MINISTRY OF AGRICULTURE, FISHERIES AND FOOD
HEALTH AND SAFETY EXECUTIVE

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A monthly listing of UK approvals and other official announcements on pesticides

The Report of the Working Party on Pesticide Residues: 1988-89

The first annual report of the Working Party on Pesticide Residues which shows the results of surveillance monitoring carried out during 1988 and 1989 is published by HMSO as a Supplement to this edition of the Pesticides Register. It is a priced publication and can be obtained from the HMSO publications centre (mail and telephone orders only), HMSO bookshops and accredited agents and through good booksellers.

Publication of WPPR reports every three years as Food Surveillance Papers will continue. The last report covering the period 1985-88 was published in March 1989 and can be obtained from HMSO at a cost of £5.90 and by quoting ISBN 0-11-242870-3.

The Working Party co-ordinates Government Surveillance of UK-produced and imported food and feeding stuffs, human tissues, wildlife and the environment for residues of pesticides, their metabolites and other degradation products. The Working Party reports to the Steering Group on Food Surveillance and the Advisory Committee on Pesticides.

Dithiocarbamate residues on protected lettuce

There has been increasing concern about pesticide residues on lettuce in recent months, particularly with the introduction of Maximum Residue Levels (MRLs) in January 1989 and the ACP's advice, in January 1990, that residues of EBDCs in some samples of treated lettuce, while at safe levels, could and should be reduced. MAFF has therefore made the following recommendations on overall limitations on the use of dithiocarbamate products.

Use of products containing mancozeb, maneb, thiram or zineb on protected lettuce

There are no restrictions governing the use of products containing dithiocarbamates during propagation. However, post-planting restrictions can be summarised as follows:

only 2 post-planting applications of any one or combination of the above chemicals are permitted either as a spray or as a dust within 2 weeks of planting out and none thereafter. The last application must not be later than 3 weeks before harvest.

Nominations for commodity chemical approval

THE Advisory Committee on Pesticides has agreed that a public consultation should be carried out to obtain data on pesticidal uses of commodity chemicals which can be considered for approval under the Control of Pesticides Regulations 1986. Details of the substances that are eligible and the data that are required to support nomination under these arrangements are set out below.

Any company wishing to market a commodity chemical as a pesticide must apply for product approval in the usual way. If a commodity chemical-based product is approved, any commodity chemical approval for the same area of use will be withdrawn.

Nominations must be in duplicate and in typescript and presented in the order listed. They should be sent to Mrs. J. Fullick in MAFF at the address on the back cover.

To enable data supporting the nominations for the same substances to be considered together, the closing date will be 31 October 1991. Chemicals nominated after this date will only be considered in special circumstances eg if they involve options for safer use. Nominated chemicals will be assessed to establish whether approval for use can be granted.

Arrangements for the Nomination of New Commodity Chemicals

1. Chemicals which meet the following criteria would be eligible for consideration:
   - it must be a substance, sold or supplied as technical material, whose major uses are non-pesticidal but which is freely available for use as a pesticide;
   - it must only be used on its own or with a diluent. Formulations will remain subject to individual product approval.

2. Nominations must detail:
   (i) Name of chemical;
   (ii) Specification, eg strength, purity, manufacturing method;
   (iii) Purpose and crops and situations on/in which used;
   (iv) Rates, method, frequency and timing of application(s) including earliest/latest dates applied;
   (v) Operator protection required;
   (vi) Method(s) of disposal of surplus substance in its original form and as prepared for application;
   (vii) Information on the commercial significance of the uses stated; how widespread and long established: alternatives;
   (viii) Reasons (including, if possible, evidence of references to other published data) for considering the pesticide to be effective;
   (ix) Available data such as safety data sheets, and references to other published data on operator exposure;
   (x) Available data/references to published data on human and environmental toxicity including residues;
   (xi) Any other information considered useful in assessing the chemical for its pesticidal use.

DH expert committee recommendations June 1990

FLOUR TREATMENT AGENTS - CHLORINE DIOXIDE AND CHLORINE

The COT has recently been reviewing the toxicity of flour treatment agents, including chlorine dioxide for use in bread flour and chlorine for use in cake flour. The COT has now recieved the advice of the COM and the advice of both Committees is given below.

Chlorine dioxide

The COM concluded that the data showed that chlorine dioxide itself was mutagenic and should be regarded as a potential human mutagen. The COM were also concerned that the chlorine component of chlorine dioxide could react with flour constituents such as amino acids and proteins to produce mutagenic compounds. In view of the COM's concerns and the compound's widespread use as a flour treatment agent, COT advised that chlorine dioxide should be classified as only provisionally acceptable for use in food (Group B). Analytical studies are needed on the fate of chlorine dioxide following reaction with flour and on residues of chlorine dioxide itself, using a sensitive method of detection; these studies should ideally be done on both treated flour and on bread baked from it under commercial conditions. Although long-term studies on chlorine dioxide are not required at this stage, further studies might be needed subsequently, depending on the outcome of the analytical work. The potential mutagenic activity of chlorinated compounds resulting from the reaction with flour components would probably best be dealt with by carrying out mutagenicity studies on extracts of cake made from chlorinated flour, which involves much higher treatment levels of chlorine than does treatment with chlorine dioxide.

Chlorine

When the COT discussed chlorine as a treatment agent for cake flour in autumn 1989, it concluded that while the existing long-term feeding studies of cake made from chlorinated flour did not show any effects which gave rise to concern, in view of the small safety margins obtained between the chlorine dose fed and the estimated intake of chlorine from consuming cake, further work was needed. The COT suggested that a 90 day feeding study should be carried out in the rat using extracts of cake made from chlorinated flour and including a detailed investigation of the immune system and a study of possible accumulation of chlorinated compounds. There have been a number of meetings with industry and a protocol for such studies was recently discussed, following

which the COT's comments were conveyed to FMBRA by the Secretariat. After hearing the COM's concerns (expressed in the context of its consideration of chlorine dioxide) that mutagenic compounds might be produced on reaction of chlorine with flour, the COT consulted the COM about the feasibility of carrying out mutagenicity studies on the extracts of cake made from chlorinated flour which will be prepared for the 90 day rat study. The COM concluded that the use of chlorine for flour treatment gives rise to concern with regard to the mutagenic potential of chlorinated products formed and that in order to assess this potential the extracts produced for use in the 90 day studies should be examined for their ability to produce both gene mutation in bacteria (after suitable "clean-up" procedures to minimise any histidine content) and chromosome aberrations, in in vitro studies. Further studies might be needed depending on the results of these studies; the precise form of any further work will need careful consideration and the COM would be happy to advise further as necessary. The COT endorsed the conclusions of the COM and has advised that the mutagenicity studies should proceed in parallel with the 90 day study.

In conclusion, COT has classified both chlorine dioxide and chlorine into Group B, with requests for further work as outlined above. COT have advised that the required work should be completed within 2 years, with an interim report produced after 1 year.

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CONTRACT REPORT M16
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Chlorine dioxide and mushrooms

PRINCIPAL WORKERS

J T Fletcher, Plant Pathologist

AUTHENTICATION

I declare that the work reported was done by me and this report represents a true and accurate record of the situation as far as I was able to establish the facts.

.....J T Fletcher
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Date 18.1.93

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SUMMARY

Discussion at the Mushroom Experiment Station Horst established that no new work is being done with chlorine dioxide. It is considered to be an excellent product for the control of bacterial blotch (Pseudomonas tolaasii) but no whitening benefits were found. Bacterial blotch and browning caused by Pseudomonas agarici are considered to be the most important diseases of the mushroom crop in The Netherlands. Sodium hypochlorite is used at 125 and 250 ppm for their control. Although these concentrations are exceeded on occasion, there was no evidence of the commercial use of chlorine dioxide. An application has been made for the registration of chlorine dioxide in The Netherlands but there is little optimism that it will succeed.

In the UK the most likely way of getting chlorine dioxide registered is as a commodity chemical, although there is very little relevant data to support such an application. It is provisionally approved as an additive to flour but this use may be withdrawn because it has been shown to be a mutagenic agent. Chlorine is similarly under suspicion.

INTRODUCTION AND BACKGROUND

Mushroom quality depends very considerably on the white appearance of the caps. Any blemishes or discolorations, however slight, reduce the quality of the product. There are many factors which affect whiteness ranging from the biotic (such pathogens as Pseudomonas tolaasii, Verticillium fungicola, Trichoderma harzianum and others) to the abiotic (chemical damage, physical damage, environmental effects). Growers are always striving for high quality mushrooms and comparisons are inevitably made between their own produce and those of their competitors. Major sources of competition are the imported mushrooms from Ireland and The Netherlands. In general, imports from these countries are of a very high quality. It is recognised that cultural methods in both Ireland and The Netherlands differ from those used on many farms in the UK but also differ from each other.

Use of chlorine dioxide

It has long been known that the use of chlorine will reduce the incidence of bacterial blotch although the concentration and conditions of application are critical in order to achieve the best results Ayers & Lambert, 1955, Royse & Wuest 1980, Wong & Preece 1985). Sodium hypochlorite is commonly used and is applied at concentrations of about 150-220 ppm. Ayers & Lambert (1955) found that the use of chlorine reduced blotch from 34% of caps affected to 7% with no detrimental effect on yield. Wong & Preece (1985) reported similar results but warned of possible phytotoxocity if high

concentrations of chlorine are used. One problem with sodium hypochlorite is its instability unless it is stored carefully. Also it is less effective at high pH and in the presence of organic matter.

Chlorine dioxide is a very powerful oxidising agent, some 2-5 times stronger than chlorine (Benarde et al. 1965). New stabilised formulations are also much easier to store. It is known to be an effective biocide under alkaline conditions and in the presence of organic matter (Geels et al. 1991). Beelman (1988) reviewed the factors influencing post harvest quality and shelf life of fresh mushrooms and considered the value of chlorine dioxide. He concluded that at low storage temperatures (3°C) bacterial growth is controlled and chemical treatment to delay browning of the caps is not necessary. But when storage temperatures are higher (13°C) bacterial growth occurs which can be controlled with a chlorine dioxide wash so that whiter colour and longer shelf life is achieved.

The effect of chlorine dioxide as a means of controlling bacterial blotch was recently reported by Geels et al. (1991). They found that 50 ppm applied three days before the first flush and with the water between flushes reduced blotch incidence from 86-93% in the innoculated controls to 15-27%. The severity on the affected mushrooms was also reduced. In comparison sodium hypochlorite at 125 and 250 ppm applied at the same timings reduced blotch to 55%. They observed no phytotoxic effects of chlorine dioxide even at very high concentrations (250ppm). They concluded that it is the best bacterial blotch control chemical so far tested.

From the literature there appears to be two possible uses for chlorine dioxide in the mushroom industry:-

1. As a means of controlling bacterial blotch: for this purpose it is applied to the growing crop.

2. As a means of preventing or minimising post harvest discoloration: for this purpose harvested mushrooms are washed in the product or the crop is sprayed shortly before harvest.

DISCUSSIONS WITH DR F P GEELS, MUSHROOM EXPERIMENTAL STATION, HORST, NETHERLANDS

Discussion with Dr Geels and with other scientists at Horst took place on 19-21 October. The most important points which arose were:-

1. The work reported by Geels, et al at the International Congress in Dublin (1991) on chlorine dioxide and bacterial blotch control has not been continued. Dr Geels concludes from the work that chlorine dioxide is a better bactericide than sodium hypochlorite although he recognises that the hypochlorite treatment used in his comparison was not according to the recommendations and general practice in the UK (ie applied at 150 ppm with every watering).

2. Dr Geels is now looking for new both non-chemical and chemical approaches to control bacterial blotch which he says is the most important disease of the crop in The Netherlands.

3. There are no new chemicals in experiments.

4. The longer term approach is to find genetic resistance and with this in mind an international collection of Agaricus bisporus isolates has been purchased from Canada. Screening these strains for blotch resistance is under way. It is hoped that resistance will eventually be incorporated into commercial strains.

5. In addition to Ps. tolaasii, Geels considers Ps. agarici to be an important cause of pale brown discoloration of mushrooms. It has also recently been reported as the cause of stalk internal necrosis.

6. An attempt is being made in The Netherlands to register chlorine dioxide for use on mushrooms. Efficacy data has been obtained (Geels et al. 1991) but the major difficulty is obtaining residue data. In the Horst work quality improvement was entirely the result of bacterial blotch control. No extra whiteness was recorded.

7. Residue data submitted with the application was obtained from the Campden Laboratory, Chipping Campden. Unfortunately this data is suspect because levels of chlorine were recorded in the untreated controls. It is presumed that the experimental crop was watered with chlorinated (mains drinking) water.

8. A Mr L P Flipse who previously worked for the registration authority is handling the chlorine dioxide application on behalf of Dutch growers.

9. During a visit to a farm with an acute blotch problem the grower was using hypochlorite and there were no signs of other products.

10. The hypochlorite used by many growers is domestic bleach (10% available chlorine) often perfumed. Domestic bleach in the UK is generally 4-5% available chlorine whereas dairy hypochlorite is 10-12%.

11. The recommendation from the Dutch advisory service is to use 125 or 250 ppm active chlorine (1.25 or 2.5 ml/litre of product) applied at the rate of 1.0 litre/m^2. Generally the 125 ppm rate is recommended as a precautionary protective treatment and the 250 ppm rate is applied when the disease occurs. The first application is made 22 days after casing and subsequently at watering during flushes.

12. I heard of one severe outbreak of blotch where 500 ppm was applied at 1.5 l/m^2 rate apparently without adverse effects on the crop. In the UK we would expect this unofficial rate to be phytotoxic.

13. Questions to researchers, growers, advisers and sales people about the use of chlorine dioxide did not suggest any illegal use of this product.

VISIT TO THE PESTICIDES SAFETY DIVISION,
HARPENDEN AND SUBSEQUENT WORK

This visit took place on 3rd November 1992. Points that arose from the discussions were:-

1. If chlorine dioxide is to be used as a disease controlling product by application to the crop, it may have to be registered under the Control of Pesticide Regulations (COPR).

2. The procedure for registration requires data covering aspects of the toxicology of the product, safety aspects for the users and efficacy data. Generally the company with the named product would be expected to submit this data package.

3. Some chemicals which are sold as the technical material and not as a product, eg sulphuric acid where major use is not pesticidal, are processed and approved as commodity chemicals. Such chemicals must be marketed on their own - once formulated as pesticides they are no longer considered to be commodity chemicals (Appendix 1).

4. Chlorine dioxide may qualify as a commodity chemical. At present there are six commodity chemicals which are permitted for use as pesticides - these are methyl bromide, sulphuric acid, formaldehyde, strychnine, ethylene dichloride and urea.

5. To make an application for the use of chlorine dioxide as a commodity chemical some data would be necessary on the toxicology

and risk to the operator, consumer and the environment as well as efficacy (the Dutch results on efficacy for the control of bacterial blotch would probably be acceptable).

6. Because chlorine dioxide is used as an additive to flour (for bleaching purposes) and also permitted as an additive to chocolate, I contacted the Department of Health, Hannibal House, London SE1 6TE to see if a toxicology package is available which might be used in a submission to MAFF for registration as a commodity chemical.

7. The advice given by the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) and its sister committee, the Committee on Mutagenicity (COM) is shown in Appendix 2. The recommendations made in June 1990 suggest that both chlorine dioxide and chlorine are classified as group B chemicals in relation to safety of use in food. The Committee concluded that chlorine dioxide is mutagenic and should be regarded as a potential human mutagen. Similarly concern was expressed that chlorine may give rise to products which are mutagenic. COT therefore advised that both chemicals should be provisionally approved for use in food (Group B) and that further data should be submitted within two years. No toxicology data package is available.

CONCLUSIONS

1. Chlorine dioxide is not approved for use on mushrooms in The Netherlands.

2. No new research work on this chemical is planned at the Mushroom Research Station, Horst.

3. Results already published show that it gives a good control of bacterial blotch but its effect on whitening is less conclusive.

4. Bacterial blotch is the main disease problem in The Netherlands and sodium hypochlorite is extensively used.

5. I saw no evidence at all of the illegal use of chlorine dioxide.

6. The Dutch are not optimistic about getting chlorine dioxide registered for use on the crop although they have made an application to the registration authorities.

7. In the UK it is possible that chlorine dioxide could be considered for registration as a commodity chemical.

8. The use of chlorine dioxide in flour is being reconsidered by the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) because there is evidence that it is mutagenic.

9. Chlorine use is also being considered by COT because it is suggested that chlorinated products may also have mutagenic properties.

10. Hypochlorite is used extensively by the Dutch at rates which we would consider to have deleterious effects on yield.

11. The presence of a newly identified cause of browning (Ps. agarici) is an added reason for the regular use of hypochlorite.

INTERPRETATION OF THE REPORT

1. There is very little evidence that the use of chlorine dioxide is worthwhile for the mushroom industry on the grounds of increasing the whiteness of the product.

2. Chlorine dioxide is at least as good as sodium hypochlorite for the control of bacterial blotch and other bacteria which may be responsible for surface browning. There is not much evidence to show that chlorine dioxide is distinctly better than hypochlorite.

3. My impression from the Dutch industry is that whiteners are not needed to improve quality but bacterial blotch control is essential. The fact that the experimental station is actively looking for new approaches suggests that they are not totally happy with hypochlorite, chlorine dioxide or biological means of control. It is also possible that they see registration of chlorine dioxide as a major obstacle to its use.

4. The fact that chlorine dioxide is a known mutagen does not auger well for its approval as a commodity chemical. If it is withdrawn from use on flour, chlorine may be withdrawn with it. This could have knock-on effects for the use of hypochlorite on mushrooms.

5. An application could be made for the approval of chlorine dioxide as a commodity chemical. A case can be made based upon the use of hypochlorite. But bearing in mind the point made under 4 this could draw attention to the use of hypochlorite and could result in the withdrawal of the current off label approval.

REFERENCES

1 Ayers, T. T. & Lambert, E. B. (1955). Controlling mushroom diseases with chlorinated water. Plant Disease Reporter, 39, 829-836.

2 Beelman, R. B. (1988). Factors influencing post harvest quality and shelf life of fresh mushrooms, The Mushroom Journal, No. 182, 455-463.

3 Bernarde, M. A., Israel, B. M., Oliveri, V. P. & Granstrom, M. L. (1965). Efficiency of chlorine dioxide as a bactericide. Applied Microbiology, 13, 776-780.

4 Geels, F. P, van Griensven, L. J. L. D., Rutjens, A. J. (1991). Chlorine dioxide and the control of bacterial blotch on mushrooms, caused by Pseudomonas tolaasii. Mushroom Science XIII, 437-442.

5 Royse, D. J. & Wuest, P. J. (1980). Mushroom brown blotch: effects of chlorinated water on disease intensity and bacterial populations in casing soil and on pilei. Phytopathology, 70, 902-905.

6 Wong, W. C. & Preece, T. F. (1985). Pseudomonas tolaasii in cultivated mushrooms (Agaricus bisporus) crops: effects of sodium hypochlorite on the bacterium and on blotch severity. Journal of Applied Bacteriology, 58, 259-267.