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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Hydroxyquinoline Derivatives and their use in Food Conservation

We, AGRIPAT S.A., a Body Corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns new conserving compositions for edible parts of plants and processes for conserving edible parts of plants.

By edible parts of plants are meant in the present invention blossoms, seeds, fruit, leaves, shoots, rods, tubers and bulbs of cultivated plants, preferably crops.

A series of microbicidally active substances for conserving fruit is known from the literature, e.g. diphenyl, alkali metal salts of o-hydroxydiphenyl, chlorohydroxydiphenyl and salicylanilide, also thiourea, ammonia, sulphur dioxide, carbon dioxide etc. [Ullmann, 3rd Edition, Vol. *11*, p. 440—462 (1960)]. Such substances, however, only partially meet the desired requirements as either the breadth and duration of action is too slight or they are too toxic to warm blooded animals or they have an unpleasant smell.

The present invention provides novel salts of 5 - acetyl - 8 - hydroxyquinoline with a polybasic, strong, inorganic acid which have excellent microbicidal properties. They are very active particularly against a broad spectrum of micro-organisms which attack utilizable parts of plants after harvesting, such as bacteria, yeasts and fungi. The new salts are particularly valuable for this reason as active substances in conserving compositions which are used, e.g. for citrus fruit such as grapefruit, oranges, lemons, also bananas, pineapple, avocados, mango, gujava, litchi, nuts, apples, pears, peaches, apricots, plums, berries, sweet potatoes, potatoes, yam tubers, carrots, onions, salads, artichokes, cabbage, asparagus and edible mushrooms. In addition, these salts also have the other properties required of active substances for food preservatives, i.e. in the concentration necessary to preserve the foodstuff they are non-toxic to man and they have no adverse effect on the taste and smell of the foodstuff. For all practical purposes, the salts are neutral compounds and they do not alter the pH of the substrate.

In a further aspect therefore the present invention provides a composition for conserving edible parts of plants comprising as active substance, at least one salt of 5 - acetyl - 8-hydroxyquinoline with a polybasic strong inorganic acid in association with suitable non-toxic solvents and/or distributing agents.

By salts of 5 - acetyl - 8 - hydroxyquinoline with polybasic, inorganic, strong acids are meant in particular the salts of sulphuric acid, phosphoric acid, and pyrophosphoric acid. Furthermore in this specification, the term "polybasic strong inorganic acid includes boric acid. Such salts have not been known hitherto. 5 - Acetyl - 8 - hydroxyquinoline itself is known from J. Am. Chem. Soc. *52*, 4433—4436 (1930); its fungicidal activity is known from German patent No. 961,668. It is also known that when using 5 - acetyl - 8-hydroxyquinoline and its hydrochloride a strong irritant action on the skin and particularly on mucous membranes is observed. In contrast to this, the new salts do not in any way irritate the skin and the mucous membranes; also they are only slightly toxic and, therefore, are particularly suitable for practical use.

The new salts can be produced by usual processes, e.g. by reaction of 5 - acetyl - 8-hydroxyquinoline with the corresponding amount of acid. They are compounds which crystallise well, they are very stable in the air, and, in contrast to 5 - acetyl - 8 - hydroxyquinoline, also in neutral or weakly acid media. The sulphate of 5 - acetyl - 8-

[*Price 5s. 0d.*]

hydroxyquinoline melts at 237—238° C. and the mono phosphate melts at 230—235° C. (with decomposition).

In particular, the salts of 5 - acetyl - 8-hydroxyquinoline with sulphuric and phosphoric acid are used as active substances for preserving utilizable parts of plants. These two salts are distinguished by good fungitoxic properties. They are soluble to a certain extent in water and in organic solvents.

The fungitoxic action of the new salts was determined by the so-called "spore-germination-test" on the following types of fungi:

Penicillium italicum
Penicillium digitatum
Aspergillus niger
Botrytis cinerea.

1 cc of a 0.1% and 0.01% solution of each active substance in a suitable solvent such as acetone is placed on 2 glass slides (26 × 76 mm) under the same conditions. The solvent is evaporated off and a uniform coating of active substance is obtained on the glass slides. The slides are inoculated with spores of the above fungi and then kept in dishes at room temperature in an atmosphere which is almost saturated with steam. The germinated spores are counted twice, once after 48 hours and the second time after 72 hours. The results are summarised in the following Tables.

TABLE I

compound	concentration %	action against					
		Penicillium italicum		*Penicillium digitatum*		*Aspergillus niger*	
		48 h	72 h	48 h	72 h	48 h	72 h
5-acetyl-8-hydroxyquinoline monophosphate	0.1	++	++	++	++	++	++
	0.01	—	—	++	++	—	—
5-acetyl-8-hydroxyquinoline sulphate	0.1	++	++	++	++	++	++
	0.01	—	—	+	+	—	—
diphenyl	0.1	—	—	+	—	—	—
	0.01	—	—	—	—	—	—
sodium-o-chlorophenyl phenolate	0.1	—	—	+	—	—	—
	0.01	—	—	+	—	—	—
tetramethyl thiuram disulphide	0.1	—	—	+	+	—	—
	0.01	—	—	+	—	—	—
Control		—	—	—	—	—	—

TABLE II

compound	concentration %	*Botrytis cinerea* 48 h	*Botrytis cinerea* 72 h
5-acetyl-8-hydroxyquinoline sulphate	0.1	++	++
	0.01	—	—
diphenyl	0.1	—	—
	0.01	—	—
tetramethyl thiuram disulphide	0.1	—	—
	0.01	—	—
Control		—	—

Legend: ++complete inhibition of germination caused by residue of 1 cc of solution of active substance,

+a 60 to 90% inhibition of germination caused by residue of 1 cc of solution of active substance,

—no inhibition of germination.

EXAMPLE 1

The preserving action of 5 - acetyl - 8-hydroxyquinoline sulphate was determined on potatoes infested with *Phytophthora infestans* (browing mildew).

48 Pin pricks are made in potato tubers which are then laid in suspension of *Phytophthora* zoo-spores. In Test 1, the tubers remain in the suspension for 60 minutes and in Test 2 for 30 minutes. After they have dried the infected tubers are dipped in either a 0.4%, 0.8% or 1.2% solution of 5-aceto-8-hydroxyquinoline sulphate. After the treatment, the tubers are allowed to dry and then planted immediately in moist vermiculite or sawdust. After 18 days the potatoes are peeled and their surface is tested for attack by *Phytophthora*.

Concentration in %	Attack by *Phytophthora* Test 1	Test 2
0.4	28%	40%
0.8	0%	3%
1.2	0%	0%
untreated	33%	75%

The edible parts of plants are preserved according to the invention by providing them with a protective coating of the new salts by either dipping, spraying, washing or painting them with liquid or wax-like preparations of the active substances. In many cases, because of their advantageous solubility in water, the new microbicidal salts can be used in the form of aqueous solutions. On the other hand, it is possible to mix the active substances together with suitable non-injurious dispersing agents such as vegetable oils, fats or waxes and to use these dispersible preparations as aqueous to anhydrous dispersions.

As solvents for such dispersions are meant non-toxic, low boiling, organic solvents such as low hydrocarbons, ketones, alcohols and ethers.

EXAMPLE 2

The following forms of compositions according to the invention serve to illustrate the present invention; where not expressly stated, parts and percentages are by weight.

a) *Paste*

20 Parts of 5 - acetyl - 8 -hydroxyquinoline sulphate,
20 parts of a 7% aqueous hydroxyethyl cellulose,
3 parts of ditertiary acetylene glycol,
57 parts of distilled water

are milled and homogenised in a mixer into a thinly flowing 20% paste. On direct addition of water, the paste dissolves into a milky dispersion. Freshly harvested oranges are dipped into a 1% dispersion; it was observed that the fruit showed no damage whatever due to micro-organisms after several days.

b) *Pulverulent Concentrate*

95 Parts of 5 - acetyl - 8 - hydroxyquinoline sulphate and 5 parts of Igepal CA 630 or another suitable, preferably ionic, wetting agent are homogenised and finely milled in a suitable mill. This pulverulent concentrate is not dusty and quickly dissolves in water. A suspension of, e.g. 1%, evenly wets fruit treated therewith.

c) *Emulsion Concentrate*

10 Parts of 5 - acetyl - 8 - hydroxyquinoline mono phosphate,
15 parts of ethoxyethanol,
15 parts of dimethyl formamide,
10 parts of emulsifying agent consisting of a mixture of Ca salt of dodecylbenzene sulphonic acid and nonylphenol polyoxyethylene (e.g. P 140 HFP),
50 parts of petroleum (boiling range 230—270°).

The mixture is a 10% emulsion concentrate which can be diluted with water to form emulsions of any concenttration desired.

A 1% aqueous emulsion is used for the treatment of mould (e.g. *Penicilium italicum*) on grapefruit. For this purpose, the fruit is dipped in the emulsion and left there for a few seconds. It is then allowed to drip dry. The attack by fungi is greatly reduced by this treatment and any new infection is prevented. We are aware of the Preservations in Food Regulations, 1962, No. 1532 and make no claims to use the invention in contravention of the law.

WHAT WE CLAIM IS:—

1. Salts of 5 - acetyl - 8 - hydroxyquinoline with a polybasic, strong, inorganic acid.
2. 5 - acetyl - 8 - hydroxyquinoline sulphate.
3. 5 - acetyl - 8 - hydroxyquinoline mono phosphate.
4. A composition, for conserving edible parts of plants, comprising, as active substance, at least one salt of 5 - acetyl - 8-hydroxyquinoline with a polybasic, strong, inorganic acid, in association with suitable non-toxic solvents and/or distributing agents.
5. A composition as claimed in claim 4 in which the active substance is 5 - acetyl - 8-hydroxyquinoline sulphate.
6. A composition as claimed in claim 4 in which the active substance is 5 - acetyl - 8-hydroxyquinoline mono phosphate.
7. A process for conserving edible parts of plants, comprising treating said parts with at least one salt of 5 - acetyl - 8 - hydroxyquinoline with a polybasic strong, inorganic acid, optionally together with suitable non-toxic solvents and/or distributing agents.
8. A process as claimed in claim 7, in which the salt of 5 - acetyl - 8 - hydroxyquinoline is the sulphate.
9. A process as claimed in claim 7, in which the salt of 5 - acetyl - 8 - hydroxyquinoline is the mono phosphate.
10. A compound as claimed in claim 1 substantially as hereinbefore described.
11. A composition as claimed in claim 4, substantially as hereinbefore described with reference to Example 1.
12. A composition as claimed in claim 4, substantially as hereinbefore described with reference to Example 2.
13. A process as claimed in claim 7, substantially as hereinbefore described with reference to Example 1.
14. A process as claimed in claim 7, substantially as hereinbefore described with reference to Example 2.

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