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(54) Title: METHOD OF MAKING A COMPLEXING AGENT FOR PLANT MICRONUTRIENTS

(57) Abstract

A method of making a chelating and complexing agent that includes the steps of mixing ground cellulose ore, such as leonardite, peat, or lignite, with sufficient alcohol, containing a small amount of mineral acid, to wet the ore, allowing the alcohol to evaporate as it oxidizes the ore, and mixing the treated ore with water, hydrogen peroxide, and potassium hydroxide to extract the chelating and complexing agent from the ore.

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METHOD OF MAKING A COMPLEXING AGENT FOR PLANT MICRONUTRIENTS

This is a continuation-in-part of Serial No. 06/650,112, filed September 13, 1984 and entitled "Method of Making a Complexing Agent for Plant Micronutrients". This invention relates to a method of making a chelating and complexing agent for plant micronutrients such as zinc and iron.

This is an improvement on the invention disclosed and claimed in my Patent No. 4,425,149, which issued on January 10, 1984 and is entitled "Method of Making a Dry Compound Containing Chelated Micronutrients and the Chelating Agent Used to Form the Compound."

As pointed out in this patent, the practice of supplying plants with chelated and complexed micronutrients separately or with fertilizers is well known. There is a large number of metal complexing agents available. Dr. Flake L. Fisher in his article entitled "No Pat Answers" that appeared in the January 1984 issue of SOLUTIONS Magazine grouped these agents according to strength. The strongest were the synthetic metal chelating agents. These include EDTA, HEEDTA, DTPA, EDDAA, NTA, and CDTA. Those considered by Dr. Fisher to be of intermediate strength were the long-chain natural organics. These are the

polyflavonoids, lignosulfonates, humic and fulvic acids, amino acids, glutamic acids, and polyphosphates. The weakest were the short-chain or small organics. These are citric acids, ascorbic acid, tartaric acid, and adipic acid.

The synthetic chelating agents are very expensive. It is also believed that they do not assist the plant in taking up or translocating the micronutrients from the leaf or ground into the plant. The long-chain natural organic chelating or complexing agents, particularly humic and fulvic acids do help the plant in translocating the micronutrients. They are pH sensitive, however. Humic acid, for example, cannot be mixed with fertilizers that are acid or neutral because humic acid is insoluble in anything other than bases. In addition, chelated metal salts using these chelating agents tend to fall out with time giving the chelated compound a relatively short shelf life.

It is an object of this invention to provide a method of making a chelating agent of the long-chain natural organic type that is very inexpensive and easy to manufacture, and when mixed with a metal salt will produce a stable product containing a higher percentage of chelated or complexed micronutrients than can be obtained with any known chelating complexing agent at the present time, including the synthetic chelating agents.

It is a further object of this invention to provide such a chelating agent that can produce a dry chelated micronutrient product using as little as 5% by weight of the chelating agent.

In addition, it is a further object of this invention and a feature thereof to produce a chelating agent that can be sprayed as a liquid on the dry micronutrient compounds to obtain a dry chelated micronutrient product thereby eliminating a liquifying and a drying step in the process.

It is a further object of this invention to provide a method of producing a chelating agent that can produce a chelated dry micronutrient compound that can contain up to 35% zinc, 19% iron, 26% manganese, and 24% copper, which are substantially higher percentages than can be obtained with EDTA, which can produce a maximum chelated material of 14% zinc, about 10% iron, 12% manganese, and 13% copper. Also, by comparison, lignosulfonate chelates can complex a maximum of 10 to 27% zinc, 23% iron, and about 20% manganese.

It is known to extract humic and fulvic acid from leonardite ore using hydrogen peroxide. Leonardite also contains various waxes, resins, and fatty acids that are also extracted and make the product unsatisfactory by decreasing its shelf life and making it pH sensitive. It has been discovered that a product can be obtained that is an excellent chelating agent that is free of waxes, resins, and fatty acids. The key factor is control of the pH to oxidize the ore and put into solution certain selected humic acids along with the waxes, resins, and fatty acids, then continuing the oxidizing process to drive off the waxes, resins, and fatty acids leaving a supernatant of selected humic acids with a pH of about 3 that is substantially free of impurities. This is accomplished as follows:

According to the method of this invention, a cellulose material, such as, peat, lignite, or leonardite ore, is finely ground and mixed with alcohol, either methyl or ethyl, and a sufficient amount of an oxidizing agent, such as a mineral acid, to oxidize the ore. For example, a mixture of 45 gallons of methanol, 95 lbs. of concentrated nitric acid, and 500 lbs. of leonardite ore. This produces a thin slurry. The amount of methanol can be reduced, but it is important that the ore be sufficiently wetted with the acid-methanol mixture to have a paste-like consistency. Preferably the ore is a well weathered, leonardite ore, and the oxidizing acid is nitric acid, although citric, acetic, tartaric, oxalic, ascorbic and phosphoric acids could also be used. After the ore, the alcohol, and the oxidizing agent have been combined, the resulting mixture is allowed to stand, preferably in the sun as much as possible, with occasional stirring, to allow the alcohol to evaporate as the ore oxidizes. The alcohol retards the oxidation process allowing it to progress slowly over a period of time without the violent reaction that would otherwise occur. This process can be shortened by adding heat. After the methanol has evaporated, the remaining dry ore will continue to oxidize. As it does, the ore turns reddish-brown. With sufficient time all of the ore will turn reddish-brown indicating that it is sufficiently oxidized for the sequential extraction of the chelating solutions from the ore. During the summer this will take about two weeks.

EXAMPLE I

Examples of the manner of extracting the chelating solutions from the treated ore and how these solutions are used to chelate metal salts are set out below:

Mix 1200 lbs. of water at a temperature of 130-140°F. with 150 lbs. of leonardite ore and 60 lbs. of 50% hydrogen peroxide. There will be little reaction at this time. Then about 8 lbs. of potassium hydroxide or about 20 lbs. of aqua ammonia in two to three gallons of water is added. This produces a violent reaction. The pH of the solution before adding the potassium hydroxide is about 3, after adding the potassium hydroxide it will be about 6. As the reaction continues, the pH will move back to a pH of 3 at which time the reaction will be substantially completed and the supernatant is separated from the remaining ore.

EXAMPLE II

An alternate method of extracting the chelating solutions without the violent reaction of EXAMPLE I is as follows:

Add 300 lbs. of the treated ore to 400 gals. (3320 lbs.) of water and slightly heated, about 110° F., to initiate additional oxidation. Add approximately 20 lbs. of a base, such as potassium hydroxide, or a sufficient amount to bring the pH to 7-7.5. Add hydrogen peroxide (50%) in 30 lb. increments to control the reaction from the base and to gradually bring the pH down to about 3-3.5.

In both examples described above after the supernatant is removed, there will be a substantial volume of solids left. Additional product can be obtained from this residue by adding additional treated ore, usually about 100 lbs. to the residue of Example II, and repeating the process. This can usually be done about two times after which only a small amount of solids will remain.

The ranges of the ingredients are between 80-95% water, 5-15% ore, 2-6% hydrogen peroxide, and 1% or less of the base.

The accumulated supernatant is an excellent chelating agent. It can be used alone or mixed with about twenty percent sodium citrate or citric acid depending on the desired pH. This produces a somewhat more stable product.

EXAMPLE III

To obtain a 35.5 dry zinc chelated material, the supernatant from Example I above is mixed with 36% zinc sulfate. Five pounds of the chelating agent is used with 100 lbs. of the zinc sulfate. The components are mixed well and then let dry. This will leave about 101.4 lbs. of material containing 35.5% chelated and complexed zinc.

EXAMPLE IV

To obtain a 7.2% zinc chelate, mix 20% by weight of 36% zinc sulfate, 1% by weight of the chelating solution obtained above and 75% water. This gives a 7.2% zinc chelate. The addition of 3 to 4% additional citric acid to this

material enhances the efficacy of the material and prevents the mixture from being somewhat cloudy.

As stated above, one of the advantages of the chelating and complexing agent is the small amount required. For example, one pint will produce twelve gallons of a chelated micronutrient in the following percentages: 7% zinc, 5% iron, 5% manganese, or 5% copper.

It is not known exactly what compounds are extracted from the ore by this method, but it is believed that it is primarily a hydroxyketocarboxylic acid. In his book PEAT-Industrial Chemistry and Technology, Academic Press (1980 p. 152), Charles H. Fuchsman, states "a partially nitrated humic acid, called 'nitro humic acid' is obtained when humic acid is oxidized with 5N HNO_3 at temperatures up to 60°C. According to Fuchsman and Stengel (1930), the product is really a nitroso derivative of a hydroxyketocarboxylic acid. Its molecular weight (about 1300) and other properties suggest strong similarity to humic acid, except that 'nitro humic acid' is soluble in acetone and other organic solvents."

As stated above, it is believed that the chelating agent obtained by the method of this invention acts to increase the ability of the plant to translocate the micronutrients into the plant. This is done by affecting the semi-permeable membranes of the plant cell, thereby enabling ions to pass through it more easily. The product also reduces the surface tension of water and therefore is a mild wetting agent. Also, as stated above, one of the great

advantages of the product produced by the method of this invention is that it forms a stable, water soluble, complex with divalent and trivalent metal ions that is not pH sensitive and can be mixed with either basic or acid fertilizers.

An example of the ability of plants to take up the micronutrients chelated with the product of this invention is demonstrated by a test in California on almond trees. There were three one-acre plots. The first one was the control plot. On the second one, a zinc lignosulfonate chelate was applied at the rate of 0.5 lbs. of zinc per acre. On the third plot, a zinc chelate using the chelating agent obtained by the method of this invention was applied at the rate of 0.32 lbs. of zinc per acre. Samples of the leaves were then tested in the laboratory and the following concentrations of zinc in the leaves were found. In the control plot, the leaves contained 40 parts per million. In the plot sprayed with the lignosulfonate zinc chelate, the leaves contained 79 parts per million. In the plot sprayed with the material of this invention, the leaves contained 119 parts per million, thereby demonstrating dramatically the ability of the product of this invention to assist the plant in taking up micronutrients.

Another field test was conducted on Rubired grapes near Fresno, California. One plot was treated one pound to the acre with a 35% zinc chelate obtained in the manner described in Example IV. A peteole sample showed 38 ppm zinc in the leaves. This compared to 27 ppm in the leaves of a

plot sprayed with a 7% zinc sulfate lignosulfonate chelate at the rate of five pounds to the acre.

Another test on Thompson seedless grapes near Fresno, California showed an increase of 33% from 54 ppm to 72 ppm after being sprayed with a 35% zinc chelate described above at the rate of one pound to the acre.

From the foregoing it will be seen that this invention is one well adapted to attain all of the ends and objects hereinabove set forth, together with other advantages which are obvious and which are inherent to the method.

The invention having been described, what is claimed is:

1. A method of making a chelating and complexing agent comprising the steps of mixing ground cellulose ore, such as leonardite, peat, or lignite, with sufficient alcohol containing a small amount of mineral acid to wet the ore, allowing the alcohol to evaporate, allowing the ore to oxidize, and mixing the treated ore with water, hydrogen peroxide and potassium hydroxide to extract the chelating and complexing agent from the ore.

2. The method of claim 1 in which the ore is allowed to oxidize until it turns reddish-brown in color.

3. The method of claim 1 or 2 in which the alcohol and mineral acid wet the ore sufficiently to form a thick slurry.

4. A method of making a chelating and complexing agent comprising the steps of mixing ground cellulose ore, such as leonardite, peat, or lignite, with sufficient alcohol containing a small amount of mineral acid to wet the ore to form a thick slurry, allowing the alcohol to evaporate as the ore oxidizes until it is reddish-brown in color, mixing about 15% by weight of the oxidized ore with 60-79% by weight of water and 6-25% by weight of 50% hydrogen peroxide and 0.5-1.0% of a strong base, such as potassium hydroxide and aqua ammonia, and separating the supernatant from the remaining solids.

5. A method of making a chelating and complexing agent comprising the steps of mixing ground cellulose ore, such as leonardite, peat, or lignite with a sufficient

amount of mineral acid to oxidize the ore and a sufficient amount of alcohol to cause the oxidizing reaction to occur over a period of time as the alcohol evaporates, allowing the alcohol to evaporate and extracting the chelating and complexing agent by mixing the ore with water, hydrogen peroxide, and a base, such as potassium hydroxide or aqua ammonia, and separating the supernatant from the remaining solids.

6. The method of claim 5 in which a sufficient amount of the base is added to change the pH of the mixture to between 7 and 7.5 and a sufficient amount of the hydrogen peroxide is added to lower the pH to between 3 and 3.5.

7. The method of claim 5 in which the supernatant is obtained by mixing 5-15% by weight of the ore with 80-95% by weight water, 2-8% by weight hydrogen peroxide, and 1% or less of the base.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/01918

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(4): C05F 11/02
U.S. Cl. 71/24, 1, 64.11, DIG. 2

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	71/1, 11, 23, 24, 27, 903, Dig.2, 64.11; 424/19; 426/74

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 3,076,291, (Gardner) 05 February 1963, See entire entire document.	1-7
X	US, A, 4.377,599. (Willard, SR.) 22 March 1983, See column 8, lines 51-69, column 9, lines 13-26. column 10, lines 35, 60-68, column 11, lines 1-6.	1-7
X	US, A, 4,425,149 (Kimbro) 10 January 1984, See entire document.	1-7

* Special categories of cited documents: [15]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
05 December 1986	15 DEC 1986
International Searching Authority [1] ISA/US	Signature of Authorized Officer [20] Ferris H. Lander

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