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Editor: Peter Taverner
Waite Research Precinct
GPO Box 397
Adelaide 5001
Phone 08-83039538

Web Address:
http://www.sardi.sa.gov.au/foodinnovation/publications/citrus_packer_newsletter

send me an e-mail :
peter.taverner@sa.gov.au

Maintaining fungicide concentrations

Peter Taverner

SARDI

The type of fungicide, application method, design of the applicator and, even, the quality of the water influence the rate of fungicide loss. An understanding of why fungicide is lost or 'stripped out' is useful to be able to maintain concentration. I try to examine these factors in this article. Let's start with water quality!

My interest was precipitated (pun intended) by a few packers asking about the need to flocculate after increased flows in the river. The short answer is; yes! Increased water flow, and therefore increased colloidal clay, will interfere with fungicides.

A common method for removing dirt and clay suspended in water is alum (aluminium sulphate). When alum is broadcast onto water that has been adjusted to pH 7, it forms a gel-like precipitate that coalesces into flocs that trap suspended particles as they fall through the water. The treated water can be carefully drained off leaving the trapped particles at the bottom.

Hang on! Did I just read 'at pH 7"? No way is river water at pH 7 during these big flows. I finally begin to understand pH issues when using sanitisers and now we have another pH issue to deal with! Give me a break! Can I just forget about pH this time?

Sorry; but you need to adjust your water before you use alum. At pH above 8 the flocs are unstable and fall apart; whereas, at pH 6.5 or below the alum just dissolves in the water. Either way, alum will be worthless unless near pH 7.

Clean water is a good start, but now you need to maintain your fungicide concentration. The following approaches are mostly aimed at high volume recalculating systems, but low volume holding tanks can still suffer from poor maintenance and fungicides 'dropping out".

The type of formulation can influence the rate of fungicide loss, especially when water has high clay content.

Soluble fungicides – Guazatine is soluble but forms a chemical bond with colloidal clay, resulting in rapid stripping from suspension, or settling to the bottom

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of the tank. When river water is flowing fast, with high clay content, as much as 40% of the guazatine can be bound up. The major reason to floculate water is to avoid this issue.

Wettable powders/granules - wettable powders tend to remain of the surface of fruit as water drains away. Great for yielding high residues, but can result in a relatively high strip out rate.

Emulsifiable concentrates – E.C.'s work well unless the emulsion breaks down. Breakdown can occur physically during strong agitation (e.g. continuous pumping of fungicide). Care must also be taken when mixing chemicals with fungicides because they may contain additives that chemically interfere with the emulsion.

The design of the applicator can also influence the rate of fungicide loss. It can trap fungicide that may have settled out. The following tips apply to large volume bin dips and low volume application holding tanks:

- A large quality of low pressure air from a spa pool blower controlled by an intermittent timer is good for mixing fungicides, especially bin dip tanks.
- Holding tanks should be deep with a cone shaped floor leading to the pump intake. Some bypass fluid can be directed into the corners of tanks to keep wettable powders from lying wastefully.
- If foam forms, the fungicides can be trapped in the foam. Use of food-grade anti-foam can alleviate this problem.
- A header tank that holds ready mixed fungicide for topping up recirculating fungicides is a good investment. If wettable powders are used the tank should be agitated. This also applies to low volume application holding tanks.
- Avoid dilution of fungicides from water draining off wet fruit going into the fungicide treatment area. At the other end, excess fungicide can be removed from fruit using sponge rollers and run back into the holding tank.
- For recalculating systems, replacing lost volume with double strength fungicide will usually maintain fungicide concentration, but you should regularly check your solutions using an analytical laboratory to be sure.
- Total replacement of the fungicide solution in small tanks is preferred to repeated topping up in large tanks.
- OMG! Not pH again! Many fungicides work well in slightly alkaline water, but if the pH becomes too high they will precipitate out. In low volume application, this can lead to blockages in spinning disks. Monitor and buffer to avoid pH getting too high.✯

Using ORP probes to monitor sanition: What is ORP anyway?

Peter Taverner
SARDI

If you are a regular reader of this newsletter, you would know that chlorine test strips only tell half the story. The sanitising activity of chlorine is dependant on the concentration (measured by test strips) and the pH (measured by pH meters). Just to make things more confusing there is another way to measure sanitiser activity called ORP.

ORP does not measure the sanitiser concentration like a test strip but measures the oxidising properties of the sanitiser. This is an important distinction in interpreting the ORP reading, but first we need to understand ORP.

ORP (or Oxidation Reduction Potential) is the potential (voltage) at which oxidation occurs on an anode (positive) and reduction occurs at the cathode (negative) of an electrochemical cell. In simple terms, when an ORP sensor is placed in water containing a sanitiser, such as chlorine or bromine, it acts like a battery and creates a small but measurable charge. The value of this potential, measured in milli-volts, depends on the type of sanitiser and its concentration.

ORP and free chlorine

Ok. Let's review to some chlorine chemistry for a minute. Sodium or calcium hypochlorite dissociates into two forms when added to water – the fast-acting hypochlorous acid (HOCl) , and the slower-acting ionic form (OCl). As mentioned earlier, test strips measure both forms as the free chlorine reading. However, the activity depends on the ratio of each, which is influenced by pH. As pH increases, the hypochlorous acid dissociates to the ionic (or slow-acting) side of the equation.

The interesting thing about the relationship between the ORP reading and free chlorine is that the ionic form has a much lower ORP reading than

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the hypochlorous acid, which is consistent with its much lower activity as a sanitiser. The ORP sensor is essentially only reading the fast-acting hypochlorous acid, which is why it is measuring sanitising activity more effectively than the ppm reading on test strips.

ORP and pH

One of the benefits of using ORP is that it responds to pH changes. Lowering the pH to 6.0 raises the ORP, as more hypochlorous acid becomes available. Raising the pH to 8.0 lowers the ORP value, as less hypochlorous acid becomes available. This means that ORP does 'compensate' for pH changes. However, it is still advisable to monitor pH to ensure that chlorine concentrations are not excessive. For instance, if the water is too alkaline, very high concentrations of chlorine would be required to obtain the appropriate ORP due to the low ratio of hypochlorous acid. It would be more effective to buffer the water back to near neutral.

ORP and cyanuric stabilsers

Cyanuric acid has been widely used in the pool industry to stablise chlorine under sunlight (UV degradation). However, there is a related product called Turcosan®, which contains chlorocyanurates, and has been marketed for water treatment in fruit packing facilities.

The chlorocyanurates readily dissociates to form hypochlorous acid and cyanuric acid. The chlorocyanurate is a reservior releasing the fast-acting hypochlorous acid (and cyanuric acid) when it is needed. The ORP reading monitors hypochlorous acid levels, which provides a measure of sanitising potential.

However, cyanuric acid levels can build up over time, and the ORP reading is correspondingly lowered. This is analogous to highly alkaline water, where buffering is required. A study by J. Steininger recommends that when the cyanuric acid level becomes too high (above 100ppm) the water should be dumped or diluted with fresh water.

ORP and bromine

Nylate®, a chloro-bromo dimethylhydantoin, is used extensively in fruit washing and processing in Australia. Bromine forms hypobromous acid (HOBr) and the hypobromous ion (OBr). The oxidation-reduction reactions are similar to chlorine and the same ORP probe can be used for either chlorine or bromine.

There are some differences: Hypobromous acid dissociates to the hypobromous ion at a higher pH than chlorine. At pH 8, there is about 80% hypobromous acid and even at pH 9, there is still 33% (compared to 4% for chlorine). As such, this chloro-bromo product should maintain a more stable ORP reading (and activity) over a wider pH range.

Advantages and disadvantages of ORP

ORP can provide 'real time' monitoring of the water disinfection. ORP probes are often linked to digital recorders, alarm systems, sanitiser injectors, pH meter and acid injectors to become fully automated systems. The ORP reading can be relied on to determine the disinfection potential across a broad range of water quality. In other words, an ORP reading of 700mV at pH 6.5 has the same disinfection potential as a reading of 700mV at pH 8.0 (although the concentration of free chlorine would be quite different).

The disadvantages are largely related to equipment maintenance and calibration of the systems. The system should be calibrated using hand-held ORP probes, pH meters and sanitiser test strips. The sensors can become fouled and need periodic cleaning. Monitor the buildup of organic matter and by-products (e.g. check turbidity) to prevent excessive dosing of chlorine to maintain the ORP reading. Dump and replace with fresh water regularly to avoid excessive buildup.

It should also be recognised that ORP is not uniform for all sanitisers. Trevor Suslow (Extension research Specialist, UC Davis) has found that ORP is not practical for monitoring hydrogen peroxide or peroxyacetic acid (eg. Tsunami®). There are also issues for its use with ozone.

Setting target ORP values

The value usually set for disinfection of 'clean' water is 650 to 700mV. This value is based in killing free floating decay or spoilage bacteria within 30 seconds. However, the packing situation is different. Trevor Suslow recommends a target value of 800mV for primary wash where high levels of organic matter are released into the water. The ORP reading is less sensitive to concentration changes at higher millivolt values. There is a plateau at 900 to 950mV where doubling free chlorine concentration does not result in a sizable gain in ORP.

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Decontamination of cold storage facilities

Peter Taverner
SARDI

The rush to remove the Valencia orange crop means an early finish for many packingsheds, and an uncharacteristic long break before the new navel orange season. This is the perfect time for major maintenance and decontamination of the cool storage facilities. Recently, seasons have been very busy, with product constantly in the cool rooms, and much more long-term storage of navel oranges to realize better prices. The opportunity to clean up and break any potential fungicide resistance issues should not be missed.

In previous issues of the newsletter, I discussed hygiene and sanitation of packingline equipment and cool rooms (see Packer Newsletter No. 84). This involved thorough cleaning and then sanitation by high rates of SOPP, chorine-based sanitizers or quaternary ammonium compounds. However, it is very difficult to thoroughly clean and decontaminate a cool room using liquid sanitizers and elbow grease. Obviously, a product with some fumigant action would be preferred. Formaldehyde has been used in the past for cleaning cool storage areas because it has a fumigant action. However, it is toxic, an irritant and has been reclassified as a human carcinogen.

In this article, I have attempted to explore some alternative treatments that may be suitable for cleaning commercial citrus cold storage facilities. Some of these treatments are untried in citrus, but are used for similar purposes, and merit further investigation.

Bactigas®

BOC Ltd has developed Bactigas as a treatment for decontaminating 'sick' buildings, and it is primarily used to treat air conditioning ducts. Bactigas contains Tea Tree oil as the active ingredient, and is injected into ducts as a high pressure 'space spray' to penetrate throughout the ducting system.

The Tea Tree oil is mixed with ethanol before adding to the carbon dioxide propellant. The resultant product is dispensed as an aerosol (with ultra-fine particles in the range of 2µm to 20µm in diameter), which should remain suspended in air for several hours, and deposit on exposed surfaces.

The antimicrobial properties of Tea Tree Oil are well documented, and the Bactigas concentrate yielded very high reductions of bacteria, yeasts and mould in antimicrobial tests in NATA accredited laboratories.

Current use of Bactigas seems to be in the maintenance of air conditioning ducts in offices and hotels against *Legionella pneumophila*, using low rates (0.5gm/m^3 for 24 hours). However, higher rates (1.0gm/m^3 for 24 hours) are suggested for general disinfection, and where the premises can be evacuated.

Bob Ryan, Development Manager, Special Products, BOC Ltd, states:

"The benefit of Bactigas is the ease of use as it can be dispensed via a manual hand gun attached to a small 6Kg cylinder or automatically dispensed using a timer – solenoid combination. The active ingredients are both low toxic and volatile so there will not be an issue with contamination of produce in treated areas.'

This is an appealing product due to its safety to humans and low residue properties. However, effective rates and exposure times to decontaminate commercial cold storage areas would need to be determined.

Vaporous Hydrogen Peroxide (VHP)

The use of VHP decontamination against biological contaminants gained considerable interest from Defense and Homeland Security following the 2001 anthrax attacks in the USA. VHP technology has been used primarily in the medical, biological and pharmaceutical industries, but is commercially capable and has demonstrated the capacity to decontaminate large spaces. The STERIS Corporation, USA and the UK based BIOQUELL Corportation have commercialized room decontamination systems using VHP technology. Information regarding equipment and application can be found on the company websites.

Commercial VHP generators have been developed as closed systems, with a process involving up to 4 phases; dehumidifying, conditioning, decontaminating and aerating. The first phase involves stabilizing the room to pre-set temperatures and (low) humidity levels, the second phase involves flash vaporisation of aqueous hydrogen peroxide (H_2O_2) into a dry air

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stream, while the following decontamination phase involves maintaining the vapour/gas concentration in the room, the final aeration phase involves the catalytic conversion of VHP to water and oxygen &/or external aeration. Prolonged (occupational) exposed to VHP should be limited to less than 1ppm, and these levels should be reached before reoccupation of the treated rooms.

Reviews on VHP disinfection of cold food storage areas are limited. Saks et. al. (2006) compared the efficacy of pulsed ultraviolet light (discussed later in this article) and ultrasonic fogging with stabilized hydrogen peroxide for decontamination of air and surfaces of cold storage facilities. They found both treatments were effective in decontaminating the walls of the cool room. However, they emphasized that more work was required to optimize the procedures for commercial conditions.

Ozone

Ozone can be used for disinfection of cold storage surfaces, but is more commonly associated with air and water disinfection. Some systems rely on the continuous presence of ozone in storage room air. The levels of ozone safe for occupational safety cannot be expected to provide effective sanitation of fruit surfaces. The levels of ozone required to surface sterilize surfaces (eg. cool room decontamination) would be toxic to humans.

In Australia, The National Environment Protection Council air quality standards is 0.10 ppm (parts per million) of ozone measured over a one hour period, with an exceedence on only one day a year, and 0.08 ppm of ozone measured over a four hour period, with an exceedence on only one day a year.

High concentrations of ozone are potentially corrosive to equipment and fruit. As such, appropriate safeguards would be employed before and during treatment. However, ozone is highly reactive and would rapidly break down into oxygen after ozone generation ceased. This is highly regarded by authorities because there are no undesirable residues or disinfection by-products.

This article is concerned with the decontamination of cold storage surfaces, but ozone has many potential uses in the food industries. Ozone is commonly used in postharvest storage facilities for air treatment and the removal of ethylene and other by-products from fruit metabolism. In these instances, the levels of ozone are regulated to very low levels or the air is isolated, sterilized with ozone and returned to the cool room through ozone scrubbers. As a consequence, ozone has been granted Generally Regarded as Safe (GRAS) status as a food processing aid.

Palou et. al. (2003) conducted work on stored citrus and found that ozone can inhibit mould sporulation. However, ozone penetration (i.e., effectiveness) was strongly dependant on the vented area of the package. Ozone could not penetrate through fiberboard cartons or plastic bags, but was acceptable for highly vented packages or open topped containers.

In Australia, companies involved in ozone in fruit and vegetable storage in 2007 include Ozoneindustries and Bioconservacion Purified air Storage. Information regarding equipment and application can be found on various company websites.

UV-C Lights

The technique of using light waves, principally UV-C light, to decontaminate surfaces and preserve foods is well established. However, there is considerably more literature on the use of UV light to decontaminate water than food and hard surfaces. More information on UV-C surface decontamination can be found in the references, especially McDonald et. al. (2000) and Gomez-Lopez et. al. (2006).

The classical UV-C treatments were achieved by using low-pressure mercury lamps designed to produce a continuous wave (CW) of energy at 254 nm (monochromatic light). More recently, medium-pressure UV lamps, which emit a polychromatic output, including germicidal wavelength from 200 to 300 nm, have been evaluated. Currently, considerable attention is on pulsed light (PL), which uses short time pulses of intense broad spectrum, rich in UV-C light.

SeriBeam Systems in Germany, and the Xenon Corporation from USA, are companies producing disinfection systems based on PL. Xenon flash lamps can produce flashes several times per second, and emit in the range from ultraviolet to infrared light. However, Gomez-Lopez et. al. (2006) conclude that the UV content from 220 to 290 nm provides the major contribution to microbial inactivation, whichever type of UV source is used.

In Australia, Wintertuhr Australia promoted their photon sanitizing system to the wine industry and looked to expand into other areas, such as citrus. They conducted trials in citrus cold stores in the

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Griffith area in 2007, but I am unaware of the results.

The advantages of UV light are the lack of any residual chemical after treatment. Pulsed UV also may provide some advantage over CW UV where rapid disinfection is required. Pulsed UV is has been recorded as having greater penetration. However, the more opaque the surface the lower the inactivation below the surface, ie, decontamination is superficial.

CW UV and pulsed UV light are safe but some precautions must be taken to avoid exposure of workers to light and to evacuate the ozone generated by shorter wavelengths.

Conclusions

There are a number of promising treatments for cold storage decontamination, and many have low toxicity to humans and/or do not produce harmful by-products. In most instances, they are in commercial and industrial use, but have not been calibrated for use in citrus. The information presented suggests the potential for good efficacy, but there has been no examination of the cost-effectiveness of any of these treatments.

A number of companies and products have been mentioned in this article. This is not an extensive list, nor is it endorsement of these products for your situation. I would highly recommend that you thoroughly research your options before committing to any particular approach or product.

These treatments have been reviewed independently, but may be combined for greater efficacy. For instance, the shorter UV wavelengths generate ozone, which may combine to improve disinfection rates. In addition, McDonald et. al. (2000) found enhanced kill of bacterial spores with combined exposure of UV and hydrogen peroxide. There are likely to be a number of combinations that will provide enhance efficacy and other advantages.

Finally, the use of these treatments should not be limited to surface decontamination of surfaces. There is the potential to use these technologies to maintain low microbial levels in cool room air, provide direct food disinfection, disinfestations of produce and reduce the overall environmental footprint. However, that is a topic for another time.

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