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March 30, 2009

VIA OVERNIGHT MAIL
Food and Drug Administration
Dockets Management Branch
5630 Fishers Lane, Room 1061
Rockville, MD 20852

RE: **Petition Requesting that FDA Amend Its Regulations for Products Composed of Engineered Nanoparticles Generally and Sunscreen Drug Products Composed of Engineered Nanoparticles Specifically [*Docket Number FDA-2006-P-0213* (originally FDA Docket No. 2006-0210/CP1)]**

COMMENTS OF PUREST COLLOIDS, INC. IN RESPONSE TO CITIZEN PETITION REQUESTING THAT FDA AMEND ITS REGULATIONS FOR PRODUCTS COMPOSED OF ENGINEERED NANOPARTICLES GENERALLY

Purest Colloids, Inc. ("Purest") hereby submits these comments in response to International Center for Technology Assessment's (ICTA's) petition requesting that the Food and Drug Administration (FDA) amend its existing regulations for products containing engineered nanotechnology. *See* FDA Docket No. 2006-P-0213. In these comments, Purest provides FDA with legal, scientific, and technical information germane to the petition.

As explained *infra*, FDA's existing regulations governing adulteration provide the agency the authority it needs to halt use of specific product ingredients that pose a cognizable risk to the health of man or animals. ICTS bases its petition on a perception

of risk that is not backed by scientific consensus, let alone competent science. It calls for categorical bans on products without proof of harm.

ICTA asks FDA to enact a de facto ban on all nanomaterials regardless of each product's safety profile without any proof whatsoever that the products pose an actual risk of cognizable injury to man or animals. FDA need not impose extensive new prior restraints on all who manufacture and distribute nanoscale products when FDA's pre-existing, case-by-case enforcement is sufficient to arrest that subset of manufacturers who distribute unsafe products.

Enacting ICTA's reforms would thus violate federal and administrative laws that prohibit unnecessary, burdensome, and arbitrary and capricious agency action and that demand competent science to support science-based regulation. *See* APA, 5 U.S.C. § 706; Data Quality Act, Pub. L. No. 106-554, § 515(a), 114 Stat. 2763.

Refusal to enact ICTA's unlawful regulations does not impose upon FDA a duty to complete an Environmental Impact Statement under the National Environmental Policy Act (NEPA). FDA's so-called "inaction" does not constitute a major federal action triggering NEPA's requirements.

I. INTERESTS OF THE COMMENTER

Purest manufactures and distributes silver colloid products, including its private label MesoSilver® silver colloid dietary supplement. Purest's colloidal silver product consists of pure elemental metal nanoparticles dispersed in ionized water. The silver particles dispersed in water range from sub-nanometer to 10 nanometers in diameter and

typically consist of 10 to 30,000 atoms per particle. The MesoSilver® product maintains a concentration of 20 parts per million of total silver.

Purest Colloids markets its MesoSilver® product as a mineral supplement. The recommended dosage is between one teaspoon and one tablespoon daily ingested orally. Purest Colloids markets its product for use in maintaining immune system health. The product has been marketed to the public for 10 years with no reports of adverse effects. Toxicity studies performed by Charles River Laboratories on the product reveal no evidence of injury even at dose levels far beyond those recommended in labeling (i.e., no adverse effects even at 30 tablespoons of MesoSilver® per daily dose); *see also* Scientific Report of Dr. George J. Maas, Ph.D. (**Attachment A**).

II. SUMMARY OF ICTA PETITION

The ICTA Petition asks FDA to impose new regulatory strictures on nanoscale materials generally. ICTA argues that nano-silver products exhibit properties that are significantly different from their bulk substances and, therefore, demands that FDA ban *all* nanomaterials.[1] ICTA asks that FDA collect safety data for each nanomaterial before such product may be lawfully marketed under the FDCA. *See* ICTA Petition at 3, 6-27.

ICTA asks FDA, in pertinent part, to:

1) Amend FDA regulations to include nanotechnology definitions necessary to properly regulate nanomaterial products, including the terms "nanotechnology," "nanomaterial," and "engineered nanoparticle;"

[1] Several of the original petitioners have received past funding from the John Merck Fund, linking petitioners with pharmaceutical giant Merck & Co, Inc. *See* John Merck Fund Top Grants, *available at*, http://www.activistcash.com/foundation.cfm?did=138.

2) Issue a formal advisory opinion explaining FDA's position regarding engineered nanoparticles in products regulated by FDA;

3) Enact new regulations directed at FDA oversight of nanomaterial products establishing and requiring, *inter alia*, that: nanoparticles be treated as new substances; nanomaterials be subjected to nano-specific paradigms of health and safety testing; and that nanomaterial products be labeled to delineate all nanoparticle ingredients; and

4) Any currently existing or future regulatory FDA programs for nanomaterial products must comply with the requirements of the National Environmental Policy Act (NEPA), including, *inter alia*, that FDA conduct a Programmatic Environmental Impact Statement (PEIS) reviewing the impacts of nanomaterial products on human health and the environment.

Id. at 3. Thus, ICTA argues that FDA should regulate nanomaterials as distinct substances from their bulk counterparts, irrespective of each nanomaterials' individual properties. *Id.*

III. EXISTING FDA REGULATORY FRAMEWORK

In 2006, after ICTA submitted its original petition, then-acting FDA Commissioner Andrew C. von Eschenbach formed an internal FDA Nanotechnology Task Force for the purpose of assessing FDA's approach to nanotechnology. *See* Nanotechnology Task Force Report at 5 (July 25, 2007) (hereinafter "Task Force Report"), *available at*, http://www.fda.gov/nanotechnology/taskforce/report2007.pdf. The Task Force concluded in part that FDA's current system was capable of addressing nanotechnology issues, as it had for past technologies. *See* Task Force Report at 20. The Task Force stated:

> Although FDA's authorities may be adequate to meet these challenges, in some cases the evolving state of the science regarding nanotechnology may warrant a case-by-case approach to assess whether sufficient

> evidence exists to show that products satisfy the applicable statutory and regulatory standards.

Id. at 20. The Task Force recommended continued case-by-case enforcement rather than categorical regulations in the absence of a thorough scientific record.

ICTA's Request for Additional Regulation

ICTA asks FDA to enact regulations declaring "new substances" those products regulated by FDA that contain "nanoparticles." *See* ICTA Petition at 3. As new substances, under the FDCA, nanoparticle containing foods, dietary supplements, cosmetics, and drugs would be deemed unmarketable unless FDA determined that specific nanomaterials were safe along with their bulk substances.

ICTA acknowledges that scientific consensus is lacking concerning whether nanomaterials pose a threat to human or animal health and concerning the means to measure nanoparticle reactivity. *Id.* at 30 ("few studies of the environmental impacts of engineered nanoparticles exist or are available in the public domain"). While experts may agree that existing evaluative methods are inadequate to comprehend the properties of all nanomaterials, there is no scientific consensus, as ICTA contends, that nanomaterials pose a risk to human or animal health. The charge is entirely speculative.

ICTA's Requested Relief is Unnecessary Because FDA's Existing Regulations Suffice

Existing FDA regulations permit the agency to arrest adulteration regardless of its course. Any product claiming to treat human disease or bodily conditions must be given premarket authorization by FDA under the agency's existing drug regulations, including products that contain nanoparticles. FDA thus assesses the safety of nanoscale drug products as part of its existing drug approval process. New regulation is thus

unnecessary because FDA presently makes a case-by-case assessment of each drug's safety as it passes through the drug approval process.

Under sections 201(s) and 409 of the FDCA, and the FDA's implementing regulations in 21 CFR 170.3 and 21 CFR 170.30, food additives may not be lawfully marketed unless generally recognized as safe (GRAS). No food, dietary supplement, or cosmetic may be lawfully marketed if it presents a risk of illness or injury to users; it is thus adulterated and illegal to sell. *See* 21 U.S.C. § 331.

Manufacturers of dietary supplements must notify FDA at least 75 days in advance of marketing a product if it contains a "new dietary ingredient," unless that ingredient has been "present in the food supply as an article used form food in a form in which the food has not been chemically altered." 21 U.S.C. § 350(b) (emphasis added); *see also* Task Force Report at 28. Because nanotechnology is novel, few, if any, engineered nanosubstances would be grandfathered under DSHEA. Indeed, almost all substances would be chemically altered and, therefore, the manufacturers would be required to submit a basis for concluding that the products are safe. Here again, FDA is afforded the opportunity to review the safety of specific nanoscale products. Under the FDCA, new dietary ingredients that have not satisfied the requisite safety levels are deemed adulterated as a matter of law. *See* 21 U.S.C. § 342(f). Accordingly, FDA's regulatory model is as capable of monitoring the safety of nanoscale substances as it is other technological developments.

IV. FDA IS PROHIBITED FROM PROMULGATING UNNCESSARY REGULATIONS

The legislative and executive branches of government have imposed limits on unnecessary and unduly burdensome agency action. Those limits prevent duplicative regulation or costly and burdensome regulation when existing schemes are appropriate. The Regulatory Flexibility Act ("RFA"), Executive Orders issued by the President of the United States, and the Administrative Procedure Act ("APA") all prohibit unnecessary regulations. Those statutes and orders command the federal agencies to employ the least burdensome means to achieve regulatory goals. New rulemaking concerning nanotechnology is not the least burdensome means to regulate nanoscale substances because, as explained *supra*, FDA's existing regulatory model is sufficient.

The Regulatory Flexibility Act

In 1980, Congress passed the Regulatory Flexibility Act. The purpose of the act was to "establish as a principle of regulatory issuance that agencies shall endeavor, consistent with the objectives … of applicable statutes, to fit regulatory and informational requirements to the scale of the businesses, organizations, and governmental jurisdictions subject to regulation." Pub. L. No. 96-354, § 2(b), 94 Stat. 164, 165 (Sept. 19, 1980). Congress passed the RFA to protect businesses from the prohibitive costs of unnecessary regulation. Indeed, the RFA is predicated on the principle that where the regulatory impact is likely to be significant, affecting a substantial number of small business entities, agencies must seek less burdensome alternatives for those entities. *See* 5 U.S.C. § 603(c) (requiring federal agencies to provide "a description of any significant alteratives to the

proposed rule which accomplish the stated objectives of applicable statutes and which minimize any significant economic impact of the proposed rule on small entities").

The RFA requires a federal agency to prepare a regulatory flexibility analysis and assessment of the economic impact of a proposed rule on small business entities. *See Environmental Defense Center, Inc. v. EPA*, 344 F.3d 832 (9th Cir. 2003). When the agency promulgates a final rule, the agency must prepare a final regulatory flexibility analysis. *See* 5 U.S.C. § 604. Among the items included in the final analysis, the agency must provide

> a description of the steps the agency has taken to minimize the significant economic impact on small entities consistent with the state objectives of applicable statutes, including a statement of the factual, policy, and legal reasons for selecting the alternative adopted in the final rule and why each one of the other significant alternatives to the rule considered by the agency which affect the impact on small entities was rejected.

See 5 U.S.C. § 604(a)(5). Congress thus requires that FDA defend its decision to choose additional regulation over a less burdensome alternative. By inference, therefore, Congress commands the agency to choose the least burdensome path when such an option will achieve the goals of the agency.

ICTA's requested regulations would force all nanosubstance manufacturers to shoulder the cost of FDA approval without evidence that specific nanosubstances exhibit significant safety risks different from their bulk counterparts. As discussed *supra*, FDA's regulatory system is adequate to determine on a case-by-case basis whether a true safety risk exists based on sound science and to prohibit the sale of specific regulated products that pose such a risk. Any additional regulation, therefore, is unduly burdensome in violation of the RFA.

The RFA is procedural in nature, and provides no independent cause of action. The RFA requires an analysis demonstrating "a reasonable, good-faith effort to carry out [RFA's] mandate." *Alenco Communications, Inc. v. FCC*, 201 F.3d 608 (5th Cir. 2000). Under the APA, the agency's decision to dismiss plausible alternatives is subject to challenge as arbitrary and capricious agency action. *See* 5 U.S.C. § 706(2)(A); *see also U.S. Cellular Corp. v. FCC*, 254 F.3d 78, 89 (D.C. Cir. 2001) (assessing FCC's RFA analysis under the APA arbitrary and capricious standard but finding FCC's chosen path reasonable). Because ICTA's regulations pertaining to nanoscale materials are redundant of present safety regulations, the cost imposed on industry far outweighs the public need for action. Accordingly, promulgation of additional rules would violate the APA's prohibition against arbitrary and capricious agency action.

Executive Order No. 12291

President Reagan signed Executive Order No. 12291 in 1981, and his order remains legally binding against executive agencies. *See* Executive Order 12291, 46 Fed. Reg. 13193. Executive Order No. 12291 revoked President Carter's Executive Order No. 12044. Like the previous order under the Carter administration, Executive Order No. 12291 limited federal agency discretion when promulgating new regulations. *See, e.g.*, Executive Order No. 12044, 43 Fed. Reg. 12661 (requiring that agencies consider alternative approaches and choose "the least burdensome of the acceptable alternatives").

Executive Order No. 12291 commands that, in promulgating new regulations, "[r]egulatory action shall not be undertaken unless the potential benefits to society for the regulation outweigh the potential costs to society." Exec. Order No. 12291 at § 2(b). In

addition, "[a]mong alternative approaches to any given regulatory objective, the alternative involving the least net cost to society shall be chosen." *Id.* at § 2(d). "Agencies shall set regulatory priorities with the aim of maximizing the aggregate net benefits to society, taking into account the condition of the particular industries affected by regulations, the condition of the national economy, and other regulatory actions contemplated for the future." *Id.* at § 2 (e).

Major rules promulgated by federal agencies must be accompanied by "[a] description of alternative approaches that could substantially achieve the same regulatory goal at a lower cost, together with an analysis of this potential benefit and costs and a brief explanation of the legal reasons why such alternatives, if proposes, could not be adopted." *Id.* at § 3(d)(4).

ICTA's requested regulations violate violating Executive Order No. 12291. Existing case-by-case enforcement has not been proven insufficient to meet new technological challenges. *See* Task Force Report at 20. The FDA's case-by-case approach permits experts to segregate nanosubstances that present significant departures from bulk substances from others with marginal, and thus acceptable, variations. FDA's case-by-case, targeted approach is more efficient that ICTA's proposed blunderbuss categorical bans.

Executive Orders are accorded the force and effect of a statute when they have a distinct statutory foundation. *Ass'n for Women in Science v. Califano*, 566 F.2d 339, 344 (D.C. Cir. 1977). The President's proclamations and orders have the force and effect of law when issued pursuant to a statutory mandate or delegation of authority from Congress. *See Independent Meat Packers Ass'n v. Butz*, 526 F.2d 228, 234 (8th Cir.

1975). President Reagan promulgated Executive Order 12291 based on authority derived from the Constitution and in his role as head of the executive branch of government. *See Building and Const. Trades Dept., AFL-CIO v. Allbuagh*, 295 F.3d 28, 32 (D.C. Cir. 2002) ("[t]he ordinary duties of officers prescribed by statute come under the general administrative control of the President by virtue of the general grant to him of the executive power, and he may properly supervise and guide their construction of the statutes under which they act in order to secure that unitary and uniform execution of the law which Article II of the Constitution evidently contemplated in vesting general executive power in the President alone").

The court in *Allbaugh* held that administrative officers are "duty-bound to give effect to the policies embodied in the President's direction, to the extent allowed by law." *Id.* at 32. The court further held that "if an executive agency … may lawfully implement the Executive Order, then it must do so." *Id.* at 33.

In *National Wildlife Federation*, the District Court for the District of Columbia recognized that agency action controlled by executive order is subject to the APA. *See National Wildlife Federation v. Babbit*, D.D.C. No. 88-0301 (July 30, 1993), *available at*, 1993 WL 304008; *see also* Steven Ostrow, Enforcing Executive Orders: Judicial Review of Agency Action under the Administrative Procedure Act, 55 G.W. L. Rev. 659, 666 (1987) (arguing that agency action or inaction in relation to an executive order can be challenged under the APA). Executive orders have the force of law and, therefore, agency action that conflicts with such orders violates the APA's prohibition against agency action that is "not in accordance with law." 5 U.S.c. § 706(2)(A).

The FDA is not free to disregard executive orders and enact unnecessary, duplicative, and burdensome regulations. Accordingly, the FDA must reject ICTA's proposals for new regulation, and continue to assess nanoscale substances on a case-by-case basis.

V. FDA IS NOT REQUIRED TO ISSUE AN ENVIRONMENTAL IMPACT STATEMENT

Under the National Environmental Policy Act ("NEPA") an Environmental Impact Statement ("EIS") is required when an agency proposes "a major Federal action[] significantly affecting the quality of the human environment." 42 U.S.C. § 4332(2)(C). NEPA requires that an agency contemplating major federal action must take a "hard look" at alternatives and environmental consequences before undertaking action. *Baltimore Gas & Elec. Co. v. Natural Resources Defense Council, Inc.*, 462 U.S. 87, 97, 103 S. Ct. 2246, 76 L. Ed. 2d 437 (1983).

> Major Federal action is a defined term under CEQ regulations.
>
> 'Major Federal action' includes actions with effects that may be major and which are potentially subject to Federal control and responsibility. Major reinforces but does not have a meaning independent of significantly (§ 1508.27). *Actions include the circumstance where the responsible officials fail to act and that failure to act is reviewable by courts or administrative tribunals under the Administrative Procedure Act or other applicable law as agency action.*

40 CFR §1508.18 (*emphasis added*). In determining whether a major federal action has occurred, under 42 U.S.C. § 4332(2)(C), courts consider three factors none of which are dispositive: "(1) whether the project is federal or non-federal; (2) whether the project receives significant federal funding; and (3) when the project is undertaken by non-federal actors, whether the federal agency must undertake 'affirmative conduct' before

non-federal actors may act." *Mineral Policy Ctr. v Norton*, 292 F. Supp. 2d 30, 54-55 (D.D.C. 2003) (citing generally *Macht v. Skinner*, 916 F.2d 13 (D.C. Cir. 1990)).

In *Alliance for Bio-Integrity v. Shalala*, 116 F. Supp. 2d 166, 174 (D.D.C. 2000), the court ruled against a coalition with the same demands currently presented by the ICTA. The coalition sued the FDA on a similar matter concerning a technological advancement involving recombinant deoxyribonucleic acid (rDNA) technology, a technology that allowed scientists to genetically alter food at the cellular and molecular level creating new breeds of plants for human and animal consumption. Those foods were designed to repel pests, retain freshness for longer periods of time, and contain more nutritional value.

In 1992, the FDA issued a policy statement announcing that it would presume that foods produced through the rDNA process were "generally recognized as safe" (GRAS) and thus not subject to regulation as food additives. The FDA encouraged that producers consult with FDA before marketing rDNA foods but made no mandates in this regard. FDA reserved the right to regulate rDNA foods on a case-by-case basis implied that it would not regulate rDNA foods differently than other foods. The coalition sued under the APA, NEPA, and First Amendment grounds. It advanced arguments concerning the environmental consequences of genetically altered food and the religious implications of eating foods produced in a genetically altered form.

FDA indicated that its rDNA policy was not a major action under NEPA and thus no Environmental Assessment (EA) or Environmental Impact Statement (EIS) was necessary. The court sided with the FDA and stated that "[w]hile declaring a rebuttable presumption that foods produced through rDNA technology are GRAS, the FDA has

neither made a final determination that any particular food will be allowed into the environment, nor taken any particular regulatory actions that could affect the environment." *Alliance for Bio-Integrity v. Shalala*, 116 F. Supp. 2d 166, 174 (D.D.C. 2000). The Court further defined "major federal action" and stated that "the agency must be prepared to undertake an 'irreversible and irretrievable commitment of resources' to an action that will affect the environment.'" *Id*. (citing *Wyoming Outdoor Council v. U.S. Forest Service*, 165 F.3d 43, 49 (D.C. Cir. 1999)). The *Bio-Integrity* court held that FDA had not bound itself to a specific regulatory action and, thus, no irreversible action had occurred necessitating an EIS. *See id*. In support of its ruling, the court cited the FDA's decision to permit additional public comment one year after the policy statement. *See id*. Moreover, the court held that "agency decisions that maintain the substantive status quo do not constitute major federal actions under NEPA." *Id.*; *see also Fund for Animals, Inc. v. Thomas*, 127 F.3d 80, 84 (D.C. Cir. 1997); *Committee for Auto Responsibility v. Solomon*, 603 F.2d 992, 1002-03 (D.C. Cir. 1979).

The *Bio-Integrity* court found that the coalition's core NEPA claim failed because the FDA's failure to act did not constitute an action under NEPA. *See id*. at 174-175. The agency must perform an "overt act." *Id*. "NEPA applies only to agency actions 'even if inaction has environmental consequences.'" *id*. at 174-75 (quoting *Defenders of Wildlife v. Andrus*, 627 F.2d 1238, 1243 (D.C. Cir. 1980)). The court stated, "Congress did not intend for agencies to perform environmental studies when the agencies were not acting," because "no agency could meet its NEPA obligations if it had to prepare an

environmental impact statement every time the agency had power to act but did not do so." *Id*. (quoting *Defenders of Wildlife*, 627 F.2d at 1246).[2]

Consequently, under the logic of *Bio-Integrity* and established precedent, FDA is not required to compile an EIS for an alleged policy of inaction in the field of nanotechnology. *C.f.* ICTA Petition at 35 (categorizing current FDA policy as policy of inaction that constitutes a "de facto" nanomaterial regulatory policy).

VI. ICTA'S PETITION CALLS FOR REGULATORY ACTIONS THAT WILL WORSEN THE RECESSION

Tens of thousands of manufacturers and distributors depend upon revenues generated from products containing nanoscale particles; some, like Purest Colloids, are wholly dependent on that revenue to remain in business. The regulatory strictures sought by ICTA are costly and burdensome. Many, like Purest, do not have the economic wherewithal to comply with the costly constraints and, so, would go out of business rather than endeavor to satisfy them. In the current marketplace, the nation's economic security hinges on cost savings. Every avenue of profit foreclosed translates directly into lost opportunities for recovery and for sustained employment. It is thus doubly imprudent for FDA, void of a sound scientific basis for action, to adopt significant and

[2] Ultimately the court granted the FDA's motion for summary judgment holding that the FDA had not preformed any overt act by creating a rebuttable presumption that rDNA foods were GRAS and thus NEPA did not apply. *Id.* at 175. *See also Int'l Ctr. for Tech. Assessment v. Thompson*, 421 F. Supp. 2d 1, 2006 U.S. Dist. LEXIS 8927 (D.D.C. 2006) (finding that the FDA's refusal to regulate a genetically engineered ornamental fish, called Glofish, was not a major Federal action or agency action that would trigger the reporting requirements under NEPA); *Cross-Sound Ferry Services, Inc. v. ICC*, 290 U.S. App. D.C. 39, 934 F.2d 327, 334 (D.C. Cir. 1991) (upholding I.C.C. finding that "a conclusion that regulation is not necessary is not a federal action, but is simply a determination not to take action").

costly new regulations that will harm all in the market, regardless of the true and provable impact each company's products have on the environment. Case-by-case evaluation of risk remains a necessary and sufficient means to address demonstrable risks.

VII. CONCLUSION

For the foregoing reasons, Purest respectfully requests that FDA issue no new regulation affecting nanoscale substances in foods, drugs, dietary supplements, and cosmetics. FDA's current regulatory framework is sufficient to address the challenges posed by nanoscale materials in all FDA regulated products.

Respectfully submitted,

PUREST COLLOIDS, INC.

By: _____/s/_____
Francis S. Key
President

ATTACHMENT A: MAAS ARTICLE

Silver Nanoparticles: Scientific Basis for Environmental Safety

George J. Maass, Ph.D. (Colloidal Science Laboratories)

Abstract:

This report will demonstrate that silver nanoparticles do not remain "nanosize" when they come in contact with normal environmental samples, such as soil and water, but they agglomerate to form much larger, much less biologically effective, silver particles which are non-toxic, non-ionic and have no history of being harmful to the environment or aquatic life. Furthermore, there is no possibility that silver nanoparticles can ever form silver ions, except in the presence of strong oxidizing substances.

Introduction:

Nanoparticles are difficult to produce; they are difficult to stabilize once they have been produced; they are not stable enough to exist in nature for very long. The purpose of this work is to prove that normal interaction of nanoparticles with various soils and different water sources is sufficient to change the size and dramatically decrease the biological activity. Specifically, the areas of examination will include experiments which will establish that silver colloids, which start out as nanoparticles, upon contact with the environment "grow" to much larger clusters, as indicated by their average particle size distribution, (a nanoparticle size measurement), and zeta potential measurements, which will establish that the zeta potential is outside of the range required for nanoparticle stability.

There are several other areas which, as recent articles have indicated, show misunderstandings about silver and its nanoparticles. At Arizona State University, Westerhoff and Benn (1) have reported "findings" which have **never** been observed during the last 10 years at Colloidal Science Laboratories (CSL). For example, they claim that nanosilver particles produce ionic silver when exposed to moisture. This is NOT true! This is tantamount to saying that silver metal is water soluble. At CSL, various forms of silver, ranging from solid silver metal to fine silver powder to colloidal nanoparticles, have been exposed to water for long periods of time with agitation. No increase in conductivity or silver ion concentration has **ever** been observed when silver metal in any form is treated with water. Silver metal requires chemical treatment with nitric acid or Aqua Regia to make silver ions. Westerhoff and Benn were working with commercially prepared socks which are prepared by treating the socks with solutions of silver in questionable form. There may have been some actual colloidal silver in the treatment solutions, but there most certainly were soluble silver compounds present, and, once the socks are rinsed, these are the substances which put silver ions back into the wash water.

As this report will show, the high biological effectiveness of colloidal silver does not persist in nature because the nanoparticles agglomerate as soon as they come in contact with the environment, specifically soil and water. Westerhoff and Benn admit that silver particles "clump" together in the fabric and in the wash water. That is precisely the point to be considered for environmental safety. How much "clumping" does it take so that the particles are no longer considered to be "nano", but much larger, therefore eliminating the continuing effect of high biological activity? These researchers, and others, are very quick to make the jump from colloidal nanoparticles, in socks for example, to ionic silver and its toxic effect, especially in zebra fish, and they speak as if the ions came from the colloidal nanoparticles. It is necessary to be very clear about this. If the researchers are finding silver ions in the wash water or anywhere else, ***then the silver ions were present in the original material***. This cannot be stated too strongly. Unless people have taken to washing their socks in nitric acid, the conversion of colloidal silver nanoparticles to silver ions is not possible.

The work at hand will examine four different environmental conditions which change the morphology and stability of silver colloids:

1. The effect of drainage of silver colloids through several soil samples.
2. The effect of interaction of silver colloids with different water samples.
3. The effect of exposure of silver colloids to sunlight.
4. The change in level of silver colloids with regard to biological activity.

Experimental:

Sample Selection

At the outset, the first two questions to be addressed were what environmental samples should be used and to what concentration of colloidal silver should these samples be exposed. Since this is a first attempt at this kind of information, it was decided to limit the environmental samples to the following:

1. Sand, taken from the New Jersey shore
2. Dirt, taken from central New Jersey,
3. Dirt, taken from Northern Pennsylvania
4. Water, local tap water from Westampton, NJ
5. Water, sea water, taken from the New Jersey shore
6. Water, taken from a northern Pennsylvania well

The soil samples represent some of the most common types found on the Eastern Coast of the United States. The sand is essentially an Entisol, which is a type of soil that is not subject to a great deal of chemical change and is common to areas where deposition and removal occur at regular intervals. The New Jersey soil is primarily an Ultisol, which contains clay, quartz, kaolinite and various iron oxides. The Pennsylvania soil is most likely a mixture of Alfisols and Inceptisols which are clays that are productive for growing most crops and are common to many areas. (2)

The water samples are Sea water, rich in many salts, NJ tap water, which has been through routine purification, and Pennsylvania well water, which most likely contains carbonates and nitrates. Therefore, the selection of samples should be sufficient to establish the effect of the environment on nanoparticles for this initial study.

Approximately 8 to 10 lbs of each environmental sample were collected. From these, 18 to 20 samples of 20.0 g each were selected, and these were randomized for the testing.

Next, in looking at the quantitative amount of colloidal silver to be used, it was decided that the initial test case should provide information with regard to an overabundance of nanoparticles being released to the environment, rather than just a trace amount. If the environment is not substantially altered by the overabundance, surely it will not be influenced by smaller amounts.

Preliminary work indicated that, at concentrations of up to 6 ppm, and probably higher, based on the weight of soil samples, no nanoparticles would survive. Therefore, a more reasonable amount, but still an enormously high concentration for a natural occurrence, was selected.

Colloidal silver samples at our disposal were of the dietary supplement type and average at least 20 ppm of silver. Most soil samples require 0.5 to 0.75 their weight in water to start draining. It was decided that the colloidal silver would be diluted 10 to 1 and then applied to each soil sample. This would make each sample contain a minimum of 2 ppm of silver nanoparticles, based on the weight of the soil. This would correspond roughly to dumping 27 liters of 20 ppm colloidal silver onto one ton of dirt. Since most colloidal silver customers are concerned with teaspoon and tablespoon quantities, it should be safe to say that this experiment covers something well above the worst case scenario.

Measurements:

In each experimental case, the selected sample of colloidal silver was mixed with the environmental sample and the change in particle size and zeta potential recorded after a specified time. The instrument used for this work was the Malvern Zetasizer, Model Nano ZS. Since the samples which were in contact with soil contained very large macroparticles and rocks, the samples all required vacuum filtration through grade 601 Ahlstrom filter paper to eliminate the particles which are 3 to 4 orders of magnitude greater than the ones of interest in this study. This filtration has no effect on nanoparticles.

For the trials in which the environmental samples were water, the colloidal silver was diluted 10 to 1 in the water in question.

Results:

The initial data in this section shows the properties of the colloidal silver used in these trials. This sample, selected at random, had 81% of its particles at 1.74 nm, and a Zeta potential of -31.7 mV. The data in Tables 1 through 6 show the results of the particles found in the **fluid** after the specified time of contact with the environmental samples in question. For example, it is shown in Table 1 that when DI water was filtered through the soil samples, no nanoparticles could be found, but only large particles on the order of 300 nm or more.

Table 2 shows that, after only 15 minutes of contact with the soil samples, a decrease in zeta potential, and the smallest particles have increased to the 3 to 8 nm range, and they still represent 80 to 90% of the total.

Table 3 indicates that, after a full 7 days of contact with the soil, but kept away from sunlight, the nanoparticles have increased 3 to 8 times in size.

In Table 4, these results are more dramatic, since the samples were all exposed to the sunlight for the 7 days, with the increases in size being 7 to 20 fold, and the smallest particles now representing only 30 to 40 % of the total.

For the data in Table 5, the colloidal silver was left in contact with the environmental water sample for 21 days in sunlight. As can be seen from the table, the particle sizes have significantly increased (3 orders of magnitude), with a corresponding drop in the zeta potential.

In Table 6, the samples were left in contact with the water samples instead of the soil samples for 7 days in the sunlight. The results of these tests show that each water sample also decreased the zeta potential and increased the particle size.

PROPERTIES OF COLLOIDAL SILVER USED IN TESTING

Smallest Particles, nm	Zeta Pot., mV	Total Ag, ppm	Ionic Ag, ppm
1.74	-31.7	21.4	9.60

TABLE 1 - DEIONIZED WATER

Filtering Medium	Smallest Particles, nm	Zeta Pot., mV	Total Ag, ppm	Ionic Ag, ppm
Sand	None found	-20.2	0.00	0.00
NJ Soil	None found	-1.5	0.00	0.00
PA Soil	None found	-31.3	0.00	0.00

TABLE 2 – COLLOIDAL SILVER – 15 MIN. CONTACT – 7 DAYS LATER

Filtering Medium	Smallest Particles, nm	Zeta Pot., mV	Total Ag, ppm	Ionic Ag, ppm
Sand	3.53	-20.6	1.14	0.00
NJ Soil	4.35	-22.2	1.57	0.20
PA Soil	8.30	-21.7	1.05	0.20

TABLE 3 – COLLOIDAL SILVER – 7 DAYS CONTACT – NO SUNLIGHT

Filtering Medium	Smallest Particles, nm	Zeta Pot., mV	Total Ag, ppm	Ionic Ag, ppm
Sand	5.4	-15.7	1.27	0.00
NJ Soil	9.7	-20.8	0.56	0.00
PA Soil	14.7	-2.8	0.17	0.00

TABLE 4 – COLLOIDAL SILVER – 7 DAYS CONTACT – SUNLIGHT

Filtering Medium	Smallest Particles, nm	Zeta Pot., mV	Total Ag, ppm	Ionic Ag, ppm
Sand	11.3	-22.8	0.94	0.00
NJ Soil	26.9	-22.2	0.41	0.00
PA Soil	34.2	-21.2	0.35	0.00

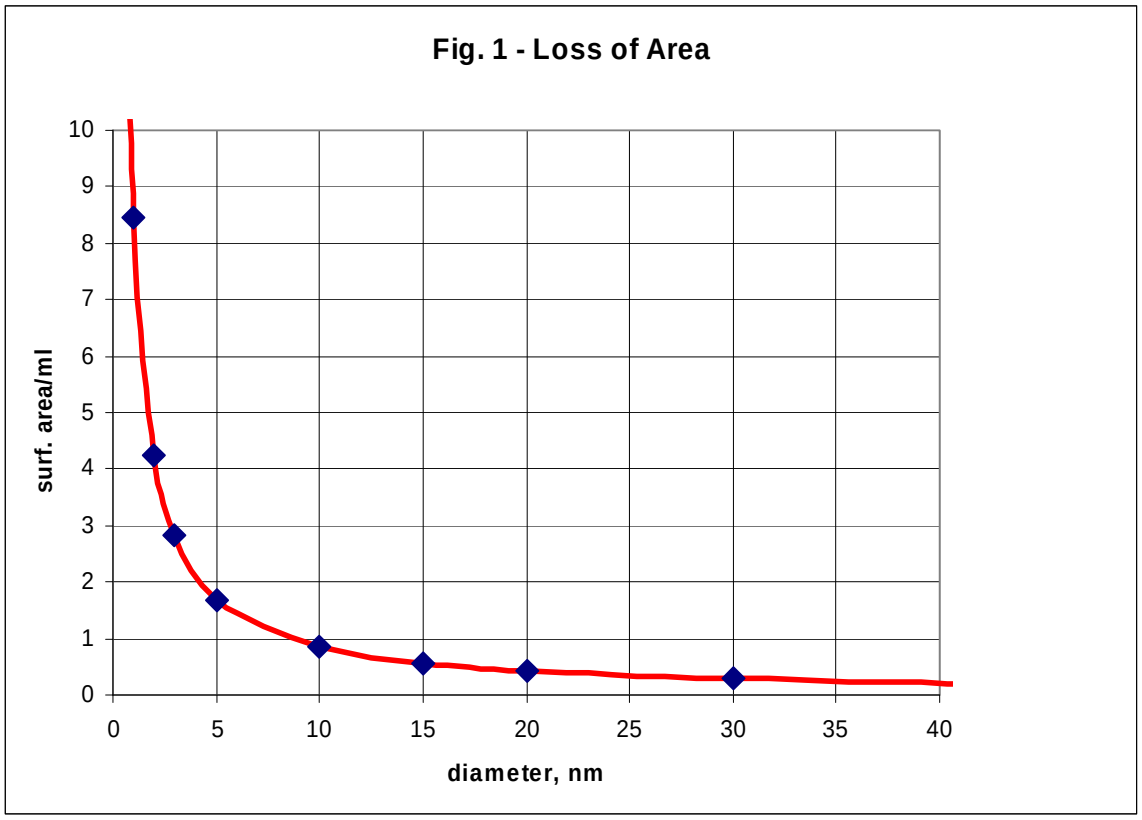
TABLE 5 – COLLOIDAL SILVER – 21 DAYS CONTACT – SUNLIGHT

Filtering Medium	Smallest Particles, nm	Zeta Pot., mV	Total Ag, ppm	Ionic Ag, ppm
Sand	>2000	-11.3	0.03	0.00
NJ Soil	>1900	-4.6	0.24	0.00
PA Soil	>1700	-7.6	0.39	0.00

TABLE 6 – COLLOIDAL SILVER – 7 DAYS CONTACT

Filtering Medium	Smallest Particles, nm	Zeta Pot., mV	Total Ag, ppm	Ionic Ag, ppm
Tap Water	113	-11.3	0.03	0.00
Sea Water	631	-4.6	1.14	0.00
Well Water	32.1	-15.7	1.47	0.20

While some of the changes in particle size seem small, one must realize that they represent large changes in loss of surface area and, since biological activity is proportional to surface area, this would correspond to large losses in biological effectiveness. In Figure 1, it can be seen that a change in particle size from 2 to 10 nm represents about an 80% loss in surface area for the same weight of particles. This is an approximation, since the exact morphology of the particles is not known. To make these calculations possible, an assumption has to be made that the particles are spherical and the spheres are close packed.



In a previous paper by F. Key and G. Maass (3), the nature of a colloid was described as being a suspension of very small particles which are stabilized by having a diffuse double layer of solution ions around them. The charge acquired by these particles gives rise to a potential difference (i.e., mutual repulsion) between them that keeps them separate and stabilizes the colloid. This potential difference is called the Zeta Potential, and has been described in countless books on electrolytic effects in solutions. When the colloid is composed of nanoparticles, the task of preventing the agglomeration is not an easy one.

As the previous paper pointed out, if the zeta potential is more negative than -30 mV, then the mutual repulsion between particles is sufficient to keep them separate and stabilize the colloid. When the zeta potential is between -15 mV and 0 mV, however, the particles agglomerate and flocculation or precipitation occurs.

In a 1996 report by the Department of the Interior by M. Elimelech and A. E. Childress (4), it was pointed out that for world average fresh water rivers, the concentration of common anions and cations across all normal pH ranges is sufficient to change the zeta potential range from about -10 mV to +5 mV, making agglomeration of nanoparticles occur. In sea water, the agglomeration would be even more pronounced.

Conclusions:

The points to be remembered are as follows:

1. This report has demonstrated that silver nanoparticles will grow to biologically far less active "clumps" even if one dumps 27 liters of 20 ppm colloidal silver on each ton of soil. In practice, this is an enormously high number which could not be expected to be reached realistically.
2. In spite of the number of manufacturers producing silver nanoparticles or claiming to be silver nanoparticles, because of the low concentrations in which these products are sold, the total amount which could be released in any part of the environment would still be expected to be very low.
3. As shown by all the experiments above, nanoparticles do not last as nanoparticles in nature for very long, but grow to harmless clumps of silver metal.
4. Silver nanoparticles are not water soluble, and therefore, silver colloids will not release silver ions into the environment.

Once agglomeration of the silver nanoparticles occurs, the result is simply silver metal; a harmless metal which has existed in nature from the beginning of our planet. Most people would not object to finding silver metal on their property.

References:

1. Environ. Sci. & Technol. 2008, 42, p 7025-7026
2. Dept. of Agriculture, Handbook 296, 2006
3. F. Key and G. Maass, "Ions, Atoms and Charged Particles", available at www.silver-colloids.com publications
4. Zeta Potential of RO Membranes by M. Elimelech and A. E. Childress, contract No. 1425-4-CR-81-19290

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Dr. Maass, a recognized problem solver, has the ability to determine the facts which cause phenomena, and to determine the methods by which they can be controlled.