

A new type of polymeric heavy metal complexing precipitant used as fishery disinfectant and antiparasitic drug

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Abstract. This paper presents a technique to produce a new kind of fishery drug that is water emulsion suspending agent containing polymeric calcium-iron-dithiocarbamate with heavy metal complexing precipitate ability, good disinfection and auxiliary insecticidal efficacy. The product has good dispersion, high efficiency and low toxicity, as well as no pollution and no harmful residues. It not only can be used in the pond waters and ornamental waters, but also can meet the high requirements of the aquaculture waters. There is non-pollutant emission in the production, which is a green environment-friendly technique without three waste discharges. This technology belongs to the ecological and environmental protection.

1. Introduction

With the development of society and economy, heavy metal pollution of the environment is more and more serious. The world's most famous minamata disease and itai-itai disease are caused by heavy metal pollution. In the past twenty years, owing to the heavy metal in excess of the standards of aquatic products caused by the existing low standards of aquaculture water environment, Chinese export of aquatic products has been repeatedly frustrated.

Table 1. The effects of polymeric N- methyl calcium-iron-dithiocarbamate.

No.	Water area	Symptom	Concentration of this drug	Effect
1	1m ³	Pd ²⁺ 0.1 mg/L, Cu ²⁺ 0.1 mg/L	0.15 mg/L	Pd ²⁺ ≤0.05 mg/L, Cu ²⁺ ≤0.01 mg/L
2	12 acres of land	dark green and odor, Cu ²⁺ 0.1 mg/L	0.12 mg/L	Color returned to normal and odor elimination, Cu ²⁺ ≤0.01 mg/L
3	8 acres of land	dark green and odor	0.09 mg/L	Color returned to normal and odor elimination
4	10 acres of land	dark green and odor	0.08 mg/L	Color returned to normal and odor elimination

The technique is to produce a water emulsion suspending agent containing polymeric N- methyl



calcium-iron-dithiocarbamate that is stereo mesh structure. From the original agents to production of a uniform dispersion of water emulsion suspending agent, there is no pollutant emission with the method of one-pot reaction, to reach 100% atomic utilization ratio. This product has good dispersion, good disinfection and auxiliary insecticidal efficacy, with high heavy metal complexing precipitation capacity and low toxicity, as well as no pollution and no harmful residues. The effects of polymeric N-methyl calcium-iron-dithiocarbamate are revealed (table 1). It not only can be used in the pond waters and ornamental waters, but also can meet the high requirements of the aquaculture waters.

Meanwhile, heavy metal as a kind of widespread pollution is a common chemical poison to fish acute poisoning death. Unfilled D orbit in the outermost electron shell mostly of heavy metal ion as a good electron acceptor has a strong affinity with many active groups of enzymes. Heavy metal ion can combine with the thiol group of the enzyme to form an insoluble thiolate, inhibit the activity of the enzyme and interfere with the metabolism after being absorbed into fish.

The Ministry of Agriculture in August 2003 issued No. 31 Decree of Regulation on Quality and Safety Management of Aquaculture, "aquaculture quality and safety management requirements". It regulates that the pollution-free aquaculture has become the minimum standards in the provisions, and aquatic drugs are under strict supervision. At the same time, a promoting plan was issued. The main content is that China's aquaculture industry has to implement standardized management and improve the quality testing system of aquatic products in a short period of 3-4 years, through the development of aquaculture standards. And in the main production areas monitoring system should be strengthened, with quality certification system of aquatic products, to comprehensively improve the international competitiveness of China's aquatic products. Therefore, research and development of pollution-free fishery drug has become the focus of the current aquaculture industry [1, 2].

In order to deal with the heavy metal pollution especially copper pollution caused by excessive use of copper sulfate and improve aquaculture water environment to meet the high requirements of Chinese aquaculture industry in aquaculture waters. Copper is an essential trace element for organism, and it is an important component of biological serum protein and cytochrome oxidase. But too much copper can have a toxic effect on organisms and cause extensive damage to the branchial gland of fish, such as increasing mucus, hypertrophy, hyperplasia, being disintegrated and covering each other, finally cause death of fish by suffocation. The Symptoms are as follows. The mouth vomits, the gill is pale green and the fish body is pale. Its autopsy revealed that a large number of cell debris and mucus in the lumen, and the columnar epithelium necrosis and ulceration were found in the digestive tract of the his body. The copper ion is above 1.0 mg/L, which will make water turbidity and odor also.

Dithiocarbamate is widely used in industry and also known as insecticidal and bactericidal drugs in agriculture [3-9]. For example, pesticides containing N, N-dimethyl dithiocarbamate, or ethylene-dithiocarbamate are also available. However, so far, these pesticides are mainly used for crops, to prevent all kinds of pests and diseases.

The existing dithiocarbamate can not meet this requirement. There have been no reports on the use of dithiocarbamate as water disinfectants and antiparasitic fishery drugs, except two papers reported by our team [1, 2]. Herein we wish to report a new type of polymer heavy metal complexing precipitant that can be used as fishery disinfectant and antiparasitic medicine. This technology belongs to the ecological and environmental protection.

2. Materials and methods

The aqueous emulsion suspending agent containing polymeric N-methyl calcium-iron-dithiocarbamate is a kind of high heavy metal complexing precipitant with good disinfection and auxiliary insecticidal efficacy. It contains 10-34% N-methyl calcium-iron-dithiocarbamate, 8-16% carrier dispersant, 5-12% multifunctional emulsifier, 0.2-5% colloidal dispersant, 1-3% antioxidant and 0.2-3% antiseptic agent and 2-3% antifreeze.

First, mix N-methylamine (870 g, 30 mol) and $\text{Ca}(\text{OH})_2$ (2442 g, 33 mol) solution, drop CS_2 (1320 g, 30 mol) slowly, after stirring 2-3 hours at room temperature, N-methyl calcium-dithiocarbamate is generated. Then add green vitriol (4170 g, 15 mol) to the calcium salt, after metathesis reaction and

polymerization catalyzed by hydroxylamine hydrochloride (208.5 g, 3 mol) in an aqueous medium product of polymeric N-methyl calcium-iron-dithiocarbamate is produced. Third, the raw aqueous product polymeric N-methyl calcium-iron-dithiocarbamate is ground to particles of less than 300 microns with a ball mill, add ultra-fine kaolin (600 g), Tween-80 (600 g), xanthan gum (250 g), propyl gallate (500 g), sodium benzoate (150 g), glycerol (250 g), and water to 20000 g, along with stirring intensively. Last, with a high-speed shearing emulsifying machine, shear and emulsify it to obtain 10% of uniform dispersed water emulsion suspending agent of polymeric N-methyl calcium-iron-dithiocarbamate, with the yield of about 91%.

From the original agents to production of a uniform dispersion of water emulsion suspending agent, there is no pollutant emission with the method of one-pot reaction, to reach 100% atomic utilization ratio (figure 1). This is a green environment-friendly production technique without three waste discharges. This technology belongs to the ecological and environmental protection.

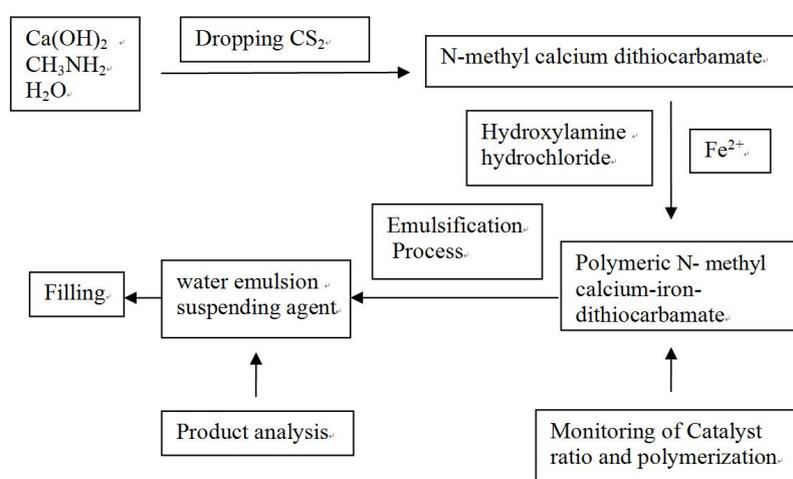


Figure 1. The production technique of water emulsion suspending agent containing polymeric N-methyl calcium-iron-dithiocarbamate.

3. Results and discussion

Not only to consider the effect of aquaculture water modifying agent, but also to avoid poisoning the human body and cultured animals, which is different from the using of industrial wastewater treatment chemicals. Therefore, water modifying agent must be efficient, no residue and good dispersion. Two low molecular dithiocarbamates (sodium and potassium salts) have strong coordination ability to heavy metal ions, can be used for complexing metal ions in wastewater treatment, but its instability and toxicity limits its application range.

We have reported that water emulsion suspending agent containing iron dithiocarbamates or copper dithiocarbamates can be used as fishery disinfectant and antiparasitic drug, but the metal complexing capability is weak.

In order to develop a kind of fishery drug that is polymeric heavy metal complexing precipitant. The structure modification to the lead compounds is changing the N-group and combining with macroelement and trace elements of the human body, so as to improve the precipitate ability but not to reduce complexing ability.

The technique is to produce a water emulsion suspending agent containing polymeric N- methyl calcium-iron-dithiocarbamate that is stereo mesh structure. From the original agents to production of a uniform dispersion of water emulsion suspending agent, there is no pollutant emission with the method of one-pot reaction, to reach 100% atomic utilization ratio. This product has good dispersion, good disinfection and auxiliary insecticidal efficacy, with high heavy metal complexing precipitation capacity and low toxicity, as well as no pollution and no harmful residues. The effects of polymeric N-methyl calcium-iron-dithiocarbamate are revealed (table 1). It not only can be used in the pond waters

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