

Alternatives to sodium metabisulphite for blackspot prevention in prawns

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In Australia, prawns are usually treated with a 1% sodium metabisulphite solution to prevent black spot. Two alternatives, *Bacterol* and *Snow Fresh*, were compared to the standard metabisulphite treatment used by industry. *Bacterol* gave similar protection to sodium metabisulphite, while *Snow Fresh* showed potential as a substitute. The concentrations most appropriate were determined from residue levels after treatment.

For many years sulphite, in the form of sodium metabisulphite, has been the main chemical treatment for controlling black spot on prawns. Because of health concerns there are restrictions on the amount of residual sulphite, measured as sulphur dioxide, allowed in prawn meat (Anon. 1992a). Accordingly any alternative which could reduce or remove sulphite or give better control over residues yet still provide sufficient protection against black spot would benefit the prawn industry. Recently two products, *HQ Bacterol F* and *Snow Fresh*, have become commercially available.

In the present study, we compared these two products with sodium metabisulphite for their ability to prevent black spot on prawns. The study investigated suitable dip concentrations for both chemicals as well as residues resulting from their application to determine the most appropriate conditions for their use.

Bacterol

In 1992 the National Food Authority approved the use of a mixture of sodium bisulphite, sodium chloride and dextrose for the treatment of uncooked prawns (Anon. 1992b). This mixture closely matches the product description of *HQ Bacterol F (Bacterol)* which is available from Hispano Quimica S.A., Barcelona, Spain. This product had been on trial by the Australian fishing industry for 12 months (Anon. 1991).

The manufacturers claimed that the saccharide component stabilises the sulphurous anhydride produced and synergistically strengthens the anti-melanotic effect. An advantage of using sodium bisulphite instead of sodium metabisulphite is that the lower dosage limits residual sulphur dioxide. They proposed that the saccharide almost forms a monomolecular layer with organic surfaces of the prawn, protecting the sulphite in contact with the crustacean surface, thereby improving sulphite stability and effectiveness (NHMRC 1990 & 1991).

The manufacturers recommended various types of application including dusting onto layers of prawns interspersed with ice. This method can result in uneven treatment and is not recommended for sodium metabisulphite by some researchers (Finne & Miget 1985, Nickelson & Cox 1977, Smith 1980) since it is difficult to

apply evenly and high local concentrations can result. Various concentrations and times for application by immersion were recommended, eg dipping in a 5% solution for 15 min, in a 4% solution for 5 or 10 min, in a 3% solution for 15 min, in a 2% solution for an unstated period, and two 3% dips and two 1% dips combined with sprinkling. No sulphite residue data have been reported. Otwell & others (1988) compared the effectiveness of *Bacterol*, sodium bisulphite and other chemical treatments and found that *Bacterol* protected against black spot.

To determine residue levels resulting from some of the manufacturer's procedures, and to determine a suitable dip concentration for use in Australia, a dip containing *Bacterol* at a sulphite level equivalent to the 1% sodium metabisulphite dip (Slattery & others 1991), and a 5% dip were evaluated for ability to prevent black spot.

Snow Fresh

Snow Fresh (Monsanto Chemical Company, St Louis, USA) is described as a product stabiliser and is used to prevent enzymic browning in vegetables. *Snow Fresh* contains sodium acid pyrophosphate, citric acid, ascorbic acid and calcium chloride. Since the mechanism of black spot development in prawns is similar to enzymic browning in other foods, this non-sulphite containing chemical was tested with prawns.

Phosphates have been used extensively by the seafood industry, for surimi, canned fish, drip loss reduction from frozen fish, scallops and prawns, cryoprotection for seafood proteins (Feltch 1990, Lampila 1992) and facilitation of shelling prawns (Sterno & others 1998, Teicher 1990). Sodium acid pyrophosphate has been approved as a food additive in Australia, not more than 1.3 g/kg measured as phosphorus being allowable in frozen fish. Prawn flesh was tested for phosphate residues.

Materials and methods

Bacterol

Freshly harvested aquacultured prawns (*Penaeus monodon*) purchased from Moreton Bay Prawn Farm, were washed, placed on ice, transported to the laboratory, then divided into 2 kg groups for one of the following treatments:

- No chemical dip.
- Dipped in a 1% sodium metabisulphite solution (theoretically 0.67% SO₂) using distilled water for a total volume of 100 L, for 30 s (a recommended practice for industry).

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- Dipped in an approximately 3% *Bacterol* solution (approx 0.67% SO₂ by analysis), total volume 100 L, for 15 min.
- Dipped in a 5% *Bacterol* solution, total volume 100 L, for 15 min.

Prawns from two harvests were randomly assigned to these treatments, after which they were drained for 5 min, divided and stored with one half placed on ice for up to 8 days and the remainder held frozen at -40°C for 14 days, thawed at room temperature for 2h and stored on ice for up to 8 days.

Snow Fresh

Trial 1: About 5kg of wild prawns, predominately banana prawns (*P. merguensis*) caught by trawler in Moreton Bay were dipped in the following solutions:

- 1% sodium metabisulphite for 30 s
- 1% *Snow Fresh* for 1 min
- 1% *Snow Fresh* for 3 min

The treatments were randomly applied to 1.5 kg batches of prawns which were drained for 5 min and stored on ice for up to 9 days.

Trial 2: After evaluation of the previous trial, a trial was conducted with a much larger catch composed entirely of tiger prawns (*P. esculentus*). Shell thickness and appearance indicated that these prawns had recently moulted. Prawns were treated using one of the following protocols:

- No chemical dip
- 1% sodium metabisulphite for 30 s
- 2% *Snow Fresh* for 1 min
- 2% *Snow Fresh* for 3 min

Four 2 kg lots of prawns were randomly assigned to a single treatment. After treatment the prawns were drained for 5 min, divided and stored. One half was placed on ice for up to 9 days and the remaining prawns held frozen at -40°C for 5 days, thawed at room temperature for 2 h and stored on ice for up to 9 days.

Visual assessment

The proportion of prawns with black discolouration on both head and abdomen was noted and expressed as a percentage according to the procedure of Ruello (1975).

Chemical analysis

Samples from each sodium metabisulphite treatment were analysed for SO₂ content at selected intervals during ice storage (in duplicate when possible). The carapace and epicuticle of the abdomen were removed from four prawns, the meat finely chopped and assayed for residual SO₂ by the method of de Vries & others (1986), modified by taking 20-50 g of chopped meat and adding 50 mL of 33% HCl.

Samples from each *Snow Fresh* treatment were processed as above and analysed for ascorbate according to the AOAC Official Methods of Analysis (1990) 967.21

Samples from each *Snow Fresh* treatment were processed as above and analysed for phosphorus according to the AOAC Official methods of Analysis (1990) 962.21. The background levels for untreated prawns were subtracted from the levels obtained for treated prawns to provide an evaluation of phosphorus residue.

Dextrose residues were not determined since Australian regulations do not state a maximum permissible concentration (MPC) of dextrose in prawns. There are no regulations permitting the use of calcium chloride or citric acid for prawns. Residues from the other components of the two products evaluated pose little safety risk.

Results

Bacterol

Figure 1 shows the development of blackspot during ice storage. The number of days in ice storage when pigmentation was observed is noted at the base of each bar. Bar height represents the percentage of prawns with melanosis. In unfrozen additive-free prawns, blackspot incidence was <20% after 4 days of storage, but by day 5, 80% of the prawns exhibited blackspot. Treatment with sodium metabisulphite markedly retarded the development of melanosis.

Treatment with 3% *Bacterol* for 15 minutes (SO₂ concentration equivalent to 1% sodium metabisulphite) was slightly more effective than sodium metabisulphite in reducing blackspot. Treatment in 5% *Bacterol* for 15 minutes was even more effective; blackspot was not observed until 5 days post-treatment and after 7 days storage the incidence was only 40%.

For frozen prawns, blackspot incidence and rate of development after all treatments was higher. Trends were similar to the fresh treatment.

SO₂ residues: Analysis of *Bacterol* indicated that it contained 23% SO₂. During storage, SO₂ concentrations (Figure 2) in unfrozen prawns treated with either sodium metabisulphite or *Bacterol* were below both export and domestic MPC, although residues in prawns treated with *Bacterol* were initially above the domestic MPC.

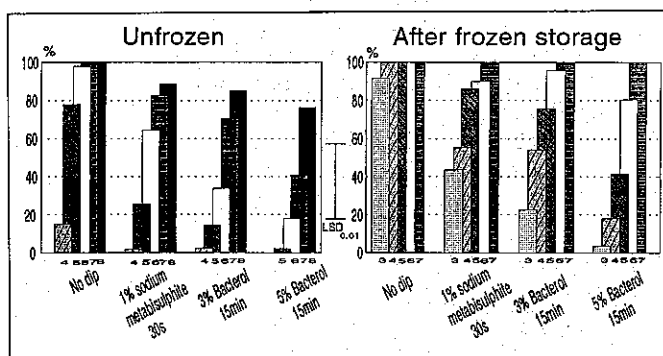


Figure 1. Comparison of *Bacterol* and sodium metabisulphite treatments. Blackspot incidence (%) on unfrozen and frozen (14d, -40°C) prawns during ice storage.

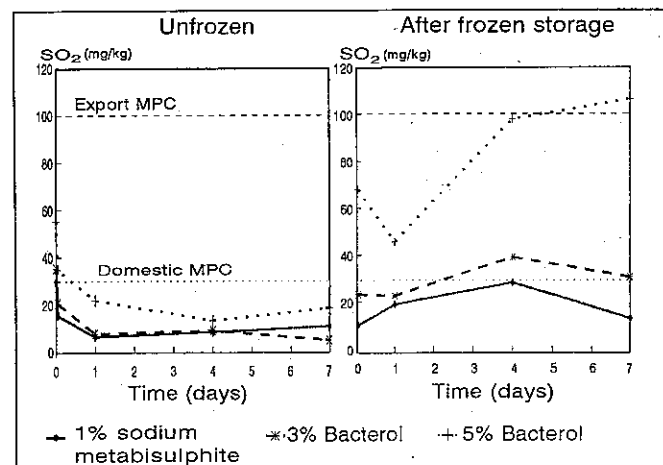


Figure 2. SO₂ residues in prawns treated with *Bacterol* and sodium metabisulphite during ice storage.

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Storage on ice can be seen as a continuous drain period, whereas freezing the prawns prevents this loss. Much higher SO_2 levels were found in prawns that were frozen. Only those prawns treated with 1% sodium metabisulphite for 30 seconds remained below the MPC for the domestic market. Residual SO_2 levels for these prawns correlate with blackspot incidence and agree with conventional wisdom that the higher the level of residual SO_2 the greater the protection given. Levels after dipping in 5% *Bacterol* were much higher and approached or exceeded the export MPC. The maximum difference between the residue levels for fresh and thawed dipped prawns equates to 0.8 mg uptake of SO_2 for 10g of peeled prawns flesh. This is equivalent to only 0.07 mL more of a 5% *Bacterol* dip being retained by 10 g of prawn flesh. We suspect that further migration of SO_2 into the flesh occurs during frozen storage.

Snow Fresh

Figure 3 shows the development of blackspot during ice storage. Ice storage time is shown on or near each bar for the pigmentation observations. Bar height represents the percentage of prawns with melanosis. For unfrozen prawns, treatment in 1% sodium metabisulphite gave results consistent with those reported above and with earlier studies (Slattery & others 1991) on blackspot

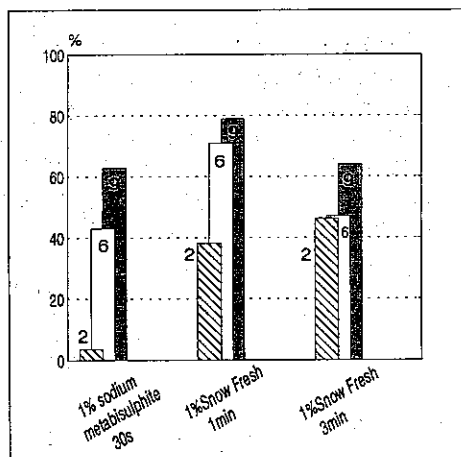


Figure 3. *Snow Fresh* trial 1. Blackspot incidence (%) on unfrozen prawns during ice storage.

incidence. Treatment with 1% *Snow Fresh* for 1 min was not as effective, but increasing treatment time to 3 min gave similar blackspot incidence to that observed with 1% sodium metabisulphite.

As seen in Figure 4, increasing the concentration to 2% *Snow Fresh* did not improve overall effectiveness. As with the earlier comparison, blackspot incidence increased when the prawns were stored frozen. In the untreated prawns almost 100% had blackspot within 3 days. Treatment with 2% *Snow Fresh* for either 1 or 3 min was slightly less effective than the standard dip in 1% sodium metabisulphite for 30 s.

SO_2 residues: Residual SO_2 levels in sodium metabisulphite treated banana and tiger prawns were below the domestic MPC for the unfrozen prawns (Figure 5). It is likely that the thinner shells and high water content of the recently moulted tiger prawns allowed a greater uptake of SO_2 than occurred in the banana prawns. Again a higher SO_2 residue level found in frozen tiger prawns was slightly above the domestic MPC on the first day after thawing.

Ascorbate residues: Base levels of ascorbate in undipped prawns were subtracted from those found in prawns dipped in *Snow Fresh* (Figure 6). Duration of dip did not affect residual ascorbate levels but higher concentrations

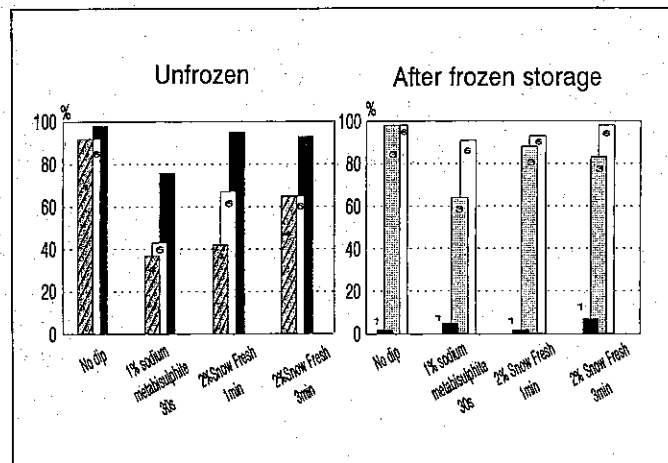


Figure 5. SO_2 residues in sodium metabisulphite-treated prawns from *Snow Fresh* trials.

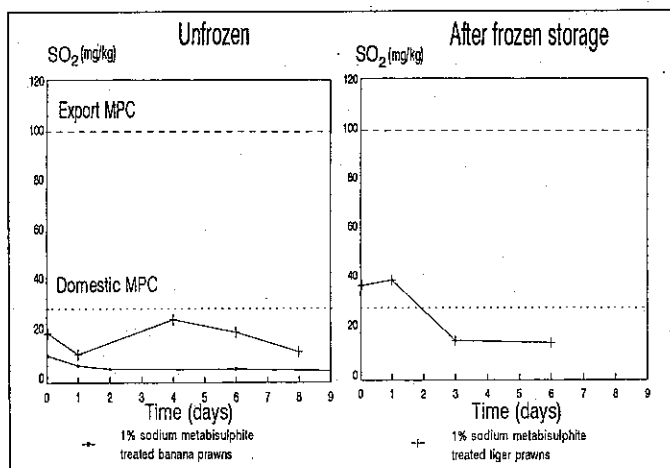


Figure 4. *Snow Fresh* trial 2. Blackspot incidence (%) on unfrozen and frozen (5d, -40°C) prawns during ice storage.

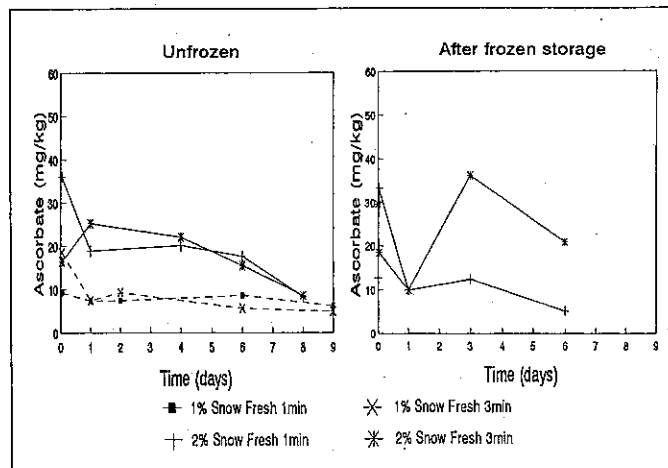


Figure 6. Ascorbate residues of *Snow Fresh*-treated prawns during ice storage.

of *Snow Fresh* resulted in higher levels of ascorbate in the flesh. There are no export limits set for ascorbate and these results are well below the MPC of 400 mg/kg for the domestic market.

Phosphate residues: Estimates of phosphate levels are inherently difficult because of large natural fluctuations in prawns. However no treatment resulted in phosphate concentrations higher than the 1.3 g/kg set by the Food Standards Code. The levels fall during storage (Figure 7).

Discussion

Both *Snow Fresh* and *Bacterol* protect against blackspot as effectively as the commonly used sodium metabisulphite. Only *Snow Fresh* represents an alternative to SO_2 ; *Bacterol* merely represents an alternative method of applying it.

The supplier recommends using *Bacterol* at 5% concentration (1.15% SO_2) for 15 min. This seems a long time in a strong solution and high residual levels above the export and domestic MPC can result when the prawns are frozen.

Previous studies showed that a 5 min drainage time was needed after dipping in 1% sodium metabisulphite solution for 30 s to prevent excessive SO_2 residues in frozen prawns (Slattery & others 1991). Effective drainage times for dips of longer duration and higher SO_2 concentration could result in extended handling times which would be detrimental to quality. After dipping in a 5% solution of *Bacterol* and one hour of storage on ice, the residue dropped markedly. One day later however, the residue level was still close to the domestic MPC.

Protection against melanosis is not permanent and as residual SO_2 levels decrease blackspot will eventually appear. Smith (1986) found that this occurred when the residual level fell to 2-8 mg/kg for fresh chilled prawns. Prawns treated with a 5% *Bacterol* dip, after thawing, exhibited extensive blackspot at day 7 of ice storage. This occurred while prawns still had SO_2 residues well above the domestic MPC. Normally the SO_2 residue would be quite low after this storage time (Finne & others 1986). The longer dip time of 15 min encourages penetration into the prawn flesh of SO_2 which is difficult to remove and which no longer provides protection at the site where melanosis occurs. Extending the drainage time by an hour might be needed to alleviate this situation. Any extension of drain-

age time after dipping however, could encourage bad handling practices and storage problems prior to freezing. A suitable dip for prawns must facilitate, not delay, the processing of the catch. A chemical treatment which produces high residues even after long term storage but does not provide any protection at the later stage can hardly be recommended.

Problems can also arise when there are different MPC for the domestic and export markets since a product which may be initially intended for export can often end up in the domestic market (Burford 1986).

Snow Fresh has the capacity to inhibit blackspot on prawns. Further experimentation may define a dosage level and application time as effective as SO_2 -based products. The suitability and safety of using phosphates on prawns needs to be assessed and all the ingredients approved by the National Food Authority before *Snow Fresh* could legally be used in Australia as an alternative to SO_2 .

Conclusions

A single dip containing no more than 3% *Bacterol* can be used as an alternative treatment to a sodium metabisulphite dip.

Snow Fresh has potential as an alternative to sodium metabisulphite but further research is needed to determine application levels.

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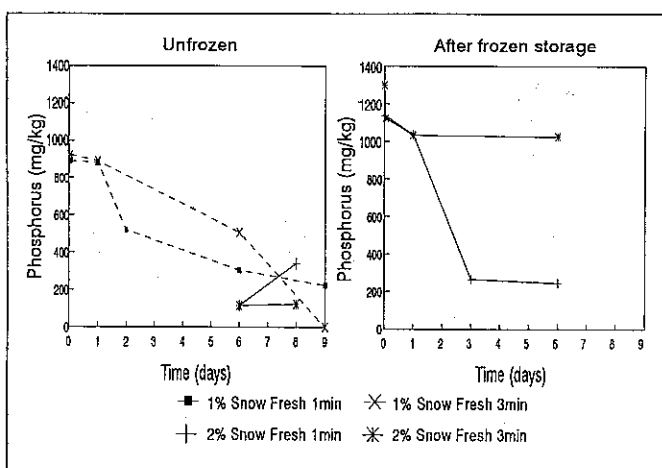


Figure 7. Phosphorus residues of *Snow Fresh*-treated prawns during ice storage.