

Humic & Fulvic Acids: The Black Gold of

Humic & Fulvic acids based specialities, mainly deriving from Leonardite, are increasingly popular in organic farming of course but also in conventional outdoors horticulture, greenhouse cropping and even in the broad acre sector. Now available from a bunch of suppliers in liquid, powder or granular form, they are applied as soil conditioners and plant growth stimulators. The market is likely to continue growing, provided a few problems are sorted out: stopping the exaggerated claims as to the miracle effectiveness of these products, setting up an international standard for their analysis and, last but not least, stopping product substitution! Using a slightly provocative wording, one can indeed unfortunately describe the market the same way soil organic matter is described: “made of humic substances and non-humic substances”. Leading Producers and Researchers from around the world all agree that they have to join forces to better face the challenge of changing a situation whose consequences –the seaweed industry has experienced them – could be highly detrimental to market expansion. Eliminating the black sheep from the market so that humic acids can be called again “the black gold of agriculture” has become a top priority among industry leaders. Distributors and Growers alike will certainly not complain!

The understanding of humic substances and the way they work are both substantially more sophisticated than the basic knowledge on fertilizers. It is thus all the more important to learn the basics – maybe a bit more – of the agronomics of humic substances before putting your fingers in this business!



Laure Metzger, Senior Research Officer, RITMO, France, has contributed the agronomic part of this feature.

WHAT ARE HUMIC ACIDS?

Soil Organic Matter is frequently said to consist of humic substances and non-humic substances.

Non-humic substances are all those materials that can be placed in one of the categories of discrete compounds such as sugars, amino acids, fats and so on.

Humic substances are the other, unidentifiable

components. Generally, humic substances are considered as a series of relatively high-molecular-weight, brown to black coloured substances formed by secondary synthesis reactions. The term is used as a generic name to describe coloured material or its fractions obtained on the basis of solubility characteristics: the fraction called humic acids is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values. They can be extracted from soil by various reagents. Humic acids are the major extractable component of soil humic substances. They are dark brown to black in colour; the fraction called fulvic acids is soluble in water under all pH conditions. They remain in solution after removal of humic acid by acidification. Fulvic acids are light yellow to yellow-brown in colour; finally the fraction called humins is not soluble in water at any pH value and in alkali. Humins are black in colour.

Many experts now believe that all dark coloured humic substances are part of a system of closely related, but not completely identical, high-molecular-weight polymers. According to this concept, differences between humic

Agriculture?



Courtesy of OMNIA Specialities, Australia



Courtesy of Humintech

acids and fulvic acids, can be explained by variations in molecular weight, the number of functional groups (carboxyl, phenolic

OH) and the extent of polymerisation.

The postulated relationships are depicted in figure 1, in which it can be seen that carbon and oxygen contents, acidity and degree of polymerisation all change systematically with increasing molecular weight.

It is apparent that humic substances consist of a heterogeneous mixture of compounds for which no single structural formula will suffice.

Humic acids are indeed thought to be complex aromatic macromolecules with amino acids, amino sugars, and peptides, aliphatic compounds involved in linkages between the aromatic groups. The hypothetical structure for humic acid contains free and bound phenolic OH groups, quinone structures, nitrogen and oxygen as bridge units and COOH groups variously placed on aromatic rings.

The average contents of

A N I N T E R V I E W W I T H

**Dr Geoff Perry, General Manager,
Omnia Specialities Australia**



Courtesy of OMNIA

“Unfortunately, in the past, humic acids have developed a bad name”

In 2003 Omnia Specialities Australia Pty Ltd was established by the Omnia group of South Africa to acquire the humate production and marketing business of the HRL Group of companies. The products result from the processing of specific deposits of Leonardite type coal identified in Victoria during coal exploration programs for the electricity industry in the 1970's.

“The technology for manufacturing of humic acid liquids - actually Potassium humate - was developed by myself and my colleagues and commercialised as the product K-humate in 1991. This was the first manufacture of humic acid products in Australia. Our K-humate is now the benchmark humate product in the Southern African market, in addition to the Australian market.

Omnia Specialities Australia is the only manufacturer of humic acid using local raw materials in Australia. Humate products are now widely distributed throughout the world with most countries having some humic acid in the agricultural market place. Unfortunately, in the past, humic

acids have developed a bad name in some regions and have been often referred to as “snake oil”. This has been caused by the marketing of low quality, highly priced products and exaggerated claims as to their effectiveness in all situations. All of the above represent a challenge for the serious marketing of humic acid products in agriculture. Our focus with K-humate and K-fulvate products is to educate the market to understand their benefits. To achieve this we use a scientific basis to explain how the products work and base our claims on proper trial data.

It must be emphasised that Leonardite based products are very different and more performing than those from any other source. In particular, recent organic matter (ROM) e.g. compost, plant waste etc., is not generally suitable as a raw material, since these products do show fast benefits, but the effect is much lower and fades very fast, at times in a few weeks. This different behaviour becomes evident when understanding the compositions – the large and complex molecules built over millions of years in Leonardite are much more

stable, compact, rich in organic matter and more efficient in all the particular performance enhancement given by humates. The cost performance is much in favour of Leonardite over ROM based products. The K-humate liquid product manufactured by Omnia Specialities Australia is a guaranteed minimum 26% w/v of the active ingredient, the highest in the world, and is organically certified.

Markets will continue to grow if the products are marketed honestly with a strong education focus based on scientific principles and commercial grower experience. Omnia Specialities Australia will continue to expand markets in Australia and overseas using these principles. We have developed a range of complimentary products, which together with humics and fulvics can play an important role in agriculture.

different humic substances and vegetal molecules in carbon, hydrogen, oxygen and nitrogen are reported in table 1.

**MULTI-FACETED FUNCTIONS
IN SOILS**

Extensive studies have shown that not much of the

humic substances in soils are in a free state but much is bound to colloidal clay. The ways in which humic substances combine with the mineral fraction of the soil may be:

- As salts of low molecular weight - organic acids (acetate, oxalate, lactate

and others) with magnesite, calcite, siderite and others.

- As salts of humic substances with alkaline cations – humic acids, fulvic acids. These are the most characteristic compounds of soil humic substances. The

Table 1: Average composition of humic substances and some vegetal molecules

Substances	% dry ash-free basis			
	C	H	O	N
Fulvic acids	44-49	3,5-5,0	44-49	2,0-4,0
Humic acids	52-62	3,0-5,5	30-33	3,5-5,0
Proteins	50-55	6,5-7,3	19-24	15,0-19,0
Lignin	62-69	5,0-6,5	26-33	-

alkaline cations (Na+, K+, Ca2+, Mg2+) are held primarily by simple cation exchange with COOH groups (RCOONa, RCOOK etc.). The humates and fulvates largely occur in soils as mixtures with Iron and Aluminium hydroxides.

- As chelate with metal ions. A chelate complex is formed when two or more coordinate positions of a metal ion are occupied by donor groups of a single ligand to form an internal ring structure. The complexing ability of humic and fulvic acids results largely from their content of oxygen-containing functional groups, such as COOH, phenolic OH and C=O groups.

Soil organic constituents form both soluble and insoluble complexes with metal ions and thereby play a dual role in soil.

Low molecular weight compounds (biochemicals, fulvic acids) bring about the solubilization of metal ions and affect their transport to plant roots.

In contrast, high molecular weight compounds (e.g. humic acids) function as a "sink" for polyvalent cations. Natural complexing agents are of considerable importance in weathering processes and in the movement of sesquioxides into the subsoil.

- As substances held on

clay mineral surfaces. The interaction of organic substances with clay has a multitude of consequences that are reflected in the physical, chemical and biological properties of the soil matrix.

Several mechanisms are involved in the adsorption of humic substances by clay minerals, the main ones being: van der Waals' forces, bonding by cation bridging, H – bonding, adsorption by association with hydrous oxides, adsorption on interlamellar spaces of clay minerals.

AN UNDISPUTABLE IMPACT ON PLANT METABOLISM

Humic substances not only impact on the physical, chemical and biological properties of soils, they also have a direct influence on plants and crops. Indeed, some recent studies have shown that humic substances contain auxin or stimulate the activity of

auxin-like molecules. They influence the uptake of ions by plants and they stimulate plant growth with efficiency comparable to auxin (AIA).

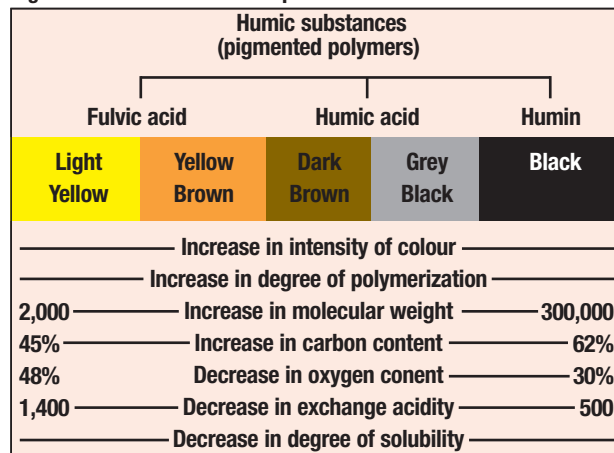
Humic substances have also been reported to activate the second metabolism of plants, to increase CO2 uptake, synthesis of ATP, and respiration of mitochondria and to influence photosynthesis.

Finally, the presence of AIA (or AIA-like molecules) in humic substances has been proved using ELISA method and liquid phase analysis.

Worth noting that studies using humic substances marked with fluorescein have shown that the impact of humic substances on plants is mostly due to the fulvic acids: indeed fulvic acids easily penetrate in plants while humic acids –with their higher molecular weight - remain outside.

EXAGGERATED CLAIMS AS TO

Figure 1 : Postulated relationships between different humic substances



Chemical properties of humic substances (Stevenson 1982)

A N I N T E R V I E W W I T H

Dr Jose Maria Garcia Mina, Research Director, Inabonos (Roullier Group)/Spain and National co-ordinator for Spain of the IHSS



Courtesy of INA

“Southern Europe markets are developing very quickly”

Aren't the promising claims of Humic Acids not just the fancies of aggressive sales personnel? It seems to me that we are experiencing similar developments to those that did so bad to the seaweed industry not so long ago?

I fully agree with you. Nowadays there are two circumstances that could negatively affect the credibility of these substances as beneficial agents to plant development: On the one hand, the lack of concordance between claims - which are mostly correct from a qualitative standpoint - and doses or type of application; and on the other hand the introduction in the market of products sold as humic substances whereas they are everything but humic acids - sometimes they are even just waste!

So, when dealing with humic acids, are we rather talking fertilizers, soil conditioners, plant biostimulants or a miracle combination of the three?

In order to have a good definition of humic acids we have to consider two complementary modes of action: a possible direct effect - an hormone like effect - on plant physiology (under discussion in this moment in the literature) and an indirect effect on the soil rhizosphere by improving both the availability of some nutrients (such as micronutrients of metallic character and phosphorus) through the formation of stable complexes and the soil porosity and aeration. Those

are the two complementary features that give humic substances their specific ability to improve plant growth under adverse conditions.

What are the main current research themes on humic & fulvic acids - by the way how do you position fulvic vs humic focusing on agriculture in the world?

When accepting that the main physical, chemical and agronomic properties of humic substances (HS) are closely related to their structure and chemical nature, it then becomes obvious how important it is to know adequately these intrinsic properties of HS. That is why the studies on the real chemical nature of HS can be considered as the main theme of research today. Another theme that is being also deeply investigated at present covers the mechanisms of action of HS on plant development.

As to the differences between humic and fulvic substances from an agronomic viewpoint, in my opinion these differences are principally related to their molecular weight and their mobility in the soil solution. Thus, humic acids - with higher molecular weight - would be more impacting on soil physic properties and local biological effects whereas fulvic acids - with lower molecular weight and higher functionality - would primarily influence micronutrient transport in the soil solution as well as the biological effects in the rhizosphere.

However, both humic and fulvic acids participate of these different actions.

Where is the research most active - I mean which regions? Is it more active in labs linked to the industry or in academic circles?

It is quite difficult to say which regions are most actively involved in research on Humic Substances. In my opinion there are many labs - e.g. in Europe and in the USA, working very hard on organic matter and HS. Regarding industry or academics, as far as I know academic labs are providing the most significant knowledge about humic substances. However there are also research labs in the Industry that are very interested in humics - this is e.g. the case of the Roullier group.

Are the Southern Europe markets quickly developing, Spain in particular?

Yes Southern Europe markets for humic products are developing very quickly. It is in my opinion a logical consequence of the specific agricultural needs and problems of these countries, which mainly derive from the low content of soil organic matter, alkalinity of soils, and abiotic stresses such as saline growth conditions, water shortages, high temperatures, etc.

“The use of humic acid based products is permanently increasing”

A N I N T E R V I E W W I T H

Müfit Tarhan, Managing Director,
Humintech, Germany

Humintech is a technology-enterprise, based in Düsseldorf, which is active in research, development and industrial production of humic matter and humic acids for agriculture, animal feed, pharmaceutical and construction industries, veterinary medicine, ecological use, such as water purification and removal of soil contamination, and other applications. The company develops products, in particular for agriculture, which have been produced under RWE/Rheinbraun AG - the world-wide largest lignite producer - since the beginning of 1970s.

“Since the rediscovery of humic acids in the agricultural sector, and especially during the last 5 years, the use of humic acid based products has been permanently increasing. Our products fulfil the demand of various agricultural and horticultural crops. We pro-

duce in fluid, granulated and concentrated form.

Our latest achievement, a worldwide innovation indeed, has been to produce after three years of development HuminFeed – a sodium humate based animal feed supplement.

Our expertise however doesn't date back to 3 years!

The first product Perlhumus, a soil conditioner, was produced already in 1971. During the 1980s further humic acid products were developed, among others Liqhumus, and Powhumus. The latter is now very popular among formulators around the world due to its easy handling and transport. We sell our product range worldwide to formulators, who resell them under their own name or process them in their own products.

Products containing humic acids will be increasingly gaining on significance in the future as they provide



Picture courtesy of Humintech

us with economical and ecologically friendly solutions for improving the quality of our lives. Our know-how in products with humic acids makes Humintech one of the worldwide leading enterprises and largest exporters in its field. With our two plants, one in Bergheim (Cologne) for Perlhumus and organo-mineral-fertilizer and one in Leipzig for liquid and soluble humates - with 5000t/annual potassium concentrate capacity - production, we are well prepared to serve the growing demand for those products on the world market”.

EFFECTIVENESS, AND PRODUCT SUBSTITUTION: BAD, HOWEVER STILL WIDESPREAD HABITS

You have just finished reading the above basics, put together by a reliable independent scientist. To cut a long story short, you know that humic acids have physical benefits (physically modifying the structure of the soil), chemical benefits (chemically change the fixation properties of the soil) and biological benefits (biologically stimulate the plant and the activities of soil

micro-organisms). You may think you're ready to go to the market and select the best products! Wait a second: you may need to know a few other things, not to talk about tricks!

Kononova, writing in the former U.S.S.R., where humus has always been a favourite research topic, made some very extravagant claims for the effects of humic acids in the soil. She has reported at length on the beneficial effects of humus on soil fertility and plant growth, but has largely

ignored the data of those workers who failed to get a response to humus, or else got a detrimental effect. However, a brief glance at the literature reveals some contradictory results; and for every reference to the success of humus could be given a reference to its failure. It is obvious that out of that broad group of soil substances that may be separated by alkaline extraction, the humic acids, there are some that promote soil fertility and some that don't! As simple as that. Not to be forgot-



Courtesy of Humintech

ten is also the fact that a claim may be correct when associated to a certain application method and/or rate, however it becomes invalid when the product is not correctly used. Not to talk about product substitution that has become a problem in a number of markets with some products sold as humic acid actually containing little or no active ingredient! As markets become more sophisticated the various players are realizing that just because it is a "black liquid" it is not necessarily humic acid and the nature of the ingredients and the concentration of humic acid are key distinguishing factors.

LEONARDITE, THE BEST RAW MATERIAL

As appears in table 2, a number of natural sources may be considered as raw material for the manufacture of humic acid/fulvic acid based commercial specialties. However, it clearly transpires that Leonardite is the best source material. What is Leonardite? Indeed a soft, earthy, medium-brown coal-like substance associated with lignite. Leonardite is organic matter, which has not reached the state of coal and differs from soft brown coal by its high oxidation degree, a result of the

process of coal formation (bog>peat>coal). The American Leonardite has often been claimed to be the benchmark standard for humic acids, that was until some unique oxidised coals were discovered in Australia (within the Gippsland Basin of Victoria). This Australian organic humate, which could well be called "Australian Leonardite", is very similar to Leonardite (USA – found in New Mexico, North Dakota, Wyoming, etc.) although being younger and more highly oxidised, hence richer in humate. Some deposits are so rich they contain 98% soluble humate. Determining the soluble humate and fulvate content of materials is relatively straightforward by extraction at high pH. The determination of humic acids is not so simple and the methods used can significantly influence the result obtained. Therefore it is difficult to compare claims from different companies (particularly in the USA, China and Russia where the largest manufacturers of humate type products can be found), regarding the humic acid content of their products.

The difference between Leonardite and other sources of humic acids lies in the fact that Leonardite is extremely bioactive through its molecular structure. This biological activity is said to be about five times stronger than other humic matter.

A VARIETY OF FINISHED PRODUCTS FOR A DIVERSITY OF APPLICATIONS

Since a number of years, many suppliers have come

to the market with a variety of commercial products (see table 3). From the powder/granulated Leonardite or humic acid concentrate all the way to powder, soluble crystalline or liquid K-humates, Amm-humates, Na –Humates and even Boron and Magnesium humates, but also Fulvic acid concentrates, Potassium Fulvates, Sodium Fulvates, etc, the potential buyer has a broad choice of offerings. In terms of humic acids content, one litre of liquid concentrate is equivalent to 7-8 metric tons of organic manure. Similarly, one kilogram of concentrated powder is equivalent to about 30 metric tons of manure. A majority of the commercial humate extracts on the market are sodium humates. Whereas sodium hydroxide extractions give an attractive end product (especially for use as feed additives and medicine material for animals 'health) also price wise, there are also claims that potassium extraction from premium quality genuine Leonardite removes more bioactive substances from the raw Leonardite material, particularly the natural growth hormones and biostimulants. An argument often used "against" the sodium Humates is also that they bring ...sodium to the plant/the soil (a sodium humate contains about 7.5 % Na on average), which in most cases is not desirable.

As important as the type of product in the effectiveness of the treatment is the type of application. Applications go from dry soil application of large quantities (like a normal fertilizer) or blending with fer-

Table 2 : Humic & Fulvic acids contents of various materials

Natural Sources	Humic Acids %	Fulvic Acids %
Leonardite/Humate	40	85
Black Peat	10	40
Sapropel Peat	10	20
Brown Coal	10	30
Dung	5	15
Compost	2	5
Soil	1	5
Sludge	1	5
Hard Coal	0	1

Source Humintech

tilizers or potting soil, all the way to foliar spraying of concentrated liquids and fertigation. And this is where suppliers have to be consistent in their approach to the buyers/ end users in order not to confuse them! Each application has its own purpose, meaning that a claim that is documented for soil application may be totally wrong when foliar spraying.

A MARKET DUE TO GROW ON

THE BASIS OF CONSISTENCY IN AGRONOMIC RESULTS

Humate products are now widely distributed throughout the world. The largest markets can be found in Europe (Germany, UK, Switzerland, Spain, Italy), in North America (USA & Canada) but also in Asia (China, Thailand, etc). Other markets are starting to develop such as the Middle East and South

America. Others have not yet started because of legal constraints, e.g. France where not even 1 product is offered in the market as the legislation in place is extremely difficult to meet for a producer (recently however one product from Spain has got the green light for sale in France and this could mark the start of market expansion in this very big potential market). Some markets are developing very fast and the reasons for such development are multifold: the expansion of organic farming almost “mechanically” calls for such products. However the development of the markets in e.g. Southern Europe is more likely linked to the specific agro-climatic, soil conditions and abiotic stress constellation (salinity,

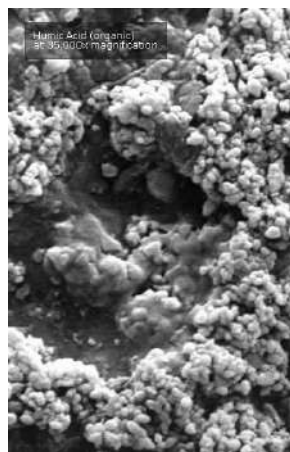
Table 3: Some Manufacturers and Suppliers of Humic & Fulvic acid products to the international markets

Company	Country	Selected Trademarks
Aglukon	Germany	Plantosam
Agrachem/Brandt	USA/France	Uptake, Leonardite Plus
Agrium	USA	Duration CR line
Agrofill	Italy	NA
Agxplore International	USA	HA-12
Biolchim	Italy	Take Up, Humidrip, Humic up
Borregard Lignotech/ Lobel	USA	Borregro Line
CIFO	Italy	Biotron Line, Cifoumic
Cosmocel	Mexico	Humicel, Humicrop, H-85
Double Dragons Humic Acid Co	China	NA
Fine-Humate Industry Co	China	Fine-Humate
Futureco	Spain	Humistrong, Humipower
GOFAR Agro Specialities	China	NA
Greenworks Technology	China	Huminova
Helena Chemicals	USA	Hydra –Hume, Trafix
Humintech	Germany	Liqhumus, Powhumus
Iteco	Spain	Humid’OR line
Jiloca Industrial	Spain	Humilig, Fulvin
Live Earth	USA	LM-32, Crop Thruster
Omnia Specialities	Australia/South Africa	K-Humate, Oxyhumate
Quimica Foliar	Mexico	Fulvicos, Fulvigran, QF Activator
Roullier Group/Inabonos	France/Spain	Fertiactyl GZ
SPA - Ret	Russia	NA
Tradecorp	Spain	Humical, Humistar
Valagro	Italy	Leonarpower

Source: New Ag International database and suppliers information.

Note: (1)This is not an exhaustive list. (2)Only Producers and suppliers of straight humates & fulvates listed. A number of those companies and others also supply multi-ingredient mixtures containing humic & fulvic acids.

drought, heat, etc.) than to anything else. There are many reasons for the markets to continue their growth. Such growth however will only take place on the basis of consistent, proven agronomic results, scientific experience, and if an international standard for testing the specifications of commercial products is agreed upon by the various parties: such standard should include the checking of humates concentration and solubility, heavy metals levels, molecule size (small fulvic molecules preferably as foliars and larger humics for soils) and possibly the percentage of oxygen in functional groups (an indication of the CEC). Then products that once had the



Courtesy of Humintech

**Humic acid at
35,000 x magnification**

reputation of being the “snake oil” will come back to what they used to be referred to before product substitution and exaggerated claims took place: “the black gold of agriculture”..■

Learning more about Humic Substances? The International Humic Substances Society

The motto of the International Humic Substances Society (IHSS) is to Advance the Knowledge, Research and Application of Humic Substances.



The Society was founded in Denver, Colorado, USA, on September 11, 198. The aims of the Society include the collection of standard samples of humic and fulvic acids from lignite, fresh water, sea water, a mineral soil, and an organic histosol soil, and the assembling of the information which is available about genesis, classification, isolation, fractionation, functionality, structures, reactivities and interactions, and the environmental influences of

humic substances. It is intended that this approach will focus on what is now known in the different areas, and it will point out what is not known but should be known.

The IHSS convenes biennially international conferences, which bring together humic scientists from the soil, coal, freshwater and marine sciences. These conferences are convened at an international location by a leading scientist whose participation is agreed on by the Board of IHSS.

For more information, browse <http://www.ihss.gatech.edu/>

“The North American Humic market still holds tremendous promise for Humic technologies”

AN INTERVIEW WITH

An interview with Rick C. Brandt, President and CEO, Brandt Consolidated, Inc - USA

Agra Chem Sales, an affiliate company of Brandt Consolidated, has been devoted to the formulation, application and marketing of humic substances derived from genuine USA Leonardite since 1970. For the past 20 years, the European Sales Office based near Paris, has been servicing clients throughout Europe and the Mediterranean Basin with Uptake, a liquid potassium Humic extract, Leonardite Plus Fine, a dry powder Humic and a number of specific nutritional formulations which contain either one of these materials.

“While still far from having reached it’s potential, even the North American Humic market still holds tremendous promise for Humic technologies. As a result of strong and innovative Humic based product development, we believe that our worldwide sales of Humic based products will increase geometrically over the next three to five years, and an additional line of products which combine humates, nutrients and other natural biostimulants such as seaweed extracts, now compliments our basic Humic product range. The synergistic effects achieved by blending these ingredients often provides even better results than any one material might provide if used alone. Other areas that Brandt/Agra Chem technologies are reaching with Humic based products are soil reclamation, nematode control and organic farming.



Picture courtesy of Brandt

As the benefits of Humic products continue to be documented, we believe that the issues of quality and experience will drive the growth of Humic substances worldwide. Rates of application, climate, soil type, specific crop and many other factors all play a role in determining those results, and those producers who possess the quality, knowledge and experience to help achieve them will prosper. We at Brandt Consolidated are also careful to advise our customers and end users that Humic products should never be considered a cure all and should be applied at certain rates, stages of growth and under certain growing conditions—just like every other product we sell for professional agriculture. Since the affiliation with Brandt in 2001, Agra Chem’s Humic products are now sold through all operating divisions on five continents. Our motto is “Professional Products for Professional Agriculture”, and Agra Chem’s products certainly fit that philosophy.