

Please Stop Telling People That Corks 'Breathe'

- Part 1 of 2

Who would have thought that wine corks would be so controversial. The voluminous reader response to our features on the pros and cons of corking wine continues long after the articles have appeared. Our learned guest columnist, Richard Grant Peterson offers some empirical evidence to prove that corks have been used for ages because...they work.

by Richard Grant Peterson, PhD

March 10, 2008

Sad to say, most articles about the pros and cons of using corks for closing wine bottles end up parroting at least one absolute untruth. Contrary to anything mystic that you may have heard, I can tell you categorically that sound corks do *not* breathe air.

I have published a simple statement to this effect many times over the years, hoping it would be memorized by all, but alas, here it is one more time:

"Show me a cork that breathes and I'll show you a bottle of vinegar."

"Show me a cork that breathes and I'll show you a bottle of vinegar." I believe I first published that in the early 1960s and it has stood the test of time scientifically. But it seems not to have withstood the unending human quest to keep regurgitating old wives' tales into the untrue lore of wine.

I agree that it sounds glamorous to say, "closures 'breathe' at some mysterious rate which controls the process of bottle-aging precisely" (as if any winemaker ever knows exactly when each bottle of wine will be opened and can time the "aging" to match the consumer's whim). The problem I have with this old fable about corks breathing is that it's pure B.S. It's high time we stop seeing it reprinted.

We did the lab work almost five decades ago! It's been repeated more than once in Australia and all those who've checked this in the lab tell the same story: Sound corks *do not* transmit oxygen! Even more important, neither is oxygen transmission through closures what we want! Wine aging and the development of "bottle bouquet" during bottle age is anaerobic, never aerobic. The effect of continued aeration of wine in bottle is something quite different, and antagonistic to the development of bottle bouquet. Aeration of wine by a leaking closure does at least three things, in steps:

- (1) It oxidizes and removes the SO₂ protection from the wine, then;
- (2) It oxidizes and removes the tannin, pigment and other polyphenolic protections from the wine;
- (3) It oxidizes and destroys the flavor of the wine, followed closely by browning, polymerization of the oxidized pigment and other polyphenols, etc.

This completes the oxidative destruction of what would have been a perfectly preserved bottle of fine wine if the closure hadn't leaked air into the bottle.

- (4) Separate from the above oxidation reactions, air, in the presence of certain bacteria, (which wine always has), allows them to grow in the wine and turn it from wine into vinegar.

I'd like to take the space here to answer one of the most prevalent questions I hear from the wine drinking public. There is a great deal of confusion about the 'good aeration' of decanting before drinking an old bottle of wine - and the 'bad aeration' that can lead to oxidation. Most people don't understand either one of them, but neither is very difficult.

First, you need to recognize something that most people have never thought about: Everything we eat or drink is bathed in air as it passes over our taste (& nose) receptors. We are used to whatever the taste of air in food and drink is. We like it. But old wine is not like most foods that we eat or drink, at least not when the bottle is first opened. Old wine has been sealed up inside a bottle for many years and something changes during that time. The wine is no longer 'bathed in air' and it will taste funny at first, until we bathe it in air before drinking. We live in a world of chemistry and that is sometimes confusing. You see, old wine has been living in a 'reducing atmosphere' in the sealed bottle, which is the chemical opposite of aeration (an aerated atmosphere).

DO NOT MISUNDERSTAND: AERATION IS NOT THE SAME AS OXIDATION.

When you aerate an old wine, you mix air into it and that makes it easy to drink and enjoy. Trust this for a minute and it will become clear. Freshly dissolved air doesn't oxidize the wine immediately - it cannot, until it has had time to do so. The oxidation of wine by dissolved oxygen takes place slowly and you won't see the effect for several hours after aerating, maybe even overnight.

Once a wine has become oxidized, it is dead and cannot be revived because the oxygen has attacked flavor and other components of the wine and changed them into something other than wine flavor. Think of an aerated wine as simply mixed with air, where the air hasn't had time enough to attack and oxidize the wine as yet. Your job is to drink the wine while it is aerated but well before it could get oxidized.

In graduate school wine research, one of the enduring chemical truths I learned from a genuine master, Professor Maynard A. Joslyn, was that "Wine in a closed container quickly becomes 'reducing' on its own (accept this chemical term for the moment), and wine lives naturally in a 'reducing atmosphere' in sealed barrels, tanks or bottles." That is extremely important to know if you want to understand bottle aging.

I've opened many bottles of 30+ year old Cabernet wine and, nearly always, those wines have a 'reducing funk' at the time they are first opened. There is no H₂S - they aren't "reduced" in that sense, but only living in a 'mildly reducing' atmosphere. They just don't smell right at first. All they need is to be decanted to remove solids, if present, and then aerated by being poured, with splashing, back into the (rinsed) original bottle. Then allow the wine to stand in its now aerated state for another few minutes before serving.

The reducing funk disappears for good reason: We are used to whatever the taste of air in food and drink is. We like it and we want to drink our wine mixed with air, same as any other food or drink. Since old wine has been sealed up inside a bottle for thirty years in a 'reducing atmosphere' - the chemical opposite of aeration - we have to get it into an aerated atmosphere before drinking. All we have to do to bring out the goodness of the wine's aroma and bouquet is aerate a little to re-establish the aerated surroundings we want to taste it in and, presto, decanting does the trick.

I tell you this so that even non-chemists will understand the truth that wine aging never takes place under aerated conditions. It's because those are the conditions that will lead only to oxidation in time, and destruction of the good things in wine. In a perfectly sealed bottle, the wine will not oxidize but will develop bottle bouquet - which it cannot do if that #%\$&@! destructive oxygen is present.

Okay, I'm a realist. I know that some people are going to continue defining "wine aging" as 'slowly oxidizing it until the wine isn't drinkable any more', if they want to. That's what those idiots do when they promote deliberate oxidation of your wine through selectively defective closures, although I don't think they do it on purpose - it's just that they lack chemical common sense.

Corks Do NOT Breathe - Part 2 of 2

by Richard Grant Peterson, PhD

October 13, 2008

Editor's Note: We received many great questions in response to guest columnist Richard Peterson's first plea to wine writers and cork promoters, asking them to cease telling people that wine corks "breathe" (Please Stop Telling People That Corks 'Breathe' 02/10/08). In this follow-up piece, Dr. Peterson hopes to answer those questions and give you the full scoop on how corks interact with wine in the bottle.

Cork Class is now in session. Read on...

Development of beautiful "Bottle Bouquet" is a primary goal of long term wine cellaring. It's well established that bottle bouquet requires the absence of oxygen to develop. Wine would die early and fail to age properly in bottle (being unable to develop bottle bouquet) if corks were to breathe air, so it's a good thing they don't. Although sound wine corks don't breathe, I admit they have a confusing way of

showing it. Just imagine: corks never inhale, and they exhale only once (right after bottling). The exhale is slow, lasts a few weeks and is only a partial one. To understand this, look at the cork structure.

Corks are cut from the thick, non-living bark of cork oak trees, *Quercus Suber*, which grow naturally on land around the Mediterranean Sea. The bark of cork differs from that of other trees in that most tree bark contains fibers running lengthwise like the wires in a cable. Cork bark does not. Rather, cork bark is made up completely of myriads of tiny cells, each imprisoning within its walls a microscopic bit of air. Those bits of air are natural, having been imprisoned there as the bark cells grew on the tree. There are about 200 million minute cells in a one inch cube of natural cork, the cells averaging 1/1000 inch in diameter. Each cell is separated from its neighbors by a thin, thread-like but extremely strong membrane of resinous materials which binds the cork cells together. Just over 50 percent of the volume of a piece of cork is this captive air within the tiny cells.

Remarkably, each cork cell is tetrakaidecahedral (14 sided). The math majors among us realize that it takes 14 sided bodies to exactly fill a space with uniform bodies of minimal surface dimensions and without interstices. The cells snug together perfectly to fill the whole space without leaving any voids at all. A piece of cork is completely cellular with no "empty" spaces between the cells. This seems to me a major reason why corks don't transmit air: the path through a cork is just too tortuous for significant numbers of gas molecules to work their way through, even if pressure is applied to one end of the cork.

CHAMPAGNE PROOF POSITIVE

Champagne people have known since Dom Perignon that carbon dioxide gas doesn't escape from a bottle of bubbly during many years' storage even though the pressure inside a bottle of Champagne or Sparkling Wine is as much as 5 atmospheres (75 psi.) If CO₂ gas can't get through a cork and out of a bottle with 75 psi of pressure pushing on it, how could O₂ get into a bottle with only a few ounces of outside pressure pushing it? CO₂ molecules are physically larger than O₂ molecules - but only a little larger, and that factor doesn't explain it. If cork contained longitudinal gaps, voids or fibers, the escape route for gases would be easier. But that only happens with damaged corks (read: cheap) which might contain cracks. Since cracks in corks are usually obvious, proper inspection and grading eliminates defective corks prior to their shipment to a winery.

Let's suppose a newly bottled wine contains a trace of air or oxygen (O₂). Fortunately, wine contains a few parts per million (ppm) of SO₂, which protects wine from oxidation by the O₂. The SO₂ and O₂ destroy each other as the two react whenever they make contact. The chemical reaction between them in wine is complex but this simplification doesn't change the gist of the story. Winemakers have long noticed that the free SO₂ content of newly bottled table wine diminishes by 5 or 6 ppm within the first month after bottling, then by only 1 ppm or less in the months after that. The accepted explanation is that this initial loss of SO₂ is due to the pickup of O₂ by the wine as it passes through pumps and hoses while moving from the bottling tank through the bottling operation. The SO₂ is lost from the wine by reacting with, and removing, any O₂ that gets in.

What if the wine was oxygen-free at the time of bottling? There should be no loss of SO₂ since there was no O₂ to remove. At Beaulieu Vineyard, I ran into a stone wall that was hard to believe at first: wine lost this SO₂ following bottling even when we carefully excluded air from pumps, hoses and equipment. That is, virtually no air had entered the wine prior to bottling, yet we still had that same loss of SO₂ in the first month after bottling. Somehow oxygen was entering the wine in the first weeks after bottling to the

extent that 5-6 ppm of SO₂ was used up in getting rid of that O₂. Where the O₂ did that O₂ come from?

Another mystery: many wines containing traces of H₂S (“rotten egg” smell) tend to lose the H₂S immediately after bottling with corks but not with screw caps. Obviously, O₂ enters the bottle and oxidizes the H₂S, getting rid of it. But where did the O₂ come from? How could O₂ enter the bottle with a cork closure and not the screw cap? Some made the obvious guess that the cork must be “breathing,” especially since that made a glamorous story, mysterious and almost apocalyptic. Just the thing to elevate the mystical attraction of wine and (ahem) sell lots more cases of it.

Unpublished experiments in 1958 showed that we were unable to force O₂ through a 1¼ inch cork, even at high pressure levels. We were left with a question: since corks weren’t porous to O₂, how could small amounts of O₂ show up in the wine immediately after bottling? The answer was suggested by early literature, though none of us recognized it at the time.

Remember that corks are made up of miniscule cells each of which contains a tiny bit of air. At bottling, corks are compressed by the corker jaws for a fraction of a second to make the corks small enough for a plunger to punch them into the bottle. This squeezing raises the air pressure inside those tiny cork cells to 3 – 4 atmospheres. That’s enough to force microscopic bits of air out of the cork cells closest to the ends of the cork. It “exhales” slowly from the cork ends over a few weeks of time – faster at first, but slowing steadily to zero after some weeks as the pressure equalizes.

Professor Jean Ribereau-Gayon reported back in 1933 that 0.1 to 0.38 mls of O₂ diffused out of the inner end of a cork into the wine bottle in the first three weeks after bottling, but less than 0.07 mls over the next four months. How could that dissipating rate be explained? It would make no sense to believe that corks “breathe” air at a high rate for 21 days, and then slowly taper off and stop. That sounds to me more like a dying gasp than breathing. Clearly, the initial air has come out of the compressed cork cells near the inside end of the cork and not “through” the cork. As this compressed air escapes (from both ends of the cork) the pressure inside the cork cells diminishes, returning to near normal in two, three or four weeks. It probably tails off to extremely low levels for a few months more before stopping entirely, but that wasn’t measured.

Ribereau-Gayon’s suggestion that oxygen diffuses out of corks into wine due to the high pressure in cork cells immediately after bottling was correct, but no one seemed to take notice immediately. He was a superb scientist and we should have kept that information in the front of our minds; somehow, nobody did. I visited him in Bordeaux three decades later and, unfortunately, I think we discussed everything except compressed corks.

WHY DON'T YOU CHILL OUT – CORKS DO

The subject of cork closures regained importance in recent years, and Caloghiris (1997) suggested that air contained within the cork cells might account for cork’s oxidative capacities. That is true, and it is easy to calculate. He reported that only a negligible volume of atmospheric O₂ enters the bottle along the boundary between the edge of the cork and the glass. That is certainly true in the first few years after bottling. *The Adventures of Mr. Cork, Part 2: The Vacation*. “Over longtime storage...corks “relax” in the bottle.” But over longtime storage, especially with rising and falling temperatures in a wine cellar, corks “relax” in the bottle and it appears that most of the air leakage into a bottle after many years storage is along the edge of the cork, between the cork and the glass.

Waters, et al (2001) reported that the main route for O₂ entry into wine bottles (ignoring the first short time period after bottling) is along this cork-glass interface. I have seen that very thing many times as older bottles show increasingly more wine stain all along the cork to the point that liquid wine droplets finally appear outside the (unopened) cork, causing corrosion under the capsule. When those corks are pulled, the cork is stained along the complete outside of the cork showing that wine has indeed seeped between the cork and the glass wall. When cut with a razor blade, these same corks were clean and unstained inside at the cut cork surface, so we know the wine did not seep through the cork but only along the outside edge next to the glass.

We also notice that corks that were “unmovable” a year or two after bottling become easier to push a few millimeters into the bottle (by thumb pressure) after the cork has gotten considerable stain along its sides. The explanation, widely recognized, is that a daily, monthly or yearly rise and fall of temperature in the cellar of even a few degrees can cause a slight movement of the cork both in and out due to pressure changes as the wine bottle storage temperature fluctuates.

Cork movement is imperceptible at first but it becomes more obvious with time. The wine in a warmer bottle expands, causing an increase in pressure inside the bottle and miniscule movement of the cork outwards. As the bottle cools the liquid contracts, and this reduces pressure in the bottle, sucking the cork back inwards ever so slightly. Each time the cork is moved a bit by these pressure changes, a tiny amount of wine moves out along the glass/cork interface. After a few years of this, the staining along the edge of the cork is extensive and the slight wine seepage between cork and glass acts as a lubricant to allow even easier cork movement. The home remedy for this is to make sure your wine cellar holds an absolutely constant temperature of storage. That isn't easy to do in most houses and, probably, none of us has done that yet.

REASONS TO RE-CORK WINE

The major problem wine collectors live with is that corks lose their ability to continue pushing against the glass over time. I've heard wine people in France say that the cork seems to “die” after several years in a bottle. They mean the cork's ability to continue pushing outwards against the glass relaxes over time until the seal isn't good enough

The Adventures of Mr. Cork, Part 3: Dam Strong: “Cork is not absolutely impervious to moisture penetration, but its cellular structure gives it high resistance to penetration by water and wine” to protect the wine any longer. To preserve their finest wines as long as possible, first-growth wineries in France and elsewhere “re-cork” fine wines about every twenty to twenty-five years. This removes the old cork and immediately replaces it with a new cork. Andre Tchelistcheff brought this practice to California and I remember doing it at Beaulieu Vineyard in 1968 to preserve his best wines of the 1940s and 50s. I did it again for my older Beaulieu wines in 1990, as they were truly irreplaceable wines.

Beaulieu was one of only three or four American wineries of world class in the late 1960s and early 70s and we were routinely visited by winemakers and owners of first-growth wineries of Bordeaux in those years. Today, of course, there are many wineries of that quality level in California but that wasn't true back then. I believe all of today's quality wineries should adhere to that type of “re-corking” regime. Also, in view of what we now know about cork exhalation at bottling time, I think they might be wise to add 15 or 20 ppm of SO₂ to each bottle at the re-corking session.

I still believe that sound corks are the preferred closure for fine wines. The TCA problem is diminishing as cork suppliers continue to improve their production methods. My hat is off to them for doing so. Modern screw caps may be OK, provided the liner seals well and continues to keep the air completely out for a

long enough time. Screw caps didn't do that thirty years ago and screw capped wines were never bottle-aged back then.

I hope this answers most of the questions engendered by the first article. Corks are one of the more interesting and unique products of nature. What else doesn't breathe but can exhale without inhaling? Come to think of it, I guess any of us would exhale a little air if squeezed hard enough. Space limits me from adding a full Bibliography but I'd be happy to send that to readers who want to study it. Contact me at APPELLATION AMERICA or www.richardgrantwine.com

Several Other Properties Of Cork Need To Be Kept In Mind

With a specific gravity of only .25, cork is one of the lightest of all solid substances.

The Cork Institute reported (1941) that a 1" cube of cork had been compressed at 14,000 psi without breaking. After release of the pressure, the cube returned to 90 percent of its original 1" height and showed no appreciable change in its other dimensions. Some of the cellular "cork air" escaped during compression but most remained trapped and compressed within the cork's cells, even at this extreme pressure. This helps us understand the myth of corks breathing.

Cork does not harden or deteriorate under ordinary pressures. This partially explains its facility for use as stoppers and flooring materials.

Cork is not absolutely impervious to moisture penetration, but its cellular structure gives it high resistance to penetration by water and wine. I have noticed many wine corks that were "wine stained" less than one inch of their length after residing in a bottle of wine for twenty years. Wine corks are mostly 1 ¾ inches long, but sometimes as long as 2 ¼ inches, which provides a sufficient length of sound cork to preserve a solid seal over time.

Cork's coefficient of friction is much greater than that of rubber or leather, because the exposed surface cells act like tiny suction cups. Because of this, it is necessary to lubricate the outsides of new wine corks with paraffin and/or silicone prior to use. We'd never get them out of a bottle otherwise.

Next to vacuum, a "dead" air space minutely divided is one of the most efficient nonconductors of heat. Cork cells, since they contain air, also tend to absorb impact or vibration which helps keep the corks well seated in wine bottles during shipping.

Letters to Author

Dick,

Thank you for your recent article — Part 2. You are a great writer and it was really easy for me to follow your ideas. As you are aware, my being a Wine Educator for the past 35 years or so, I've been lying to my students. I've got it straight now!

One thing I still have a question on. Why was it important to keep a bottle of wine on its side or upside down for storage? I always said it kept the cork expanded and didn't allow the cork to shrink and allow air in. Is that true? It sounds like the cork will shrink anyways in 20 to 25 years? Is the industry wasting its time to keep wines upside down in cases? Do we need to keep screw cap wines upside down or does it matter?? (Just when you thought you had answered all the questions!)

Thanks for all your knowledge; I really enjoy hearing all your stories,
Pooch

Hi Pooch,

In a message dated 10/28/2008 3:58:03 P.M. Pacific Daylight Time, gmpooch@pacbell.net writes:

Why was it important to keep a bottle of wine on its side or upside down for storage?

We really don't know, but it seems unlikely that it could have any effect. Moisture doesn't penetrate cork well at all and there's no evidence that "keeping a cork wet" has any effect on the cork's ability to keep trying to hold its original structure. It seems to hold its original shape because of the fundamental features of the 14-sided 'spherical' shapes of the cork cells. They keep their shape because anything trying to deform them will have to stretch the outside skin of each cell in order to change the shape permanently. Cork retains its shape primarily because of the extremely strong and unstretchable membranes between the cells (surrounding each cell).

A perfectly round object has minimal surface area. It's like a ball: Any other shape has more surface area. As long as the outside skin doesn't stretch, the ball remains round. A ball stays round because any force trying to flatten the ball will only transmit its force to the other sides of the ball, which would push back against the flattening force. As long as the outside wall (the cover or skin) keeps its strength and doesn't stretch, the ball will stay more or less round.

I always said it (the moisture) kept the cork expanded and didn't allow the cork to shrink and allow air in. Is that true?

Again, we don't know. That belief assumes that cork cells would shrink if they "dried out." But corks never have more than about 7% of moisture in the wettest of cases -- it's hard to believe that they need moisture to hold their tiny amounts of air inside. I think it probably depends on the chemistry of the resin-like membranes that cork cell skins are made of. I haven't seen any published evidence that moisture would have an effect on whether cork cells stay expanded. The cork cells are like tiny basketballs that aren't quite perfectly round. If they were perfectly round they wouldn't snug together so precisely without having tiny empty spaces left over between the cells. The surfaces of cork cells are very nearly round but have 14 tiny FLAT sides instead of perfect curves. The flat sides match and cling to each other exactly and that adds an immense amount of strength to the skin of each cork cell; the result is the mass of cells tends to keep the whole thing from changing shape -- or losing their tiny bits of air. If forced to make a guess, I'd say moisture may not have much to do with it.

It sounds like the cork will shrink anyways in 20 to 25 years?

It may not be properly called "shrinking." The cells hold their shape against the compression they're under inside the bottle neck for two decades or more at cellar temperatures. I imagine the membranes between cells get old very slowly, holding out that long but then finally giving up (one at a time) and just say the hell with it -- like each of the cells in our bodies. Nothing can keep its composition forever and they just slowly decompose until the cork wakes up one day and says, "Shit! I've lost the battle!"

Is the industry wasting its time to keep wines upside down in cases?

Maybe not. Storing upside down allows you to see when the cork is leaking in time to use the wine before it goes over the hill.

Do we need to keep screw cap wines upside down or does it matter??

No. Assuming the metal of the screw cap retains its strength for as long as it's stored in your cellar, the position of the cap should make no difference. I hope these answers are helpful. Dick Peterson

-----Original Message-----

From: GM Pucilowski

To: Dick Peterson\87

Sent: Tue, Jul 2, 2019 10:12 am

Subject: Update your article?

Hello Dick,

Thank you for entertaining Heidi and myself with your great Pinot Noir. That is a trip I am willing to make anytime!! Thank you also for the bottle of 2016 which I am excited to try.

I mentioned that I wanted to distribute your article, Please Stop Telling People That Corks 'Breathe.' I was wondering if you might have updated information that maybe you wanted to add? This was written in 2008 and I was thinking there might be new information — or not.

So here is what I have in a Word document. If you want to glance at this and update it, that would be great. If you are okay with it as is, that's fine also. The conference is in August, so you have at least a month to take a look.

Thank you,

Pooch

Hi Pooch,

Well, another thing you might want to mention is that lots of wineries, especially those bottling expensive wines, waste their time packing bottles upside down in the cases on the bottling line. The reason they do it is that some absolute fool told them many years ago that the corks have to be kept wet to insure that they do not leak air into the bottle. So they pack the bottles upside down, which only increases the chances of a bad cork emitting the horrible flavor of cork taint into the wine inside that bottle. Even if a cork is taint-free, that practice is crazy, because it makes the cases hard to handle due to their lack of balance.

Any cork producer ought to know better if they keep parroting that falsehood to wineries -- and to the public. Cork companies know very well that cork is mostly wax, with a little connective fiber between cells to hold all those wax cells in place. Cork is about 93%+ insoluble stuff, mostly wax. The water content of a cork that you find in a wine bottle is ONLY between 6 and 7 % water! You can soak a cork for centuries and it still will not absorb more than 7% water. In other words, it isn't the wetness of a cork that makes it impermeable to air -- it is the waxy makeup of all cork bark that is used to seal bottles. Cork is an interesting substance: It is naturally composed of tiny 14-sided wax cells, each containing a microscopic bubble of air surrounded by wax and held together by the insoluble skin of each cell. The 14-sided cells cling tightly together so that there is no space between any of the cells in any direction, making it a very tortuous pathway for any molecule of air that might try to move through the cork -- it simply cannot do it, which is why "CORKS DO NOT BREATHE."

What about that microscopic bubble of air that occurs naturally in the middle of every cork cell? It cannot escape under normal conditions and it is those tiny bubbles of air inside the cork cells that make the corks feel 'spongy' to the touch and why the corks can be compressed a little when a cork is inserted into a bottle. (It's also why corks float.) To be completely accurate, a tiny fraction of the air from bubbles actually DOES escape from the cells located near the ends of any cork when it is compressed for inserting into a wine bottle. At the inside end, a tiny bit of this "cork air" does go into the bottle, but it is quickly destroyed by about 5 ppm of the SO₂ in the wine, so it does no damage to the wine. Of course, at the outside end of the cork a tiny bit of the cork air escapes to the outside because of the pressure of the corker jaws at the instant of inserting the cork into a bottle. But after bottling, no further air can enter a bottle until you open that bottle.

As you can tell, I have a serious brain flaw which makes me unable to forget many tons of this useless information. I've had to live with it all my life. The good news is "it's kind of interesting." Dick Peterson