FAQs Concerning Zinc Oxide (PW 4) in Oil Paints (2018)

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Zinc Oxide's Use in the Past

When did artists start using Zinc White?

Zinc White was first introduced in watercolors in 1834, and was available as a single color in oil paint in 1860, although it existed in blends and mixtures for at least a decade before that.

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Why was Zinc used in oil paint, what does it offer?

Zinc provided several advantages that were attractive in the past:

- Zinc Oxide was the first major alternative to lead white, whose health risks were well
 documented and of increasing concern in the 19th century, and was championed as a safer
 choice for use in both artist and commercial paints
- Produced a harder, more durable surface, especially when added for paints that produced notoriously soft films, like Titanium White.
- Imparted a dense, bodied feel to paint when being milled.
- Shown to lessen the yellowing of oil paints, particularly for both Lead and Titanium Whites.
- Was not prone to the darkening that lead paints experienced when exposed to Sulphurcontaining air pollution – a problem in 19th and early 20th centuries. This was particularly important in commercial paint industry.
- Acts as a mildewcide and adds UV protection to paint films. Still used for UV protection in sunscreens.
- Helps keep pigments in suspension and acts as a dispersing agent when milling.
- It is more translucent that other whites and so allowed for brighter, cleaner tints.
- Cooler in color (more bluish) than other whites

Are older paintings containing Zinc Oxide falling apart?

It is important to keep in mind that most paintings done over the last hundred years have some level of zinc, often at low percentages, and still appear to be fine. That said, the full extent of the issue is not known and is the subject of ongoing research. Problems can range anywhere from very small, limited patches of cracking, which might not threaten an entire work, to major problems with delamination. Issues with zinc can also be hidden underneath the surface and not readily visible. So more research is needed to account for this as well. That said, we also do not want to minimize the potential problems. At the present time conservators do consider this issue a major concern as museum collections have turned up significant number of instances where cracking and cleavage have been linked to the use of zinc oxide.

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Why do some older paintings look good?

This is still being investigated and researchers are trying to understand the roles that paint formulation, changes in particle size and shape, environmental conditions, and painting techniques all play. Also keep in mind that issues with zinc can be hidden under the surface and a painting can look fine until it gets rolled, stretched, suffers a sudden blow or dramatic change in the environment, or some other source of sudden stress.

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How does zinc oxide cause cracking?

• The actual mechanisms which cause zinc to form a brittle paint, and have a high risk of cracking or delamination, are still a subject of research but a broad picture starts to emerge. Most oil paints, as they cure, form an intricate web of intermingled, crosslinked chains of fatty acids. However the particular crystalline structure of zinc oxide interferes with this process; its stiff and plate-like layers are densely packed and entrap unsaturated free fatty acids, preventing them from oxidization and crosslinking. They are essentially cut off from connecting to the rest of the polymer network. Because of this, the film remains structurally fragile, with hard and brittle formations only weakly linked to each other. This makes the zinc-bearing paints very prone to cracking, as well intralayer cleavage, a pulling apart that happens inside a single layer of paint, as opposed to separating from another layer below it.

In addition, zinc oxide is also an extremely reactive pigment that rapidly creates metallic soaps from the fatty acids found in drying oils. This is a process known as saponification. The dangers from these soaps are two-fold. They can form agglomerates or pustules that interfere with the appearance of a painting by becoming mobile and breaking through to the surface. In this they are not unlike lead soaps, which have shown similar issues, albeit over a longer period of time. More importantly, these zinc soaps display a preference to accumulate at the interfaces between layers of paint, or between the paint and ground. These accumulations of soaps at these interfaces have been linked to instances of delamination and peeling.

What Has Been GOLDEN's History with the Issues of Zinc Oxide?

• GOLDEN became increasingly involved in the issues surrounding Zinc Oxide and oil paints once we acquired Williamsburg Handmade Oil Colors in mid-2010. At that time there were still only a handful of modern conservation studies focused on the brittleness of Zinc Oxide, although the topic had been gaining attention after 2007, when a 28-year study by Marion Mecklenburg, Senior Research Scientist at the Smithsonian, began to be publicized and discussed (Mecklenburg 2005, 2007). After consulting with Mecklenburg and other colleagues in the field, it was suggested that reducing the percentage of zinc wherever possible should lower overall risk and increase performance. While there was never evidence of a specific 'safe level' one could use, it was suggested to us and others that 15% was a reasonable target to aim for. This is something we did almost immediately, with the exception, of course, of Zinc White itself. With these new formulations in place, we soon started longer-term, controlled testing, although for oil paints, even initial results can unfortunately take many years to bear fruit and validate our decisions.

The core issues with zinc oxide, namely its tendency to form brittle films and increase the risk of cracking, have been well-known since the pigment was introduced in the 19th century. Those aspects in themselves were not particularly new, and research confirming this not particularly alarming. However, it had also long been assumed by painters and researchers alike that smaller additions were not only safe but could also be shown to play a desirable and beneficial role; a position that even today enjoys a broad following. Against this backdrop, any new research needed to overcome more than a century of practice that seemed to be solidly supported by a wealth of empirical evidence. It was and remains a particularly high bar to overcome, and one wants to approach overturning these longstanding positions with particular care.

We also want to point out that we are not completely eliminating zinc oxide from our line. Instead, we will be removing it from all mixtures where we feel it is not needed, as one way to responsibly reduce risk, while continuing to offer it in 150ml and larger sizes for both Zinc and Titanium-Zinc White. The larger sizes will be clearly labeled to make sure artists are aware of the potential risks in using these colors.

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Which Williamsburg Paints Are Being Discontinued or Reformulated?

 Which of your paints contained zinc? Which ones have newer zinc-free versions, and which are being discontinued?

Colors that Contained Zinc Oxide (PW 4):

These colors have new zinc-free versions available:

Brilliant Yellow Pale Canton Rose Jaune Brilliant King's Blue Montserrat Orange Naples Yellow
Naples Yellow Reddish
Persian Rose
Provence Violet Bluish
Provence Violet Reddish
Sevres Blue
Turquoise
Zinc Buff

These colors are being discontinued:

Silver White SF Silver White SF Titanium-Zinc White Zinc Buff Yellowish

These colors will be sold in 150ml size only:

Titanium-Zinc White Zinc White

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Ongoing Availability of Zinc Oxide in Williamsburg

Why will Williamsburg still offer Zinc White and Titanium-Zinc White?

Zinc White continues to be an important paint for a lot of artists, who use it as a way to counter the yellowing associated with Titanium and Lead White, and as a more translucent mixing white for creating cleaner, brighter tints. During this period when research is still ongoing and inconclusive, we feel it is more important to educate artists about the risks of using zinc oxide than to remove it completely from our offerings. It remains, after all, one of the most important white pigments in continual use for over a hundred and fifty years. This situation is not unlike other art materials, such as rabbit skin glue and Alizarin Crimson, which have been used for very long periods of time despite being linked to well-known problems.

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Why will Williamsburg only sell 150ml tubes of Zinc White and Titanium-Zinc White?

While we are committed to making Zinc and Titanium-Zinc White available to artists, we also wanted to limit the number of products that contained zinc oxide, including the range of sizes they came in. This will hopefully reduce the casual or inadvertent use of these products while still making them available to those who truly want them. Larger size 150 ml labels also allow for a clear warning statement to support artists' awareness of zinc issues.

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What percentage of Zinc Oxide is in your current Titanium-Zinc White?

While there is currently no acknowledged safe level of zinc in conservation literature, we have continued to reduce the percentage to a minimum and still achieve the benefits of adding Zinc Oxide to Titanium White – namely less yellowing and a harder, less tacky surface. Starting in February 2018 that percentage has been set at 2% by weight and we will continue to make further adjustments as needed based on testing and research.

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What to Do With the Zinc I Have?

What should I do with any Williamsburg paints I own that contain zinc?

We are happy to exchange any of our paints containing Zinc Oxide for one of our new zinc-free formulations or for any other color of similar value.

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How can I tell if there is Zinc Oxide (PW 4) in my paints?

We list all the pigments for each of our paints on the label, where you would find both the common name, "Zinc Oxide", as well as the official Color Index Name, "PW 4". This practice is followed by most manufacturers but is not a legal requirement. If you have any questions about any of your paints, we recommend contacting the manufacturer of that brand for more information.

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Zinc in Other Mediums

• Does Zinc in acrylic or watercolors have the same issues?

No. The problems with Zinc Oxide are unique to oil paints, where it interacts with free fatty acids found in the drying oil to form metallic soaps. Because acrylics do not have fatty acids, this particular issue is avoided altogether. That said, one area where more research is needed is whether any zinc oxide in an acrylic film could interact and cause issues with a layer of oil paint applied on top. Until this can be fully investigated, we do not recommend using acrylics containing zinc oxide under oil paints.

Pigments That Are Similar

What other white can I use that is most similar to zinc?

In terms of translucency, the best options are Flake White (made with basic lead carbonate) or our Safflower Porcelain White (made with PW5, lithopone). Neither of these, however, will lessen yellowing nor appear as cool in temperature – properties unique to Zinc White.

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Does Zinc Sulfide have similar issues to Zinc Oxide?

No evidence points to them having similar issues. Unlike Zinc Oxide, Zinc Sulfide is considered chemically stable and does not form metallic soaps when exposed to fatty acids. And ultimately it is the formation of these metallic soaps that causes the problems we see with Zinc Oxide.

Zinc Sulfide is most often encountered as a component of PW5, lithopone, which is a complex coprecipitation of barium sulfate and zinc sulfide and the pigment found in our Porcelain White. Lithopone has been used in coatings for almost 150 years and during this time has not been linked to issues of cracking or delamination.

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Best Practices and How to Minimize Problems

What are the Best Practices for Using Zinc?

Coming up with a set of Best Practices is difficult on several fronts. First, it is impossible to predict what any one painting will do, especially given our current understanding and the complexity of the issues involved. Secondly, current conservation research has not identified a safe level of zinc, or reached consensus on all the factors that might lessen or increase the risk of cracking and delamination. So what remains is undeniably broad and general.

To limit problems linked to the use of Zinc Oxide, we would recommend the following:

- Use zinc sparingly and only when needed.
- Do not use it in underpaintings or lower layers.
- Keep applications thin. Do not apply thickly.
- Avoid stretching, bending, or flexing of the surface.
- Limit shipping whenever possible due to the potential for vibration, sudden shocks from dropping, or extreme changes in environmental conditions.
- Protect the paintings from anything pressing from the rear by using a backing board. Likewise, when shipping or moving, protect the front by use of a travel frame or shipping collar.
- Maintain the painting in as stable an environment as possible, following similar ranges recommended for museums and galleries of 16-25°C (60-77°F) and 40-60% RH.

• Work on an inflexible support. Ideally, one that is unresponsive to humidity and temperature, such as aluminum composite panel.

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• I used Williamsburg paints containing Zinc Oxide in my painting. What is going to happen to it? What about works in galleries and collections?

There is really no way to predict what might happen to any particular painting. There are simply too many variables. Keep in mind that the majority of paintings containing some level of zinc still appear to be fine, and there might be any number of factors beyond simply using Zinc Oxide that could greatly lessen or increase the risk. The best thing to do at this point is to keep it in a stable environment and try to avoid any flexing, stress, or keying out of the painting. Never roll the painting and try to limit any shipping, where the piece will be exposed to vibration and shocks. Anyone who currently owns or deals with oil paintings containing Zinc Oxide should handle them with extra care and monitor them closely for any signs of cracking or cleaving. If signs of these appear, a conservator should be consulted about possible treatments.

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• Can I remove the paint from my painting and start over?

We would not recommend this as a reliable solution.

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Can I just paint a new layer of paint or can I put varnish on top to stop the flaking?

No. Painting on top of zinc oxide can cause those layers to crack or delaminate later on, so we do not recommend it, while varnish will not inhibit or stop the processes that make zinc oxide brittle.

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What if I add a lot of flexible binder into my zinc paints?

This remains unknown, although some current research and literature point to heat-bodied oils, such as Stand Oil, as potentially being helpful.

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Art Conservation / ASTM

What studies can I read from conservation or other sources?

A complete bibliography of major articles on the issue of zinc oxide is included in the Supplementary Materials at the end of this document.

Unfortunately, very few of those articles are available online for easy access. However the following can provide a good introduction to some of the literature that can be easily accessed:

Mecklenburg, M., Tumosa, C. S., Vicenzi, E. P. (2010) The influence of pigments and ion migration on the durability of drying oil and alkyd paints. In Cleaning 2010: New insights into the cleaning of paintings, ed. L. Fuster-López, A.E. Charola, M. F. Mecklenburg, M. T. Coménech-Carbó. València: Universitat Politènica de València. 27-28.

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Osmond, G., Ebert, B. Drennan, J. (2013) Zinc oxide-centred deterioration in 20th century Vietnamese paintings by Nguyễ Trọng Kiệm (1933–1991), AICCM Bulletin Vol. 34, Issue 1,2013 https://aiccm.org.au/sites/default/files/docs/Bulletin2014/BulletinVol34/6932%20AICCM%20Bulletin%20v34-osmond.pdf

Pratali E (2013)Zinc oxide grounds in 19th and 20th century oil paintings and their role in picture degradation processes, CeROArt [Online], EGG 3 | 2013, https://ceroart.revues.org/3207

Anderson, C., Taube, M., Vila A., Baadsgaars, E. (2016), Zinc, Paint loss and Harmony in blue: Degradation problems in Peder Severin Krøyer's paintings and the possible role of zinc white, Perspective, The National Gallery of Denmark http://www.re-ad.dk/ws/files/60370947/zink paint loss and harmony in blue 9.pdf

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Are Conservation groups expected to speak out on this issue? Are they already? If not, why not?

They are, and a lot of the current articles and presentations conferences are increasingly being devoted to this topic. GOLDEN is committed to staying up to date on the newest developments in this area, attending the annual American Institute of Conservation, and relevant conferences put on by the International Institute of Conservation, and will be in attendance at the major international conference on the Conservation of Modern Oil Paintings, in Amsterdam, Netherlands, in 2018, which will have a large focus on this topic. Please also see the complete bibliography in the online version of our Just Paint article on Zinc for a better sense of the conservation literature and the extent of their concerns about zinc oxide.

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Will this issue be addressed in the ASTM Quality Standard for Oil Paint (D 4302)?

No, not currently, but we feel this will likely need to be a future topic that the ASTM Sub Committee on Artists' Materials will need to address. In the meantime, we encourage you to let all paint manufacturers know that this issue is important to you and that you would like to see more action taken by the ASTM Committee in this area.

Definitions and Examples

Glossary

- Backing Board: A rigid board attached to the back of a painting's frame or stretchers.
 (see <u>Backing Boards for Paintings on Canvas Canadian Conservation Institute (CCI) Notes</u>
 10/10 for more information)
- Cleaving/Cleavage: A separation between layers. In painting, any separation between paint layers, between paint film and ground or between ground and support. Cleavage occurs where adhesion between layers has deteriorated; it is commonly due to faulty materials or improper methods of application. It causes blisters, wrinkles, and flaking of paint. (Mayer, 1969)
- Crack: A visible separation on a surface that extends through one or more layers. Cracks may be
 due to stress, pressure, temperatures, or humidity variations or mechanical defects. Cracks are
 described by the size (hairline, wide) and direction (parallel, radial, spiral, etc.). See for
 example <u>crackle</u> and <u>crazing</u>. (CAMEO)
- Delamination: The separation of one or more layers in a multiple layer material. In most cases, delamination indicates a failure within the adhesive or with its bond to the adherend. (CAMEO)
- Interlayer cleaving: A separation or cleaving (see above) that happens between different layers
- o Intralayer cleavage: A splitting that occurs within a single layer
- o **Peeling**: The delamination of paint from a surface
- Flaking: The separation of small, thin pieces of a coating from its substrate. (AIC Wiki)
- Shipping collar: Another term for a travel frame.
- Travel frame: A raised collar attached to the back of a frame so that any protective covering or wrapping material does not touch the painting during storage or shipment. (see <u>Wrapping a</u> <u>Painting – CCI Notes 10/16</u> for more information)

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• Can you show me pictures?

Please refer to our Just Paint article, *Zinc Oxide: Warnings, Cautions, and Best Practices*, as well as our online JustPaint.org article, *Zinc Oxide - Reviewing the Research*, for images of our testing.

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