

Humic Acids

Crops

Identification of Petitioned Substance

Chemical Names:	15	Trade Names:
NA	16	NA
Other Name:		CAS Numbers:
Humic acid		1415-93-6
Humic acid, sodium salt		68131-04-4
Humic acid, potassium salt		68514-28-3
Humates		(EPA, 2004)
		Other Codes:
		NA

Characterization of Petitioned Substance

Composition of the Substance:

Humic substances are a group of complex organic compounds consisting of humic acids, fulvic acids, natural salts of these acids (e.g., calcium humates), and sponge-like substances called humin (Weber, undated). Humic substances (which includes humic acids) naturally constitutes a large fraction of the organic matter in soil, and is formed through the process known as "humification." Humification is the natural conversion of organic matter into humic substances by microorganisms in the soil (Mayhew, 2004). This process begins with microorganisms separating out sugars, starches, proteins, cellulose, and other carbon compounds from the organic matter. The microorganisms use these components in their own metabolic processes. Subsequently, the microorganisms transform the majority of the organically bound nutrients into a mineral form that are used by plants and other organisms. The portions of the organic matter that are not digested by the microorganisms accumulate as humic substances (Sachs, undated). Humification does not occur in one step, but involves an intermediate substance called compost, which consists of a mixture of humic substances and partially decomposed organic matter. As the humification process proceeds, various chemicals dominate at different times until conversion to humic substances is complete (Mayhew, 2004).

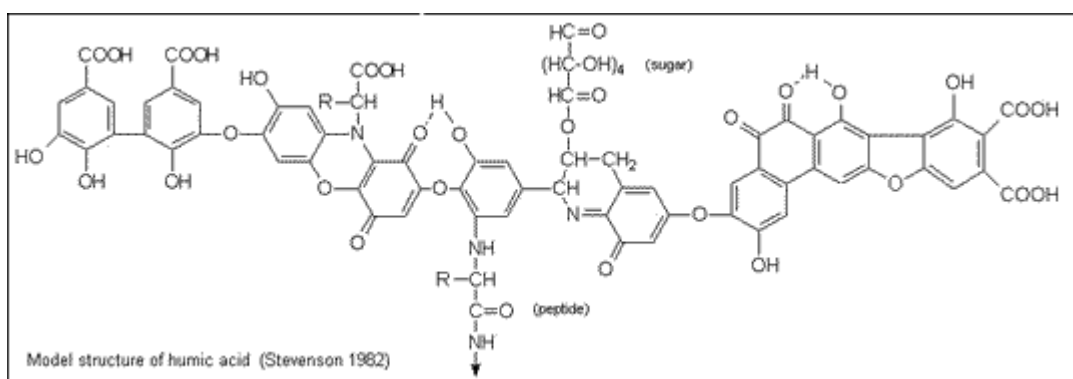
The decomposition of organic matter in soil is dependent on several factors, including the amount of available free oxygen, the amount of moisture present in the soil, and the temperature of the soil. The amount of free oxygen determines whether aerobic or anaerobic microorganisms will conduct the decomposition process. Aerobic microorganisms decompose organic material at a faster rate than do anaerobic organisms. However, greater amounts of humic substances are found in soils produced by anaerobic organisms because in these conditions accumulation is favored over destruction of humic substances. Although microorganisms need moisture to function, too much or too little water can decrease the rate of decomposition. Increasing soil temperature leads to greater microbial activity and decreased humic substance content because decomposition is occurring at a faster rate than accumulation (Sachs, undated).

In addition to humic substances originating from soil, commercially available humic substances are derived from coal. Leonardite is a highly oxidized low-rank coal originating from plant matter that serves as a key mined source for the production of humic acids. The humification process that yields leonardite may take 70 million years. In comparison, peat can be formed in about a few thousand years. Leonardite possesses a high humic substance content as a result of being highly decomposed by microorganisms. At 40 to 85 percent humic and fulvic acids, leonardite-sourced humic substances have a

54 much higher humic/fulvic acid content than other sources (such as black peat at 10 to 40 percent,
 55 sapropel peat at 10 to 20 percent, manure at 5 to 15 percent, and compost at 2 to 5 percent). Natural soil
 56 typically has 1 to 5 percent humic and fulvic acids. Additionally, in contrast to compost, leonardite-
 57 sourced humic acids do not compete with plants for nutrients, because leonardite-sourced humic acids
 58 are completely decomposed (Humintech, undated).

59
 60 Humic acids are not a substance with a single molecular formula. Figure 1 shows one example of a humic
 61 acids molecule. Humic acids may be described as “complex colloidal supermixtures” (Mayhew, 2004)
 62 that are characterized by their functional groups (Heise and Brendler., undated). The composition and
 63 structure of humic acids can vary from one soil to another (Sachs, undated). Generally, humic acids are
 64 considered to be aromatic in structure with amino acids, amino sugars, peptides, and aliphatic
 65 compounds linking the aromatic groups. The hypothetical structure of humic acid, as shown by the
 66 example in Figure 1, is believed to consist of free and bound phenolic hydroxyl groups, quinines, oxygen
 67 and nitrogen bridges, and carboxy groups (Weber undated). Adding to their complexity, the structure of
 68 humic acids is continuously influenced by their surroundings. For example, changes in pH can result in
 69 broken hydrogen bonds. (Heise and Brendler, undated).

70
 71 **Figure 1. An Example of the Chemical Structure of Humic Acids**



74 Source: Weber, Jerzy. Undated. Definition of soil organic matter. Available online at:
 75 http://www.humintech.com/001/articles/article_definition_of_soil_organic_matter.html. Last Accessed:
 76 January 10, 2006.

77
 78 The surface of humic substance particles consists of compounds that contain hydrogen ions
 79 capable of being replaced by cations (positively charged ions) like calcium, magnesium, potassium
 80 or sodium. In soil with high hydrogen ion activity (low pH), humic substances are saturated with
 81 hydrogen ions forming humic acid. Humic acid, in turn, reacts with mineral particles in the soil
 82 causing these particles to release basic cations (e.g., calcium, potassium, and magnesium). Humic
 83 acid then replaces its hydrogen ions with the basic cations and is converted into a salt called
 84 humate (Sachs, undated).

85
 86 **Properties of the Substance:**

87
 88 As previously stated, humic substances consist of humic acid, fulvic acid, and a sponge-like
 89 substance called humin. Humic substances are divided into three fractions on the basis of their
 90 solubility characteristics. These fractions are soluble over a wide pH range. The first fraction,
 91 humic acid, is not soluble in water under acidic conditions (pH < 2), but is soluble at higher pH
 92 values. Humic acid is the major extractable fraction of humic substances and ranges from dark
 93 brown to black in color. It can be extracted from soil by various reagents. The second fraction,
 94 fulvic acid, is soluble in water under all pH conditions. Fulvic acid, which stays in solution after
 95 the extraction of humic acid, ranges from light yellow to yellow-brown in color. After the first two
 96 fractions have been extracted, the third fraction, called humin, remains. This fraction, which is
 97 black in color, is not soluble in water at any pH, nor in any alkali solution (Weber, undated).

98

99 Generally, the humin fraction of humic substances is the dominant organic material in soils and
100 sediments. However, little information exists regarding the properties of this fraction (Kohl and
101 Rice, 1996). Variations between humic and fulvic acids include differences in molecular weight,
102 number of functional groups, and extent of polymerization. Humic acid has a higher molecular
103 weight, fewer functional groups that are acidic in nature (e.g. COOH and OH), greater carbon
104 content, and lower oxygen content than fulvic acid. Finally, the majority of oxygen in humic acid
105 is located as a structural constituent of its nucleus, while the oxygen in fulvic acid is found
106 predominantly in the functional groups (Weber, undated).

107

108 **Specific Uses of the Substance:**

109

110 Humic acids (naturally occurring deposits, water and alkali extracts only) are currently on the National
111 List for use as a plant or soil amendment. Specifically, humic acids are used by organic growers as a
112 component of traditional fertilizers.

113

114 Although humic acids are most commonly used as a soil amendment, they are also used as a foliar spray
115 (Jackson, undated). In general, plants are capable of absorbing small amounts of nutrients from the use of
116 foliar sprays on leaves. However, it is not possible to supply significant amounts of nutrients this way;
117 root uptake is more efficient (Witney, 1996). Application of humic acid as a foliar spray is believed to
118 promote the photosynthesis of leaves; increase yield and quality of plants; promote root development;
119 and improve nutrient uptake through the root system (HumaTech, Inc, undated).

120

121 Commercially available humic substances do not provide additional nutrients to plants, but rather affect
122 soil fertility by making micronutrients (e.g., iron) more readily available to plants. By chelating (or
123 binding) nutrients (especially iron), humic substances cause insoluble and unstable, and therefore
124 unavailable, compounds in the soil to remain available for plant uptake (Obreza et al, 1989).

125

126 The use of humic acids for agricultural purpose continues to grow, and as result, the number of products
127 and vendors continues to grow. However, there is currently a lack of standardized analysis for
128 substances marketed as humic substances, resulting in the marketing of some products that produce
129 minimal to no results. However, the benefits of using humic acid substances in agriculture have been
130 researched and documented by scientists (Mayhew, 2004).

131

132 **Approved Legal Uses of the Substance:**

133

134 As stated above, humic acids (naturally occurring deposits, water and alkali extracts only) are currently
135 on the National List for use as a plant or soil amendment.

136

137 The US Environmental Protection Agency (EPA) granted an exemption from the requirement for a
138 tolerance for residues of humic acids, sodium salts, used as an inert ingredient (adjuvant, UV protectant)
139 in pesticide formulations applied to growing crops and raw agricultural commodities after harvest (EPA,
140 2000).

141

142 In 2003, the EPA proposed to amend the existing tolerance exemption for humic acid, sodium salt to
143 include humic acid, potassium salt and humic acid. The EPA stated that such humate materials would be
144 used as inert ingredients in pesticide formulations applied to growing crops under the Federal Food,
145 Drug, and Cosmetic Act (FFDCA), as amended by the Food Quality Protection Act of 1996 (FQPA) (EPA,
146 2003). In 2004, the existing tolerance exemption was amended eliminating the need to establish a
147 maximum permissible level for residues of humic acid; humic acid, sodium salt; and humic acid,
148 potassium salt (EPA, 2004).

149

Action of the Substance:

According to Mayhew (2004), humic substances have demonstrated the ability to:

- Chelate (bind) soil nutrients;
- Improve nutrient uptake;
- Reduce the need for nitrogen fertilizer;
- Remove toxins from soils;
- Stimulate soil biological activity;
- Solubilize minerals;
- Improve soil structure; and
- Improve water holding capacity.

In general, commercially-available humic substances do not promote plant growth by providing substantial amounts of nutrients to plants. Instead, humic substances affect soil fertility by making nutrients (e.g., iron) more readily available to plants. In order for plants to take up nutrients, the nutrients need to be in solution, or dissolved in water. However, nutrients predominantly exist in soil as the insoluble forms of soil minerals and organic matter. Humic substances, which are negatively charged, make nutrients more available by attracting the positively charged nutrients and holding them in reserve. These readily available nutrients are subsequently released into solution to replace nutrients taken up by the plant roots (Cogger, 2000; Obreza et al., 1989; Senn and Kingman, undated).

Humic acids also promote plant growth by enabling root penetration in soils with high clay content. These types of soil can become extremely dense and compact due to salts located on their surface. The salts cause the negatively-charged clay particles to become neutral and move together. This compaction can create resistance to plant rooting. The addition of humic acids results in the removal of the salts, which causes the clay soil to loosen up for greater root penetration (Bio Ag, 1999). Seed germination and top growth also are stimulated (Obreza et al 1989). In the presence of humic acid, both a larger percentage of seeds germinate and germination occurs at a faster rate. This increased rate and occurrence of germination is related to the greater efficiency of binding of nutrients and water that takes place in the presence of humic substances (Bio Ag, 1999).

Additionally, the same action described in the previous paragraph allows for greater water penetration in clay soils. Humic acid also acts in decreasing water evaporation from soils. This is essential in arid areas with sandy soils that retain little to no water. With water present, the compounds that were previously bound by humic acid are partially ionized (or given a charge). As a result, the bonded compound's positive attractive force is partly restored. Subsequently, the negatively-charged oxygen atom of the water molecule loosely bonds to the positively charged compound, while the hydrogen end of the water molecule becomes more positive. This leads to another negatively charged oxygen from a water molecule binding to the positively charged hydrogen ion of the original water molecules. This continues until the attractive forces of the water molecules are stabilized (Bio Ag, 1999).

Status

International

Canada - Canadian General Standards Board -
http://www.pwgsc.gc.ca/cgsb/032_310/32.310epat.pdf
 No information was identified at the listed site.

The Certified Organic Associations of British Columbia (undated) allows:

- Humates (if not fortified with synthetic nutrients); and

- 203 • Humic acid derivatives (non-synthetic or using potassium hydroxide as an extractant but not to
204 fortify the product – no other sources are allowed)
205

206 They prohibit humic acids extracted by ammonium or sodium hydroxide or synthetic bases other than
207 potassium hydroxide.
208

209 **CODEX Alimentarius Commission –**

210 <ftp://ftp.fao.org/docrep/fao/005/Y2772e/Y2772e.pdf>

211 No information was identified at the listed site.
212

213 **European Economic Community (EEC) Council Regulation 2092/91 –**

214 http://europa.eu.int/eur-lex/en/consleg/pdf/1991/en_1991R2092_do_001.pdf

215 No information was identified at the listed site.
216

217 Humic acids are not allowed in the EU. However, some certifiers/authorities may consider the extracts
218 from certain fossilized organic matter to be 'peat' products, which are covered under Annex IIA. This is
219 more common in recognized third countries like Hungary than in the EU (Organic Trade Association
220 2002).
221

222 **Japan Agricultural Standard for Organic Production –**

223 <http://www.ams.usda.gov/nop/NOP/TradeIssues/JAS.html>

224 No information was identified at the listed site.
225

226 **California Certified Organic Growers International (CCOF) –**

227 <http://www.ccof.org/pdf/GlobalMarketAccessDraftForReview.pdf>
228

229 According to the 2005 CCOF's Draft Manual III: Global Market Access Program, alkali-extracted humic
230 acids are prohibited and/or restricted on crops for the USDA/Export, European Union Export, and
231 International Federation of Organic Agriculture Movements (IFOAM) export programs.
232

233 **Washington State Department of Agriculture: European Organic Verification Program (EOVP) –**

234 <http://agr.wa.gov/FoodAnimal/Organic/default.htm>
235

236 According to this program, alkali-extracted humic acid may not be used on raw or processed organic food
237 exported to Japan.
238

239 **Evaluation Questions for Substances to be used in Organic Crop or Livestock Production**

240

241 **Evaluation Question #1: Is the petitioned substance formulated or manufactured by a chemical**
242 **process? (From 7 U.S.C. § 6502 (21))**
243

244 Extraction of humic substances from terrestrial sources, such as soil, peat, compost, oxidized lignites, and
245 other coals (Karr, 2001), is commonly conducted using potassium hydroxide, water, or (rarely) ammonia
246 (Original TAP Database Form, 1995). Various extraction processes are described in the following
247 paragraphs:
248

249 **Alkali Extraction of Humic Substances:**
250

251 The process begins with the separation of organic matter from the inorganic matrix of sand, silt,
252 and clay. The terrestrial source is leached with hydrochloric acid (HCL) to remove calcium and
253 other positively-charged ions and to increase the efficiency of extraction of organic matter with
254 alkaline reagents. Next, a stronger sodium hydroxide solution is used to create a liquid solution
255 (Weber, undated). The extracted liquid solution is incompatible with acids because it is very
256 alkaline, in the range of 8 to 12 pH, and can be treated with an acid to precipitate out the humic
257 acid portion (Mayhew, 2004).

258

259 Alkali extraction can also be conducted using potassium hydroxide, which is a typical alkali used by
260 manufacturers to extract humic acid from leonardite. The extracted liquid solution is also incompatible
261 with acids because it is very alkaline, in the range of 8 to 12 pH, and can be treated with an acid to
262 precipitate out the humic acid portion (Mayhew, 2004).

263

264 **Processes Inconsistent with the Current Listing**

265

266 Continued experimentation has led to development of a recently patented process that solubilizes the
267 "humin" fraction of leonardite and mixes it with liquid phosphate fertilizer. This solution is used as an
268 early-season soil treatment or as a foliar spray, and enhances the efficiency of the phosphate in the
269 fertilizer. (Kline and Wilson, 1994)

270

271 Lignite and other coals serve as a natural source that can now be synthetically oxidized to produce
272 biochemically active humic substances. The coal is converted to humic substances through either "dry or
273 wet oxidative depolymerization" or "nitric acid oxidation and ammonation."

274

275 A recent innovation in extraction of humic acid uses microbial digestion of lignite to form a humic
276 substance with the trade name Actosol (Kline and Wilson, 1994).

277

278 **Evaluation Question #2: Is the petitioned substance formulated or manufactured by a process that**
279 **chemically changes the substance extracted from naturally occurring plant, animal, or mineral sources?**
280 **(From 7 U.S.C. § 6502 (21).)**

281

282 Humates and humic acids are extremely complex and varied in chemical structure. Some chemical
283 reactions do occur during the processes by which humic materials are obtained from terrestrial sources,
284 such as soil, peat, compost, oxidized lignites, and other coals (Karr, 2001). However, it may not be
285 possible to characterize the reactions and the extent to which there is a chemical change beyond the
286 simple effects of shifting pH on hydrogen ion availability for displacement.

287

288 **Evaluation Question #3: Is the petitioned substance created by naturally occurring biological**
289 **processes? (From 7 U.S.C. § 6502 (21).)**

290

291 In nature, organic matter is converted into humic substances by microorganisms. This natural
292 humification process, however, does not occur as a result of the specific process (i.e., application of
293 NaOH) used for commercial manufacturing.

294

295 **Evaluation Question #4: Is there environmental contamination during the petitioned substance's**
296 **manufacture, use, misuse, or disposal? (From 7 U.S.C. § 6518 (m) (3).)**

297

298 Humic acids are a natural substance that can also be manufactured from natural sources (e.g., coals).
299 There is no information available from EPA to suggest that environmental contamination results from the
300 manufacture, use, misuse, or disposal. Improper disposal of acids or bases used in the extraction process
301 could be a source of environmental contamination, and the mining of lignite/leonardite or other source
302 materials has environmental impacts.

303

304 **Evaluation Question #5: Is the petitioned substance harmful to the environment? (From 7 U.S.C. §**
305 **6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i).)**

306

307 No. Humic acids are a primary component of soil. Humic acids are nearly completely broken down by
308 soil organisms, and are not known to produce toxicity to plants, soil organisms, or higher animals (Original
309 TAP Database Form, 1995). According to Humintech (undated), humic acids will not harm soil or
310 contaminate groundwater or soil. As discussed above (see "Action of the Substance"), humic acids have a
311 number of beneficial properties in soil.

312

313 **Evaluation Question #6: Is there potential for the petitioned substance to cause detrimental chemical**
314 **interaction with other substances used in organic crop or livestock production? (From 7 U.S.C. § 6518**
315 **(m) (1).)**
316

317 Based on the intended use of the substance, no information was uncovered to suggest that use of humic
318 substances could cause detrimental chemical interaction with other substances used in organic crop
319 production. Humic acids are naturally occurring and are a primary component of soil.
320

321 **Evaluation Question #7: Are there adverse biological or chemical interactions in the**
322 **agro-ecosystem by using the petitioned substance? (From 7 U.S.C. § 6518 (m) (5).)**
323

324 Based on the intended use of humic acids, no evidence of adverse biological or chemical interaction in the
325 agro-ecosystem was identified.
326

327 **Evaluation Question #8: Are there detrimental physiological effects on soil organisms, crops, or**
328 **livestock by using the petitioned substance? (From 7 U.S.C. § 6518 (m) (5).)**
329

330 Soil organisms are affected positively by the addition of humic acids (Original TAP Database file, 1995).
331 Crops generally benefit from, or do not react to, addition of humic acids.
332

333 **Evaluation Question #9: Is there a toxic or other adverse action of the petitioned substance or its**
334 **breakdown products? (From 7 U.S.C. § 6518 (m) (2).)**
335

336 Soil humic acids in nature undergo biochlorination, facilitated by ubiquitous soil enzyme
337 chloroperoxidase. The reaction yields chlorinated humic acid, which in turn is converted to
338 chlorophenols, chloroacetic acids, and chloroform. The chlorophenols have been shown in nature to
339 dimerize to form dioxins. However, this process is natural, and since humic acid is a primary component
340 of soil the intended use would not significantly affect the environment through this process. (Euro Chlor,
341 undated)
342

343 **Evaluation Question #10: Is there undesirable persistence or concentration of the petitioned substance**
344 **or its breakdown products in the environment? (From 7 U.S.C. § 6518 (m) (2).)**
345

346 Humic acids are nearly completely broken down by soil organisms, and are not known to produce
347 toxicity to plants, soil organisms, or higher animals (Original TAP Database Form, 1995).
348

349 **Evaluation Question #11: Is there any harmful effect on human health by using the petitioned**
350 **substance? (From 7 U.S.C. § 6517 (c) (1) (A) (i), 7 U.S.C. § 6517 (c) (2) (A) (i) and 7 U.S.C. § 6518 (m) (4).)**
351

352 Based on the intended use, no adverse effects on human health from use of humic acids were identified.
353

354 **Evaluation Question #12: Is there a wholly natural product which could be substituted for the**
355 **petitioned substance? (From 7 U.S.C. § 6517 (c) (1) (A) (ii).)**
356

357 Manures and yard waste compost also contain humic acids and can be applied to soil as alternatives to
358 humic acid as a fertilizer. However, no alternatives are listed for use of humic acids as a soil amendment
359 (Maryland Cooperative Extension, 2003).
360

361 **Evaluation Question #13: Are there other already allowed substances that could be substituted for the**
362 **petitioned substance? (From 7 U.S.C. § 6518 (m) (6).)**
363

364 Other allowed plant or soil amendments on the National List include:
365

- 366 • Aquatic plant extracts (other than hydrolyzed) - Extraction process is limited to the use of
367 potassium hydroxide or sodium hydroxide; solvent amount used is limited to that amount
368 necessary for extraction;

- 369 • Elemental sulfur;
- 370 • Lignin sulfonate - chelating agent, dust suppressant, floatation agent;
- 371 • Magnesium sulfate - allowed with a documented soil deficiency;
- 372 • Micronutrients - not to be used as a defoliant, herbicide, or desiccant. Those made from nitrates or
- 373 chlorides are not allowed. Soil deficiency must be documented by testing;
- 374 • Soluble boron products;
- 375 • Liquid fish products - can be pH adjusted with sulfuric, citric or phosphoric acid. The amount of
- 376 acid used shall not exceed the minimum needed to lower the pH to 3.5; and
- 377 • Vitamins, B1, C, and E (USDA 2005).
- 378

379 **Evaluation Question #14: Are there alternative practices that would make the use of the petitioned**

380 **substance unnecessary? (From 7 U.S.C. § 6518 (m) (6).)**

381

382 Potential alternative practices include composting or use of an alternative soil organic soil amendment (see

383 Evaluation Questions #12 and #13). Other soil building practices that could be considered as alternatives

384 to the use of added humic acids (and soil amendments) include tilling, rotating crops, and planting cover

385 crops (Giannangelo Farms Southwest, 2005).

386

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