Nanoparticles in Children's Sunscreens

2018 test results, health concerns and recommendations for parents, companies and regulators

Laboratory results commissioned by Friends of the Earth find engineered nanoparticles in all four major U.S. children's sunscreen products tested.

What are manufactured nanoparticles and why are they used in sunscreens?

Manufacturers are adding nanoparticles to sunscreens to make mineral-based sun-blocking ingredients like titanium dioxide (TiO2) and zinc oxide (ZnO) rub on "cosmetically clear" instead of white. These novel ingredients are being used despite a lack of appropriate oversight, labeling requirements or reliable safety information.

The physical and chemical properties of nanoscale materials, such as reactivity, persistence or bioavailability, can differ significantly from their larger-scale counterparts. The safety of nanoscale ingredients remains poorly understood and a growing body of scientific research raises concerns about their use in food and consumer products.

Nanotechnologies are the convergence of chemistry, physics and engineering at the nanoscale to take advantage of unique properties associated with small-sized particles. One nanometer (nm) is one billionth of a meter. One nm is roughly 100,000 times smaller than the width of a human hair.

[See the Friends of the Earth U.S. website for information about other consumer products that contain engineered nanoparticles including baby formula, popular food products and cosmetics.]

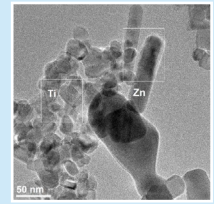
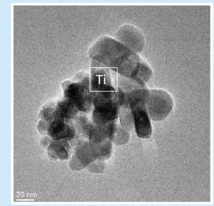
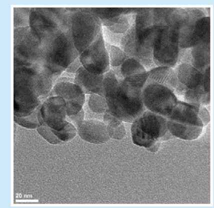
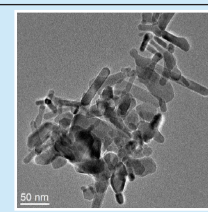
Major children's sunscreen brands contain nanoparticles

This analysis by Friends of the Earth reveals the use of engineered nanoparticles in children's sunscreens sold throughout the United States. We commissioned independent laboratory studies with a world-class nanotechnology research facility at Arizona State University to learn more about the presence of engineered nanoparticles in popular children's sunscreens.

Friends of the Earth tested a selection of four children's sunscreen products purchased from Walmart and Babies R Us. We found nanoparticles of potential concern in all four sunscreens tested, including nano titanium dioxide (TiO2) and nano zinc oxide (ZnO).

Nanoparticles are being used in hundreds of consumer products including sunscreens, cosmetics, baby formula and other food products ahead of safety assessment, regulation and labeling

Nanoparticles are now being used in nearly every personal care product on the market, including deodorant, soap, toothpaste, shampoo, hair conditioner, sunscreen, anti-wrinkle cream, moisturizer, foundation, face powder, lipstick, blush, eye shadow, nail polish, perfume and after-shave lotion (see the Friends of the Earth U.S. website for information about other consumer products that contain engineered nanoparticles). Friends of the Earth has also found nanoparticles of concern in baby formula, see "Nanoparticles in Baby Formula: Tiny New Ingredients are a Big Concern."

Product	Product type	Nanoparticles found (size and shape)	Laboratory analysis image of nanoparticles
Aveeno® Baby Natural Protection®	Children's Sunscreen	Nano titanium dioxide (TiO2) and Nano zinc oxide (ZnO) **Size:** 117.7 ± 21.6 nm 22.8 ± 4.2 nm **Shape:** rod (ZnO), spherical (TiO2)	
Banana Boat® Kids	Children's Sunscreen	Nano titanium dioxide (TiO2) and Nano zinc oxide (ZnO) **Size:** 64.1 ± 13.9 nm 29.9 ± 6.1 nm **Shape:** rod (ZnO) spherical (TiO2)	
Neutrogena® Pure and Free® Baby	Children's Sunscreen	Nano zinc oxide (ZnO) **Size:** 29.2 ± 5.1 nm **Shape:** spherical	
Thinksport™ Kid's Safe	Children's Sunscreen	Nano zinc oxide (ZnO) **Size:** 60.8 ± 19.1 nm **Shape:** rod	

Serious ethical and social justice concerns must be addressed in the regulation of nanotechnology, especially when it comes to products marketed for children. Children may be at greater risk of suffering health harms from exposure to toxics like nanomaterials because of their more vulnerable physiology.[1] Children's immune, central nervous, reproductive and digestive systems are still developing, and at certain early stages of development, exposure to toxicants can lead to irreversible damage which can increase risk of disease later in life. Workers involved in the manufacture of nanomaterials or products containing them also face increased risk of exposure to harmful nanomaterials.

Research and regulation are not keeping up with the pace of commercialization of nanotechnologies. Yet, governments, scientists and scientific bodies such as the U.S. National Research Council have presented more than sufficient evidence to justify a proactive regulatory regime and a properly funded research program that will effectively target areas of greatest environmental and health concern.

In stark contrast to the precautionary action being taken in the European Union, the U.S. response has largely been one of regulatory inaction. The U.S. Food and Drug Administration is charged with ensuring the safety of sunscreens and other food and cosmetic products, yet the agency has not developed binding guidance for industry on the use of nanomaterials in consumer products. U.S. consumers remain in the dark about the presence of nanomaterials in products they purchase. No product registry or labeling requirements are in place. The lack of established regulations allows products with nano ingredients to remain on the market while the public unknowingly takes on potential health risks. It is important for U.S. consumers to know that manufacturers are not required to list nanomaterial ingredients on product packaging in the United States.

Health concerns: Novel risks of nanoparticles

Materials manufactured at the nanoscale can exhibit different physical, biological and chemical properties than bulk materials (e.g. stable compounds can become highly reactive). One reason for these fundamentally different properties is that quantum physics governs at the nanoscale. But just as the size and chemical characteristics of manufactured nanomaterials can give them exciting properties for manufacturers, those same new properties — tiny size, vastly increased surface area to volume ratio, high reactivity — can also create unique and unpredictable human health and environmental risks.

Although very few nanoparticles have been adequately tested, from the limited data that is available, we have learned that their small size makes them more amenable to enter the lungs and pass through cell membranes.[2] Once in the blood stream, they seem to have unlimited access to all tissues and organs, including the brain, and possibly fetal circulation where they may disrupt normal cell activity.[3] When ingested, some nano

materials may pass through the gut wall and circulate through our blood.[4] It has been demonstrated that nano TiO2 can be absorbed by the gastrointestinal tract once in the body and can be distributed to various organs.[5] Animal studies suggest that some nanomaterials can cause inflammation, damage brain cells and cause pre-cancerous lesions.[6]

Specific nano titanium dioxide (TiO2) health concerns

Two of the children's sunscreen tested contains nano TiO2 (Aveeno® Baby Natural Protection® and Banana Boat® Kids). In contrast to bulk particles of titanium dioxide, nanoscale titanium dioxide is biologically very active. Studies show that titanium dioxide can damage DNA,[7] disrupt the function of cells, interfere with defense activities of immune cells and, by adsorbing fragments of bacteria and "smuggling" them across the gastrointestinal tract, can provoke inflammation.[8] A single high oral dose of titanium dioxide nanoparticles was found to cause significant lesions in the kidneys and livers of female mice.[9] Nano titanium dioxide is highly mobile in the body and has been detected in both humans and animals in the blood, liver and spleen.[10] A 2015 study found that food grade TiO2 can be absorbed in the bloodstream.[11] A study using pregnant mice found that nanoparticles of titanium dioxide were transferred from mother to offspring and were associated with brain damage, nerve system damage and reduced sperm production in male offspring.[12]

The European Commission's Scientific Committee on Consumer Safety recommended that certain nano titanium dioxide (TiO2) ingredients not be used in sunscreen because they strongly react with sunlight to produce free radicals.[13] It also recommended that nano TiO2 and nano zinc oxide (ZnO) not be used in powder or sprayable products because of the toxicity risk associated with inhalation.[14]

Specific nano zinc oxide (ZnO) health concerns

All children's sunscreen products tested contain nano ZnO. A 2010 study by Gulson et al. found small amounts of zinc from sunscreen in the blood and urine of human trial found small amounts of zinc from sunscreen in the blood and urine of human trial participants.[15] Some scientists have argued that since the amounts of zinc found in the blood and urine were small, there is no cause for concern.

However, one interesting finding reported in a later paper by Gulson et al. was that the highest levels of zinc isotope were actually found nine days after the five-day application period ended. The scientists were not sure why this was the case. They suggested that the nanoparticles could be accumulating in the skin and acting as a long-term chemical reservoir. This is obviously of concern if they react with sunlight and produce free radicals while they are there. Or, they could be accumulating elsewhere in the body — such as the liver or muscle.[16]

The study was not able to show whether the zinc oxide was absorbed in nanoparticle form or whether it dissolved, so this requires further research. Zinc oxide is fairly soluble so it is possible that it dissolves in the body. This may mean that the body's defenses will be able to deal with it — since our body has mechanisms to regulate zinc levels. A study has shown that in the lab, white blood cells may be able to take up and dissolve zinc oxide nanoparticles.[17] However, further studies are needed before conclusions can be drawn about what really happens in the body.

Furthermore, these findings cannot be extrapolated to other nanomaterials used in sunscreen such as titanium dioxide. Titanium dioxide, for example, is less soluble than zinc oxide and not a chemical that our body is naturally exposed to.

Can nanoparticles be absorbed by skin?

Though studies to date suggest mineral nanoparticles in sunscreen may not fully penetrate intact skin, children are likely to ingest nanoparticles from sunscreen during application. We don't know if nanoparticles would more likely penetrate thinner skin, e.g. in elderly people or babies, or whether deep penetration is always necessary to elicit toxic effects.

Environmental concerns

A 2014 study published in the American Chemical Society's Journal of Environmental Science and Technology demonstrates the harmful effects of nanoparticles from sunscreens on ocean ecosystems.[18] The researchers found that when nanoparticles of titanium dioxide and zinc oxide react with ultraviolet light in water, they create hydrogen peroxide, which can stunt the growth of phytoplankton.[19] Phytoplankton are a critical species of tiny algae at the base of marine food chains, sustaining animals ranging from small fish, which feed dolphins and other sea life, to whales. Other studies have demonstrated the potential for nano TiO2 in sunscreens to have a negative impact on marine ecosystems including another 2014 study that shows potential decrease of coral populations due to bioaccumulation of TiO2 in microflora of coral.[20]

Some “non-nano” sunscreens may actually contain nano-ingredients

There is a growing market for nano-free sunscreens, with many brands choosing to market nano-free options. Accordingly, sunscreen ingredient suppliers have been marketing ingredients to sunscreen brands as nano-free. Unfortunately, it seems that the claims of some sunscreen manufacturers and ingredients suppliers may not be accurate. For example, the manufacturer of “Thinksport Kid’s Safe Sunscreen SPF 50+” claimed its product contained non-nano ZnO (as of February 2018 this product included non-nano labeling). Our testing found that the average particle size in this product is 60.8 ± 19.1 nm (a size that is considered nanoscale). It is possible that this manufacturer and others are not aware of this problem. However, it is concerning, and manufacturers should closely monitor their ingredients to ensure accuracy if making non-nano product claims.

Conclusion and recommendations

Our test results demonstrate that many sunscreens marketed for our most vulnerable population, babies and children, contain engineered nanoparticles that a growing body of science indicates may be harmful. These and many other products and food intended for children (and the rest of us) are entering the market ahead of adequate safety assessment, oversight and labeling.

What industry and government must do

- **Test and require approval for these products before commercialization**
  Because of their capacity to have fundamentally different properties, nano-ingredients in sunscreens should be classified as new chemicals; they should be regulated as new products and new ingredients that require pre-market safety assessment. Governments should review all relevant data and approve the safety of these substances before commercialization is permitted.

- **Transparency and labeling**
  Industry should make information on nanomaterial ingredients in its products available to the public. The fundamental right of consumers to make informed purchasing choices is compromised by the lack of transparency regarding the use of nanomaterials in nano-formulated sunscreens and other products and the limited disclosure of information regarding safety. At a minimum, consumers need a list of ingredients, including any nanoscale ingredients in the products they buy and use on themselves and their families. In addition to that, however, nano-ingredient labeling is necessary for health professionals and others in order to assess causation and provide traceability in the event that adverse health or environmental effects occur.

- **Support much more vigorous EHS research**
  Publicly available, peer-reviewed, and independent studies of human health and environmental impacts are urgently needed to protect public health and the environment and provide the basis for adequate regulatory oversight of nanomaterials. Crucially, the lack of data or evidence of specific harm should not be a proxy for reasonable certainty of safety.

- **Look at the whole life cycle**
  Because of their presence in all environmental media, nanomaterials affect every area of environmental concern. Environmental impacts can occur at any stage of a nanomaterial’s life cycle — R&D, manufacturing, transportation, product use, recycling, disposal or some time after disposal — and a nanomaterial life cycle framework helps assess how various statutory frameworks apply and where regulatory gaps exist. To address all possible exposures and environmental impacts adequately, a nanomaterial’s complete life cycle must be considered.

- Manufacturers should refer to the Nanomaterials Policy Recommendations published by a coalition of domestic and international advocacy groups, including Friends of the Earth, to help inform companies and consumers about the potential risks of nanomaterials.

- Manufacturers and policymakers should also refer to our guidance document published in 2007 called Principles for the Oversight of Nanotechnologies and Nanomaterials (more than 70 groups from six continents have endorsed these principles).

Recommendations for parents and other consumers:

Many parents are choosing to avoid sunscreens with nano-ingredients in an effort to reduce their children's exposure to these potentially toxic ingredients. Apart from nanomaterials, some other sunscreen ingredients, such as oxybenzone, a hormone disruptor,[21] also pose health concerns. Some of these ingredients are also hazardous to coral reefs.[22] However, consumers need to know that engineered nanoscale zinc and titanium oxides are not the only choice and are not necessarily the most effective or safest choice for sun protection.

Besides several different carbon-based active ingredients, consumers can also look for larger-scale, more opaque metal-oxide based sunscreens, although without mandatory labeling these may be very hard to find (at least in the U.S.).

We recommend using a nano-free zinc-based SPF 30+ broad-spectrum sunscreen in conjunction with protective clothing, a broad-brimmed hat, sunglasses and shade to stay sun safe. You can also urge sunscreen and other companies that market products for children to avoid the use of nanomaterials. In addition, we need your help to push regulators to make sure products with potentially risky nanomaterials do not hit store shelves without labels and ahead of proper safety and environmental assessment. For more information and to take action, see our website: www.foe.org.

Testing methodology

A careful analysis was conducted for each sample. Tiered approaches were used for the systematic detection, quantification and characterization of nanomaterials in these products. Specifically, products were first subject to the analysis by an X-ray fluorescence (XRF) analyzer (Niton XL3t GOLDD+, Thermo Scientific) to detect the presence of titanium and zinc elements, which are reported as a weight percentage. Scanning (SEM) or transmission (TEM) electron microscopy was further utilized to image the size, shape and morphology of nanomaterials in, or extracted from, each product. Energy-dispersive X-ray spectroscopy (EDS) was used in conjunction with electron microscopy to confirm the chemical composition of nanomaterials. The number and dimensions of nanomaterials are reported along with these images.

Prior to TEM characterization, TiO_2 and/or ZnO particles were extracted from the sunscreens. The materials were briefly extracted by dichloromethane (DCM) solvent through repeated sonication and centrifugation to remove organic constituents. The extracted pellets were then rinsed by ultrapure water to remove salts and surfactants. The extracted materials were finally resuspended in isopropanol and dropped onto TEM grids for analysis.

Particle size analysis was performed using ImageJ, a free image-processing program available from the National Institute of Health. The number of primary particles was noted and these were sized. The scale bar was used to set the scale for calculating each particle's diameter. In the case of high aspect ratio structures, both a width and length were measured. Error is reported as +/- 1 standard deviation. Percent of particles below 100nm was calculated based on the primary particles imaged.

Additional details about the study are included in the Analysis Report prepared by the laboratory.

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