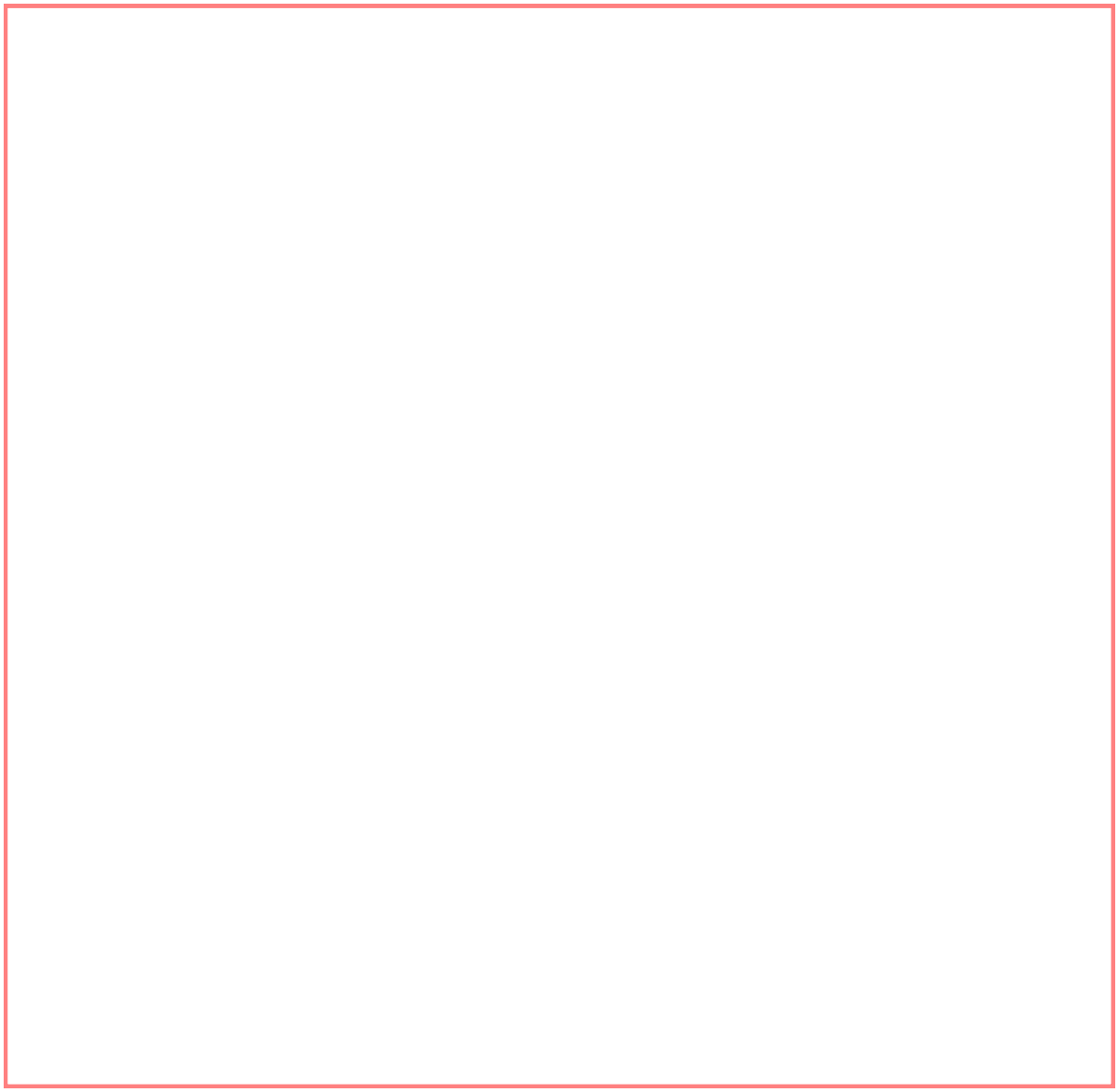
5. Identification of the substance that is the subject of the proposed action

The FCS that is subjected to this notification is titanium nitride with an average particle size of < 20 nm. It is classified as a nanoscalic ceramic powder.

CAS Reg. No. :	25583-20-4
Molecular formula:	TiN
Molecular weight:	61.9 g/mol
Melting point:	approx. 2950 °C
Particle size:	< 20 nm
Specific surface area:	[redacted] m²/g
Morphology:	Spherical
Physical appearance:	The FCS is a black solid powder. [redacted]
Solubility:	insoluble in water, ethanol, hydrochloric -, sulfuric -, nitric acid as well as in alkali solutions

Intended technical effect:

[redacted]



Discussion of particle size:

The FCS titanium nitride is homogenously incorporated into the PET resin. It is being used as a ceramic powder with a particle size < 20 nm and therefore it can be classified as a nanoscalic material.

Due to the smaller particle size nanoscalic titanium nitride possesses an increased surface area per unit mass compared to conventional titanium nitride with a particle size in the micron range and above. Attributed to the particle size the coloration of titanium nitride particles is black-grey in the nano range and golden-brown for larger particle sizes.

In the chart below characteristics of conventional and nanoscalic titanium nitride are presented:

	Nano TiN	TiN
Purity	> 99 %	> 90 %
Average particle size	20 nm	1 µm
Specific surface area	[redacted] m^2/g	10 m^2/g
Colour	Black	Yellow - brown
Morphology	Spherical	spherical
Bulk density	0.08 g/cm^3	3.1 g/cm^3
True density	5.22 g/cm^3	5.22 g/cm^3
flammability	Flammable solid	Non-flammable solid

Certificate of Analysis	Nano TiN	TiN
Ti (%)	77.83	> 77.8
N (%)	21.91	21.5
C (%)	0.03	0.1
Fe (%)	< 0.001	< 0.20
O (%)	0.22	0.22
Ni (%)	< 0.001	
Si (%)	< 0.003	

Due to its high melting point, extreme hardness, excellent wear resistance and corrosion resistance, titanium nitride is widely used in composites, cermets and as thin coating film for cutting tools, medical and surgical devices (e.g. implants) and microelectronic applications, rather than as a monolithic ceramic material. The major advantage of titanium nitride nanoparticles is the possibility to produce dense TiN bodies at lower temperature and improve the mechanical properties of sintered monolithic compacts[2].

Several categories of nanoparticles like nanotubes, nanowires, nanocrystals and quantum dots exhibit unique (novel) properties e.g. in regard to their electronic, optical, magnetic and catalytic characteristics. These changes in physical and chemical behaviour can be attributed to the reduced particle size and increased surface (e.g. by alteration of thermodynamic properties) of nanoparticles[3].

In contrast, ceramics like titanium nitride are classified as "other nanoparticles", which also include existing common nanoparticles such as ultrafine carbon black

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[2] Wang, L. et al.: Consolidation of Nano-Sized TiN Powders by Spark Plasma Sintering. J. Am. Ceram. Soc. (2006), Vol. 89, No. 7, 2364-2366

[3] Powers, K.W. et al.: Research Strategies for Safety Evalution of Nanomaterials. Part VI. Characterization of Nanoscale Particles for Toxicological Evaluation. Toxicological Sciences (2006), Vol. 90, No. 2, 296-303

and fumed silica which are synthesised in bulk form through flame pyrolysis methods. Nanoparticles of this type may be formed from many materials including metals, oxides, ceramics, semiconductors and organic materials[4]. These nanoparticles do not necessarily differentiate from conventional sized particles in respect to their chemical and physical properties[5].

Like conventional sized titanium nitride, nanoscalic titanium nitride must be regarded as chemically and physiologically inert. As described in the literature, TiN nanopowders do not interact with various biochemical medias (like blood and gastric juice) nor with water, diluted NaOH and HCl solutions [6]. Solubility properties of nanoscalic titanium nitride are similar to or even the same as the solubility properties of titanium nitride in the conventional scale.

Catalytic properties of high surface area titanium nitrides (up to 200 m²/g) have been reported for hydrogen transfer reactions, where titanium nitride is used in a co-catalytic system together with $NaAlH_4$. The supposed role of TiN in the hydrogenation of diphenylethyne (DPE) is to facilitate the dissociation of $NaAlH_4$ into NaH and AlH_3 if a suitable substrate is present. Hereafter, AlH_3, formed on the TiN particle surface, adds to DPE and forms *Z*-stilbene after hydrolysis of the hydroalumination intermediate[7]. These co-catalytic properties apply to titanium nitride nanoparticles used under specific laboratory conditions.

To our knowledge and based on a further literature research, there is no data available stating unique chemical or physical properties of used nanoscalic titanium nitride (particle size < 20 nm, average surface area [redacted] m²/g) that could distinguish the used FCS from titanium nitride with a larger particle size.

Titanium nitride is generally considered to be physiologically inert. EC_{50}-, LC_{50}-values or any other relevant toxic endpoints could not be established for titanium nitride. There are no cases reported in the literature that titanium nitride has caused human intoxication (regardless of the particle size). However, exposure to fine particulate dusts is known to lead to pulmonary diseases. Therefore general precautions must be taken preventing the inhalation of titanium nitride aerosols (dust) from the aspect of occupational safety. This is necessary for both conventional sized and nanoscalic titanium nitride. Once embedded in the PET polymer matrix, titanium nitride of either size causes no health concerns as all particles are immobilised.

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[4] UK Health and Safety Executive - Institute of Occupational Medicine: Nanoparticles: An occupational hygiene review (2004) Research Report 274

[5] Please refer to foot note 3

[6] Lavrenko, V.A. et al.: Stability and corrosion resistance of titanium nitride in biochemical media. Key Engineering Materials (2002) Vols. 206-213, 1571-1574

[7] Kasel, S. et al.: Catalytic properties of high surface area titanium nitride materials. Journal of Molecular Catalysis A: Chemical (2004) Vol. 208, 291-298

6. Introduction of the substance into the environment

6 a. Introduction of the FCS into the environment as a result of manufacture

Based on the manufacture's and ColorMatrix's declaration all applicable emission and occupational safety requirements are being respected both for the manufacture of the nanoscalic titanium nitride powder by [redacted] and for the application of the nanoscalic titanium nitride in the polymerisation process of PET. Besides good general industrial hygiene, protective gloves and clothing, no eating and drinking in the work area and washing after handling of the material, this includes e.g. avoidance of the generation and inhalation of titanium nitride dusts and precautionary measures against static discharges.

The titanium nitride (TiN) with a particle size < 20 nm is being used as a dispersion [redacted] This dispersion is sold to PET resin manufacturers who add this dispersion directly during polymerisation. The resin manufacturer will empty the entire contents of the drum or intermediate bulk container (IBC). The drum or IBC is then returned to ColorMatrix Group Inc. and is re-used for the same product. Therefore it can be anticipated that there is no release of nanoscalic titanium nitride into the environment during the handling and production of the respective PET material.

In conclusion, no significant environmental release of the FCS nanoscalic titanium nitride is expected during the manufacture of the FCS and during the production process of PET containing the nanoscalic titanium nitride.
In addition, information available to the Notifier does not suggest that there are any extraordinary circumstances in this case that indicate any adverse environmental impact as a result of the manufacture of the FCS and of its use in the production of PET bottles.
Therefore this environmental assessment of nanoscalic titanium nitride will focus on the relevant issues relating to the use and disposal of FDA-regulated articles as described under 21 CFR 25.40 (a).

6 b. Introduction of the FCS into the environment as a result of use/disposal

It can be assumed that the introduction of the FCS nanoscalic titanium nitride into the environment occurs in general as a result of the disposal of PET bottles that are formulated with this FCS. Therefore PET bottles manufactured with the FCS nanoscalic titanium nitride are expected to be disposed of in patterns similar to conventional PET bottles.

No environmental release is expected upon the use of nanoscalic titanium nitride to produce polyethylene terephthalate (PET) bottles. In this application the FCS is entirely homogenously incorporated in the polyethylene terephthalate polymer resin (PET). Therefore any waste material generated in the process of the polymerisation of PET and of the bottle blowing, e.g. plant scraps, are expected

to be disposed as part of the bottle manufacturer's overall non-hazardous solid waste in accordance with established procedures.
Due to titanium nitride's chemical inertness and insolubility in water, ethanol and acids and due to the low diffusion characteristics of the PET polymer, the titanium nitride is immobilized in the PET matrix and therefore it can not be released upon the use of food-contact articles (PET bottles) manufactured with this FCS. Consequently the FCS nanoscalic titanium nitride will remain with the food packaging throughout the use of the package by consumers.

PET bottles containing up to 20 ppm of nanoscalic titanium nitride are expected to be disposed in patterns similar to the current disposal of conventional PET bottles. As PET bottles formulated with titanium nitride and conventional PET bottles are chemically identical with regard to the polymer resin, it is anticipated that PET bottles formulated with titanium nitride will bear the resin identification code used for PET and are expected to be disposed of similarly to conventional PET. Following established disposal patterns the disposal of PET bottles, either conventional or containing the additive titanium nitride, by the ultimate consumer will be by conventional rubbish disposal including sanitary landfill and incineration. PET bottles will enter the recycling process as well.

Based on data evaluated by U.S. Environmental Protection Agency on Municipal Solid Waste in the United States: 2005 Facts and Figures, an overall amount of 850 thousand tons of PET were generated for the use as soft drink bottles in the U.S. in the year 2005. 290 thousand tons corresponding 34.1 % of these PET bottles disposed in the U.S. were subjected to the recycling process, while 560 thousand tons of PET (65.9 %) were being discarded.
In accordance with usual solid waste disposal pattern about 80 % of the solid waste that is not recycled or composted will be disposed of by means of landfill and about 20 % will be incinerated[8]. The use of nanoscalic titanium nitride as an additive in PET is not expected to have an impact on this figure.

Once PET bottles containing the additive nanoscalic titanium nitride are disposed of via sanitary landfills, no significant leaching of any substance, including the FCS nanoscalic titanium nitride, from the PET material into the environment is expected to take place. This assessment is based on the fact that the additive nanoscalic titanium nitride is entirely homogenously incorporated in the polyethylene terephthalate polymer resin (PET). Due to titanium nitride's chemical inertness and insolubility in water, ethanol and acids (regardless of the particle size) and due to the diffusion characteristics of the PET polymer, the titanium nitride is immobilized in the PET matrix and therefore will not be released from the PET bottle in significant quantities.
This conclusion was confirmed by the results of the migration testing under exaggerated exposure conditions using 95 % ethanol as an extraction simulant (as shown in the migration study conducted on PET bottles containing 20 ppm of titanium nitride with a particle size < 20 nm, submitted to FDA in support of FCN No. 716). Leaching / migration of nanoscalic titanium nitride from PET was not observed at a detection limit of 5 ppb (5 µg/kg). It was demonstrated that the use of titanium nitride in its nanoscalic form has no impact on the migration

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[8] Please refer to footnote 1

properties of titanium nitride used in a PET matrix.
Considering this lack of leaching of nanoscalic titanium nitride from PET bottles even under conditions that exaggerate environmental conditions, it is concluded that there will be no environmental impact of nanoscalic titanium nitride due to leaching. Thus, it is expected that the FCS will not threaten a violation of EPA's regulations in 40 CFR Part 258 that pertain to landfills.

When incinerated, there are not expected to be any toxic combustion products originating from the additive titanium nitride, as non-toxic titanium oxide (TiO_2)[9] is described to be formed from conventional sized titanium nitride as well as from nanoscalic titanium nitride under oxidative conditions and under temperature conditions in the range of temperatures typically achieved in the decomposition process in incinerators[10,11].
Therefore we do not expect the FCS to cause municipal waste combustors to threaten a violation of applicable emission laws and regulations, e.g. 40 CFR part 60 and/or relevant state and local laws.

The proposed use of nanoscalic titanium nitride is described in the section 5 "Intended technical effect" (please refer to page 3 of this document).

Considering the production process of PET bottles, possible industrial scrap and the intended and predictable use of the PET bottles formulated with titanium nitride, the estimated yearly market volume of titanium nitride that will remain with the packaging is more than 99 %. Therefore less than 1 % will enter the waste stream at the PET and PET bottles production site(s).

Taking the fact into account that nanoscalic titanium nitride is not leaching significantly from the PET bottles, that no toxic thermal decomposition products are being formed from titanium nitride during incineration and that only extremely small quantities of nanoscalic titanium nitride may enter the waste stream at the production site, it can be concluded that the use and disposal of nanoscalic titanium nitride used as additive for PET bottles do not adversely effect the environment.

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[9] Titanium oxide is an inert solid.
[10] Chuprina, V.G., Shalya, I.M. Oxidation of porous nanocrystalline titanium nitride – II: Scale Structure and composition. Powder Metallurgy and Metal Ceramics (2006) Vol. 45, No. 3-4, 168-172
[11] Gmelin Handbuch der anorganischen Chemie: System Nr. 41 (1951) Titan, 272-285

7. Fate of Emitted Substances in the Environment

The used FCS "nanoscalic titanium nitride" is a non-volatile inert powder. For achieving the intended technical effect it is incorporated into the polyethylene terephthalate matrix of food-contact article (PET bottles). Due to its chemical inertness and insolubility in water, ethanol and acids and due to the diffusion characteristics of the PET polymer, the titanium nitride is immobilized in the PET.

As discussed above, considering the application, use and disposal of the FCS and the respective food-contact articles, nanoscalic titanium nitride is not expected to be released into the environment. Therefore no information on the fate of the substance in the atmosphere, in marine and terrestrial ecosystems need to be provided.

8. Environmental effects of released substance

No information need to be provided on the environmental effects of substances released into the environment as a result of the use and disposal of food-contact articles containing the FCS in landfills and by combustion, because, as discussed above, the FCS is not expected to be introduced into the environment. Therefore, the use and disposal of the food-contact articles in landfills or by combustion are not expected to threaten a violation of applicable laws and regulations, e.g., the Environmental Protection Agency's regulations in 40 CFR Parts 60 and 258.

9. Use of resources and energy

The use of resource and energy in the manufacture of PET polymers containing nanoscalic titanium nitride and in their conversion to finished PET bottles is expected to be equal to or lower than similar conventional PET bottles already on the market. The intended technical effect of nanoscalic titanium nitride including the aspects of resources and energy are provided in section 5 "Intended technical effect" of this document (please refer to page 3).

The (partial) replacement of conventional PET bottles with PET bottles containing nanoscalic titanium nitride is not expected to have any adverse impact on the use of energy and resources.

PET bottles produced by comparable technologies using the incorporation of [redacted] into the PET matrix in order to achieve the described technical effect are commercially on the market.

[redacted]

Therefore the replacement of [redacted] by (nanoscalic) titanium nitride is not expected to have any adverse effect, [redacted], on the use of natural resources and energy in the production of PET bottles.

PET bottles containing the additive nanoscalic titanium nitride are expected to be recycled along with conventional PET containers: As the polymer structure of PET containing nanoscalic titanium nitride does not differ chemically from conventional PET, it is anticipated that PET bottles formulated with titanium nitride will bear the resin identification code used for PET and are expected to be included in the same post-consumer stream as conventional PET. The presence of nanoscalic titanium nitride in the PET matrix is not expected to have any adverse impact on the recyclability of PET. [redacted]

In summary, it is expected that the incorporation of nanoscalic titanium nitride will have no significant adverse impact on natural resources and energy required for the manufacture of PET resins and PET bottles.

10. Mitigation measures

As shown above, no significant adverse environmental impacts are expected to result from the use of nanoscalic titanium nitride as additive in PET bottles and from the disposal of such PET bottles. This is primary due to the non-leaching properties of the nanoscalic titanium nitride incorporated in the PET polymer, the formation of a non-toxic combustion product (titanium oxide) and the non-adverse impact on the use of resources and energy compared to conventional PET. Thus, the use of nanoscalic titanium nitride as proposed is not reasonably expected to result in any new environmental problem requiring mitigation measurements of any kind.

11. Alternatives to the proposed action

No potential adverse effects have been identified that would require any alternative actions to those proposed in this Notification.
Non-approval of the proposed action would result in the continued use of alternative additives (see confidential part of section 9 "Use of resources and energy" for an example) in PET for achieving the intended technical effect (as described in section 5 "Intended technical effect" of this document; please refer to page 3) or PET bottles would continue to be produced without the benefit of such an additive, respectively.

Considering the fact that the FCS nanoscalic titanium nitride is not expected to enter the environment in significant quantities upon the use and disposal of PET bottles and the absent of any significant environmental impact which would result from its use, the establishment of an effective Food Contact Notification to permit the use of "nanoscalic titanium nitride" as additive in PET bottles is safe from an environmental perspective.

12. List of preparers

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13. Certification

The undersigned official certifies that the information presented is true, accurate, and complete to the best of her knowledge.

May 2, 2007

Dr. Diana Kemmer

Scientist

14. Attachment

- Material safety data sheet (MSDS) for nanoscalic titanium nitride dispersion.