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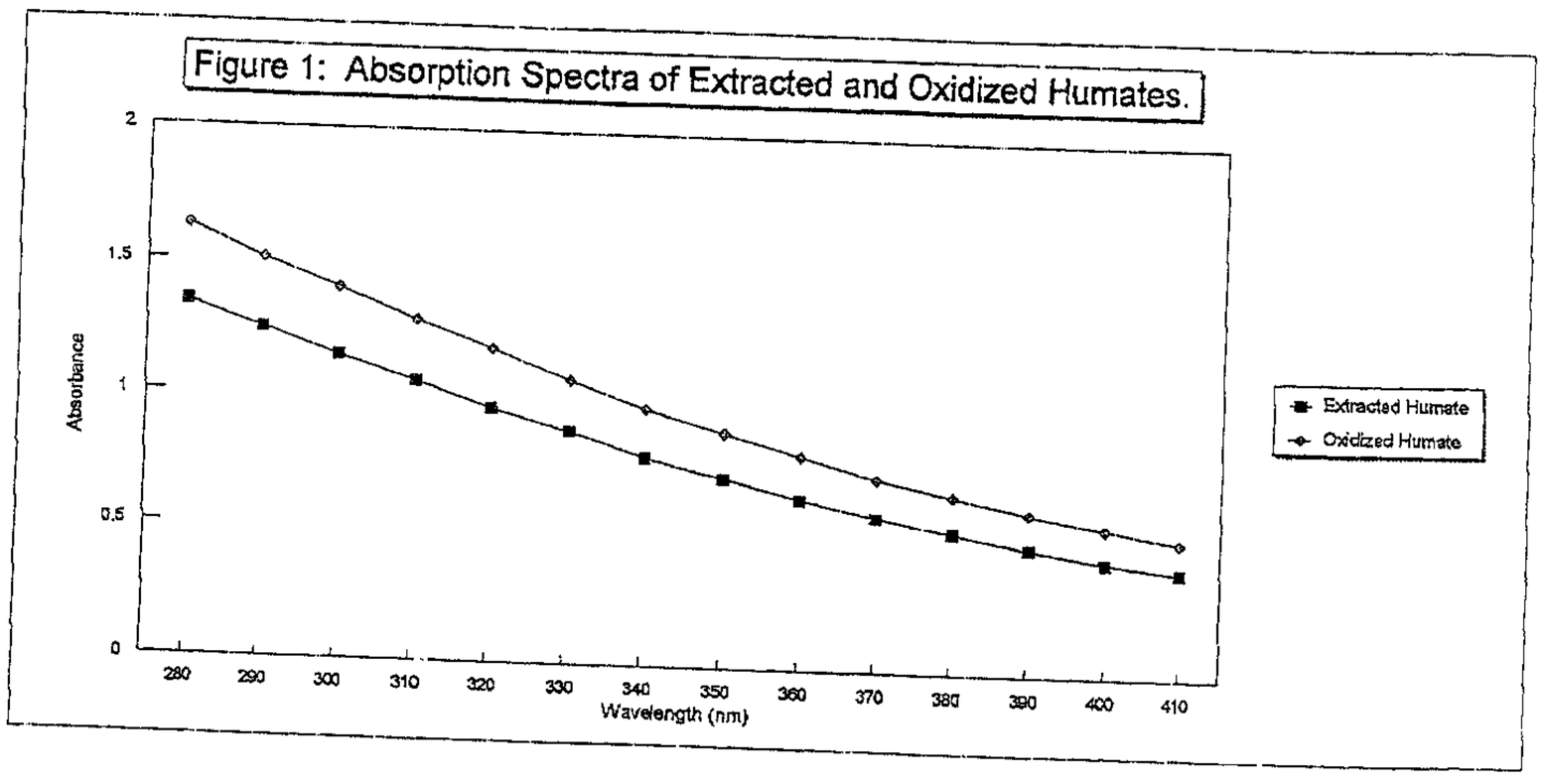
(54) **UTILISATION D'HUMATES ET D'HUMATES MODIFIES COMME ADJUVANTS DANS LES PESTICIDES**

(54) **USE OF HUMATES AND MODIFIED HUMATES AND ADJUVANTS IN PESTICIDES**



(57) Description d'une méthode d'utilisation des humates et des humates modifiés comme adjuvants dans les pesticides. Des quantités efficaces d'adjuvants d'humates et/ou d'humates modifiés sont ajoutées à des formulations de pesticides ou, de préférence, de biopesticides durant la préparation, ou encore sont mélangées avec les pesticides ou les biopesticides au moment de l'application. Une telle adjonction fournit une protection supérieure contre les dommages causés par les rayons ultraviolets et, de ce fait, permet de stabiliser les pesticides et d'augmenter leur activité.

(57) A method of using humates and/or modified humates as adjuvants in pesticides is disclosed. Effective amounts of the humate and/or modified humate adjuvants are added to the pesticide or, more preferably, biopesticide formulations at the time of formulation or are mixed with the pesticide or biopesticide at the time of application. Such addition provides superior protection from damage caused by UV light and, thereby, stabilizes the pesticide and enhances activity.

USE OF HUMATES AND MODIFIED HUMATES AS ADJUVANTS IN PESTICIDES

Abstract of the Invention

A method of using humates and/or modified humates as adjuvants in pesticides is disclosed. Effective amounts of the humate and/or modified humate adjuvants are added to the pesticide or, more preferably, biopesticide formulations at the time of formulation or are mixed with the pesticide or biopesticide at the time of application. Such addition provides superior protection from damage caused by UV light and, thereby, stabilizes the pesticide and enhances activity.

USE OF HUMATES AND MODIFIED HUMATES AS ADJUVANTS IN PESTICIDES

Background and Summary of the Invention

The present invention relates to the use of humates and/or modified humates as adjuvants in pesticides to provide superior protection from damage caused by UV light.

Humates, as used here, refer to the alkaline extracts of humic acid bearing ores. Peat, lignites (e.g. leonardite), bituminous coal, brown coal, collinite, exinite, and sapropelic coal have been cited as sources of humates, and thus, can be considered humic acid bearing ores (Kirk-Othmer, "Encyclopedia of Chemical Technology", 3rd Ed., vol. 14, John Wiley & Sons, 1981). Extraction of such ores with sodium hydroxide, potassium hydroxide and/or ammonium hydroxide yields the humates disclosed herein as UV protectants. A specific example of such an extraction is given by U.S. Patent No. 4,319,041. The humates disclosed herein can also be obtained by precipitation from runoff water containing high organic contents as described in U.S. Patent No. 5,213,692. A third source of such humates is the so called artificial humates produced by the oxidative polymerization of quinones.

Modified humates, as used here, refer to humates obtained from oxidized coal as described in U.S. Patent Nos. 4,912,256 and 5,004,831. Humates oxidized after isolation by extraction are also considered modified humates as are sulfonated humates. Sulfonation reactions included in the preparation of the later class of modified humates include reaction with sulfur dioxide as described in U.S. Patent 4,502,868, concentrated sulfuric acid as described by Zhambal (Khim Tverd. Topl. (Moscow 1991, (2), 70-2), sodium sulfite as

described by Sharanova et al (Khim Tverd. Topl. (Moscow) 1987, (3), 38-43), sodium sulfite and sodium bisulfite as described in Spanish Patent 495,426 and by sulfomethylation as described by Pobedonostseva et al (Khim Tverd. Topl. (Moscow) 1978, (6), 97-102).

The humates and modified humates disclosed herein are heterocyclic in nature and, hence, are characterized by high UV absorbance in both the UV-A (i.e. 320-410nm) and the UV-B (i.e. 280-320nm) regions of the spectrum. (Kirk-Othmer, "Encyclopedia of Chemical Technology", 3rd Ed. vol. 14, John Wiley & Sons, 1981). Amador et al (Appl. Environ. Microbiol., 55 (11), 1989, 2843-2349) has studied the light absorbing properties of humates in some detail and found that they absorb across the entire solar spectrum.

Nielson and Ekelund (Limnol. Oceanogr., 38 (7), 1993, 1570-1575) studied the effect of added humates on the growth rate of gyridinuim aureolum solutions irradiated with UV-B light. At lower concentrations of added humate (i.e. 1.2 and 4.2 mg/L) growth rates increased with the observed increases attributed to the UV-B screening effect of the added humates. No claims were made, however, as to the effectiveness of humates in the solid state or to their possible use as adjuvants in pesticides.

In addition to their UV absorbing properties, the chemical structure of these substances enables them to function as anti-oxidants. Since many of the photochemical reactions involved in the UV light induced degradation of pesticides involve free radical intermediates, the anti-oxidant properties of humates should contribute to their ability to act as an adjuvants in pesticides.

The present invention thus relates to the use of humates and modified humates as adjuvants in pesticides. The humate-based and/or modified humate-based adjuvants disclosed herein can be added to a pesticide at the time of formulation or mixed with the pesticide at the time of application, such as in a spray tank. Such addition provides superior protection from damage caused by UV light and, thereby, stabilizes the pesticide and enhances activity.

In a preferred embodiment of the invention, an effective amount of humate prepared by alkaline/air oxidation of leonardite is mixed with a pesticide, e.g. insecticide, herbicide, fungicide, acaricide, or combination thereof. Most preferably the adjuvant is mixed with a biopesticide such as Bacillus thuringiensis, or toxin crystals, spores, or a recombinately expressed toxin therefrom. The adjuvants of the invention are also particularly effective when mixed with baculoviruses such a nuclear polyhedrosis virus. When mixed with such a pesticide, the adjuvants disclosed herein inhibit the UV light induced degradation of the pesticide and increases its effectiveness over time.

Brief Description of the Drawing

Fig. 1 is a graph illustrating the UV-light absorbing capacity of a humate prepared by extraction of leonardite ore, and a humate prepared by alkaline air oxidation of leonardite ore.

Detailed Description of the Invention

The invention claimed here is the use of humates and/or modified humates as adjuvants for pesticides. The humates and/or modified humates described herein function as adjuvants by inhibiting the UV light induced degradation of the pesticide.

By inhibiting such degradation, they in turn increase the pesticide's effectiveness over time.

The humates disclosed herein include the alkaline extracts of humic acid bearing ores, e.g. lignites especially leonardite,peat, bituminous coal, brown coal, collinite, exinite, and sapropelic coal, humates obtained by precipitation from runoff water containing high organic contents, and artificial humates produced by the oxidative polymerization of quinones. The preferred ore is leonardite due to its ready availability and relatively inexpensive cost. The mean particle size of the ore will normally be less than about 3 mm. Preferably, the mean particle size of the ore varies in the range of 10 to 1000 microns and most preferably, the mean particle size is in the range of 10 to 100 microns. Thus, finer particles of ore result in the reaction occurring with relative ease enabling the reaction to be completed in a relatively shorter period of time.

The modified humates disclosed herein include humates obtained from oxidized coals, humates oxidized after isolation by extraction, and sulfonated humates. Sulfonation reactions included in the preparation of the later class of modified humates include reaction with sulfur dioxide, concentrated sulfuric acid, sodium sulfite, sodium bisulfite, potassium bisulfite, ammonium bisulfite, magnesium bisulfite, sodium meta-bisulfite, potassium meta-bisulfite, ammonium meta-bisulfite and magnesium meta-bisulfite, and sulfomethylation.

The humates and modified humate based adjuvants disclosed herein can be added to the pesticide at the time of formulation or mixed with the pesticide at the time of application, such as in a spray tank. The amount of adjuvant which must be added to a given pesticide may vary with the type

of pesticide and the specific type of adjuvant. Typically, the adjuvant is added to the pesticide at a dosage of 0.5-95 weight percent, preferably 5-25 weight percent, and most preferably 8-12 weight percent. In all cases, however, effective amounts of adjuvant must be added for optimum performance.

The use of the adjuvants described in the present invention may be further supplemented by combination with other compounds commonly used in the formulation and/or application of pesticides. Such compounds include, but are not limited to deposition agents, stickers/adhesives, feeding attractants, penetrants, spreaders, drift control agents, and preservatives. It will be understood by one skilled in the art, however, that such additional components are not essential to the activity of the adjuvant. Their proportions, therefore, are not critical and may be optimized for the purpose and method of application by one skilled in the art. It should also be apparent to one skilled in the art that the adjuvants of the present invention may be used in combination with other UV protectants such as lignosulfonates, kraft lignins and synthetic UV protectants.

As previously noted, pesticides as used herein refer to an insecticide, a fungicide, an acaricide, a herbicide or a combination thereof. Preferably, the pesticide is selected from a chemical pesticide, a fungal insecticide, a viral insecticide or a *Bacillus*-based insecticide. The chemical pesticide is selected from carbamates, avermectins, insect growth regulators, pyroles, organophosphates, pyrazoles, chlorinated organics or pyrethroids. The viral insecticide is preferably a polyhedrosis or a granulosis virus.

While the adjuvants of the present invention may be used in the application of any pesticide, they are particularly useful in the application of pesticides that are sensitive to UV light induced degradation. Examples of pesticides which can benefit from use of these adjuvants include but not limited to pyrethrum extracts, pyrethroids, avermectins, organophosphates, carbamates, pyrazoles and pyroles.

Another class of pesticides which can particularly benefit from the use of the adjuvants disclosed herein are biopesticides. In fact, the use of the present adjuvants in biopesticides is envisioned as one of the preferred uses. It is further envisioned that biopesticides which can benefit from use of these adjuvants include but are not limited to baculoviruses such as nuclear polyhedrosis virus (NPV).

Examples of biopesticides include but are not limited to baculoviruses, such as nuclear polyhedrosis virus (NPV), e.g. *Autographa californica* NPV, *Syngrapha falcifera* NPV, *Heliothis zea* NPV, *Lymantria dispar* NPV, *Spodoptera exigua* NPV, *Neodiprion lecontei* NPV, *Neodiprion sertifer* NPV, *Harrisina brillians* NPV, *Endopiza viteana* Clemens NPV; granulosis viruses e.g., *Cydia pomonella* granulosis virus (GV), *Pieris brassicae* GV, *Pieris rapae* GV; entomopathogenic fungi, such as *Beauveria bassiana, Metarhizium anisopliae, Verticillium lecanii,* and *Paecilomyces* spp. and various *Bacillus*-based products.

Examples of *Bacillus*-related pesticides include but are not limited to pesticides produced by *Bacillus thuringiensis* subsp. *kurstaki, Bacillus thuringiensis* subsp. *aizawai, Bacillus thuringiensis* subsp. *israelensis, Bacillus thuringiensis* subsp. *tenebrionis, Bacillus sphaericus, Bacillus cerius, Bacillus thuringiensis kurstaki/tenebrionis, Bacillus thuringiensis aizawai/kurstaki,* and *Bacillus thuringiensis kurstaki/kurstaki.*

Application of the adjuvants of the present invention can be in dry or liquid form. They can be applied directly to the plant and are effective when applied to a number of different plant types including, but not limited to, cereal crops such as wheat, pomes and soft fruit such as apples, legumes such as beans, cucurbots such a cucumbers, vegetables such as potato, deciduous trees and conifers such as oak and pine and other plants such as ornamentals.

One process for producing humates is described in U.S. Patent No. 4,912,256. It involves mixing coal with an aqueous medium to produce a slurry having a pH in the range of 4-9. The slurry thus produced is reacted with a gaseous oxidant such as air or oxygen under conditions of temperature and pressure for a time sufficient to cause the oxidation of the coal. Separation of the reaction product from the aqueous medium produces an oxidized coal containing humates. Under the conditions used in this process, however, the humic acids contained in such coals are only mildly oxidized.

Another oxidative process described in South African Patent No. 87/9232 involves oxidation of coal in the dry state in a fluid bed reactor. Coal with a particle size in the 100 micron to 3 mm range is heated to 150 to 300°C under a partial pressure of oxygen for a time of 30 to 600 minutes to produce oxidized coals containing humates. No alkali is used in this process.

Yet another method for producing humates from oxidized coals is described in U.S. Patent No. 5,004,831. The process involves mixing oxidized coal with aqueous alkali, heating the mixture to 100 to 180°C under sufficient pressure to prevent evaporation of water, and maintaining the elevated temperature

for a time sufficient to extract a substantial amount of the available humates. Like the other methods described above, however, this method does not use conditions which promote extensive oxidation of the humic acids contained in the coal.

Traditional methods for producing humates from humic acid bearing ores involve extraction with alkali. An example of such an extraction process is described in U.S. Patent No. 4,319,041. It involves mixing humic acid containing ores with water and caustic soda and extraction of the humic acids by agitation at pH 6.5-8.0. The times required in this process are quite lengthy, however, and the humates produced are not oxidized.

A simple process for producing oxidized humates is the alkaline air oxidation of a humic bearing ore wherein the modified humate is obtained by extracting a humic bearing ore with alkali and simultaneously oxidizing the humate obtained thereby. This process comprises the steps of (a) dissolving a humic acid containing ore in alkali to form a reaction mixture; (b) reacting the reaction mixture with an oxidant under conditions of temperature and pressure and for a time sufficient to cause the oxidation of the humic acid containing ore to produce an oxidized humic acid concentrate; and (c) separating the oxidized humic acid concentrate from the reaction mixture. Optionally, the reaction mixture may be saturated with oxygen prior to the start of the oxidation reaction.

The process particularly comprises reacting humic acid bearing ores with oxygen under alkaline conditions at a temperature between 100°C and 200°C for at least 0.5 hour, but usually for 1-6 hours, to produce oxidized humates which are soluble at pH as low as 2.9 and are formed in yields of at least

70%. Suitable oxygen pressures in the process are 5 to 200 psi and suitable sources of alkali for the process include sodium hydroxide, potassium hydroxide, ammonium hydroxide, lithium hydroxide and/or combinations of these materials. The process, particularly, calls for reacting a humic acid bearing ore such as leonardite with oxygen in the presence of 15 to 30% sodium hydroxide and at 170°C for 1 hour. Removal of insolubles by filtration, centrifugation or settling gives oxidized humates soluble at pH 3.0 or greater at yields of at least 70%. If desired, the oxidized humates may be formed into a powder, preferably, by spray drying.

The first step of the alkaline air oxidation process involves dissolving the humic acid containing ore in alkali. Any alkali may be employed that provides sufficient alkalinity to adjust the pH high enough to dissolve the humic acid containing ore. Preferably, the pH of the reaction mixture is 9-13 with 10-12 being preferred and pH 11 most preferred. Examples of alkali that may be used to dissolve the humic acid containing ore include sodium hydroxide, potassium hydroxide, ammonium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate, lithium carbonate, and mixtures thereof. Most preferably, sodium hydroxide is used due to its ready availability. It should be noted that calcium hydroxide probably should not be employed since it will form an insoluble component. If the alkali employed is sodium hydroxide, it preferably comprises 10-30% by weight of the reaction mixture. If the alkali employed is ammonium hydroxide, it preferably comprises 9-26% by weight of the reaction mixture. If the alkali employed is lithium hydroxide, it preferably comprises 6-18% by weight of said reaction mixture.

The second step of the alkaline air oxidation process involves reacting the reaction mixture under conditions of temperature and pressure and for sufficient time to produce an oxidized humate concentrate. The reaction is preferably carried out in a pressurized closed vessel equipped with a suitable distributor or stirring mechanism to insure effective mass and heat transfer between the liquid, solid and gaseous phases contained therein. The closed vessel should be rated at 2-1000 psi, preferably 2-400 psi to prevent evaporation of water. The reaction takes place at a temperature of between about 100°C to 200°C. Preferably, the reaction temperature ranges between 140°C to 180°C and most preferably between 160°C to 170°C. The mixture is reacted for about 0.5-6 hours with the preferred reaction time being 1-4 hours depending upon the reaction temperature. In any event, the reaction step is continued for a period of time sufficient to produce an oxidized humate concentrate in yields of at least about 70%. These oxidized humate concentrates are soluble at pH as low as about 2.9.

The oxidant employed in the oxidation step of the present process is preferably a gaseous oxidant which is bubbled through the reaction mixture at a charge of 5-200 psi. The oxidant is selected from oxygen, air and mixtures thereof with the preferred oxidant being oxygen. The oxidation step is carried out for sufficient time and under sufficient pressure and temperature to insure substantially complete oxidation of the humic acid containing ore.

After the reaction is complete, the undissolved solids present in the reaction mixture are separated from the oxidized humic acid concentrate by filtration, settling and/or centrifugation. Upon completion of the process, a liquid product

is formed which is a minimum of 5%, preferably a minimum of 16%, oxidized humate in aqueous solution. The pH of said product typically is between 7-9, but pH 8.5 is preferred.

The invention is further illustrated in the following non-limiting examples.

Example 1

This example demonstrates the UV-light absorbing capacity of the humate and modified humate adjuvants disclosed herein. UV-visible spectroscopic analysis shows that the absorbance of a humate prepared by extraction of lignite (leonardite ore) was strong in both the UV-A (i.e. 320-410nm) and the UV-B (i.e. 280-320nm) regions of the spectrum (see Fig. 1). The absorbance of a modified humate prepared by sulfomethylation of the same ore was also strong in these regions.

UV-visible spectroscopic analysis further shows that the absorbance of a humate prepared by the preferred embodiment of the invention, alkaline air oxidation of lignite (e.g. leonardite ore), was exceptionally strong in both the UV-A (i.e. 320-410nm) and the UV-B (i.e. 280-320nm) regions of the spectrum (see Fig. 1). Since it is envisioned that higher absorbance in these regions translates into improved performance, it is easily seen that modified humates prepared by this preferred embodiment will offer superior protection from UV light induced degradation.

Example 2

This example describes the procedure involved in the preparation of the preferred embodiment of the invention. Two hundred grams of leonardite ore with an average particle size

less than 100 microns was slurried in 1000 grams of water. Sixty seven grams of 45% sodium hydroxide solution was added to the leonardite slurry, and the mixture was mixed for 30 minutes. During this time, the mixture was saturated with oxygen. The saturated leonardite/caustic mixture was then reacted at 165°C for one hour in a sealed reactor. After cooling, the soluble portion of reaction mixture was isolated from the reaction mixture by settling. Contained therein was approximately 180-190 grams of the preferred embodiment.

Example 3

This example demonstrates the effectiveness of the present adjuvants as UV protectants for pesticides. One gram of the insecticide permethrin and 0.1g of the adjuvant prepared as described in Example 2 were dissolved in 5ml of dimethylsulfoxide. One gram of the resulting mixture was spread evenly on a glass plate, and the solvent was removed by evaporation under vacuum. The solvent free mixture was then irradiated with UV light filtered through a pyrex glass filter. An equivalent weight sample of permethrin without adjuvant was prepared by the same method and exposed to UV light under identical conditions. Irradiation time was 14 days at low intensity.

After exposure the samples were collected by extraction with hexane and analyzed. The results of the analysis showed that the active level in the control sample decreased by 9.7%. Their was no change in activity in the sample containing the adjuvant. Thus, it can be concluded that the addition of adjuvant to the permethrin insecticide inhibited the UV light induced degradation of the pesticide and increased its effectiveness over time.

CLAIMS

1. A method for stabilizing pesticides against ultraviolet light comprising incorporating from 0.5 to 95 weight percent of a modified humate with a pesticide to inhibit degradation of the pesticide by ultraviolet light, wherein said modified humate is obtained by sulfonation or oxidation of a humate.

2. The method of claim 1 wherein said modified humate is incorporated with said pesticide when formulating said pesticide.

3. The method of claim 1 wherein said modified humate is incorporated with said pesticide when applying said pesticide.

4. The method of claim 1 wherein the modified humate is obtained from oxidized lignite, peat, bituminous coal, brown coal, collinite, exinite or sapropelic coal, or a mixture thereof.

5. The method of claim 1 wherein the modified humate is obtained by oxidizing a humate after obtaining said humate by alkali extraction of humic bearing ore.

6. The method of claim 1 wherein the modified humate is obtained by sulfonation of a humate after obtaining said humate by alkali extraction of humic bearing ores.

7. The method of claim 6 wherein said sulfonation can be achieved by reaction with sulfur dioxide, concentrated sulfuric acid, sodium sulfite, sodium bisulfite, potassium bisulfite, ammonium bisulfite, magnesium bisulfite, sodium meta-bisulfite, potassium meta-bisulfite, ammonium meta-bisulfite or magnesuim meta-bisulfite, or combinations thereof.

8. The method of claim 6 wherein said sulfonation is achieved by sulfomethylation.

9. The method of claim 1 wherein the modified humate is obtained by extracting a humic bearing ore with alkali and simultaneously oxidizing the humate obtained thereby.

10. The method of claim 1 wherein said pesticide is an insecticide, a fungicide, an acaricide or a herbicide or a combination thereof.

11. The method of claim 10 wherein the pesticide is selected from the group consisting of a chemical pesticide, a fungal insecticide, a viral insecticide or a *Bacillus*-based insecticide.

12. The method of claim 11 wherein the chemical pesticide is selected from the group consisting of carbamates, avermectins, insect growth regulators, pyroles, organophosphates, pyrazoles, chlorinated organics and pyrethroids.

13. The method of claim 11 wherein the viral insecticide is a polyhedrosis or a granulosis virus.

14. The method of claim 11 wherein the *Bacillus*-based insecticide is obtained from a *Bacillus* selected from the group consisting of *Bacillus thuringiensis* subspecies *kurstaki, aizawai, israelensis, tenebrionis, kurstaki/tenebrionis, aizawai/kurstaki* or *kurstaki/kurstaki, Bacillus sphaericus* and *Bacillus cerius*.

15. The method of claim 1 wherein the modified humate is incorporated with the pesticide at a dosage of 5 to 25 weight percent.

Figure 1: Absorption Spectra of Extracted and Oxidized Humates.

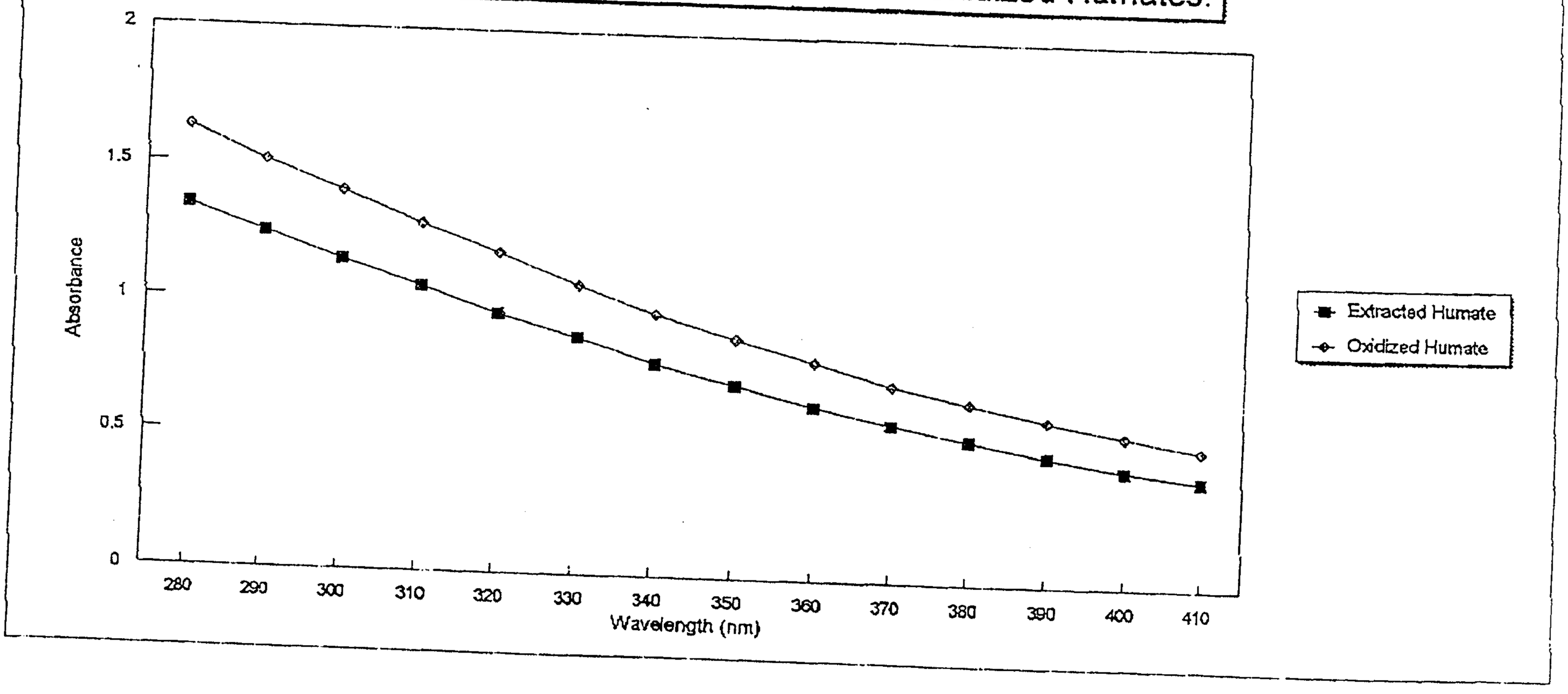


Figure 1: Absorption Spectra of Extracted and Oxidized Humates.