

### **Ferric Humate Patents & Licenses**

Vigiron and its affiliate Agro-Iron, Inc. have the exclusive world-wide license to the following patents, copies of which are attached hereto:

<b><u>Patent #</u></b>	<b><u>Title</u></b>
5,213,692	Process for preparing preferred iron humate
5,302,180	Iron Humate Product
5,354,350	Citrate Soluble Slow Release Iron Humate
5,411,569	Iron Humate Product and Method of Use

These patents reserve certain rights to the patent-owner, which have been exclusively licensed to Vigiron and its affiliate Agro-Iron, Inc., with respect to preparation of iron humate and the beneficial use of iron humate product as a chemical material and for use as a nutrient in animal feed and to promote growth of agricultural crops and turf grasses.



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## United States Patent [19]

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Hjersted

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## [54] IRON HUMATE PRODUCT

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## Related U.S. Application Data

[63] Continuation of Ser. No. 751,872, Aug. 28, 1991, Pat. No. 5,213,692.

[51] Int. Cl.<sup>5</sup> ..... C05F 11/02[52] U.S. Cl. .... 71/24; 71/28;  
71/DIG. 2; 71/59; 210/710; 210/724; 210/917[58] Field of Search ..... 71/24, 28, DIG. 2, 59;  
210/609, 702, 709, 710, 723-728, 770, 917

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## [57]

## ABSTRACT

A process is provided for preparing preferred iron humate products. The preferred iron humate products provide iron and other nutrients and organic matter for vegetation. The preferred iron humate products are produced by using an iron salt coagulant that is relatively free of heavy metal contaminants and reacting the iron salt coagulant with naturally occurring humic substances such as those found in natural surface waters used in drinking water treatment facilities. According to the invention, iron is stoichiometrically reacted at a controlled pH with the humic and fulvic acid fractions in the water to precipitate an iron humate product precipitate. A preferred concentration of iron salt coagulants is used in order to minimize the formation of iron hydroxides which generally provide low iron availability to the plant. A more readily soluble iron humate complex is produced by the reacting and or blending of the iron humate residue with various nitrogen containing sources.

4 Claims, No Drawings

## IRON HUMATE PRODUCT

### CROSS REFERENCE TO RELATED APPLICATION

The present application is a continuation of U.S. Ser. No. 07/751,872, filed Aug. 28, 1991 entitled PROCESS FOR PREPARING PREPARING PREFERRED IRON HUMATES, Now U.S. Pat. No. 5,213,692.

### BACKGROUND OF THE INVENTION

The present invention relates to a process for preparing a preferred iron humate product, compositions of preferred iron humate products and a method for treating chlorosis in vegetation using preferred iron humate products.

Many agricultural crops and turf grasses must have commercial applications of iron nutrients in order to prevent or correct for iron deficiency otherwise known as plant chlorosis. Chlorosis can be physically detected by yellowing of leaves in trees, shrubs, and vegetables and yellowing of blades within turf grasses. Chlorosis hinders plant growth or yields and can also lessen food quality. Additionally, many soils are deficient in organic substances which can have a favorable effect on soil moisture retention, plant nutrient uptake and plant growth. There are many commercial iron nutrient sources available to correct for iron chlorosis such as ferrous sulfate and chelated irons such as sodium ferric ethylenediamine di-(0-hydroxy-phenol-acetate) ("FeEDDHA") sold under the trade names Sequesterene 138-Fe and Libfer SP.

A separate problem has been the disposal of sludge or precipitates formed by coagulating raw water contaminants with iron and aluminum salts or the like at potable water treatment plants and at plants designed to remove the organic color from effluents from such sources as paper mills. This is especially true for surface waters which are characterized by their high content of dissolved organic color from the natural decaying of aquatic vegetation. These potable water treatment plants must use high coagulant dosages, which in turn, generate large quantities of sludge residue for disposal. Often the water treatment sludges are simply dumped back into the water source causing degradation of the water quality. Other currently preferred options for disposal of water treatment sludges are lagoon storage, disposal in landfills and discharge into sanitary sewers. Inadequacies in these disposal methods has led to an increased interest in the land application of water treatment sludge.

Important constituents of natural surface waters are aquatic humic substances. Humic substances are formed from the decomposition of plant and animal materials and comprise the largest fraction of natural organic matter in natural surface waters accounting for 40 to 60 percent of the dissolved organic carbon ("DOC"; DOC is defined as organic carbon particles smaller than 0.45 micrometers in diameter and may be in colloidal suspension rather than in solution).

Humic substances comprise a complex heterogeneous mixture of compounds that are not readily separated into discrete components. However, three subfractions of humic substances are generally recognized. These subfractions comprise humic acid, fulvic acid and humin. Humic acid is defined as the fraction of humic substances that is not soluble in water under highly acidic Conditions (pH < 2.0) but is soluble at higher pH

values. Fulvic acid is defined as the fraction of humic substances that is soluble in water under all pH conditions. Humin is defined as the fraction of humic substances that is not soluble in water at any pH value.

Humic substances are removed from raw drinking water due to several problems associated with their presence. Humic substances are responsible for the yellow or brown organic color of natural surface waters. Humic substances act as a vehicle for the transport of toxic, water insoluble elements and organic micropollutants. Chlorine combines with aquatic humic substances to form chlorinated organic compounds, such as chloroform and complex chlorinated compounds, that may have negative effects on health. Humic substances also precipitate in water distribution systems where they lead to deterioration of tap water quality and increase the need for interior cleaning of pipes.

Traditionally, colored surface waters have been treated with alum (aluminum sulfate) which generates an aluminum containing sludge, which after dewatering, must be deposited in a secure landfill. Iron salt coagulants have been effectively used but often produce a sludge high in heavy metals due to the quality of the iron salt coagulant. Many of the commercial iron salt coagulants are produced from by-products from such sources as TiO<sub>2</sub> production or steel pickling and are typically high in heavy metals and organic contaminants.

When an iron salt coagulant is used as the primary coagulant to remove humic substances, it reacts to precipitate an iron humate residue. The inferior quality of many iron salt coagulants, in terms of concentration of heavy metal contaminants, often results in iron humate products having unacceptable concentrations of heavy metals so as to prevent land application of the iron humate products.

Another problem with current potable water treatment methods is that these methods generally result in a water treatment sludge having unnecessarily high concentrations of hydrous metal oxides, such as iron hydroxides. Hydrous metal oxides are strong adsorbents of trace metals and phosphorus. When applied to the soil surrounding vegetation at high concentrations and high pH, iron hydroxides can result in metal deficiencies in the vegetation including iron deficiency. Also the presence of hydrous metal oxides results in the sorption of phosphorous from the soil reducing the availability of phosphorous to vegetation. Phosphorous is necessary for vegetation growth. Additionally, iron hydroxides do not dewater as well as iron humate products. The iron hydroxides form a somewhat gelatinous mass making sludge containing excess iron hydroxides harder to handle and more expensive to transport.

### SUMMARY OF THE INVENTION

The present invention provides preferred iron humate products and processes for preparing preferred iron humate products adapted for use in treating chlorosis in vegetation.

Existing water treatment processes focus primarily on producing high quality drinking water with little regard for the quality of the resultant sludge. The goal of the water treatment process of the present invention is to produce both high quality drinking water and a high quality sludge that is particularly well adapted for land application to provide useful nutrients to plants.

The concentration of heavy metal contaminants in the resultant iron humate product is reduced by selecting a relatively pure iron salt coagulant that is free of or has a relatively low concentration of heavy metal contaminants.

The concentration of iron hydroxides in the resultant iron humate product is minimized by using a minimum dosage of iron salts to effect the required color removal of the raw water. The iron salt dosage is minimized by identifying and then coagulating the raw water at an optimum reaction or coagulation pH. The optimum coagulation pH is identified, preferably by analytical tests of water samples. A typical optimum coagulation pH ranges from 3.8 to 5.5 for most iron salt coagulants and most colored surface waters.

The resultant iron humate products are relatively insoluble but still function as a source of iron nutrients during interactions with plants in soil media. More soluble iron humate products may be produced by contacting, the resultant iron humate products with a nitrogen source so as to produce a nitrogen enriched iron humate product that contains nitrogen in the range of 0.5 to 12 percent by weight as nitrogen with a minimum water soluble iron content of 50 ppm as iron. Both the unmodified iron humate product and the nitrogen enriched iron humate product are relatively inexpensive and beneficial sources of iron and humic substances for application to and use by plants.

#### OBJECTS AND ADVANTAGES OF THE INVENTION

Therefore, the objects of this invention are to provide a method for running a water purification facility to produce high quality drinking water and to produce a high quality sludge useable in providing needed nutrients to vegetation; to produce commercial, high quality, low cost, iron humate products especially suitable for addition to soil as an iron nutrient and organic soil additives for the benefit of vegetation; to produce such iron humate products having a relatively low concentration of heavy metal contaminants; to produce such iron humate products through the use of high quality iron salts as coagulants in the water treatment process; to produce such iron humate products having a minimum concentration of iron hydroxides; to produce such iron humate products through the controlled addition of iron salt coagulants; and to produce a modified iron humate product with more soluble iron which is more rapidly available for plant uptake and the correction of iron deficiency.

Other objects and advantages of this invention will become apparent from the following description wherein are set forth, by way of illustration and example, certain embodiments of this invention.

#### DETAILED DESCRIPTION OF THE INVENTION

As required, detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which may be embodied in various forms. Therefore, specific composition and functional details disclosed herein are not to be interpreted as limiting, but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present invention in virtually any appropriately detailed embodiment.

The present invention concerns the production of preferred iron humate products from water treatment processes to be used in treating vegetation and in particular crops and the like suffering from iron deficiencies generally referred to as chlorosis. The preparation of the iron humate products or residuals involves the controlled addition of a iron salt coagulant to raw water in a water treatment plant. The iron salt coagulant reacts with organic color producing aquatic humic substances or species in the raw water to form an iron humate product or precipitate which when applied to plants provides useful organic matter and nutrients such as iron. The preferred iron salt coagulant for the process is ferric sulfate or polyferric sulfate. Other acceptable iron salts are ferric chloride, ferrous chloride, polyferric chloride, and ferrous sulfate and the like. In order to be acceptable the iron salt coagulant used should be of high purity in terms of generally being free of or having a relatively low heavy metal and organic contamination such as organic corrosion inhibitors and tri-halomethane precursors.

Preferably the iron salt coagulant is produced from virgin iron sources and virgin acid sources so as to minimize the extraneous contaminants which may not be environmentally safe to apply to soil or may be harmful to vegetation. Table I gives a typical specification of a ferric sulfate coagulant that is suitable for treating at least some raw surface water under the present invention. However, allowable contaminant levels may differ depending on the water to be treated and the desired end use application of the recovered iron humate product. The allowable contaminants specified in Table I are stricter than the American Water Works Association (AWWA) current standard for ferric sulfate because this standard only addresses the effects of contaminants in the coagulant on the resultant treated water and not the quality of the resultant sludge residue.

TABLE I

Impurity	Maximum Impurity Concentration (mg/kg)
Arsenic	2
Cadmium	2
Chromium	5
Lead	10
Mercury	1
Selenium	3
Silver	5
Nitrites	75
Total Organic Carbon	15
Copper	5
Zinc	10
Manganese	90
Barium	6
Chloride	100
Fluoride	60
Titanium	50
Nitrates	150
Sodium	1000

The most critical parameter affecting the quality of the resultant iron humate product is the reaction or coagulation pH. The optimum coagulation pH will vary depending on the type of surface water, the concentration of organic species present and the type of iron salt coagulant used. The optimum pH in an actual water treatment plant is determined using analytical jar tests of water samples in an iterative approach. A selected quantity of water to be treated is collected in several jars. The pH of the water in the jars is adjusted by the addition of an acid such as sulfuric acid such that the pH

of each of the jars is different. A selected quantity of iron salt coagulant is added to each jar and the contents are agitated and then allowed to react or coagulate and then settle. The pH of the jar having the greatest raw water color reduction is identified. Several more jars are filled with a selected quantity of the water to be treated. The pH of the water in these jars is adjusted to match the pH identified in the first jar test as resulting in the greatest raw water color reduction. Various quantities of iron salt coagulant are then added to these jars. The contents are agitated and then allowed to react or coagulate and then settle. The smallest quantity of iron salt coagulant effecting a preselected or desired level of color reduction is identified. Using the identified minimum quantity of iron salt coagulant resulting in the desired color reduction another set of jar tests can be conducted to identify the pH resulting in the greatest color reduction with the identified minimum quantity of iron salt coagulant. Typically two iterations of the jar tests are completed to identify an optimum coagulation pH for effecting color reduction and the minimal quantity of iron salt coagulant at that pH to effect the desired reduction. Typical optimum coagulation pH values range from 3.8 to 5.5 for most iron salt coagulants and most colored surface waters.

Controlling the optimum pH insures using the minimum dosage of iron salt coagulant to effect the required color removal of the raw water. It is theorized that excess iron salts form insoluble iron hydroxides which are not taken up by plants as opposed to the preferred iron humate products. Because iron hydroxides are strong adsorbents of trace metals and phosphorous, the presence of the hydroxides in the sludge applied to vegetation can result in metal deficiencies in plants including phosphorous and iron deficiencies. The adsorption of iron from the soil by iron hydroxides may reduce the availability of iron from the preferred iron humate product. Additionally, iron hydroxides do not dewater as well as iron humate products and form a gelatinous mass. The production of excess iron hydroxides results in a product that is more difficult to handle and more expensive to transport. Although the iron humate products are also very insoluble, they can still function as a source of iron nutrients during interactions with plants in soil media. Although it is not the intent of applicant to be bound to any specific theory of how such iron is used by the vegetation, it is theorized that in the soil, the iron humate products are converted into a useable form by vegetation allowing the uptake of iron by the vegetation.

In an actual water treatment plant application, analytical jar tests should be conducted frequently to verify the optimum treatment pH setpoint and minimum effective iron dosage rate and to compensate for changes in the chemical composition of the raw water to be treated. Although an excess iron salt coagulant dosage will still produce a high quality drinking water, it will produce excess and undesirable iron hydroxides in precipitates removed from the water and used herein to provide nutrients to vegetation.

The preferred water treatment process of the present invention may be incorporated into a continuous flow water treatment system or a batch water treatment system. The steps of the process of the present invention are essentially the same when incorporated into either a continuous flow or batch treatment system except that the steps are time based in a batch reactor and position or location based in a continuous flow reactor.

In a continuous flow water treatment system the pH of the raw water in an influent raw water stream is initially lowered to a previously identified optimum coagulation pH in an acidification zone. The pH may be lowered by the addition of an auxiliary acid such as sulfuric acid or by means such as bubbling CO<sub>2</sub> into the raw water to form carbonic acid and by other means generally known in the art.

The efficiency of the treatment process appears to improve when the pH of the raw water is lowered prior to the addition of an iron salt coagulant as opposed to lowering of the pH concurrently with or after the addition of an iron salt coagulant. However, the pH of the raw water may be lowered before, after or during the addition of the iron salt coagulant. Also, for pH control and iron salt coagulant dosage efficiency purposes, it is preferred to use an iron salt coagulant with very low free acidity, so that the pH may be controlled independent of the iron salt dosage. As discussed above, the optimum coagulation pH may change due to changes in the composition of the raw water. Analytical jar tests are conducted regularly to identify changes in the optimum coagulation pH and the pH of the water to be treated is adjusted accordingly.

Downstream of the acidification zone, an iron salt coagulant is added to the influent raw water stream in a flash mixing zone to form a treatment solution. The iron salt coagulant is added to the influent raw water stream at a rate previously calculated to provide the minimum dosage of iron salt coagulant necessary to effect the required color removal from the raw water. As discussed above analytical jar tests are conducted regularly to identify any changes in the minimum dosage necessary to effect the required color removal due to changing characteristics of the raw water. The rate of addition of iron salt coagulant is adjusted to correspond to any identified changes in the minimum dosage requirement.

Impellers are preferably used in the flash mixing zone to provide rapid, thorough mixing of the raw water and the iron salt coagulant, however it is foreseeable that other rapid mixing means may be incorporated into the process of the present invention. The iron salt coagulant and the raw water are preferably mixed in the flash mixing zone for a minimum of 15 seconds. This initial mixing is followed by at least 3 minutes and preferably at least 10 minutes of additional mixing such as is available in a flocculation type mixing zone located downstream of the flash mixing zone. The reaction of the iron salt coagulant with the humic substances and other organic matter in the raw water is nearly complete within three minutes for temperate water and longer for colder waters. The reaction of iron salt coagulant and humic substances forms iron humate products.

After the reaction is complete, the treatment solution is allowed to settle with the iron humate products precipitating out of the solution to form a solids residue. After settling, the resultant treated water is separated from the solids residue (whether as a floating flocculant or as a precipitate that forms a lower solids or sludge layer in the water). The treated water is preferably chlorinated after separation from the solids residue to minimize the formation of chlorinated organics which will contaminate the residue and the drinking water.

The iron humate product in the form of the solid residue is concentrated and dried by conventional equipment being used in the water treatment industry such as settling basins, clarifiers, mechanical filters,

sludge drying beds and commercial sludge dryers. The resultant iron humate product typically dewateres very effectively and can achieve air dry solids concentrations up to 88% by weight solids. The iron-humate product of the present invention is characterized by a high iron concentration ranging from 15 to 45 percent by weight on a dry solids basis and preferably 28 to 33 percent by weight on a dry solids basis, low toxic organic and heavy metal contamination, high concentration of humic substances (an elemental carbon concentration generally greater than 30 percent by weight on a dry and ash free basis) and minimal concentration of iron hydroxides. The solids residue is characterized by a concentration of iron complexed as iron hydroxide of less than 25 percent by weight and preferably less than 10 percent by weight of the total iron present. After air drying, it has a medium brown color and has the consistency of a fine porous soil. The iron humate remains nearly insoluble in water (less than 1 ppm) or when stored in segregated piles, but slowly releases iron to the vegetation in mixed soil conditions.

More soluble, nitrogen enriched iron humate products are produced by contacting the partially hydrated iron humate products with a commercially available nitrogen source such as ammonia, ammonium hydroxide, urea, ammonium nitrate, and potassium nitrate. The resultant nitrogen enriched iron humate preferably contains nitrogen in the range of 0.5 to 12 percent by weight as nitrogen with a minimum water soluble iron content of 50 ppm a iron. The nitrogen enriched iron humate also turns from a medium brown color to rich dark brown color. The mixture of the nitrogen enriched iron humate with water forms a dark brown solution, while the filtrate from mixing water with the iron humate is colorless.

Examples of the processes in accordance with the invention which follow are for the purpose of demonstrating specific processes in accordance with the invention and are not intended to be limiting in scope on the invention or claims.

#### EXAMPLE 1

A plant trial was conducted to treat the Hillsborough River Water in Tampa, Florida with ferric sulfate for color removal. Sulfuric acid was added upstream of a flash mix tank to maintain a desired coagulation pH at a setpoint of 4.5 pH units. A high purity ferric sulfate in accordance with the invention was added at the entrance of the flash mix tank to maintain an average iron dosage of 21 milligrams/liter to treat an average raw water color of 105 standard color units (SCU) to a maximum of 15 standard color units before chlorination. The raw water dissolved organic carbon (DOC) averaged 15.9 ppm (an indication of the dissolved humic substances present) with reduction of the DOC in the water by application of ferric sulfate in accordance with the invention averaged over 72% by weight. The resultant iron humate sludge precipitate was concentrated using a clarifier, mechanically dewatered using a belt filter press to 18% by weight solids and then dried in a conventional sludge drying bed to a dry solids content of 88% by weight. This unmodified iron humate contained 32% by weight iron on a dry solids basis. The humate material, when mixed with excess water, produced a clear filtrate with less than 1 milligram/liter soluble iron. Additional elemental and composition data relating to the unmodified iron humate product are provided in Tables 2 and 3. Data for Tables 2 and 3

were taken from samples of unmodified iron humate taken, randomly from the resultant iron humate product.

#### EXAMPLE 2

The unmodified iron humate product from above Example 1 was contacted with anhydrous ammonia in excess in a pressure vessel at 50 pounds per square inch (psi) for 48 hours at ambient temperatures and then dried. The resultant nitrogen content was 4.71% by weight on a dry weight basis. The nitrogen enriched iron humate had turned to a rich dark brown. The iron solubility had increased by a factor of greater than 500. Elemental and compositional analysis of the ammonia-nitrogen enriched iron humate product are provided in Tables 2 and 3. Data for Tables 2 and 3 were taken from samples of nitrogen enriched iron humate taken randomly from the resultant iron humate product.

TABLE 2

	pH	COMPOSITIONAL ANALYSIS*			
		Percent by weight			
		Ash	Moisture	Volatiles	Iron
Unmodified	4.8	49	12	39	32
Nitrogen Enriched	8.3	36	14	50	23

\*The weight percents for ash, moisture, volatiles and iron were determined after roasting the resultant unmodified and ammonia-nitrogen enriched iron humate products at 1000° Centigrade until dry.

TABLE 3

Element	ELEMENTAL ANALYSIS	
	Percent by weight of dry and ash free humate	
	Unmodified Iron Humate	Nitrogen Enriched Iron Humate
Carbon	40	43
Hydrogen	4	6
Nitrogen	0.9	4
Oxygen	55	46

#### EXAMPLE 3

100 pounds (dry weight) of the unmodified iron humate product from above Example 1 was mixed with 29 pounds of urea and then stored at ambient temperature and pressure for 24 hours in a closed atmosphere to produce a nitrogen enriched iron humate product. The nitrogen content of the nitrogen enriched iron humate had risen from 0.6 to 10.9 percent by weight. The nitrogen enriched iron humate had turned to a rich dark brown. The iron solubility had increased by a factor of more than 100.

#### EXAMPLE 4

Plugs of turf grass and soil from a horticultural field laboratory were prepared for testing in triplicate with dosages of 2.5, 7.5 and 25.0 pounds of iron humate products made in accordance with Example 1 and Example 3 per acre applied to separate plots. Uniform rates of nitrogen, phosphorous, and potassium were applied to all plots. Visual ratings were performed bi-weekly and clippings for growth rate and iron uptake measurements were conducted weekly for two weeks. Both the urea-nitrogen enriched iron humate of Example 3 and the unmodified iron humate of Example 1 were compared against equivalent iron dosages from other iron sources, in particular, ferrous sulfate, a commercial iron chelate sold under the trademark Sequesterene 138-Fe and a control group with no added iron. The results of the iron uptake and vegetation growth measurements for

the first two weeks are shown on Table 4. In general, the nitrogen enriched iron humate samples outperformed the unmodified iron humate samples. Although the commercial iron products outperformed the iron humates on an efficiency basis, higher dosages of the iron humates outperformed the lower dosages of the commercial organic chelate. All the iron humate samples outperformed the control samples and also had a much greener appearance.

TABLE 4

Iron Source	lbs Fe /Acre	Fe Uptake (mg Fe/pot*)	Week 1 Growth(g/pot)	Week 2 Growth(g/pot)	Total Growth
1. Iron Humate	2.5	0.182	.42	.60	1.02
2. Iron Humate	7.5	0.151	.43	.60	1.03
3. Iron Humate	25.0	0.183	.51	.59	1.10
4. Nitrogen Enriched Iron Humate	2.5	0.201	.46	.69	1.15
5. Nitrogen Enriched Iron Humate	7.5	0.148	.40	.54	.94
6. Nitrogen Enriched Iron Humate	25.0	0.224	.42	.69	1.11
7. Sequesterene 138-Fe	2.5	0.176	.52	.67	1.19
8. Sequesterene 138-Fe	7.5	0.301	.58	.64	1.22
9. Ferrous Sulfate	25.0	0.245	.59	.65	1.24
10. Control	0	0.099	.35	.51	.86

\*Plant growth is expressed in g/pot which indicates the mass of the plant growth per pot in which plants are grown.

## EXAMPLE 5

Iron uptake in young citrus trees was tested for the nitrogen enriched and unmodified iron humates of Examples 2 and 1 respectively and compared against two commercial iron chelates sold under the trademarks Sequesterene 138-Fe and LibFer SP and a control group with no added iron nutrients in a soil incubation study over 70 days. The results of the tissue analysis for iron are shown in Table 5. In Table 5, the headings Carrizo and Swingle represent the root stock of the young citrus trees on which the iron sources were applied. The ammonia-nitrogen enriched iron humate of Example 2 showed dramatically higher content than all other iron sources tested. The unmodified iron humate of Example 1 showed slightly lower to equivalent performance in comparison to the commercial iron chelates. All tested iron sources performed better than the control group.

The preliminary economics indicate that the iron humate products of the present invention are commercially viable compared to available iron sources. The analysis for iron of tissue samples from the citrus leaves of trees treated with the nitrogen enriched iron humate product indicate that these leaves contained more iron than the leaves of trees treated with Sequesterene 138-Fe. The cost of an effective amount of the nitrogen enriched iron humate product would be a fraction of the cost for a similarly effective amount of Sequesterene 138-Fe based upon the price thereof at the time of filing

of this application, while still maintaining a healthy profit for the iron humate producer.

TABLE 5

Concentration of Iron in Leaves of Two Citrus Rootstocks 45 Days After Application of Iron Source			
Iron Source	Rate g Iron/plant	Iron in Leaves (mg/kg)	
		Carrizo	Swingle
Nitrogen Enriched	2	390	240

Iron Humate			
Nitrogen Enriched	1	338	213
Iron Humate			
Nitrogen Enriched	0.5	241	104
Iron Humate			
Unmodified Iron Humate	2	235	67
Sequesterene 138-Fe	0.5	225	98
Sequesterene 138-Fe	1	218	61
Sequesterene 138-Fe	0.25	216	112
Unmodified Iron Humate	1	205	98
Unmodified Iron Humate	0.5	198	70
LibFer SP	0.25	198	58
Libfer SP	1	190	61
Libfer SP	0.5	180	139
CONTROL	0	164	44

It is to be understood that while certain forms of the present invention have been illustrated and described herein, it is not to be limited to the specific forms or arrangement of parts described and shown.

What is claimed and desired to be secured by Letters Patent is as follows:

1. An iron humate product having:

- (a) an iron concentration ranging from fifteen to forty-five percent by weight on a dry solids basis;
- (b) a concentration of humic substances equal to or greater than thirty percent by weight; and
- (c) said product has a concentration of iron hydroxides that is less than 25 percent by weight of total iron present, wherein said iron humate product is produced by adding a sufficient concentration of an iron salt coagulant to a quantity of raw water having a pH between about 3.8 and 5.5 to reduce

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the organic color of the water and form a solid residue containing said iron humate product.

2. The iron humate product as described in claim 1 wherein:

(a) said iron humate product includes a nitrogen source.

3. The iron humate product described in claim 2 wherein:

(a) said nitrogen source is selected from the group consisting of ammonia, ammonium hydroxide, 10

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urea, ammonium nitrate, potassium nitrate and mixtures thereof to produce a nitrogen enriched iron humate product.

4. The iron humate product as described in claim 1 wherein:

(a) said iron hydroxides are present in a concentration of less than 10 percent by weight of total iron present.

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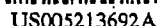
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[57] **ABSTRACT**

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A process is provided for preparing preferred iron humate products. The preferred iron humate products provide iron and other nutrients and organic matter for vegetation. The preferred iron humate products are produced by using an iron salt coagulant that is relatively free of heavy metal contaminants and reacting the iron salt coagulant with naturally occurring humic substances such as those found in natural surface waters used in drinking water treatment facilities. According to the invention, iron is stoichiometrically reacted at a controlled pH with the humic and fulvic acid fractions in the water to precipitate an iron humate product precipitate. A preferred concentration of iron salt coagulants is used in order to minimize the formation of iron hydroxides which generally provide low iron availability to the plant. A more readily soluble iron humate complex is produced by the reacting and or blending of the iron humate residue with various nitrogen containing sources.

### 15 Claims, No Drawings

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## PROCESS FOR PREPARING PREFERRED IRON HUMATES

### BACKGROUND OF THE INVENTION

The present invention relates to a process for preparing a preferred iron humate product, compositions of preferred iron humate products and a method for treating chlorosis in vegetation using preferred iron humate products.

Many agricultural crops and turf grasses must have commercial applications of iron nutrients in order to prevent or correct for iron deficiency otherwise known as plant chlorosis. Chlorosis can be physically detected by yellowing of leaves in trees, shrubs, and vegetables and yellowing of blades within turf grasses. Chlorosis hinders plant growth or yields and can also lessen food quality. Additionally, many soils are deficient in organic substances which can have a favorable effect on soil moisture retention, plant nutrient uptake and plant growth. There are many commercial iron nutrient sources available to correct for iron chlorosis such as ferrous sulfate and chelated irons such as sodium ferric ethylenediamine di-(O-hydroxy-phenol-acetate) ("FeEDDHA") sold under the trade names Sequesterene 138-Fe and Libfer SP.

A separate problem has been the disposal of sludge or precipitates formed by coagulating raw water contaminants with iron and aluminum salts or the like at potable water treatment plants and at plants designed to remove the organic color from effluents from such sources as paper mills. This is especially true for surface waters which are characterized by their high content of dissolved organic color from the natural decaying of aquatic vegetation. These potable water treatment plants must use high coagulant dosages, which in turn, generate large quantities of sludge residue for disposal. Often the water treatment sludges are simply dumped back into the water source causing degradation of the water quality. Other currently preferred options for disposal of water treatment sludges are lagoon storage, disposal in landfills and discharge into sanitary sewers. Inadequacies in these disposal methods has led to an increased interest in the land application of water treatment sludge.

Important constituents of natural surface waters are aquatic humic substances. Humic substances are formed from the decomposition of plant and animal materials and comprise the largest fraction of natural organic matter in natural surface waters accounting for 40 to 60 percent of the dissolved organic carbon ("DOC"; DOC is defined as organic carbon particles smaller than 0.45 micrometers in diameter and may be in colloidal suspension rather than in solution).

Humic substances comprise a complex heterogeneous mixture of compounds that are not readily separated into discrete components. However, three subfractions of humic substances are generally recognized. These subfractions comprise humic acid, fulvic acid and humin. Humic acid is defined as the fraction of humic substances that is not soluble in water under highly acidic conditions ( $\text{pH} < 2.0$ ) but is soluble at higher pH values. Fulvic acid is defined as the fraction of humic substances that is soluble in water under all pH conditions. Humin is defined as the fraction of humic substances that is not soluble in water at any pH value.

Humic substances are removed from raw drinking water due to several problems associated with their

presence. Humic substances are responsible for the yellow or brown organic color of natural surface waters. Humic substances act as a vehicle for the transport of toxic, water insoluble elements and organic micropollutants. Chlorine combines with aquatic humic substances to form chlorinated organic compounds, such as chloroform and complex chlorinated compounds, that may have negative effects on health. Humic substances also precipitate in water distribution systems where they lead to deterioration of tap water quality and increase the need for interior cleaning of pipes.

Traditionally, colored surface waters have been treated with alum (aluminum sulfate) which generates an aluminum containing sludge, which after dewatering, must be deposited in a secure landfill. Iron salt coagulants have been effectively used but often produce a sludge high in heavy metals due to the quality of the iron salt coagulant. Many of the commercial iron salt coagulants are produced from by-products from such sources as  $\text{TiO}_2$  production or steel pickling and are typically high in heavy metals and organic contaminants.

When an iron salt coagulant is used as the primary coagulant to remove humic substances, it reacts to precipitate an iron humate residue. The inferior quality of many iron salt coagulants, in terms of concentration of heavy metal contaminants, often results in iron humate products having unacceptable concentrations of heavy metals so as to prevent land application of the iron humate products.

Another problem with current potable water treatment methods is that these methods generally result in a water treatment sludge having unnecessarily high concentrations of hydrous metal oxides, such as iron hydroxides. Hydrous metal oxides are strong adsorbents of trace metals and phosphorus. When applied to the soil surrounding vegetation at high concentrations and high pH, iron hydroxides can result in metal deficiencies in the vegetation including iron deficiency. Also the presence of hydrous metal oxides results in the sorption of phosphorous from the soil reducing the availability of phosphorus to vegetation. Phosphorous is necessary for vegetation growth. Additionally, iron hydroxides do not dewater as well as iron humate products. The iron hydroxides form a somewhat gelatinous mass making sludge containing excess iron hydroxides harder to handle and more expensive to transport.

### SUMMARY OF THE INVENTION

The present invention provides preferred iron humate products and processes for preparing preferred iron humate products adapted for use in treating chlorosis in vegetation.

Existing water treatment processes focus primarily on producing high quality drinking water with little regard for the quality of the resultant sludge. The goal of the water treatment process of the present invention is to produce both high quality drinking water and a high quality sludge that is particularly well adapted for land application to provide useful nutrients to plants.

The concentration of heavy metal contaminants in the resultant iron humate product is reduced by selecting a relatively pure iron salt coagulant that is free of or has a relatively low concentration of heavy metal contaminants.

The concentration of iron hydroxides in the resultant iron humate product is minimized by using a minimum

dosage of iron salts to effect the required color removal of the raw water. The iron salt dosage is minimized by identifying and then coagulating the raw water at an optimum reaction or coagulation pH. The optimum coagulation pH is identified, preferably by analytical tests of water samples. A typical optimum coagulation pH range from 3.8 to 5.5 for most iron salt coagulants and most colored surface waters.

The resultant iron humate products are relatively insoluble but still function as a source of iron nutrients during interactions with plants in soil media. More soluble iron humate products may be produced by contacting the resultant iron humate products with a nitrogen source so as to produce a nitrogen enriched iron humate product that contains nitrogen in the range of 0.5 to 12 percent by weight as nitrogen with a minimum water soluble iron content of 50 ppm as iron. Both the unmodified iron humate product and the nitrogen enriched iron humate product are relatively inexpensive and beneficial sources of iron and humic substances for application to and use by plants.

#### OBJECTS AND ADVANTAGES OF THE INVENTION

Therefore, the objects of this invention are to provide a method for running a water purification facility to produce high quality drinking water and to produce a high quality sludge useable in providing needed nutrients to vegetation; to produce commercial, high quality, low cost, iron humate products especially suitable for addition to soil as an iron nutrient and organic soil additives for the benefit of vegetation; to produce such iron humate products having a relatively low concentration of heavy metal contaminants; to produce such iron humate products through the use of high quality iron salts as coagulants in the water treatment process; to produce such iron humate products having a minimum concentration of iron hydroxides; to produce such iron humate products through the controlled addition of iron salt coagulants; and to produce a modified iron humate product with more soluble iron which is more rapidly available for plant uptake and the correction of iron deficiency.

Other objects and advantages of this invention will become apparent from the following description wherein are set forth, by way of illustration and example, certain embodiments of this invention.

#### DETAILED DESCRIPTION OF THE INVENTION

As required, detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which may be embodied in various forms. Therefore, specific composition and functional details disclosed herein are not to be interpreted as limiting, but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present invention in virtually any appropriately detailed embodiment.

The present invention concerns the production of preferred iron humate products from water treatment processes to be used in treating vegetation and in particular crops and the like suffering from iron deficiencies generally referred to as chlorosis. The preparation of the iron humate products or residuals involves the controlled addition of a iron salt coagulant to raw water in a Water treatment plant. The iron salt coagulant reacts

with organic color producing aquatic humic substances or species in the raw water to form an iron humate product or precipitate which when applied to plants provides useful organic matter and nutrients such as iron. The preferred iron salt coagulant for the process is ferric sulfate or polyferric sulfate. Other acceptable iron salts are ferric chloride, ferrous chloride, polyferric chloride, and ferrous sulfate and the like. In order to be acceptable the iron salt coagulant used should be of high purity in terms of generally being free of or having a relatively low heavy metal and organic contamination such as organic corrosion inhibitors and tri-halomethane precursors.

Preferably the iron salt coagulant is produced from virgin iron sources and virgin acid sources so as to minimize the extraneous contaminants which may not be environmentally safe to apply to soil or may be harmful to vegetation. Table I gives a typical specification of a ferric sulfate coagulant that is suitable for treating at least some raw surface water under the present invention. However, allowable contaminant levels may differ depending on the water to be treated and the desired end use application of the recovered iron humate product. The allowable contaminants specified in Table I are stricter than the American Water Works Association (AWWA) current standard for ferric sulfate, because this standard only addresses the effects of contaminants in the coagulant on the resultant treated water and not the quality of the resultant sludge residue.

TABLE I

Impurity	Maximum Impurity Concentration (mg/kg)
Arsenic	2
Cadmium	2
Chromium	5
Lead	10
Mercury	1
Selenium	3
Silver	5
Nitrites	75
Total Organic Carbon	15
Copper	5
Zinc	10
Manganese	90
Barium	6
Chloride	100
Fluoride	60
Titanium	50
Nitrates	150
Sodium	1000

The most critical parameter affecting the quality of the resultant iron humate product is the reaction or coagulation pH. The optimum coagulation pH will vary depending on the type of surface water, the concentration of organic species present and the type of iron salt coagulant used. The optimum pH in an actual water treatment plant is determined using analytical jar tests of water samples in an iterative approach. A selected quantity of water to be treated is collected in several jars. The pH of the water in the jars is adjusted by the addition of an acid such as sulfuric acid such that the pH of each of the jars is different. A selected quantity of iron salt coagulant is added to each jar and the contents are agitated and then allowed to react or coagulate and then settle. The pH of the jar having the greatest raw water color reduction is identified. Several more jars are filled with a selected quantity of the water to be treated. The pH of the water in these jars is adjusted to match the pH identified in the first jar test as resulting in

the greatest raw water color reduction. Various quantities of iron salt coagulant are then added to these jars. The contents are agitated and then allowed to react or coagulate and then settle. The smallest quantity of iron salt coagulant effecting a preselected or desired level of color reduction is identified. Using the identified minimum quantity of iron salt coagulant resulting in the desired color reduction another set of jar tests can be conducted to identify the pH resulting in the greatest color reduction with the identified minimum quantity of iron salt coagulant. Typically two iterations of the jar tests are completed to identify an optimum coagulation pH for effecting color reduction and the minimal quantity of iron salt coagulant at that pH to effect the desired reduction. Typical optimum coagulation pH values range from 3.8 to 5.5 for most iron salt coagulants and most colored surface waters.

Controlling the optimum pH insures using the minimum dosage of iron salt coagulant to effect the required color removal of the raw water. It is theorized that excess iron salts form insoluble iron hydroxides which are not taken up by plants as opposed to the preferred iron humate products. Because iron hydroxides are strong adsorbents of trace metals and phosphorous, the presence of the hydroxides in the sludge applied to vegetation can result in metal deficiencies in plants including phosphorous and iron deficiencies. The adsorption of iron from the soil by iron hydroxides may reduce the availability of iron from the preferred iron humate product. Additionally, iron hydroxides do not dewater as well as iron humate products and form a gelatinous mass. The production of excess iron hydroxides results in a product that is more difficult to handle and more expensive to transport. Although the iron humate products are also very insoluble, they can still function as a source of iron nutrients during interactions with plants in soil media. Although it is not the intent of applicant to be bound to any specific theory of how such iron is used by the vegetation, it is theorized that in the soil, the iron humate products are converted into a useable form by vegetation allowing the uptake of iron by the vegetation.

In an actual water treatment plant application, analytical jar tests should be conducted frequently to verify the optimum treatment pH setpoint and minimum effective iron dosage rate and to compensate for changes in the chemical composition of the raw water to be treated. Although an excess iron salt coagulant dosage will still produce a high quality drinking water, it will produce excess and undesirable iron hydroxides in precipitates removed from the water and used herein to provide nutrients to vegetation.

The preferred water treatment process of the present invention may be incorporated into a continuous flow water treatment system or a batch water treatment system. The steps of the process of the present invention are essentially the same when incorporated into either a continuous flow or batch treatment system except that the steps are time based in a batch reactor, and position or location based in a continuous flow reactor.

In a continuous flow water treatment system the pH of the raw water in an influent raw water stream is initially lowered to a previously identified optimum coagulation pH in an acidification zone. The pH may be lowered by the addition of an auxiliary acid such as sulfuric acid or by means such as bubbling CO<sub>2</sub> into the raw water to form carbonic acid and by other means generally known in the art.

The efficiency of the treatment process appears to improve when the pH of the raw water is lowered prior to the addition of an iron salt coagulant as opposed to lowering of the pH concurrently with or after the addition of an iron salt coagulant. However, the pH of the raw water may be lowered before, after or during the addition of the iron salt coagulant. Also, for pH control and iron salt coagulant dosage efficiency purposes, it is preferred to use an iron salt coagulant with very low free acidity, so that the pH may be controlled independent of the iron salt dosage. As discussed above, the optimum coagulation pH may change due to changes in the composition of the raw water. Analytical jar tests are conducted regularly to identify changes in the optimum coagulation pH and the pH of the water to be treated is adjusted accordingly.

Downstream of the acidification zone, an iron salt coagulant is added to the influent raw water stream in a flash mixing zone to form a treatment solution. The iron salt coagulant is added to the influent raw water stream at a rate previously calculated to provide the minimum dosage of iron salt coagulant necessary to effect the required color removal from the raw water. As discussed above analytical jar tests are conducted regularly to identify any changes in the minimum dosage necessary to effect the required color removal due to changing characteristics of the raw water. The rate of addition of iron salt coagulant is adjusted to correspond to any identified changes in the minimum dosage requirement.

Impellers are preferably used in the flash mixing zone to provide rapid, thorough mixing of the raw water and the iron salt coagulant, however it is foreseeable that other rapid mixing means may be incorporated into the process of the present invention. The iron salt coagulant and the raw water are preferably mixed in the flash mixing zone for a minimum of 15 seconds. This initial mixing is followed by at least 3 minutes and preferably at least 10 minutes of additional mixing such as is available in a flocculation type mixing zone located downstream of the flash mixing zone. The reaction of the iron salt coagulant with the humic substances and other organic matter in the raw water is nearly complete within three minutes for temperate waters and longer for colder waters. The reaction of iron salt coagulant and humic substances forms iron humate products.

After the reaction is complete, the treatment solution is allowed to settle with the iron humate products precipitating out of the solution to form a solids residue. After settling, the resultant treated water is separated from the solids residue (whether as a floating flocculant or as a precipitate that forms a lower solids or sludge layer in the water). The treated water is preferably chlorinated after separation from the solids residue to minimize the formation of chlorinated organics which will contaminate the residue and the drinking water.

The iron humate product in the form of the solid residue is concentrated and dried by conventional equipment being used in the water treatment industry such as settling basins, clarifiers, mechanical filters, sludge drying beds and commercial sludge dryers. The resultant iron humate product typically dewateres very effectively and can achieve air dry solids concentrations up to 88% by weight solids. The iron-humate product of the present invention is characterized by a high iron concentration ranging from 15 to 45 percent by weight on a dry solids basis and preferably 28 to 33 percent by weight on a dry solids basis, low toxic organic and

heavy metal contamination, high concentration of humic substances (an elemental carbon concentration generally greater than 30 percent by weight on a dry and ash free basis) and minimal concentration of iron hydroxides. The solids residue is characterized by a concentration of iron complexed as iron hydroxide of less than 25 percent by weight and preferably less than 10 percent by weight of the total iron present. After air drying, it has a medium brown color and has the consistency of a fine porous soil. The iron humate remains nearly insoluble in water (less than 1 ppm) or when stored in segregated piles, but slowly releases iron to the vegetation in mixed soil conditions

More soluble, nitrogen enriched iron humate products are produced by contacting the partially hydrated iron humate products with a commercially available nitrogen source such as ammonia, ammonium hydroxide, urea, ammonium nitrate, and potassium nitrate. The resultant nitrogen enriched iron humate preferably contains nitrogen in the range of 0.5 to 12 percent by weight as nitrogen with a minimum water soluble iron content of 50 ppm as iron. The nitrogen enriched iron humate also turns from a medium brown color to a rich dark brown color. The mixture of the nitrogen enriched iron humate with water forms a dark brown solution, while the filtrate from mixing water with the iron humate is colorless.

Examples of the processes in accordance with the invention which follow are for the purpose of demonstrating specific processes in accordance with the invention and are not intended to be limiting in scope on the invention or claims.

#### EXAMPLE 1

A plant trial was conducted to treat the Hillsborough River Water in Tampa, Fla. with ferric sulfate for color removal. Sulfuric acid was added upstream of a flash mix tank to maintain a desired coagulation pH at a set-point of 4.5 pH units. A high purity ferric sulfate in accordance with the invention was added at the entrance of the flash mix tank to maintain an average iron dosage of 21 milligrams/liter to treat an average raw water color of 105 standard color units (SCU) to a maximum of 15 standard color units before chlorination. The raw water dissolved organic carbon (DOC) averaged 15.9 ppm (an indication of the dissolved humic substances present) with reduction of the DOC in the water by application of ferric sulfate in accordance with the invention averaged over 72% by weight. The resultant iron humate sludge precipitate was concentrated using a Clarifier, mechanically dewatered using a belt filter press to 18% by weight solids and then dried in a conventional sludge drying bed to a dry solids content of 88% by weight. This unmodified iron humate contained 32% by weight iron on a dry solids basis. The humate material, when mixed with excess water, produced a clear filtrate with less than 1 milligram/liter soluble iron. Additional elemental and composition data relating to the unmodified iron humate product are provided in Tables 2 and 3. Data for Tables 2 and 3 were taken from samples of unmodified iron humate taken randomly from the resultant iron humate product.

#### EXAMPLE 2

The unmodified iron humate product from above Example 1 was contacted with anhydrous ammonia in excess in a pressure vessel at 50 pounds per square inch (psi) for 48 hours at ambient temperatures and then

dried. The resultant nitrogen content was 4.71% by weight on a dry weight basis. The nitrogen enriched iron humate had turned to a rich dark brown. The iron solubility had increased by a factor of greater than 500. Elemental and compositional analysis of the ammonia-nitrogen enriched iron humate product are provided in Tables 2 and 3. Data for Tables 2 and 3 were taken from samples of nitrogen-enriched iron humate taken randomly from the resultant iron humate product.

TABLE 2

	pH	Percent by weight			
		Ash	Moisture	Volatiles	Iron
Unmodified	4.8	49	12	39	32
Nitrogen Enriched	8.3	36	14	50	23

\*The weight percents for ash, moisture, volatiles and iron were determined after roasting the resultant unmodified and ammonia-nitrogen enriched iron humate products at 1000° Centigrade until dry.

TABLE 3

Element	Percent by weight of dry and ash free humate	
	Unmodified Iron Humate	Nitrogen Enriched Iron Humate
Carbon	40	43
Hydrogen	4	6
Nitrogen	0.9	4
Oxygen	55	46

#### EXAMPLE 3

100 pounds (dry weight) of the unmodified iron humate product from above Example 1 was mixed with 29 pounds of urea and then stored at ambient temperature and pressure for 24 hours in a closed atmosphere to produce a nitrogen enriched iron humate product. The nitrogen content of the nitrogen enriched iron humate had risen from 0.6 to 10.9 percent by weight. The nitrogen enriched iron humate had turned to a rich dark brown. The iron solubility had increased by a factor of more than 100.

#### EXAMPLE 4

Plugs of turf grass and soil from a horticultural field laboratory were prepared for testing in triplicate with dosages of 2.5, 7.5 and 25.0 pounds of iron humate product made in accordance with Example 1 and Example 3 per acre applied to separate plots. Uniform rates of nitrogen, phosphorous, and potassium were applied to all plots. Visual ratings were performed bi-weekly and clippings for growth rate and iron uptake measurements were conducted weekly for two weeks. Both the urea-nitrogen enriched iron humate of Example 3 and the unmodified iron humate of Example 1 were compared against equivalent iron dosages from other iron sources, in particular, ferrous sulfate, a commercial iron chelate sold under the trademark Sequestrene 138-Fe and a control group with no added iron. The results of the iron uptake and vegetation growth measurements for the first two weeks are shown on Table 4. In general, the nitrogen enriched iron humate samples outperformed the unmodified iron humate samples. Although the commercial iron products outperformed the iron humates on an efficiency basis, higher dosages of the iron humates outperformed the lower dosages of the commercial organic chelate. All the iron humate sam-

ples outperformed the control samples and also had a much greener appearance.

TABLE 4

Iron Source	lbs Fe/Acre	Fe Uptake (mg Fe/pot*)	Week 1 Growth (g/pot)	Week 2 Growth (g/pot)	Total Growth
1. Iron Humate	2.5	0.182	.42	.60	1.02
2. Iron Humate	7.5	0.151	.43	.60	1.03
3. Iron Humate	25.0	0.183	.51	.59	1.10
4. Nitrogen Enriched Iron Humate	2.5	0.201	.46	.69	1.15
5. Nitrogen Enriched Iron Humate	7.5	0.148	.40	.54	.94
6. Nitrogen Enriched Iron Humate	25.0	0.224	.42	.69	1.11
7. Sequesterene 138-Fe	2.5	0.176	.52	.67	1.19
8. Sequesterene 138-Fe	7.5	0.301	.58	.64	1.22
9. Ferrous Sulfate	25.0	0.245	.59	.65	1.24
10. Control	0	0.099	.35	.51	.86

\*Plant growth is expressed in g/pot which indicates the mass of the plant growth per pot in which plants are grown.

## EXAMPLE 5

Iron uptake in young citrus trees was tested for the nitrogen enriched and unmodified iron humates of Examples 2 and 1 respectively and compared against two commercial iron chelates sold under the trademarks Sequesterene 138-Fe and LibFer SP and a control group with no added iron nutrients in a soil incubation study over 70 days. The results of the tissue analysis for iron are shown in Table 5. In Table 5, the headings Carrizo and Swingle represent the root stock of the young citrus trees on which the iron sources were applied. The ammonia-nitrogen enriched iron humate of Example 2 showed dramatically higher content than all other iron sources tested. The unmodified iron humate of Example 1 showed slightly lower to equivalent performance in comparison to the commercial iron chelates. All tested iron sources performed better than the control group.

The preliminary economics indicate that the iron humate products of the present invention are commercially viable compared to available iron sources. The analysis for iron of tissue samples from the citrus leaves of trees treated with the nitrogen enriched iron humate product indicate that these leaves contained more iron than the leaves of trees treated with Sequesterene 138-Fe. The cost of an effective amount of the nitrogen enriched iron humate product would be a fraction of the cost for a similarly effective amount of Sequesterene 138-Fe based upon the price thereof at the time of filing of this application, while still maintaining a healthy profit for the iron humate producer.

TABLE 5

Concentration of Iron in Leaves of Two Citrus Rootstocks  
45 Days After Application of Iron Source

Iron Source	Rate g Iron/plant	Iron in Leaves (mg/kg)	
		Carrizo	Swingle
Nitrogen Enriched Iron Humate	2	390	240
Nitrogen Enriched Iron Humate	1	338	213
Nitrogen Enriched Iron Humate	0.5	241	104
Unmodified Iron Humate	2	235	67
Sequesterene 138-Fe	0.5	225	98
Sequesterene 138-Fe	1	218	61
Sequesterene 138-Fe	0.25	216	112
Unmodified Iron Humate	1	205	98
Unmodified Iron Humate	0.5	198	70
LibFer SP	0.25	198	58
Libfer SP	1	190	61
Libfer SP	0.5	180	139
CONTROL	0	164	44

It is to be understood that while certain forms of the present invention have been illustrated and described herein, it is not to be limited to the specific forms or arrangement of parts described and shown.

What is claimed and desired to be secured by Letters Patent is as follows:

1. A method for the production of an iron humate product in a treatment process for treating a quantity of colored raw water; said iron humate product adapted for use in providing nutrients and organic matter to soil for use by vegetation grown in said soil; said method comprising the steps of:

- (a) adding an iron salt coagulant to said raw water to form a treatment solution;
- (b) controlling the pH of said treatment solution between 3.8 and 5.5 to provide for the addition of a minimum amount of said iron salt coagulant to the raw water to reduce the color of the raw water to a preselected level and to produce an iron humate product wherein the concentration of iron complexed as iron hydroxide in the iron humate product is less than 25 percent by weight on a dry solids basis;
- (c) separating said iron humate product from said treatment solution;
- (d) concentrating and drying said iron humate product; and
- (e) contacting said iron humate product with a nitrogen source to produce a nitrogen enriched iron humate product that contains nitrogen in the range of 0.5 to 12 percent by weight as nitrogen with a minimum water soluble iron content of 50 ppm as iron.

2. The method as defined in claim 1 wherein said step of controlling includes:

- (a) periodically sampling the raw material;
- (b) finding the pH value of the sampled water to produce an optimum coagulation effect in the water;
- (c) adding iron salt coagulant to find the optimum concentration of iron salt coagulant to coagulate components of the water to form iron humate without producing substantial quantities of iron hydroxides; and
- (d) adjusting the addition of the iron salt coagulant for producing said optimum concentration within said water.

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3. The method as described in claim 1 including the step of:
  - (a) applying the iron humate product to soil to provide nutrients and organic matter to said soil for use by vegetation grown in said soil.
4. The method as described in claim 1 including the step of:
  - (a) applying said iron humate product to soil in which vegetation having an iron deficiency is being grown to provide iron to the vegetation.
5. The method as described in claim 1 including the step of:
  - (a) selecting said iron salt from the group consisting of ferric sulfate, ferrous sulfate, polyferric sulfate, ferric chloride, ferrous chloride and polyferric chloride.
6. The method as described in claim 5 including the step of:
  - (a) contacting said iron humate product with a nitrogen source selected from the group consisting of ammonia, ammonium hydroxide, urea, ammonium nitrate and potassium nitrate so as to produce a nitrogen enriched iron humate product.
7. The method as described in claim 6 including the step of:
  - (a) applying the nitrogen enriched iron humate product to soil to provide nutrients and organic matter to said soil for use by the vegetation grown in said soil.
8. The method of claim 1 wherein:
  - (a) the concentration of iron complexed as iron hydroxide in the iron humate product is less than 10 percent by weight on a dry solids basis.
9. A method for the production of an iron humate product from a treatment process for treating a quantity of colored raw water; said iron humate product adapted for use in providing nutrients and organic matter to soil for use by vegetation grown in said soil; said method comprising the steps of:
  - (a) lowering the pH of the raw water to within approximately a pH range between 3.8 and 5.5 to form an acidified solution;
  - (b) adding an amount of an iron salt coagulant to said acidified solution while controlling said adding so as to produce an iron humate product with a concentration of iron complexed as iron hydroxide in the iron humate product of less than 10 percent by weight of said product on a dry solids basis; said iron humate product precipitating out of said acidified solution to form a solid residue containing said iron humate product and a liquid layer comprising treated water;
  - (c) separating said iron humate product from said treated water;

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- (d) concentrating and drying said iron humate product; and
  - (e) adding a source of nitrogen to said iron humate product selected from the group consisting of ammonia, ammonium hydroxide, urea, ammonium nitrate and potassium nitrate so as to produce a nitrogen enriched iron humate product that contains nitrogen in the range of 0.5 to 12 percent by weight as nitrogen with a minimum water soluble iron content of 50 ppm as iron.
  10. The method as described in claim 9 including the step of:
    - (a) selecting said iron salt from the group consisting of ferric sulfate, ferrous sulfate, polyferric sulfate, ferric chloride, ferrous chloride and polyferric chloride.
  11. The method as described in claim 9 including the step of:
    - (a) applying the nitrogen enriched iron humate product to soil in which vegetation having an iron deficiency is being grown to provide iron to the vegetation having an iron deficiency.
  12. A method for providing nutrients and organic matter to vegetation comprising the step of applying to the soil in which the vegetation is grown a nitrogen enriched iron humate product produced by adding a sufficient concentration of an iron salt coagulant to a quantity of raw water having a pH between from 3.8 and 5.5 to reduce the organic color of the water to a preselected level while producing an iron humate product such that the concentration of iron complexed as iron hydroxide in the iron humate product is less than 25 percent by weight of said product on a dry solids basis and contacting said iron humate product with a nitrogen source to produce said nitrogen enriched iron humate product that contains nitrogen in the range of 0.5 to 12 percent by weight as nitrogen with a minimum water soluble iron content of 50 ppm as iron.
  13. The method as described in claim 12 including the step of:
    - (a) selecting said iron salt from the group consisting of ferric sulfate, ferrous sulfate, polyferric sulfate, ferric chloride, ferrous chloride, polyferric chloride and mixtures thereof.
  14. The method as described in claim 13 including the step of:
    - (a) contacting said iron humate product with a nitrogen source selected from the group consisting of ammonia, ammonium hydroxide, urea, ammonium nitrate, potassium nitrate and mixtures thereof so as to produce a nitrogen enriched iron humate product.
  15. The method of claim 12 wherein:
    - (a) the concentration of iron complexed as iron hydroxide in the iron humate product is less than 10 percent by weight on a dry solids basis.
- \* \* \* \* \*



US005411569A

**United States Patent** [19][11] Patent Number: **5,411,569****Hjersted**[45] Date of Patent: \* **May 2, 1995**[54] **IRON HUMATE PRODUCT**[75] Inventor: **Lawrence N. Hjersted, Bartow, Fla.**[73] Assignee: **Kemiron, Inc., Bartown, Fla.**

[\*] Notice: The portion of the term of this patent subsequent to Apr. 12, 2011 has been disclaimed.

[21] Appl. No.: **213,180**[22] Filed: **Mar. 14, 1994****Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 18,287, Feb. 16, 1993, Pat. No. 5,302,180, which is a continuation of Ser. No. 751,872, Aug. 28, 1991, Pat. No. 5,213,692.

[51] Int. Cl.<sup>6</sup> ..... **C05F 11/02**[52] U.S. Cl. .... **71/24; 71/28; 71/59; 71/DIG. 2; 210/710; 210/724; 210/917**[58] Field of Search ..... **71/24, 28, 59, DIG. 2; 210/609, 702, 710, 723-728, 770, 917**[56] **References Cited****U.S. PATENT DOCUMENTS**

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[57] **ABSTRACT**

A process is provided for preparing preferred iron humate products. The preferred iron humate products provide iron and other nutrients and organic matter for vegetation and supplementation of animal feedstocks. The preferred iron humate products are produced by using an iron salt coagulant that is relatively free of heavy metal contaminants and reacting the iron salt coagulant with naturally occurring humic substances such as those found in natural surface waters used in drinking water treatment facilities. According to the invention, iron is stoichiometrically reacted at a controlled pH with the humic and fulvic acid fractions in the water to precipitate an iron humate product precipitate. A preferred concentration of iron salt coagulants is used in order to minimize the formation of iron hydroxides.

**11 Claims, No Drawings**



## IRON HUMATE PRODUCT

## CROSS REFERENCE TO RELATED APPLICATION

The present application is a continuation-in-part of U.S. Ser. No. 08/018,287, entitled IRON HUMATE PRODUCT, filed Feb. 16, 1993, now U.S. Pat. No. 5,302,180, which is a continuation of U.S. Ser. No. 07/751,872, entitled PROCESS FOR PREPARING PREFERRED IRON HUMATES, filed Aug. 28, 1991, now U.S. Pat. No. 5,213,692.

## BACKGROUND OF THE INVENTION

The present invention relates to a process for preparing a preferred iron humate product, compositions of preferred iron humate products and a method for treating chlorosis in vegetation and a method of providing nutrients to animals using preferred iron humate products.

Many agricultural crops and turf grasses must have commercial applications of iron nutrients in order to prevent or correct for iron deficiency otherwise known as plant chlorosis. Chlorosis can be physically detected by yellowing of leaves in trees, shrubs, and vegetables and yellowing of blades within turf grasses. Chlorosis hinders plant growth or yields and can also lessen food quality. Additionally, many soils are deficient in organic substances which can have a favorable effect on soil moisture retention, plant nutrient uptake and plant growth. There are many commercial iron nutrient sources available to correct for iron chlorosis such as ferrous sulfate and chelated irons such as sodium ferric ethylenediamine di-(O-hydroxy-phenol-acetate) ("FeEDDHA") sold under the trade names Sequesterene 138-Fe and Libfer SP.

Livestock and poultry similarly require commercial addition of iron supplements to feedstocks in order to prevent anemia, a deficiency of red blood cells. Red blood cells contain hemoglobin, a protein which employs iron atoms to bind oxygen and transport it from the lungs to the tissues. An adequate supply of iron is essential to the production of hemoglobin, and a deficiency in hemoglobin results in anemia. The young of certain species, such as piglets, are especially susceptible to iron deficiency. Animals with mild forms of anemia exhibit retarded growth, while animals with severe anemia are at risk of death. Iron deficiency may also lower the resistance of the animal to disease. During the first days of life it is standard practice to supplement animals such as piglets with iron supplied orally, parenterally or by injection. In addition, the feed industry routinely adds iron compounds to supplement that which naturally occurs in feedstocks. Typical iron supplementation of animal feedstocks in the United States employs about 15 parts per million (ppm) of iron for beef cattle and sheep, 25 ppm for dairy cattle, 40 ppm for poultry feed and 80 ppm for swine feed. Most current iron feed supplements employ iron sulfate, which is unpalatable to animals and can cause stomach upset.

A separate problem has been the disposal of sludge or precipitates formed by coagulating raw water contaminants with iron and aluminum salts or the like at potable water treatment plants and at plants designed to remove the organic color from effluents from such sources as paper mills. This is especially true for surface waters which are characterized by their high content of dissolved organic color from the natural decaying of

aquatic vegetation. These potable water treatment plants must use high coagulant dosages, which in turn, generate large quantities of sludge residue for disposal. Often the water treatment sludges are simply dumped back into the water source causing degradation of the water quality. Other currently preferred options for disposal of water treatment sludges are lagoon storage, disposal in landfills and discharge into sanitary sewers. Inadequacies in these disposal methods has led to an increased interest in the land application of water treatment sludge.

Important constituents of natural surface waters are aquatic humic substances. Humic substances are formed from the decomposition of plant and animal materials and comprise the largest fraction of natural organic matter in natural surface waters accounting for 40 to 60 percent of the dissolved organic carbon ("DOC"; DOC is defined as organic carbon particles smaller than 0.45 micrometers in diameter and may be in colloidal suspension rather than in solution).

Humic substances comprise a complex heterogeneous mixture of compounds that are not readily separated into discrete components. However, three subfractions of humic substances are generally recognized. These subfractions comprise humic acid, fulvic acid and humin. Humic acid is defined as the fraction of humic substances that is not soluble in water under highly acidic conditions ( $\text{pH} < 2.0$ ) but is soluble at higher pH values. Fulvic acid is defined as the fraction of humic substances that is soluble in water under all pH conditions. Humin is defined as the fraction of humic substances that is not soluble in water at any pH value.

Humic substances are removed from raw drinking water due to several problems associated with their presence. Humic substances are responsible for the yellow or brown organic color of natural surface waters. Humic substances act as a vehicle for the transport of toxic, water insoluble elements and organic micropollutants. Chlorine combines with aquatic humic substances to form chlorinated organic compounds, such as chloroform and complex chlorinated compounds, that may have negative effects on health. Humic substances also precipitate in water distribution systems where they lead to deterioration of tap water quality and increase the need for interior cleaning of pipes.

Traditionally, colored surface waters have been treated with alum (aluminum sulfate) which generates an aluminum containing sludge, which after dewatering, must be deposited in a secure landfill. Iron salt coagulants have been effectively used but often produce a sludge high in heavy metals due to the quality of the iron salt coagulant. Many of the commercial iron salt coagulants are produced from by-products from such sources as  $\text{TiO}_2$  production or steel pickling and are typically high in heavy metals and organic contaminants.

When an iron salt coagulant is used as the primary coagulant to remove humic substances, it reacts to precipitate an iron humate residue. The inferior quality of many iron salt coagulants, such that the coagulants may include high concentrations of heavy metal contaminants, often results in iron humate products having unacceptable high concentrations of heavy metals so as to prevent land application of the iron humate products as well as use of such products in animal feed supplements.

Another problem with current potable water treatment methods is that these methods generally result in a water treatment sludge having unnecessarily high concentrations of hydrous metal oxides, such as iron hydroxides. Hydrous metal oxides are strong adsorbents of trace metals and phosphorus. When applied to the soil surrounding vegetation at high concentrations and high pH, iron hydroxides can result in metal deficiencies in the vegetation including iron deficiency. Also the presence of hydrous metal oxides results in the sorption of phosphorous from the soil reducing the availability of phosphorous to vegetation. Phosphorous is necessary for vegetation growth. Additionally, iron hydroxides do not dewater as well as iron humate products. The iron hydroxides form a somewhat gelatinous mass making sludge containing excess iron hydroxides harder to handle and more expensive to transport.

### SUMMARY OF THE INVENTION

The present invention provides preferred iron humate products and processes for preparing preferred iron humate products adapted for use in treating chlorosis in vegetation and for use in supplementing animal feedstocks.

Existing water treatment processes focus primarily on producing high quality drinking water with little regard for the quality of the resultant sludge. The goal of the water treatment process of the present invention is to produce both high quality drinking water and a high quality sludge that is particularly well adapted for land application to provide useful nutrients to plants and for addition to animal feedstocks as an iron supplement.

The concentration of heavy metal contaminants in the resultant iron humate product is reduced by selecting a relatively pure iron salt coagulant that is free of or has a relatively low concentration of heavy metal contaminants.

The concentration of iron hydroxides in the resultant iron humate product is minimized by using a minimum dosage of iron salts to effect the required color removal of the raw water. The iron salt dosage is minimized by identifying and then coagulating the raw water at an optimum reaction or coagulation pH. The optimum coagulation pH is identified, preferably by analytical tests of water samples. A typical optimum coagulation pH ranges from 3.8 to 5.9 for most iron salt coagulants and most colored surface waters.

The resultant iron humate products are relatively insoluble, but still function as a source of iron nutrients during interactions with plants in soil media. The musty odor and low water solubility of such iron humate products are more attractive to animal palates than conventional iron sulfate animal feed additives. More soluble iron humate products may be produced by contacting the resultant iron humate products with a nitrogen source, so as to produce a nitrogen-enriched iron humate product that contains nitrogen in the range of 0.5 to 12 percent by weight as nitrogen with a minimum water soluble iron content of 50 ppm as iron. Both the unmodified iron humate product and the nitrogen-enriched iron humate product are relatively inexpensive and beneficial sources of iron and humic substances for application to and use by plants and animals.

### OBJECTS AND ADVANTAGES OF THE INVENTION

Therefore, the objects of this invention are to provide a method for running a water purification facility to produce high quality drinking water and to produce a high quality sludge usable in providing needed nutrients to vegetation and to animals; to produce commercial, high quality, low cost, iron humate products especially suitable for addition to soil as an iron nutrient and organic soil additives for the benefit of vegetation; to produce commercial, high quality, low cost, iron humate products especially suitable for addition to animal feedstocks as an iron nutrient for the benefit of animals; to produce such iron humate animal feed products having iron available for animal metabolism and hemoglobin synthesis; to produce such iron humate animal feed products having increased palatability to animals; to produce such iron humate feed products which cause less stomach upset in animals than conventional iron feed supplements; to produce such iron humate feed products which increase digestibility of animal feeds such as hay and silage; to produce such iron humate products having a relatively low concentration of heavy metal contaminants; to produce such iron humate products through the use of high quality iron salts as coagulants in the water treatment process; to produce such iron humate products having a minimum concentration of iron hydroxides; to produce such iron humate products through the controlled addition of iron salt coagulants; and to produce a modified iron humate product with more soluble iron which is more rapidly available for plant uptake and the correction of iron deficiency.

Other objects and advantages of this invention will become apparent from the following description wherein are set forth, by way of illustration and example, certain embodiments of this invention.

### DETAILED DESCRIPTION OF THE INVENTION

As required, detailed embodiments of the present invention are disclosed herein. However, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which may be embodied in various forms. Therefore, specific composition and functional details disclosed herein are not to be interpreted as limiting, but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present invention in virtually any appropriately detailed embodiment.

The present invention concerns the production of preferred iron humate products from water treatment processes to be used in treating vegetation and in particular crops and the like suffering from iron deficiencies generally referred to as chlorosis, and to be used as an animal feed supplement to provide iron for animal metabolism and hemoglobin synthesis.

The preparation of the iron humate products or residuals involves the controlled addition of an iron salt coagulant to raw water in a water treatment plant. The iron salt coagulant reacts with organic color-producing aquatic humic substances or species in the raw water to form an iron humate product or precipitate which when applied to plants or added to animal feed provides useful organic matter and nutrients such as iron. The preferred iron salt coagulant for the process is ferric sulfate or polyferric sulfate. Other acceptable iron salts are

ferric chloride, ferrous chloride, polyferric chloride, and ferrous sulfate and the like. In order to be acceptable the iron salt coagulant used should be of high purity in terms of generally being free of or having a relatively low heavy metal and organic contamination, such as organic corrosion inhibitors and trihalomethane precursors.

Preferably the iron salt coagulant is produced from virgin iron sources and virgin acid sources so as to minimize the extraneous contaminants which may not be environmentally safe to apply to soil or may be harmful to vegetation or animals. Table I gives a typical specification of a ferric sulfate coagulant that is suitable for treating at least some raw surface water under the present invention. However, allowable contaminant levels may differ depending on the water to be treated and the desired end use application of the recovered iron humate product. The allowable contaminants specified in Table I are stricter than the American Water Works Association (AWWA) current standard for ferric sulfate because this standard only addresses the effects of contaminants in the coagulant on the resultant treated water and not the quality of the resultant sludge residue.

TABLE I

Impurity	Maximum Impurity Concentration (mg/kg)
Arsenic	2
Cadmium	2
Chromium	5
Lead	10
Mercury	1
Selenium	3
Silver	5
Nitrites	75
Total Organic Carbon	15
Copper	5
Zinc	10
Manganese	90
Barium	6
Chloride	100
Fluoride	60
Titanium	50
Nitrates	150
Sodium	1000

The most critical parameter affecting the quality of the resultant iron humate product is the reaction or coagulation pH. The optimum coagulation pH will vary depending on the type of surface water, the concentration of organic species present and the type of iron salt coagulant used. The optimum pH in an actual water treatment plant is determined using analytical jar tests of water samples in an iterative approach. A selected quantity of water to be treated is collected in several jars. The pH of the water in the jars is adjusted by the addition of an acid such as sulfuric acid such that the pH of each of the jars is different. A selected quantity of iron salt coagulant is added to each jar and the contents are agitated and then allowed to react or coagulate and then settle.

The pH of the jar having the greatest raw water color reduction is identified. Several more jars are filled with a selected quantity of the water to be treated. The pH of the water in these jars is adjusted to match the pH identified in the first jar test as resulting in the greatest raw water color reduction.

Various quantities of iron salt coagulant are then added to these jars. The contents are agitated and then allowed to react or coagulate and then settle. The small-

est quantity of iron salt coagulant effecting a preselected or desired level of color reduction is identified.

Using the identified minimum quantity of iron salt coagulant resulting in the desired color reduction another set of jar tests can be conducted to identify the pH resulting in the greatest color reduction with the identified minimum quantity of iron salt coagulant. Typically two iterations of the jar tests are completed to identify an optimum coagulation pH for effecting color reduction and the minimal quantity of iron salt coagulant at that pH to effect the desired reduction. Typical optimum coagulation pH values range from 3.8 to 5.9 for most iron salt coagulants and most colored surface waters.

Controlling the optimum pH ensures using the minimum dosage of iron salt coagulant to effect the required color removal of the raw water. It is theorized that excess iron salts form insoluble iron hydroxides which are not taken up by plants as opposed to the preferred iron humate products. Because iron hydroxides are strong adsorbents of trace metals and phosphorous, the presence of the hydroxides in the sludge applied to vegetation can result in metal deficiencies in plants including phosphorous and iron deficiencies. The adsorption of iron from the soil by iron hydroxides may reduce the availability of iron from the preferred iron humate product. Additionally, iron hydroxides do not dewater as well as iron humate products and form a gelatinous mass. The production of excess iron hydroxides results in a product that is more difficult to handle and more expensive to transport.

Although the iron humate products are also very insoluble, they can still function as a source of iron nutrients during interactions with plants in soil media and will also function as an oral source of iron nutrients available to animals. Although it is not the intent of applicant to be bound to any specific theory of how such iron is used by the vegetation, it is theorized that in the soil, the iron humate products are converted into a useable form by vegetation allowing the uptake of iron by the vegetation. There is empirical evidence that iron humate products supply animals with a viable source of elemental iron which is available for hemoglobin synthesis.

In an actual water treatment plant application, analytical jar tests should be conducted frequently to verify the optimum treatment pH setpoint and minimum effective iron dosage rate and to compensate for changes in the chemical composition of the raw water to be treated. Although an excess iron salt coagulant dosage will still produce a high quality drinking water, it will produce excess and undesirable iron hydroxides in precipitates removed from the water and used herein to provide nutrients to vegetation.

The preferred water treatment process of the present invention may be incorporated into a continuous flow water treatment system or a batch water treatment system. The steps of the process of the present invention are essentially the same when incorporated into either a continuous flow or batch treatment system except that the steps are time-based in a batch reactor and position or location-based in a continuous flow reactor.

In a continuous flow water treatment system the pH of the raw water in an influent raw water stream is initially lowered to a previously identified optimum coagulation pH in an acidification zone. The pH may be lowered by the addition of an auxiliary acid such as sulfuric acid or by means such as bubbling CO<sub>2</sub> into the

raw water to form carbonic acid and by other means generally known in the art.

The efficiency of the treatment process appears to improve when the pH of the raw water is lowered prior to the addition of an iron salt coagulant as opposed to lowering of the pH concurrently with or after the addition of an iron salt coagulant. However, the pH of the raw water may be lowered before, after or during the addition of the iron salt coagulant. Also, for pH control and iron salt coagulant dosage efficiency purposes, it is preferred to use an iron salt coagulant with very low free acidity, so that the pH may be controlled independent of the iron salt dosage. As discussed above, the optimum coagulation pH may change due to changes in the composition of the raw water. Analytical jar tests are conducted regularly to identify changes in the optimum coagulation pH and the pH of the water to be treated is adjusted accordingly.

Downstream of the acidification zone, an iron salt coagulant is added to the influent raw water stream in a flash mixing zone to form a treatment solution. The iron salt coagulant is added to the influent raw water stream at a rate previously calculated to provide the minimum dosage of iron salt coagulant necessary to effect the required color removal from the raw water. As discussed above analytical jar tests are conducted regularly to identify any changes in the minimum dosage necessary to effect the required color removal due to changing characteristics of the raw water. The rate of addition of iron salt coagulant is adjusted to correspond to any identified changes in the minimum dosage requirement.

Impellers are preferably used in the flash mixing zone to provide rapid, thorough mixing of the raw water and the iron salt coagulant, however it is foreseeable that other rapid mixing means may be incorporated into the process of the present invention. The iron salt coagulant and the raw water are preferably mixed in the flash mixing zone for a minimum of 15 seconds. This initial mixing is followed by at least 3 minutes and preferably at least 10 minutes of additional mixing such as is available in a flocculation type mixing zone located downstream of the flash mixing zone. The reaction of the iron salt coagulant with the humic substances and other organic matter in the raw water is nearly complete within three minutes for temperate waters and longer for colder waters. The reaction of iron salt coagulant and humic substances forms iron humate products.

After the reaction is complete, the treatment solution is allowed to settle with the iron humate products precipitating out of the solution to form a solids residue. After settling, the resultant treated water is separated from the solids residue (whether as a floating flocculent or as a precipitate that forms a lower solids or sludge layer in the water). The treated water is preferably chlorinated after separation from the solids residue to minimize the formation of chlorinated organics which will contaminate the residue and the drinking water.

The iron humate product in the form of the solid residue is concentrated and dried by conventional equipment being used in the water treatment industry such as settling basins, clarifiers, mechanical filters, sludge drying beds and commercial sludge dryers. The resultant iron humate product typically dewateres very effectively and can achieve air dry solids concentrations up to 88% by weight solids. The iron humate product of the present invention is characterized by an iron concentration ranging from about 5 to about 45 percent by

weight on a dry solids basis and preferably about 28 to about 33 percent by weight on a dry solids basis, low toxic organic and heavy metal contamination, high concentration of humic substances (an elemental carbon concentration generally greater than about 15 percent by weight on a dry and ash free basis, with a preferred concentration greater than about 30 percent) and minimal concentration of iron hydroxides. The solids residue is characterized by a concentration of iron complexed as iron hydroxide of less than 25 percent by weight and preferably less than 10 percent by weight of the total iron present. After air drying, it has a medium brown color and has the consistency of a fine porous soil. The iron humate remains nearly insoluble in water (less than 1 ppm) or when stored in segregated piles, but slowly releases iron to the vegetation in mixed soil conditions.

More soluble, nitrogen-enriched iron humate products are produced by contacting the partially hydrated iron humate products with a commercially available nitrogen source such as ammonia, ammonium hydroxide, urea, ammonium nitrate, and potassium nitrate. The resultant nitrogen-enriched iron humate preferably contains nitrogen in the range of 0.5 to 12 percent by weight as nitrogen with a minimum water soluble iron content of 50 ppm as iron. The nitrogen-enriched iron humate also turns from a medium brown color to a rich dark brown color. The mixture of the nitrogen-enriched iron humate with water forms a dark brown solution, while the filtrate from mixing water with the iron humate is colorless.

Iron humate products can also be employed to provide iron and humic acid to animals such as cattle, swine, poultry, sheep, horses, turkeys, household pets and the like. Iron humate can be fed to animals of all ages, either directly, by mixing with a conventional feedstock, or by blending with an animal feed premix, that is, a uniform mixture of one or more micro-ingredient additives with a diluent, such as a carrier or binder, which is in turn blended with a conventional feedstock. Premixes can also be employed for preparation of fertilizer products for application to vegetation.

Such premixes may include about 1% to about 35% elemental iron on a dry weight basis. Especially preferred premixes contain about 15% to about 20% iron on a dry weight basis. Such premixes also include a concentration of humic substances of about 2% to about 70%, with an especially preferred concentration of about 20% to about 60%. Suitable micro-ingredients include iron, phosphorus, calcium, potassium, sodium, zinc, copper, magnesium, manganese, selenium, iodine, cobalt, fluorine, or any other suitable element or element-containing mineral or mixture thereof. Where the premix is to be fed to animals, Vitamin A, Vitamin B12, Vitamin C, Vitamin D, Vitamin E, or any other suitable vitamin, or mixture thereof may also be employed as a micro-ingredient.

Where iron humate is added to conventional feedstocks, sufficient humate is added to provide a feedstock having from about 15 to about 100 parts per million of elemental iron, depending on the species to be fed. Sheep and beef cattle are typically fed about 15 parts per million of elemental iron, while dairy cattle are fed about 25 parts per million, poultry about 40 parts per million and swine about 80 parts per million.

Examples of the processes in accordance with the invention which follow are for the purpose of demonstrating specific processes in accordance with the inven-

tion and are not intended to be limiting to the scope of the invention or claims.

### EXAMPLE 1

A plant trial was conducted to treat water from the Hillsborough River in Tampa, Fla. with ferric sulfate for color removal. Sulfuric acid was added to the water upstream of a flash mix tank to maintain a desired coagulation pH at a setpoint of 4.5 pH units. A high purity ferric sulfate in accordance with the invention was added at the entrance of the flash mix tank to maintain an average iron dosage of 21 milligrams/liter to treat an average raw water color of 105 standard color units (SCU) to a maximum of 15 standard color units before chlorination. The raw water had a dissolved organic carbon (DOC) content that averaged 15.9 ppm (an indication of the dissolved humic substances present). The DOC in the water was reduced by application of ferric sulfate in accordance with the invention by an average of over 72% by weight. The resultant iron humate sludge precipitate was concentrated using a clarifier, mechanically dewatered using a belt filter press to 18% by weight solids and then dried in a conventional sludge drying bed to a dry solids content of 88% by weight. This unmodified iron humate contained 32% by weight iron on a dry solids basis. The humate material, when mixed with excess water, produced a clear filtrate with less than 1 milligram/liter soluble iron. Additional elemental and composition data relating to the unmodified iron humate product are provided in Tables 2 and 3. Data for Tables 2 and 3 were taken from samples of unmodified iron humate taken randomly from the resultant iron humate product.

### EXAMPLE 2

The unmodified iron humate product from above Example 1 was contacted with anhydrous ammonia in excess in a pressure vessel at 50 pounds per square inch (psi) for 48 hours at ambient temperatures and then dried. The resultant nitrogen content was 4.71% by weight on a dry weight basis. The nitrogen-enriched iron humate had turned to a rich dark brown. The iron solubility had increased by a factor of greater than 500. Elemental and compositional analysis of the ammonia-nitrogen enriched iron humate product are provided in Tables 2 and 3. Data for Tables 2 and 3 were taken from samples of nitrogen-enriched iron humate taken randomly from the resultant iron humate product.

TABLE 2

#### COMPOSITIONAL ANALYSIS\*

	Percent by weight				
	pH	Ash	Moisture	Volatiles	Iron
Unmodified	4.8	49	12	39	32
Nitrogen-Enriched	8.3	36	14	50	23

\*The weight percents for ash, moisture, volatiles and iron were determined after roasting the resultant unmodified and ammonia-nitrogen enriched iron humate products at 1000° Centigrade until dry.

TABLE 3

#### ELEMENTAL ANALYSIS

Element	Percent by weight of dry and ash free humate	
	Unmodified Iron Humate	Nitrogen-Enriched Iron Humate
Carbon	40	43
Hydrogen	4	6
Nitrogen	0.9	4

TABLE 3-continued

Element	Percent by weight of dry and ash free humate	
	Unmodified Iron Humate	Nitrogen-Enriched Iron Humate
Oxygen	55	46

### EXAMPLE 3

100 pounds (dry weight) of the unmodified iron humate product from above Example 1 was mixed with 29 pounds of urea and then stored at ambient temperature and pressure for 24 hours in a closed atmosphere to produce a nitrogen-enriched iron humate product. The nitrogen content of the nitrogen-enriched iron humate had risen from 0.6 to 10.9 percent by weight. The nitrogen-enriched iron humate had turned to a rich dark brown. The iron solubility had increased by a factor of more than 100.

### EXAMPLE 4

Plugs of turf grass and soil from a horticultural field laboratory were prepared for testing in triplicate with dosages of 2.5, 7.5 and 25.0 pounds of iron humate product made in accordance with Example 1 and Example 3 per acre applied to separate plots. Uniform rates of nitrogen, phosphorous, and potassium were applied to all plots. Visual ratings were performed bi-weekly and clippings for growth rate and iron uptake measurements were conducted weekly for two weeks. Both the urea-nitrogen enriched iron humate of Example 3 and the unmodified iron humate of Example 1 were compared against equivalent iron dosages from other iron sources, in particular, ferrous sulfate, a commercial iron chelate sold under the trademark Sequesterene 138-Fe and a control group with no added iron. The results of the iron uptake and vegetation growth measurements for the first two weeks are shown on Table 4. In general, the nitrogen-enriched iron humate samples outperformed the unmodified iron humate samples. Although the commercial iron products outperformed the iron humates on an efficiency basis, higher dosages of the iron humates outperformed the lower dosages of the commercial organic chelate. All the iron humate samples outperformed the control samples and also had a much greener appearance.

TABLE 4

Iron Source	lbs Fe/Acre	Fe Uptake (mg Fe/pot*)	Week		Total Growth
			1 Growth (g/pot)	2 Growth (g/pot)	
1. Iron Humate	2.5	0.182	.42	.60	1.02
2. Iron Humate	7.5	0.151	.43	.60	1.03
3. Iron Humate	25.0	0.183	.51	.59	1.10
4. Nitrogen Enriched Iron Humate	2.5	0.201	.46	.69	1.15
5. Nitrogen Enriched Iron Humate	7.5	0.148	.40	.54	.94
6. Nitrogen Enriched Iron Humate	25.0	0.224	.42	.69	1.11

TABLE 4-continued

Iron Source	lbs Fe/Acre	Fe Uptake (mg Fe/pot*)	Week 1 Growth (g/pot)	Week 2 Growth (g/pot)	Total Growth
7. Sequesterene 138-Fe	2.5	0.176	.52	.67	1.19
8. Sequesterene 138-Fe	7.5	0.301	.58	.64	1.22
9. Ferrous Sulfate	25.0	0.245	.59	.65	1.24
10. Control	0	0.099	.35	.51	.86

\*Plant growth is expressed in g/pot which indicates the mass of the plant growth per pot in which plants are grown.

## EXAMPLE 5

Iron uptake in young citrus trees was tested for the nitrogen-enriched and unmodified iron humates of Examples 2 and 1 respectively and compared against two commercial iron chelates sold under the trademarks Sequesterene 138-Fe and LibFer SP and a control group with no added iron nutrients in a soil incubation study over 70 days. The results of the tissue analysis for iron are shown in Table 5. In Table 5, the headings Carrizo and Swingle represent the root stock of the young citrus trees on which the iron sources were applied. The ammonia-nitrogen enriched iron humate of Example 2 showed dramatically higher content than all other iron sources tested. The unmodified iron humate of Example 1 showed slightly lower to equivalent performance in comparison to the commercial iron chelates. All tested iron sources performed better than the control group.

The preliminary economics indicate that the iron humate products of the present invention are commercially viable compared to available iron sources. The analysis for iron of tissue samples from the citrus leaves of trees treated with the nitrogen-enriched iron humate product indicate that these leaves contained more iron than the leaves of trees treated with Sequesterene 138-Fe. The cost of an effective amount of the nitrogen-enriched iron humate product would be a fraction of the cost for a similarly effective amount of Sequesterene 138-Fe based upon the price thereof at the time of filing of this application, while still maintaining a healthy profit for the iron humate producer.

The iron humate compositions of the present invention are usable in conjunction with a variety of vegetation and is usable not just in conjunction with plants grown in fields or the like, but also in such related areas as potting soil.

TABLE 5

Concentration of Iron in Leaves of Two Citrus Rootstocks 45 Days After Application of Iron Source			
Iron source	Rate g Iron/plant	Iron in Leaves (mg/kg)	
		Carrizo	Swingle
Nitrogen-Enriched Iron Humate	2	390	240
Nitrogen-Enriched Iron Humate	1	338	213
Nitrogen-Enriched Iron Humate	0.5	241	104
Unmodified Iron Humate	2	235	67
Sequesterene 138-Fe	0.5	225	98
Sequesterene 138-Fe	1	218	61
Sequesterene 138-Fe	0.25	216	112
Unmodified Iron Humate	1	205	98

TABLE 5-continued

Concentration of Iron in Leaves of Two Citrus Rootstocks 45 Days After Application of Iron Source			
Iron source	Rate g Iron/plant	Iron in Leaves (mg/kg)	
		Carrizo	Swingle
Unmodified Iron Humate	0.5	198	70
LibFer SP	0.25	198	58
Libfer SP	1	190	61
Libfer SP	0.5	180	139
CONTROL	0	164	44

## EXAMPLE 6

Sow's milk contains only about 1 part per million of elemental iron. In addition, piglets are born with a relatively low total body iron content, most of which is already incorporated into hemoglobin. Consequently, nursing piglets raised in a confined environment without access to soil as an iron source are well known to be subject to iron deficiency anemia. Piglets with chronic anemia may exhibit poor growth, listlessness, rough hair coat, wrinkled skin, and paleness of the snout, ears and mucous membranes. Blood hemoglobin levels in piglets with chronic anemia may range from about 5 to about 8 grams/deciliter (g/dl). Piglets with acute anemia may experience labored breathing or a spasmodic movement of the diaphragm known as "thumps". Blood hemoglobin levels in piglets with acute anemia may fall to 3 to 5 g/dl and the piglets may die suddenly.

For this reason, an iron supplement such as ferrous sulfate may be conventionally administered to nursing piglets.

Availability of elemental iron from iron humate for animal metabolism and hemoglobin synthesis in piglets in accordance with the present invention was evaluated in comparison with equivalent iron dosages from other iron sources, e.g., Pig Oral Iron (supplied by Carl S. Akey, Inc.) and Iron Dextran (supplied by Durvet, Inc.). A total of twelve litters of nursing piglets were randomly assigned to three groups. Two groups were fed daily for 28 days with 75 grams/litter of elemental iron supplied from either iron humate or Pig Oral Iron. Aliquots of 25 grams of the respective supplement were set out in small pans in the farrowing crates three times daily. Piglets in the third group were injected with 100 mg of elemental iron supplied in 1.0 milliliter of Iron Dextran within 24 hours after birth.

## Hemoglobin concentrations

Blood samples were drawn from each piglet on day 1, prior to initiation of the treatments and subsequently on days 3,5,7,10,14,21, and 28. Three to five milliliters of whole blood were drawn from each piglet and frozen until analysis. Hemoglobin was measured using a kit (Sigma Diagnostics, St. Louis, Mo., kit number 525). Sows were fed a standard lactation diet and piglets had minimal access to sow feed. The piglets were not creep fed. As shown in Table 6-1, hemoglobin levels were approximately equal on day 1. They decreased by day 3, and began to increase by day 5 or 7. This pattern was repeated for all piglets, regardless of the iron source. By day 10, iron humate-fed piglets exhibited greater hemoglobin concentrations than the other piglets, and this pattern prevailed throughout the remainder of the trial. Piglets fed Pig Oral-Iron exhibited a plateau in hemoglobin concentrations about day 10 or 14 and piglets receiving Iron-Dextran peaked on day 10 or 14 and decreased steadily to day 28. By day 28 hemoglobin

concentrations for iron-humate fed piglets were 17% and 42% higher than for piglets receiving Pig Oral Iron or Iron Dextran, respectively. Blood hemoglobin levels increased by 3.77% in the Iron Humate-fed group, decreased by 16.4% in the Pig Oral Iron group, and decreased by 26.4% in the Iron Dextran group. Since no other source of iron was available to the piglets for hemoglobin synthesis other than the negligible amount present in sow's milk, it can be concluded that iron humate provides a source of supplemental iron that is available for hemoglobin synthesis in the nursing piglet.

TABLE 6-1

HEMOGLOBIN LEVELS OF PIGLETS 0-28 DAYS OF AGE FED EITHER IRON-HUMATE OR PIG ORAL-IRON OR INJECTED WITH IRON DEXTRAN AS THE SOLE SOURCE OF IRON DURING A 28 DAY LACTATION

HEMOGLOBIN LEVELS OF PIGLETS 0-28 DAYS OF AGE FED EITHER IRON-HUMATE OR PIG ORAL-IRON OR INJECTED WITH IRON DEXTRAN AS THE SOLE SOURCE OF IRON DURING A 28 DAY LACTATION			
HEMOGLOBIN LEVEL, G/DL			
DAY/TREATMENT	IRON-HUMATE <sup>a</sup>	PIG ORAL-IRON <sup>b</sup>	IRON DEXTRAN <sup>c</sup>
1	10.08	10.69	10.00
3	7.44	7.59	7.97
5	7.98	7.25	8.10
7	8.16	8.25	8.78
10	9.83	8.39	9.33
14	10.34	8.33	9.34
21	11.28	9.07	8.44
28	10.46	8.94	7.36

<sup>a</sup>Each value represents an average pooled from thirty-nine piglets from four replicate litters.

<sup>b</sup>Each value represents an average pooled from forty-one piglets from four replicate litters.

<sup>c</sup>Each value represents an average pooled from thirty-five piglets from four replicate litters.

#### Growth Performance

Litters were weighed weekly on days 1,7,14,21, and 28. As shown in Table 6-2, litter weights were approximately equal on day 1 and all litters exhibited relatively steady growth. Iron-humate fed piglets showed an increase in litter weight at days 14 and 28 as compared to either Pig Oral Iron or Iron-Dextran. On day 28 the Iron humate-fed group had increased in weight by 369%, the Pig Oral Iron group by 319%, and the Iron Dextran group by 343%.

TABLE 6-2

LITTER GROWTH OF PIGLETS 0-28 DAYS OF AGE FED EITHER IRON-HUMATE OR PIG ORAL-IRON OR INJECTED WITH IRON DEXTRAN AS THE SOLE SOURCE OF IRON DURING A 28 DAY LACTATION.			
LITTER WEIGHT <sup>a</sup> , KG			
DAY/TREATMENT	IRON-HUMATE	PIG ORAL-IRON	IRON DEXTRAN
0	28.5	31.6	29.3
7	49.3	50.3	51.2
14	80.9	78.6	75.3
21	111.1	105.7	103.6
28	133.8	132.3	129.7
LITTER GAIN, KG			
0-14 DAYS	52.4	47.0	46.0
0-28 DAYS	105.3	100.7	100.4

<sup>a</sup>Each weight represents four replicate litters.

Individual piglet weights were recorded on days 1 and 28. As shown in Table 6-3, the Iron Humate fed piglets gained an average of 433%, the Pig Oral Iron fed piglets an average of 361%, and the Iron Dextran-injected piglets an average of 395%.

TABLE 6-3

GROWTH OF PIGLETS 0-28 DAYS OF AGE FED EITHER IRON-HUMATE OR PIG ORAL-IRON OR INJECTED WITH IRON DEXTRAN AS THE SOLE SOURCE OF IRON DURING A 28 DAY LACTATION			
PIGLET WEIGHT <sup>a</sup> , KG			
DAY/TREATMENT	IRON-HUMATE	PIG ORAL-IRON	IRON DEXTRAN
0	1.29	1.40	1.46
28	6.88	6.46	7.22
PIGLET GAIN, KG			
0-28 DAYS	5.59	5.06	5.76

<sup>a</sup>Each weight represents the piglets from four replicate litters.

Table 6-4 shows survival rates for litters fed with iron humate or Pig Oral Iron or injected with Iron Dextran. The Iron humate and Pig Oral Iron fed litters were slightly larger at birth than the Iron Dextran injected group.

TABLE 6-4

LITTER SIZE OF SOWS WHERE PIGLETS 0-28 DAYS OF AGE WERE FED EITHER IRON-HUMATE OR PIG ORAL-IRON OR INJECTED WITH IRON DEXTRAN AS THE SOLE SOURCE OF IRON DURING A 28 DAY LACTATION.			
LITTER SIZE <sup>a</sup> , KG			
DAY/TREATMENT	IRON-HUMATE	PIG ORAL-IRON	IRON DEXTRAN
0	11.3	11.3	10.0
28	9.8	10.3	9.0
% SURVIVAL	86.7	91.2	90.0

<sup>a</sup>Each number represents the piglets from four replicate litters.

Although the numbers of piglets and litters is small, the growth data depicted in Tables 6-2 through 6-4 provide evidence that the elemental iron in Iron Humate is available to the piglet for growth and hemoglobin synthesis. Piglets fed iron Humate grew faster than those fed Pig Oral Iron and similarly to those receiving Iron Dextran.

It is to be understood that while certain forms of the present invention have been illustrated and described herein, it is not to be limited to the specific forms or compositions described.

What is claimed and desired to be secured by Letters Patent is as follows:

1. An iron humate product having:
  - (a) an iron concentration ranging from about five to about forty-five percent by weight on a dry solids basis;
  - (b) a concentration of humic substances equal to or greater than about fifteen percent by weight; and
  - (c) said product has a concentration of iron complexed as iron hydroxides that is less than about 25 percent by weight of total iron present, wherein said iron humate product is produced by adding a sufficient concentration of an iron salt coagulant to a quantity of raw water having a pH between about 3.8 and about 5.9 to reduce the organic color of the water and form a solid residue containing said iron humate product.
2. The iron humate product as described in claim 1 wherein:

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(a) said product has a concentration of iron complexed as iron hydroxides that is less than about 10 percent by weight of total iron present.

3. The iron humate product as described in claim 1 wherein:

(a) said iron salt coagulant is selected from the group consisting of ferric sulfate, ferrous sulfate, polyferric sulfate, ferric chloride, ferrous chloride, polyferric chloride, and mixtures thereof.

4. An iron humate product prepared in accordance with a method for treating a quantity of colored raw water including humic substances comprising the steps of:

(a) adding an iron salt coagulant to said raw water to form a treatment solution;

(b) controlling the pH of said treatment solution between about 3.8 and about 5.9 to provide for the addition of a minimum amount of said iron salt coagulant to the raw water to reduce the color of the raw water to a preselected level and to produce an iron humate product wherein the concentration of iron complexed as iron hydroxide in the iron humate product is less than about 25 percent by weight on a dry solids basis;

(c) separating said iron humate product from said treatment solution; and

(d) concentrating and drying said iron humate product so as to form a solid residue having a concentration of humic substances greater than about 15% by weight.

5. An iron humate product prepared in accordance with the method of claim 4 wherein said step of controlling includes:

(a) periodically sampling the raw water;

(b) finding the pH value of the sampled water to produce an optimum coagulation effect in the water;

(c) adding iron salt coagulant to find the optimum concentration of iron salt coagulant to coagulate components of the water to form iron humate without producing substantial quantities of iron hydroxides; and

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(d) adjusting the addition of the iron salt coagulant for producing said optimum concentration with said water.

6. An iron humate product prepared in accordance with the method of claim 4 wherein said method includes the step of:

(a) selecting said iron salt from the group consisting of ferric sulfate, ferrous sulfate, polyferric sulfate, ferric chloride, ferrous chloride, polyferric chloride, and mixtures thereof.

7. An iron humate product prepared in accordance with the method of claim 4 wherein the concentration of iron complexed as iron hydroxide in the iron humate product is less than about 10 percent by weight on a dry solids basis.

8. An iron humate product prepared in accordance with the method of claim 4 wherein the concentration of humic substances in said product is at least 15 percent by weight.

9. An iron humate product prepared in accordance with a method comprising the steps of:

(a) adding a sufficient concentration of an iron salt coagulant to a quantity of raw water containing humic substances and having a pH of from about 3.8 to about 5.9 to reduce the organic color of the water to a preselected level while producing a solid residue iron humate product such that the concentration of iron complexed as iron hydroxide in the iron humate product is less than about 25 percent by weight of said product on a dry solids basis and the concentration of humic substances is greater than about 15% by weight.

10. An iron humate product prepared in accordance with the method of claim 9 wherein said method includes the step of:

(a) selecting said iron salt from the group consisting of ferric sulfate, ferrous sulfate, polyferric sulfate, ferric chloride, ferrous chloride, polyferric chloride and mixtures thereof.

11. An iron humate product prepared in accordance with the method of claim 10 wherein the concentration of iron complexed as iron hydroxide in the iron humate product is less than about 10 percent by weight on a dry solids basis.

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US005354350A

**United States Patent** [19][11] **Patent Number:** **5,354,350****Moore**[45] **Date of Patent:** **Oct. 11, 1994**[54] **CITRATE SOLUBLE SLOW RELEASE IRON HUMATE**

5,302,180 4/1994 Hjersted ..... 71/DIG. 2

[75] **Inventor:** William P. Moore, Hopewell, Va.*Primary Examiner*—Ferris Lander[73] **Assignee:** The Vigoro Corporation, Chicago, Ill.[21] **Appl. No.:** 165,958[22] **Filed:** Dec. 14, 1993[51] **Int. Cl.<sup>5</sup>** ..... C05F 11/02; C05B 21/00; C05G 3/00[52] **U.S. Cl.** ..... 71/24; 71/33; 71/34; 71/64.11; 71/DIG. 2; 210/710; 210/724; 210/770; 210/917; 426/807[58] **Field of Search** ..... 71/24, DIG. 2, 64.11, 71/33, 34; 210/710, 724, 720, 917; 426/807[56] **References Cited****U.S. PATENT DOCUMENTS**

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[57] **ABSTRACT**

A new slow releasing particulate iron humate agricultural nutrient composition exhibiting substantially complete solubility of its iron content in soil solutions as indicated by neutral citrate solubilities, and almost no solubility in water, and a new method for preparing the composition. The method comprises admixing and co-reacting iron humate with about equimolar amounts of a divalent metal oxide, an aqueous hydroxide of a monovalent Lewis acid, and a water soluble inorganic phosphate. The iron humate amounts to between 20 and 70 percent of the nutrient particles, and the reaction is carried out at temperatures between 60° and 150° C. for between 4 and 25 minutes.

**18 Claims, No Drawings**

## CITRATE SOLUBLE SLOW RELEASE IRON HUMATE

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention relates to slow release iron agricultural nutrients based on iron humate, and a method for their preparation. More particularly, this invention relates to a composition and a method for preparing the new slow releasing iron humate agricultural nutrient composition, which substantially completely releases its iron contents in soil solutions. The new method relates to the discovery that the coreaction of iron humate, a divalent metal oxide, an aqueous hydroxide of a monovalent Lewis acid, and a water soluble inorganic phosphate, produces hard, homogeneous, particles containing iron which is substantially insoluble in water, but soluble in agricultural soil solutions.

#### 2. Description of Related Art

Iron is an essential nutrient in the growth of plants. It is usually absorbed by the roots of plants in ionic form from soil solutions. Iron deficiencies have been observed in many plant species where iron solubilities in the soil solution are insufficient to provide the plant iron requirements.

The amount of iron in the soil solution in relation to the amounts of other elements is as important in some instances as the absolute quantities of iron. Excess iron in the soil solution can cause plant deficiencies in other nutrients, such as manganese, copper, and molybdenum, even though ordinarily sufficient amounts of those nutrients are present in the soil.

Where fertilizers containing substantially water soluble iron are used around cement, brick, or ceramic walks, roads, floors, and walls, the surfaces are frequently stained with dark brown colored spots where the fertilizer granules contact the surfaces. The term substantially is used herein to mean mainly or more than one half.

The need for carbon in soils in which plants are grown has been well proved, and investigators have shown quantitatively the effectiveness of optimum ratios of carbon to nutrient, particularly nitrogen, ratios in the soil. Humates and humic acids are effective sources of soil carbon and additionally improve the condition of soils for growing plants.

Hjersted, in U.S. Pat. No. 5,213,692, disclosed a method for providing nutrients and organic matter to soil for use by vegetation, and a method for the preparation of iron humate by treatment of humate colored raw water, under controlled pH conditions, with an iron salt coagulant. Hjersted separated the precipitated iron humate product, concentrated and dried it. The iron humate recovered exhibited an iron solubility of less than 1 part per million parts of water. When he mixed the iron humate with nitrogen from urea or ammonia, he increased iron solubility in water to about 0.05 percent.

Soil is a heterogeneous, polydisperse system of solid, liquid and gaseous components. In this heterogeneous system, the soil solution acts as a medium by which chemical reactions between members of the different and the same soil phases are made possible, even when the reactants are not in direct contact. Nutrients to be effective in the growth of plants must be soluble in the soil solution which comprises soluble and insoluble cation exchange moieties, and organic and inorganic moieties. Soil solutions vary considerably in nature, and

one solution may not be used to exactly duplicate each one's properties. However, neutral citrate solutions are used to indicate availability of nutrients to plants through the soil solutions, particularly in the cases of phosphate and iron nutrients.

To find iron nutrients with good availability of iron to plants, it has been a goal of researchers to find and produce iron nutrient compositions which have substantially complete solubilities in neutral aqueous citrate solution. The method to determine Citrate-Soluble Phosphorous in Fertilizers is defined in AOAC Official Methods of Analysis, 15th Edition, 1990 in Method 960.01. The same method may be used for Citrate-Soluble Iron using the AOAC Method 980.01 for iron instead of the phosphorous determination.

There exists an important need for an iron agricultural nutrient composition which is practically insoluble in water and substantially completely soluble in soil solution as indicated by solubility in aqueous neutral citrate solution, and for a method for effectively preparing such a composition.

In the preparation of agricultural nutrients, reactions involving acids and bases have been used. The term Lewis acid is used to define an ion, or molecule, that can combine with another ion, or molecule, by forming a covalent bond with two electrons from the second ion, or molecule. Hydrogen ion (proton) is the simplest substance which will do this, but many other ions such as ammonium ion, potassium, and sodium will also do this. Ammonium, sodium, and potassium hydroxides are hydroxides of Lewis acids.

### SUMMARY OF THE INVENTION

I have discovered that iron humate, exhibiting low iron solubility in aqueous neutral citrate solution and poor handling and use physical properties, may be chemically coreacted with divalent metal oxide, aqueous hydroxide of a Lewis acid, and water soluble inorganic phosphate, in a new method to form a new particulate, slow releasing, agricultural nutrient composition, which exhibits water insolubility and substantially complete solubility in soil solutions, as indicated by solubility in aqueous neutral citrate solution, and excellent handling and physical properties.

It was found that the slow releasing particulate solid iron humate agricultural nutrient composition, containing between 20 and 70 percent iron humate and between 30 and 80 percent chemically coreacted divalent metal oxide, hydroxide of a monovalent Lewis acid, and a water soluble inorganic phosphate formed in the new method, and exhibiting water insolubility and substantially complete solubility in soil solutions of its iron content, are excellent agricultural nutrients for plants and animals.

### DETAILED DESCRIPTION OF THE INVENTION

I have discovered a new and effective method of preparing a slow releasing particulate iron humate agricultural nutrient composition which is practically insoluble in water yet is substantially completely soluble in soil solutions. Iron contents between 5 and 25 percent in the composition are required to provide a useful amount of iron and to allow sufficient reactants to make the iron soluble in the soil solution. The variation in iron content is caused to some extent by the variations of iron con-

centrations in the iron humates available for use in the instant method.

Iron humate, amounting to between 20 and 70 percent of the final agricultural nutrient, is admixed with a divalent metal oxide. That mixture is then admixed and reacted with an aqueous hydroxide of a monovalent Lewis acid, and then reacted with a water soluble inorganic phosphate.

For the method to effectively form iron nutrient, soluble in soil solution, the divalent metal oxide, the hydroxide of a monovalent Lewis acid, and the water soluble inorganic phosphate moieties must be admixed and reacted in about equimolar amounts, and the chemically coreacted moieties must amount to between 30 and 80 percent of the dry particulate agricultural nutrient.

Temperatures between 60° and 150° C. are necessary during the coreaction so that the reactants react sufficiently to form homogeneous particles of iron humate agricultural nutrients which are practically water insoluble yet substantially completely soluble in soil solutions.

The term practically water insoluble is used to denote iron solubilities of a few hundredths of a percent, or less, and substantially completely soluble in soil solution is used to denote iron solubilities of more than half in neutral aqueous citrate solution using the AOAC Method 980.01 method for available iron.

The divalent metal oxide may be used effectively in the hydrated or hydroxide form because the reaction is carried out in aqueous media. However, it is usually more convenient to handle the dry metal oxides and allow hydration to occur during the admixing with the other aqueous ingredients.

Divalent metal oxides are usually valuable agricultural nutrients, and those oxides found to be most effective in the instant method are oxides of magnesium, manganese, zinc, copper, iron, cobalt, and calcium.

Iron humate may be obtained in any practical manner and used effectively. It may be formed by, for example, the coagulation-clarification of humate colored raw water.

Lewis acids define a very large number of electron accepting ions or molecules. The materials which perform effectively as reactants in the instant method are only the hydroxides of monovalent Lewis acids. The preferred hydroxides are potassium hydroxide, sodium hydroxide, and ammonium hydroxide. The divalent hydroxides such as calcium hydroxide are ineffective.

Phosphates, to be effective in the instant invention, must be water soluble. Only inorganic, water soluble, phosphates provide the reactivity required to produce the coreaction to form water insoluble-citrate soluble iron in slow release particles. Organic phosphates and insoluble phosphates do not react effectively in the method.

The water soluble inorganic phosphates may be reacted with the aqueous hydroxide of monovalent Lewis acid prior to its use in the instant method, so long as the phosphate remains water soluble before its reaction with the divalent metal oxide and iron humate.

The preferred water soluble inorganic phosphates are one, or a combination, of the following phosphates: phosphoric acid, monoammonium phosphate, diammonium phosphate, monopotassium phosphate, dipotassium phosphate, polyphosphoric acid, and ammonium polyphosphate.

Although the instant method is conveniently performed in a stepwise batch manner, it is economically carried out in a continuous manner whereby iron humate, divalent metal oxide, monovalent hydroxide of a Lewis acid and a water soluble inorganic phosphate are continuously charged to a continuous reactor in which admixing and coreacting steps are continuously conducted under the same closely controlled conditions as in the batch method, and from which the homogeneous particles of iron humate agricultural nutrients are continuously discharged.

Surprisingly, by use of the instant method iron humate exhibiting low iron solubility in aqueous citrate solution and poor physical properties is converted to a new slow releasing particulate iron humate agricultural nutrient composition exhibiting a high degree of water insolubility and substantially complete solubility in soil solutions of its iron content, as indicated by solubility in neutral aqueous citrate solution. The new composition must contain between 20 and 70 percent iron humate and between 30 and 80 percent of chemically combined divalent metal oxide, aqueous hydroxide of a monovalent Lewis acid, and a water soluble inorganic phosphate to provide an iron content of between 5 and 20 percent.

The new composition functions well to provide iron slowly and continuously through the soil solutions to growing plants and does not cause iron toxicity, and does not cause interactions to create deficiencies of other metallic plant nutrients. The new composition may be used around walls, floors, and walkways without rusty looking discoloration by occasional particles contacting the surfaces.

Iron is an essential nutrient in animal feeds. The new composition functions effectively as an animal feed source of iron. The iron of this composition enters the blood stream of animals more effectively than other commercial iron sources now in use in the feed industry.

Plant nutrients are used more effectively as granules than as random particles in commercial operations requiring minimum labor, and machinery. Attrition resistant granules produce a minimum amount of dust and plant food segregation. The new method provides attrition resistant granules of iron humate which preferably contain between 6 and 20 percent iron, with substantially all of the iron insoluble in water and soluble in neutral aqueous citrate. In this preferred method, iron humate powder, amounting to between 40 and 60 percent of the granular plant nutrient, is admixed with a divalent metal oxide powder, and with a water soluble salt formed by reaction of a hydroxide of a monovalent Lewis acid and phosphoric acid. This mixture is then reacted with phosphoric acid. To be effective, the divalent metal oxide, the hydroxide of monovalent Lewis acid, and the total phosphate moieties must be used in closely controlled molecular ratios. The molar ratios must be held between 1 and 1.2 for each of the three moieties, so that each will participate in the coreaction with iron humate. The total amounts of these reactants must be controlled so that they form between 60 and 40 percent of the granular plant nutrient. The term powder is used to denote finely divided solid particles.

Excellent operations and nutrient effectiveness are obtained when the salt of phosphoric acid and a hydroxide of a monovalent Lewis acid, and phosphoric acid are combined in a ratio to form plant nutrient granules exhibiting a near-neutral pH between 6 and 7.5.

Homogeneous, attrition resistant granules of iron humate plant nutrients are best formed where the admixing and reacting is carried out at a temperature between 80° and 125° C. for a period of time amounting to between 4 and 25 minutes. Lower reaction temperatures provide soft, damp granules and higher temperatures damage the physical integrity of the iron humate, with combustion of the humates sometimes occurring at temperatures slightly above 150° C. The reaction and mixing is incomplete with less than 4 minutes reaction time and more than 25 minutes causes finer than desired granular nutrients.

It is possible to carry out the instant method where all of the phosphate moieties are admixed and reacted as a water soluble salt of a hydroxide of a monovalent Lewis acid and phosphoric acid, and the method may be used effectively where a soluble phosphate salt, such as monoammonium phosphate, is economically available. However, the method may also be operated for reasons of method efficiency and economics where about half of the admixed and reacted phosphate moieties are derived from a water soluble salt of a hydroxide of a monovalent Lewis acid and phosphoric acid, and about half from phosphoric acid.

In the preferred method of producing attrition resistant granules of iron humate plant nutrient, the iron humate may be derived as a precipitated coagulation product resulting from the clarification of humate colored water by treatment with iron salts. Where such a precipitated product is unavailable, or where higher concentrations of iron in iron humate are desired, iron humate derived from other sources may be used.

The reactions in the instant method are exothermic and create sufficient heat to evaporate moisture from the granular product. It is possible to increase the moisture removal by supplying hot air directly to the reaction mixture. Depending somewhat upon the amount of water included in the iron humate and the other reactants used in the instant method, it is usually desirable, for optimization of nutrient concentrations and physical properties, to dry the iron humate plant nutrients further in a separate dryer using air at temperatures between 100° and 200° C., until the moisture content in the nutrient is between 1 and 7 percent. Granule friability increases rapidly at moisture contents below 1 percent, and handleability and nutrient concentrations undesirably decrease with more than 7 percent moisture. Drying is slow with air temperature below 80° C. and fire hazards occur at temperatures above 200° C.

The method of preparing attrition resistant granules of iron humate plant nutrient may be economically and effectively carried out on a continuous basis whereby the iron humate powder, divalent metal oxide powder, water soluble salt formed by reaction of a hydroxide of a monovalent Lewis acid and phosphoric acid, and aqueous phosphoric acid are continuously charged to, admixed in, coreacted in, and discharged from, a continuous reactor as homogeneous attrition resistant granules of iron humate. The continuous reactor must provide for high-shear mechanical mixing and plug flow dynamics in the system. Plug flow dynamics preclude appreciable back-mixing and the presence of unreacted ingredients in the product discharged from the reactor. Plug flow dynamics are best achieved by use of a long thin tubular reactor having a length to diameter ratio higher than 3 to 1. Alternatively, plug flow dynamics may be approached by use of a compartmented mixer-reactor to prevent back mixing.

When the preferred method is used, an attrition resistant granular iron humate plant food composition is formed which comprises between 40 and 60 percent iron humate and between 60 and 40 percent of chemically combined divalent metal oxide, water soluble salt of a monovalent Lewis acid hydroxide and phosphoric acid, containing between 6 and 20 percent iron, substantially all of which is insoluble in water and soluble in aqueous neutral citrate solution. The composition functions well as a slow releasing iron plant nutrient.

#### MODE OF OPERATION OF THE INVENTION

Having described the basic concepts of the instant invention, reference is now made to the following examples which are provided to illustrate the new method of preparing a slow releasing particulate iron humate agricultural nutrient exhibiting practically zero iron water solubility and substantially complete solubility in aqueous neutral citrate solution, and to illustrate the efficacy as agricultural nutrients of the new compositions prepared by the instant method.

#### EXAMPLE 1

This example demonstrates the instant invention by providing specific ingredients and conditions for the batch method.

Preparation of slow releasing particulate iron humate agricultural nutrient was carried out in an Eirich Model R-08 mixer reactor constructed of stainless steel 304, consisting of a 92 centimeter (cm) diameter by 92 cm tall pan equipped with a drive apparatus and sealing ports on the top and bottom of the pan. The pan contained an agitator consisting of 6 flat blades made from 7.6 cm high by 1.25 cm thick hardened steel bars welded to the end of a hardened steel shaft. The bar agitator describes a diameter of 30 cm when it rotates with the bottom of the agitator located at 7.5 cm above the floor of the pan. Arrangements were made for the pan to operate in a clockwise manner and the agitator also rotated in a clockwise manner. The blades of the agitator operated within about 1.25 cm of the rotating pan's vertical wall. The pan was equipped with a stationary scraper to remove material from the wall, located at about 3 o'clock compared to the closest point of the agitator at 8 o'clock. The pan was fitted with a vent to discharge vapors through a scrubber and stack. The apparatus was operated at about atmospheric pressure.

The pan was charged at ambient temperatures with iron humate powder admixed with the divalent metal oxide powder, magnesium oxide powder, and the water soluble phosphate, diammonium phosphate powder, in the amounts listed as follows:

Materials	Kilograms
Iron Humate, 20% Fe, 20% H <sub>2</sub> O	28.1
DAP, 18-46-0	7.0
Magnesium Oxide, 57% Mg	3.8

While the pan was rotating at 15° from its vertical axis at 46 RPM, and the agitator was rotating at 533 RPM, black phosphoric acid preheated to 65° C., containing 53 percent P<sub>2</sub>O<sub>5</sub> and amounting to 6.1 kilograms, was added evenly through a two minute period. The molecular ratios of the magnesium, phosphate, and ammonium moieties were 1.00, 1.00, and 0.992, respectively, and the iron humate amounted to 60 percent of the final product on a dry basis.

The temperature of the mixture increased to 107° C. as the exothermic coreaction took place. The apparatus continued to operate for 10 minutes after addition of the phosphoric acid was completed, and the system cooled on completion of the reaction as moisture evaporated from the homogeneous granules formed.

The granular products were discharged at 91° C. and dried in a Witte vibratory fluid bed dryer operating with an exit air temperature of 88° C. Granular product recovered amounted to 37.0 kilograms. It was analyzed for the chemical properties, which are listed as follows:

Component	Wt %
Nitrogen, total N	3.24
CWIN	2.21
Phosphate, total P <sub>2</sub> O <sub>5</sub>	16.6
Citrate soluble P <sub>2</sub> O <sub>5</sub>	12.1
Magnesium, total Mg	5.6
water soluble Mg	0.5
EDTA soluble Mg	4.9
Iron, total Fe	14.4
water soluble Fe	<0.01
citrate soluble Fe	12.00
Moisture	4.01

Water solubility of the iron was about 0.01 percent of the total iron while the iron soluble in soil solution, as indicated by the iron soluble in neutral citrate solution, was substantially complete at 87.5 percent.

The initial iron humate which was recovered from iron coagulation-clarification of humate colored water was dried before use to 80 percent dry matter and analyzed. It contained 20.9 percent iron, of which 32 percent was soluble in neutral citrate solution, indicative of availability to plants by solubility in the soil solution.

The granular product exhibited a pH of 6.9. The granules which were primarily in the -6+16 U.S. mesh screen size range required an average of 1.7 kilograms weight to fracture, and showed little tendency to form dust after extended handling. The original iron humate exhibited no physical integrity.

#### EXAMPLE 2

This example demonstrates the instant invention by providing specific ingredients and conditions for the continuous method for reacting aqueous hydroxide of monovalent Lewis acid, manganous metal oxide powder, phosphoric acid and iron humate to form highly available iron nutrient granules.

A steam jacketed horizontal cylinder having an internal volume of 300 liters with a length to diameter ratio of 3.2/1 was used to prepare granular nutrient from the same iron humate starting material used in Example 1. The cylinder was fitted with 2 plows rotating tangentially to the inside wall of the cylinder at 500 RPM and shaped to throw the contents toward the center of the cylinder. The cylinder was also fitted with two choppers operating perpendicularly to the internal wall at a speed of 3000 RPM, describing chopping circles of 15 centimeters on shafts entering the cylinder at the 3 o'clock position 25 and 75 percent of the way along the length of the cylinder. The choppers consisted of 4 sharp steel blades attached to a shaft as close to the wall of the cylinder as possible. The cylinder was equipped with a fluid addition nozzle 10 percent along from the inlet end, and with a level controlling overflow dam at

the discharge end. The dam was set to allow the cylinder to operate about 40 percent full of solids.

Premixed powder and aqueous hydroxide of a monovalent Lewis acid reactants were continuously charged to the inlet end of the steam jacketed reactor as follows:

Reactants	Continuous Feed Rate, KG/Min
Iron Humate, 20.9% Fe, 80DM	4.33
Manganous Oxide, 62% Mn	2.00
Potassium hydroxide, 47% KOH	2.69

To this mixed material was admixed by spraying through the fluid addition nozzle, black phosphoric acid containing 53 percent P<sub>2</sub>O<sub>5</sub> at the rate of 3.0 KG per minute. Admixing and exothermic coreaction took place as the reactants moved in a near-plug-flow manner with high shear mixing through the cylindrical, steam jacket heated, reactor for a retention time of 7 minutes, reaching a maximum temperature of 85° C. near the discharge end of the reactor.

The iron humate based agricultural nutrient flowed continuously over the discharge dam, and was continuously dried to a moisture content of 5.1 percent in a Witte fluid bed dryer, and analyzed to provide the results recorded as follows:

Component	Wt %
Potassium, total K <sub>2</sub> O	11.5
Water insoluble K <sub>2</sub> O	8.4
Phosphate, total P <sub>2</sub> O <sub>5</sub>	17.4
Citrate soluble P <sub>2</sub> O <sub>5</sub>	9.9
Manganese, total Mn	13.4
water soluble Mn	0.7
EDTA soluble Mn	5.9
Iron, total Fe	9.9
water soluble Fe	<0.01
citrate soluble Fe	8.9

The iron in the granular nutrients, most of which was in the -6+16 U.S. mesh screen size range, was practically insoluble in water and substantially completely available to plants as indicated by the 89.5 percent solubility in neutral citrate solution.

The physical integrity of the product granules was indicated by the 1.7 kilograms average force required to crush a granule. The pH of the product was about neutral at 6.6.

#### EXAMPLE 3

This example demonstrates the utility and effectiveness of the new agricultural composition as an agricultural nutrient for feeding animals. The product from Example 1 was fed orally as an iron source, along with two other commercially available iron sources, to six litters of pigs which were randomly given one of the three treatments. One third the pigs were orally fed with 75 grams per litter per day with the agricultural nutrient granules containing 14.4 percent iron from Example 1, another third of the pigs were fed 75 grams per litter per day of commercial Pig Oral-Iron, and the final third were injected intravenously with 100 mg iron per day from commercial Iron Dextran.

Blood samples were drawn from each pig in each litter throughout a 30 day test period with hemoglobin determinations made on each sample. The results indi-

cate the excellent availability of the iron nutrient as follows:

Days after Treatment	Hemoglobin Level, G/DL		
	Iron Humate	Pig Oral-Iron	Iron Dextran
1	10.42	10.41	9.39
3	7.72	7.60	8.44
5	9.00	7.10	9.13
10	11.25	9.84	9.44
15	11.40	10.42	10.26
22	13.75	11.22	9.14
30	11.59	10.91	7.50

#### EXAMPLE 4

This example demonstrates the utility and effectiveness of the new agricultural composition as an agricultural nutrient for plants.

A plot of iron deficient Merion bluegrass golf fairway turf in western Virginia displayed a light green color and was given a color rating of 5.0 on a scale where 0 indicates dead grass and 9 indicates dark green color, although the well irrigated and drained loam soil contained more than sufficient macronutrients in mid-June. Treatment of the plot with 100 grams per 1000 square foot area of the product from Example 2 containing 9.9 percent iron on June 15, resulted in improving color after 10 days. Color improvement continued so that dark green color and a rating of 8.5 was achieved by the plot by September 1.

I claim:

1. A method of preparing a slow releasing particulate iron humate agricultural nutrient composition which contains between 5 and 25 percent iron which is practically insoluble in water and substantially completely soluble in soil solutions, the method comprising:

- admixing iron humate, amounting to between 20 and 70 percent of the agricultural nutrient composition, with a divalent metal oxide;
- admixing and coreacting with the mixed divalent metal oxide and iron humate, an aqueous hydroxide of a monovalent Lewis acid;
- admixing and coreacting the iron humate, divalent metal oxide, and hydroxide of monovalent Lewis acid with a water soluble inorganic phosphate;
- providing the divalent metal oxide, the hydroxide of monovalent Lewis acid, and the water soluble inorganic phosphate moieties in about equimolar amounts so that they coreact to form between 30 and 80 percent of the agricultural nutrient composition;
- continuing the admixing, and reaction at temperatures between 60° and 150° C. until homogeneous particles of iron humate agricultural nutrients are formed which are practically water insoluble and substantially completely soluble in soil solutions.

2. The method of claim 1 wherein the divalent metal oxide is in a hydrated form.

3. The method of claim 1 wherein the divalent metal oxide is selected from the group of agricultural nutrients consisting of magnesium oxide, manganous oxide, zinc oxide, cupric oxide, ferrous oxide, cobaltous oxide, and calcium oxide.

4. The method of claim 1 wherein the iron humate is a precipitated coagulation product resulting from clarification of humate colored water by treatment with soluble iron salts.

5. The method of claim 1 wherein the aqueous hydroxide of a monovalent Lewis acid is selected from the group consisting of potassium hydroxide, sodium hydroxide, and ammonium hydroxide.

6. The method of claim 1 wherein the water soluble inorganic phosphate is selected from the group consisting of phosphoric acid, polyphosphoric acid, monoammonium phosphate, diammonium phosphate, monopotassium phosphate, dipotassium phosphate, and ammonium polyphosphate.

7. The method of claim 1 wherein the water soluble inorganic phosphate is chemically reacted with the aqueous hydroxide of the monovalent Lewis acid to form a water soluble salt before admixing and reacting with the divalent metal and the iron humate.

8. The method of claim 1 wherein the iron humate, divalent metal oxide, monovalent hydroxide of a Lewis acid, and the water soluble inorganic phosphate are continuously charged to a continuous reactor, in which the admixing and coreacting steps are continuously conducted, and from which the homogeneous particles of iron humate agricultural nutrients are continuously discharged.

9. The slow releasing particulate iron humate agricultural nutrient composition containing between 20 and 70 percent iron humate and between 30 and 80 percent chemically coreacted divalent metal oxide, aqueous hydroxide of a monovalent Lewis acid, and a water soluble inorganic phosphate, which exhibits water insolubility and substantially complete solubility in soil solutions of its iron content of between 5 and 20 percent, prepared by the method of claim 1.

10. The composition of claim 9 wherein the slow releasing iron humate is a new improved plant nutrient.

11. The composition of claim 9 wherein the slow releasing iron humate is a new improved animal feed nutrient.

12. A method of preparing attrition resistant granules of iron humate plant nutrient containing between 6 and 20 percent iron which is substantially insoluble in water and soluble in neutral aqueous citrate, the method comprising:

- admixing iron humate powder, amounting to between 40 and 60 percent of the granular plant nutrient, with a divalent metal oxide powder and a powder of water soluble salt formed by reaction of a hydroxide of a monovalent Lewis acid, and phosphoric acid;
- admixing and reacting the mixed divalent metal oxide powder, the iron humate powder, and the powder of water soluble salt of a monovalent Lewis acid and phosphoric acid, with aqueous phosphoric acid;
- providing the divalent metal oxide, the hydroxide of monovalent Lewis acid, and total phosphate moieties in respective molecular ratios between 1 and 1.2, so that they coreact to form between 60 and 40 percent of the granular plant nutrient;
- providing the water soluble salt of phosphoric acid and the hydroxide of a monovalent Lewis acid, and phosphoric acid in a ratio to form plant nutrient granules with a near-neutral pH between 6 and 7.5;
- continuing the admixing and reaction at a temperature between 80° and 125° C. for a period of time amounting to between 4 and 25 minutes until homogeneous attrition resistant granules of iron humate plant nutrients are formed.

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13. The method of claim 12 wherein all of the phosphate moieties are admixed and reacted as a water soluble salt of a hydroxide of a monovalent Lewis acid and phosphoric acid.

14. The method of claim 12 wherein about half of the admixed and reacted phosphate moieties are derived from a water soluble salt of a hydroxide of monovalent Lewis acid and phosphoric acid, and about half from phosphoric acid.

15. The method of claim 12 wherein the iron humate powder is derived as a precipitated coagulation product resulting from clarification of humate colored water by treatment with iron salts.

16. The method of claim 12 wherein the particulate iron humate plant nutrients are dried with hot air at temperatures between 80° and 200° C. until moisture content is between 1 and 7 percent.

## 12

17. The method of claim 12 wherein the iron humate powder, divalent metal oxide powder, water soluble salt formed by reaction of a hydroxide of a monovalent Lewis acid and phosphoric acid, and aqueous phosphoric acid are continuously charged to, admixed in, coreacted in, and discharged from as homogeneous attrition resistant granules of iron humate plant nutrients, a continuous reactor which provides high shear mechanical mixing and plug flow.

18. The attrition resistant granular iron humate plant food composition prepared by the method of claim 12 comprising between 40 and 60 percent iron humate, and between 60 and 40 percent of chemically combined divalent metal oxide, water soluble phosphate salt of a monovalent Lewis acid hydroxide, and phosphoric acid, containing between 6 and 20 percent iron, substantially all of which is insoluble in water and soluble in aqueous neutral citrate solution.

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