



AU9667970

(12) PATENT ABRIDGMENT (11) Document No. AU-B-67970/96  
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 701296

(Modified Examination)

- (54) Title  
BORDEAUX MIXTURE, PROCESS FOR ITS MANUFACTURE AND CUPRIC FUNGICIDAL COMPOSITIONS CONTAINING IT
- International Patent Classification(s)  
(51)<sup>6</sup> A01N 059/20
- (21) Application No. : 67970/96 (22) Application Date : 02.10.96
- (30) Priority Data
- (31) Number (32) Date (33) Country  
95 11593 03.10.95 FR FRANCE
- (43) Publication Date : 10.04.97
- (44) Publication Date of Accepted Application : 21.01.99
- (71) Applicant(s)  
ELF ATOCHEM AGRI S.A.
- (72) Inventor(s)  
MICHEL COURTADE; GEORGES RAMEL
- (74) Attorney or Agent  
SPRUSON & FERGUSON, GPO Box 3898, SYDNEY NSW 2001
- (57) Claim

1. Bordeaux mixture in which substantially all the copper is in the form of brochantite and which, in dry form, contains not more than 20% by weight of bassanite.

6. Process for the manufacture of a Bordeaux mixture as defined in Claim 1, which process comprises reacting an aqueous copper sulphate solution and an aqueous suspension of lime in a  $\text{Ca(OH)}_2/\text{CuSO}_4$  molar ratio of between 0.60 and 0.75, at a temperature and for a period of time which are sufficient to convert substantially all the copper complexes into brochantite.

**AUSTRALIA**  
**PATENTS ACT 1990**

**COMPLETE SPECIFICATION**

**FOR A STANDARD PATENT**

**ORIGINAL**

Name and Address  
of Applicant:

Elf Atochem Agri S.A.  
1, Rue des Freres Lumiere  
78370 Plaisir  
FRANCE

Actual Inventor(s):

Michel Courtade and Georges Ramel

Address for Service:

Spruson & Ferguson, Patent Attorneys  
Level 33 St Martins Tower, 31 Market Street  
Sydney, New South Wales, 2000, Australia

Invention Title:

Bordeaux Mixture, Process for its Manufacture and  
Cupric Fungicidal Compositions Containing It

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

The present invention relates to plant protection products. In particular the present invention relates to a novel Bordeaux mixture, its manufacture and its use for the preparation of cupric  
5 fungicidal compositions in the form of powders, granules or concentrated suspensions, which are dispersible in water.

The fungicidal treatments for vines currently in common practice find their origin in the appearance,  
10 in the 19th century, of two original fungal parasites from America:

- powdery mildew (*Uncinula necator*)  
introduced into France in 1847
  - downy mildew (*Plasmopara viticola*)  
15 introduced into France in 1878
- which have since become endemic parasites.

In order to control these parasites, use is still made of two products of inorganic origin (sulphur to combat powdery mildew and copper to combat downy  
20 mildew), since their use in successive treatments does not induce any phenomenon of resistance, as is often the case with synthetic fungicides.

As regards copper, the sulphate form is seen to be the simplest to use on account of its solubility  
25 in water. However, since the acidity of this solution leads to burns on the vine leaves, it has proven necessary to incorporate a product of basic nature therein in order to decrease the acidity by



neutralization. Lime and calcium carbonate have been used for this purpose, giving rise to what is known as:

- Bordeaux mixture for the mixture of copper sulphate with a milk of lime,

5                   - Burgundy mixture for the mixture of copper sulphate with calcium carbonate.

Bordeaux mixture has become, little by little, the product most widely used in viticulture and its use as a fungicide has even extended to other  
10 cultures (vegetables and fruits) and to other parasites, in particular bacteriosis and scab.

The two most common processes for the industrial production of a Bordeaux mixture are:

- the direct process consisting of the  
15 introduction of a milk of lime into an aqueous copper sulphate solution,

- the reverse process, according to which an aqueous copper sulphate solution is introduced into a milk of lime.

20                   However, irrespective of the process used and despite the technical improvements made, the fungicidal compositions formulated from current industrial Bordeaux mixtures often have drawbacks at the time of their use, in particular:

25                   - poor dispersion in water  
                  - production of a sticky deposit in the spray tank, leading to plugging of nozzles  
                  - appearance of burns on the leaves on



account of the acidity of the product.

The use of a standard Bordeaux mixture in the formulation of a concentrated aqueous suspension (liquid formulation of the SC type) leads, on storage, to the gelation and settling and caking of the suspension to a solid. In the formulation of water-dispersible granules (formulation of WG type), the use of a standard Bordeaux mixture leads, on storage, to a reinforcement of the cohesion of the granules with, as an effect, poor redispersion of these granules during use. The use of a standard Bordeaux mixture in the formulation of a wettable powder (formulation of WP type) leads, on suspending this powder in water, to the formation of a sticky deposit.

X-ray analysis of a standard Bordeaux mixture reveals a polyphasic and variable composition of copper complexes, consisting of:

- devillite:  $\text{Ca}[\text{Cu}_4(\text{SO}_4)_2(\text{OH})_6] \cdot 3\text{H}_2\text{O}$
- posnjakite:  $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}$
- brochantite:  $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$
- antlerite:  $\text{Cu}_3(\text{SO}_4)(\text{OH})_4$

as well as a polyphasic and variable composition of calcium complexes, consisting of:

- gypsum:  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- bassanite:  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ .

It has now surprisingly been found that the abovementioned drawbacks are essentially due to the presence of cupric complexes other than brochantite and

to an excess of bassanite, and that these may be overcome or at least mitigated by the use of a Bordeaux mixture in which substantially all the copper is in the form of brochantite and which, in the dry form,  
5 contains not more than 20% by weight of bassanite.

According to one aspect the present invention provides a Bordeaux mixture in which substantially all the copper is in the form of brochantite and which, in dry form, contains not more than 20% by weight of  
10 bassanite.

According to another aspect the present invention provides a Bordeaux mixture in the form of an aqueous suspension whose solids comprise essentially approximately 47% by weight of brochantite and 53% by  
15 weight of gypsum, as well as a dry Bordeaux mixture comprising approximately 47% by weight of brochantite, 33 to 53% by weight of gypsum and 0 to 20% by weight of bassanite.

A further aspect of the invention comprises  
20 the manufacture of a Bordeaux mixture by a method which comprises reacting an aqueous copper sulphate solution and an aqueous suspension of lime in a  $\text{Ca(OH)}_2/\text{CuSO}_4$  molar ratio of between 0.60 and 0.75, at a temperature and for a period of time which are sufficient to  
25 convert substantially all the copper complexes into brochantite. Using this method a Bordeaux mixture of constant quality can be obtained.

Another aspect of the invention relates to



use of the Bordeaux mixture for the preparation of formulated products in commercial demand such as:

- Bordeaux mixture as sole fungicide
- combination of this Bordeaux mixture with

5 at least one synthetic fungicide  
in the following presentations:

- formulations of WP type (wetable powder)

which are dispersible in water

10 - formulations of WG type (dispersible  
granule) of higher apparent particle size (from about  
50 to 400  $\mu\text{m}$ ) which are dispersible in water and  
release little or no dust at the time of use

- liquid formulations of SC type (suspension  
concentrate) which are also dispersible in water.

15 A wet Bordeaux mixture according to the  
invention may be obtained by reacting an aqueous copper  
sulphate solution and an aqueous suspension of lime at  
a temperature and for a period of time which are  
sufficient to convert substantially all of the copper  
20 complexes into brochantite.

In order to obtain the exclusive formation of  
brochantite, it is necessary for the  $\text{Ca}(\text{OH})_2/\text{CuSO}_4$  molar  
ratio to be between 0.60 and 0.75 and, preferably,  
between 0.65 and 0.70, approximately.

25 The copper concentration of the aqueous  
copper sulphate solution is not a critical parameter  
and is limited principally by the solubility of the  
copper sulphate at the implementation temperature.



Industrially, an aqueous copper sulphate solution having a copper content ranging from 20 to 100 g/l may be used. However, in order to avoid too large a dilution of the reaction medium, it is preferable to  
5 use a copper sulphate solution whose copper content is between 50 and 100 g/l and, more particularly, between 75 and 85 g/l.

The calcium hydroxide concentration of the aqueous suspension of lime is not a critical parameter  
10 either, and may vary within a wide range as a function of the particle size of the lime used. Industrially, an aqueous suspension having a  $\text{Ca}(\text{OH})_2$  content ranging from 20 to 200 g/l and, preferably, of between 100 and 150 g/l may be used.

15 Although the process according to the invention may be performed by simultaneously mixing the milk of lime and the aqueous copper sulphate solution or by introducing the milk of lime into the aqueous copper sulphate solution (direct process), it is  
20 preferred to work according to the reverse process consisting in introducing the aqueous copper sulphate solution into the milk of lime.

The reaction may be performed at a temperature ranging from room temperature to  $90^\circ\text{C}$ , but  
25 is preferably performed at between approximately  $40^\circ\text{C}$  and  $70^\circ\text{C}$ . The reaction time which is sufficient to convert all the copper complexes into brochantite depends on many factors, in particular on the temperature, the





stirring and the concentration of the reaction medium. Under certain conditions, substantially complete conversion of the copper complexes into brochantite may be obtained in about 30 minutes. It is, however,  
5 recommended to maintain the mixture in reaction for at least two hours and, optionally, to ensure the absence of copper complexes other than brochantite by X-ray examination of the reaction product.

The reaction product is in the form of a more  
10 or less concentrated aqueous suspension which contains no bassanite and which, after possible concentration in paste form (for example by centrifugation), may be used directly for the manufacture of fungicidal formulations of SC type (suspension concentrate) or of WG type  
15 (granules) which are dispersible in water and stable on storage.

For the manufacture of wettable powders of the WP type, the paste obtained after concentration needs to be dried. In accordance with the present  
20 invention, this drying may be performed under conditions such that the bassanite content of the dry product does not exceed 20%. The content of bassanite formed on drying depends on many factors, in particular on the temperature, the duration and the drying  
25 equipment used (oven, drying tower, drying tunnel). It may readily be controlled by analysis of the copper titre of the dry product, which should not exceed 27.3% by weight.



Starting with the Bordeaux mixture (paste or powder) according to the invention, fungicidal formulations may be manufactured in a manner which is known per se, using common adjuvants (dispersing agents, wetting agents, anti-foaming agents, dyes, thickeners, inert fillers and pH modifiers). It suffices to replace the standard Bordeaux mixture (paste or powder) by a Bordeaux mixture according to the invention with an equivalent amount of copper.

10           The invention also provides a method of combatting fungus in a crop which method comprises applying to the crop or the locus where the crop is growing a fungicidal composition according to the invention.

15           In the examples which follow, which illustrate the invention without limiting it, the parts and percentages are by weight except where otherwise mentioned.

**EXAMPLE 1**

20           8 litres of an aqueous suspension of lime containing 130 g/l (i.e. 14 mol of calcium hydroxide) were loaded into a reactor. Into this stirred suspension maintained at 40-50°C were then introduced, over 5 minutes, 16 litres of an aqueous copper sulphate solution containing 80 g/l of copper (i.e. 20 mol of  $\text{CuSO}_4$ ).

25

After reacting for 5 hours, the mixture was filtered and 9.66 kg of a Bordeaux mixture paste



containing 50% solids (referred to hereinbelow as "BM 50 paste") were thus obtained, which paste, on drying in an oven at a temperature not exceeding 90°C, gave a solid (referred to hereinbelow as "dry BM") having the

5 following characteristics:

- copper content:  $26.5\% \pm 0.5$
- plaster content: traces
- water content:  $< 1\%$
- pH at 1% in distilled water:  $6.5 \pm 0.5$

10 X-ray analysis shows that this solid consists of a coprecipitate of brochantite (46.7%) and gypsum (53.3%), with only traces of bassanite and other copper complexes.

#### EXAMPLE 2 (Comparative)

15 The process is performed as in Example 1, but with the drying being carried out at 100°C for 10 hours. A solid, not in accordance with the invention, was thus obtained consisting of brochantite (51%) and bassanite (49%), having the following characteristics:

- 20
- copper content:  $28\% \pm 0.5$
  - gypsum content: 0%
  - water content: 0%
  - pH at 1% in distilled water:  $6.5 \pm 0.5$

#### EXAMPLE 3

25 75.5 parts of "dry BM", 6 parts of sodium lignosulphonate (dispersing agent), 0.5 part of sodium naphthalenesulphonate (wetting agent), 0.5 part of an anti-foaming agent (silicone) and 17.5 parts of kaolin



were successively introduced into a mixer and the mixture was then ground and a wettable powder of Bordeaux mixture containing 20% of copper was obtained having, according to the CIPAC methods, the following

5 physical characteristics:

- wettability: < 60 s
- 45  $\mu$ m wet oversize: < 1%
- suspensibility: > 80%
- foam: < 20 ml

10 In this water-dispersible formulation it is possible, without drawback, to add a dye such as Prussian blue.

EXAMPLE 4

45.5 parts of "dry BM", 35.3 parts of  
15 technical-grade 85% mancozebe, 6 parts of sodium lignosulphonate, 0.5 part of sodium naphthalenesulphonate, 0.5 part of silicone, 1 part of Prussian blue and 11.2 parts of kaolin were loaded into the same apparatus as in Example 3.

20 After grinding, a wettable powder containing 12% of copper and 30% of mancozebe and having physical characteristics similar to those of the powder of Example 3 was obtained.

In this formulation, which is intended more  
25 particularly for treatment to combat downy mildew, all or part of the mancozebe may be replaced by another synthetic fungicide such as manebe, zinebe or folpel.

EXAMPLE 5



56.7 parts of "dry BM", 22 parts of technical-grade 91% zinebe, 2.5 parts of technical-grade 96% cymoxanil, 6 parts of sodium lignosulphonate, 0.5 part of sodium naphthalenesulphonate, 0.5 part of silicone and 11.8 parts of kaolin were loaded into the same apparatus as in Example 3, and the mixture was then ground.

A wettable powder containing 15% of copper, 20% of zinebe and 2.4% of cymoxanil and having physical characteristics similar to those of the powder of Example 3 was thus obtained.

In this formulation more particularly intended for treatment to combat downy mildew, all or part of the zinebe may be replaced by another synthetic fungicide such as mancozebe or folpel.

#### EXAMPLE 6

151 parts of "BM 50 paste" and 38 parts of water were mixed together in a tank fitted with a stirrer, in order to obtain a fluid paste (slurry) of low viscosity (about 100 mPa s at a shear rate of  $111 \text{ s}^{-1}$ ) and of low particle size (2 to 5  $\mu\text{m}$ ).

14 parts of sodium lignosulphonate, 0.5 part of sodium naphthalenesulphonate, 0.5 part of silicone and 9.5 parts of kaolin were then introduced into this fluid paste.

The mixture was then conveyed into a drying tower (spray dryer) and granules were thus obtained which were readily dispersible in water, having the



following characteristics (CIPAC method):

- copper content: 20%
- wettability: < 30 s
- 45  $\mu$ m wet oversize: < 1%
- 5      - suspensibility: > 80%
- foam: < 20 ml

EXAMPLE 7

Working as in the first paragraph of Example 6 with 129 parts of "BM 50 paste" and 32 parts of  
10      water, a fluid paste was prepared which was mixed with:

- 11 parts of technical-grade 91% manebe
- 14 parts of sodium lignosulphonate
- 0.5 part of sodium naphthalenesulphonate
- 0.5 part of silicone
- 15      - 9.5 parts of kaolin

After drying the mixture as in Example 6, WG granules containing 17% of copper and 10% of manebe and having physical characteristics similar to those of the granules of Example 6 were obtained.

20      EXAMPLE 8

Example 7 is repeated, but using the following constituents:

- 114 parts of "BM 50 paste"
- 28 parts of water
- 25      - 24 parts of technical-grade 85% mancozebe
- 2.5 parts of technical-grade 96% cymoxanil
- 14 parts of sodium lignosulphonate
- 0.5 part of sodium naphthalenesulphonate



- 0.5 part of silicone
- 1.5 parts of kaolin

WG granules containing 15% of copper, 20% of mancozebe and 2.4% of cymoxanil, which were readily dispersible in water and had physical characteristics very close to those of the granules of Examples 6 and 7 were obtained.

#### EXAMPLE 9

1132 g of "BM 50 paste" and 126 g of water were introduced simultaneously into a tank fitted with a stirrer, and to the fluid paste (slurry) thus obtained were then added 40 g of sodium lignosulphonate, 7.5 g of Prussian blue, 3.8 g of silicone anti-foaming agent and 90 g of an aqueous solution containing 2.5% of a thickener (polysaccharide of the xanthan gum type).

A liquid Bordeaux mixture was thus obtained containing 150 g/l of copper and having the following characteristics (CIPAC method):

- 45  $\mu$ m wet oversize: < 1%
- suspensibility: > 80%
- foam: < 20 ml

#### EXAMPLE 10

Example 9 was repeated, but using the following constituents:

- 755 g of "BM 50 paste" diluted with 230 g of water
- 40 g of sodium lignosulphonate



- 5 g of sodium naphthalenesulphonate
  - 7.5 g of Prussian blue
  - 3.8 g of silicone anti-foaming agent
  - 223 g of technical-grade folpel containing
- 5 90% of active material
- 90 g of an aqueous solution containing 2.5% of polysaccharide

A stable, liquid, ready-to-use mixture containing 100 g/l of copper and 200 g/l of folpel and

10 which had the same characteristics as the formulation of Example 9 was thus obtained.

#### EXAMPLE 11

Example 9 was repeated, but with the following constituents:

- 15 - 1132 g of "BM 50 paste" diluted with 106 g of water
- 40 g of sodium lignosulphonate
  - 5 g of sodium naphthalenesulphonate
  - 7.5 g of Prussian blue
  - 3.8 g of silicone anti-foaming agent
  - 21 g of technical-grade cymoxanil
- 20 containing 96% of active material
- 90 g of an aqueous solution containing 2.5% of polysaccharide

25 A stable, liquid, ready-to-use mixture containing 150 g/l of copper and 20 g/l of cymoxanil and which had the same characteristics as the



formulation of Example 9 was thus obtained.

All the formulations of Examples 3 to 11  
formed the subject of tropicalization tests (storage at  
54°C for 14 days) and showed excellent stability on  
5 ageing.

5

6

7

8  
9  
10  
11

The claims defining the invention are as follows:

1. Bordeaux mixture in which substantially all the copper is in the form of brochantite and which, in dry form, contains not more than 20% by weight of  
5 bassanite.

2. Aqueous suspension of Bordeaux mixture according to Claim 1, the solids of the suspension comprising essentially approximately 47% by weight of brochantite and 53% by weight of gypsum.

10 3. Dry Bordeaux mixture according to Claim 1, which dry mixture comprises approximately 47% by weight of brochantite, 33 to 53% by weight of gypsum and 0 to 20% by weight of bassanite.

4. Bordeaux mixture according to any one of  
15 claims 1 to 3 substantially as hereinbefore described.

5. Bordeaux mixture according to any one of claims 1 to 3 substantially as described in any one of Examples 1 and 3 to 11.

6. Process for the manufacture of a  
20 Bordeaux mixture as defined in Claim 1, which process comprises reacting an aqueous copper sulphate solution and an aqueous suspension of lime in a  $\text{Ca(OH)}_2/\text{CuSO}_4$  molar ratio of between 0.60 and 0.75, at a temperature and for a period of time which are sufficient to  
25 convert substantially all the copper complexes into brochantite.

7. Process according to Claim 6, in which the aqueous copper sulphate solution is added to the



aqueous suspension of lime.

8. Process according to Claim 6 or 7, in which the  $\text{Ca(OH)}_2/\text{CuSO}_4$  molar ratio is between 0.65 and 0.70.

5 9. Process according to any one of Claims 6 to 8, in which the reaction is performed at a temperature ranging from room temperature to  $90^\circ\text{C}$ .

10 10. Process according to any one of Claims 6 to 8 in which the reaction is performed at a temperature between  $40$  and  $70^\circ\text{C}$ .

11. Process according to any one of Claims 6 to 10, in which a copper sulphate solution whose copper content is between 50 and 100 g/l is used.

15 12. Process according to any one of Claims 6 to 10, in which a copper sulphate solution whose copper content is between 75 and 85 g/l is used.

13. Process according to any one of Claims 6 to 12, in which a suspension of lime having a  $\text{Ca(OH)}_2$  content ranging from 20 to 200 g/l is used.

20 14. Process according to any one of Claims 6 to 12 in which a suspension of lime having a  $\text{Ca(OH)}_2$  content ranging from 100 to 150 g/l is used.

25 15. Process for the manufacture of a Bordeaux mixture according to Claim 3 which process comprises, optionally after concentration, drying an aqueous suspension as defined in Claim 2 under conditions such that the weight content of copper in the product does not exceed 27.3%.



16. Process for the manufacture of a Bordeaux mixture as defined in Claim 1 substantially as hereinbefore described.

17. Bordeaux mixture as defined in Claim 1  
5 manufactured by the process claimed in any one of Claims 6 to 16.

18. Use of a Bordeaux mixture according to Claim 1 or 2 for the manufacture of cupric fungicidal compositions in the form of granules or concentrated  
10 suspensions, which are dispersible in water.

19. Use of a Bordeaux mixture according to Claim 1 or 3, for the manufacture of cupric fungicidal compositions in the form of wettable powders, which are dispersible in water.

20. A cupric fungicidal composition based on  
15 a Bordeaux mixture as claimed in any one of Claims 1 to 5 and 17.

21. A cupric fungicidal composition  
according to Claim 20 substantially as hereinbefore  
20 described.

22. A cupric fungicidal composition  
according to Claim 20 substantially as described in any one of Examples 4 to 11.

23. A method of combatting fungus in a crop  
25 which method comprises applying to the crop or the locus where the crop is growing a fungicidal composition as claimed in any one of Claims 20 to 22.

24. A method according to Claim 23 wherein the fungicidal composition is applied to vines.

## ABSTRACT

### BORDEAUX MIXTURE, PROCESS FOR ITS MANUFACTURE AND CUPRIC FUNGICIDAL COMPOSITIONS CONTAINING IT

The invention relates to a Bordeaux mixture  
5 for use in crop protection.

According to the present invention in the  
Bordeaux mixture substantially all the copper is in the  
form of brochantite and which, in dry form, contains  
not more than 20% by weight of bassanite.

10 The absence of cupric complexes other than  
brochantite and a small amount of bassanite in the dry  
product makes it possible to avoid the drawbacks of  
conventional Bordeaux mixtures.