



SOIL WATER REPELLENCY MANAGEMENT SYSTEM

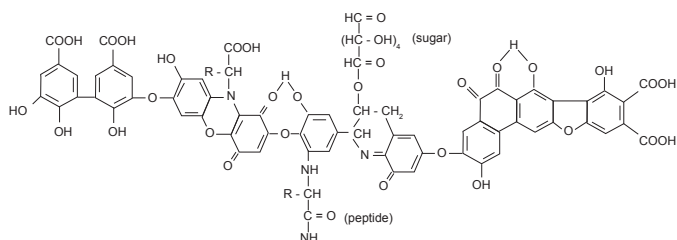
Technical Information

SOIL WATER REPELLENCY

Humic Substances

The build-up of water repellent, non-polar organic coatings on mineral surfaces in the upper root zone has been identified by the general scientific community as the primary cause of soil hydrophobicity.

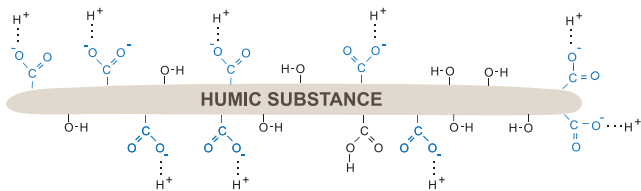
Many scientists point to humic substances as an example of organic polymer materials that will adopt conformational changes in order to facilitate their adsorption to the soil particle interface and ultimately form non-polar (water repellent) films. As a result, the surface of the soil particle surface can quickly be covered with adjoining sequences of these adsorbed, non-polar polymer chains.



Model structure of humic acid (Stevenson 1982)

Conformational Changes

Humic substances are usually present as negatively charged polymers (due to the presence of weak acid functional groups such as carboxylic acid, -COOH). Carboxylic acid functional groups are called weak acids, meaning that they only partially dissociate into H⁺ cations and RCOO⁻ anions in aqueous solution.



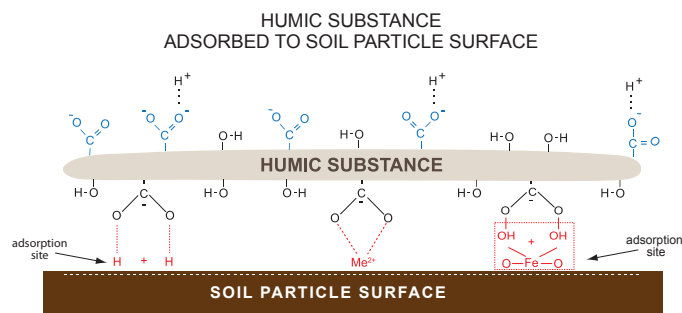
Since the carboxylic acids are weak acids, in water, both non-polar and anionic (negative charge) forms exist in an equilibrium.



Theoretically humic substances should be repelled from the sand particle surface which also has a negative charge. However, humic substances will undergo changes to their molecular configuration to overcome this similar charge repellency at the soil interface.

Scientists have found humic substances commonly initiate adsorption to the sand particle surface through segment-surface bonds such as:

- Cationic bridges
- Association with hydrous oxides
- Hydrogen bonds

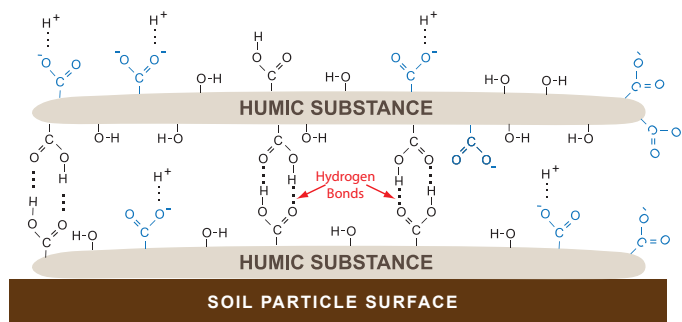


These bonds effectively reverse the surface charge of humic substance adhesion points to positive values that allows them to adsorb to particle surfaces through electrostatic interactions. Once segment-surface bonds are formed, temporary induced polarity of non-polar sites on organic substances (via van der Waals' forces) also contribute to adsorption.

Layer-on Layer Deposition

During later stages of development, hydrophobic humic substances continue to build on sand particles as layer-on-layer depositions.

Layered humic substance build-up occurs as organic polymers are attracted to each other and held to each other through hydrogen bonds, hydrophobic interactions and non-polar attraction (van der Waals' forces).

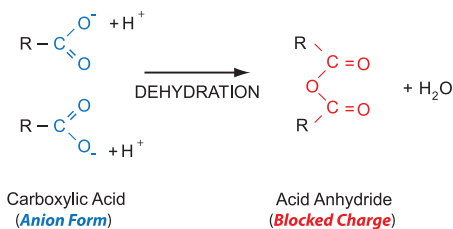


Wet / Dry Cycles

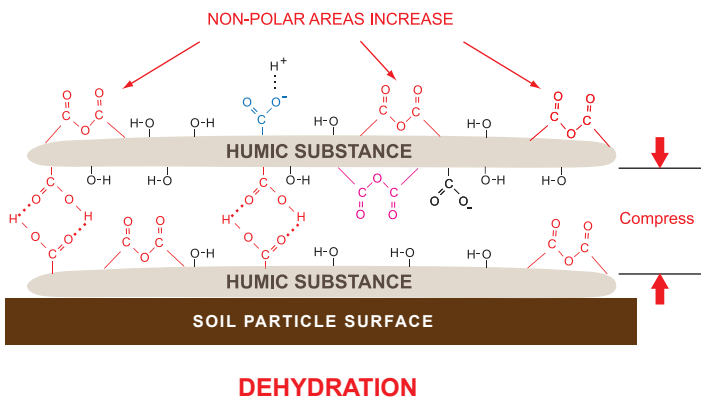
Initially, very few sites on the humic substance polymer chain bind the molecule to the particle surface. However, if the system is allowed to dehydrate, such as occurs during cyclic wet/dry periods of irrigation, the humic substance's molecular structure collapses and flattens on the sand particle surface as oxygen and hydrogen atoms are removed from binding sites. This intimate contact with the particle surface allows a greater area of the humic substance molecule to be held to the particle surface by van der Waals' forces -- resulting in the humic substance being held very tightly to the soil particle surface.

The dehydration process also causes polar sites at the humic substance - water interface to lose their negative "charge" as hydrogen and oxygen are removed from the surface of the humic substance molecule.

Functional groups such as carboxylic acids that are critical for hydration of the soil profile are often rendered non-polar as their anionic negative charges are "blocked" by the removal of their hydrogen and oxygen atoms during the dehydration process (acetylation).



As the dehydration process continues, non-polar sites on the humic substances surface increase and spaces between the layered humic substrates compress -- rendering early stage films and later stage polymer layers of humic substances to become water repellent.



MANAGING WATER REPELLENT SOILS

The standard practice for treating water-repellent sand root zones is the systematic application of nonionic soil surfactants. The use of block copolymers have become the preferred surfactant treatment chemistries. However, it should be remembered that these treatments are used to address the symptoms of water repellency -- localized dry spot, infiltration and water movement problems.

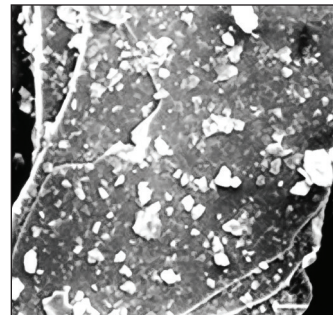
Addressing the cause of water repellency -- the build-up of water repellent organic coatings -- will require newer technology. **And that technology is available now! RETRO SWR Management System.**



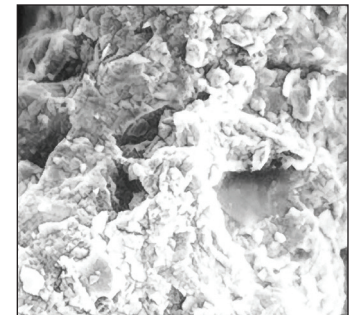
RETRO is a unique formulation of DEPRO¹²⁹⁹, a blend of unique organic coating removal agents, combined with a best-in-class surfactant complex designed to provide the golf course superintendent with a broad, proactive approach to address the cause and problems associated with soil water repellency. RETRO represents a new concept of deploying complementary technologies directed at both helping to correct the build-up of water repellent organic coatings on sand particles (the cause of water repellency) and providing relief from localized dry spots, poor infiltration of applied water and non-uniform water movement into the root zone (the symptoms of water repellency).

MODE OF ACTION

Development of water repellent organic coatings on soil particles is progressive in nature. As a result, these coatings exist as thin films on the particle surface (early stages of development) that progress to a layer-on-layer build-up ("caking") of water repellent organic substances during later stages of development.



Electron micrograph of wettable (hydrophilic) soil particle. Little humic substance is visible.

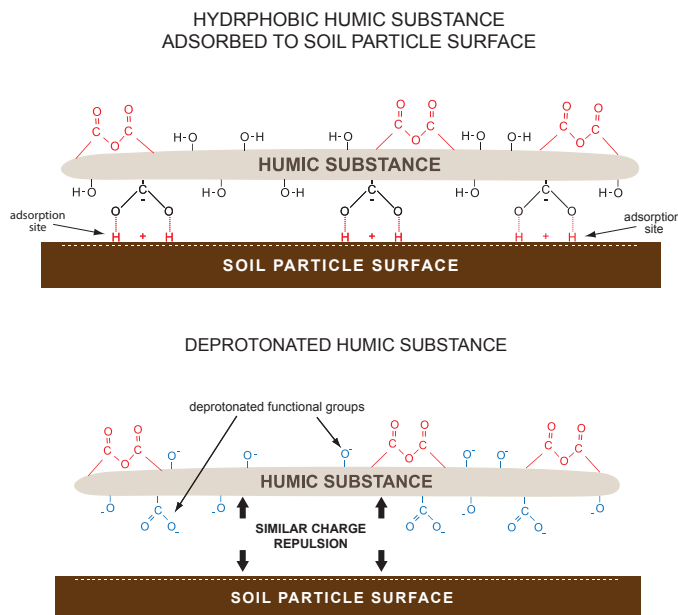


Electron micrograph of non-wettable (hydrophobic) soil particle. Layer-on-layer deposition of humic substances is very visible.

In RETRO's Soil Water Repellency Management System, both its surfactant complex and the organic coating removal agents found in DEPRO¹²⁹⁹ participate in the dissolution of hydrophobic organic coatings on particle surfaces -- both early stage films and later stage polymer build-up ("caking").

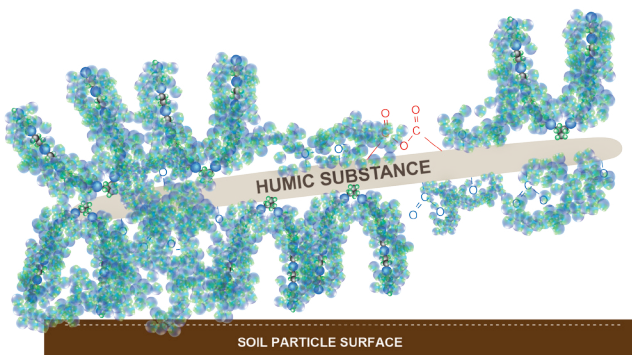
Particle Surface Film Coating

DEPRO's Organic coating removal agents. The DEPRO¹²⁹⁹ organic coating removal agents found in RETRO deprotonate (remove) hydrogen atoms from areas on humic substances. As a result, the net negative charge of the humic substance is increased. Since most soil particles have a negative charge, both the surface and the humic substance repel each other. This begins the process of separating the humic film from the soil particle surface. The negative charge on the humic substance also makes it more water soluble.



Since the bond types between the particle surface and humic substances are diverse, establishing repulsive forces strong enough for complete separation and removal may not be possible in all cases. What probably occurs is that some bonds are broken, some bonds are compromised and some bonds remain intact.

Surfactant Complex. The surfactant complex used in the RETRO formulation has an affinity for humic substances. They are included in the RETRO formulation to assist in moving the coating removal agents in a uniform manner throughout the rootzone as well as enhancing the removal process by loosening and solubilizing the humic substances into the bulk solution.



Graphic showing how surfactants in RETRO aid in the removal of hydrophobic humic substance from the surface of soil particle following deprotonation and initial separation from surface by organic coating removal agents.

The surfactants also stay attached to humic substances that remain on the particle surface. Subsequent irrigations will rehydrate the surfactants and aid in additional removal of humic substances as well as contribute to a return of uniform patterns of infiltration, percolation, retention and favorable wetting patterns.

Layer-on-Layer Polymer Build-up ("Caking")

Organic coating removal agent. Where layer-on-layer coating of water repellent organic polymers occur, RETRO's components act together to separate the molecular fractions of these organic coatings (primarily humic substances in combination with other organic materials) and solubilize these parts into the bulk soil solution.

Hydrogen-based intermolecular bonds form the attraction between individual molecules of humic substances. They also confer a conformational rigidity to humic associations and depress molecular reactivity (non polarity).

The DEPRO¹²⁹⁹ organic coating removal agents in RETRO deprotonate (remove) critical hydrogen atoms from areas on humic substances. Removal of the hydrogen atoms promotes conformational decay. Deprotonation also increases the net negative charge on the humic substance molecules (increasing reactivity) that leads to *layer separation and dissolution due to repulsive forces*.

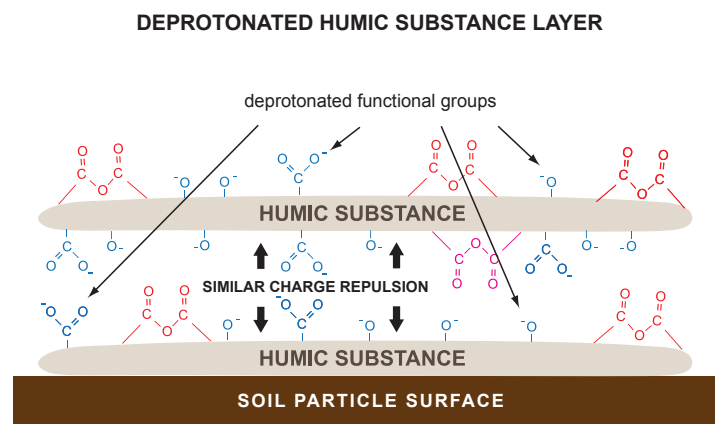


Illustration depicting separation of humic substance layers following deprotonation by DEPRO's organic coating removal agents.

Surfactant Complex. The amphiphilic nature of surfactants and humic substances can easily lead to their mutual attraction. The binding can be either electrostatic or hydrophobic attraction. Surfactants in the RETRO formulation attach to hydrophobic fractions of the humic substances. As these surfactants attract water molecules (hydrate), **they facilitate further separation of layered humic substance molecules.** The surfactant complex also promotes transport into the bulk solution. This is often referred to as "flaking off" of the non-polar organic layers.

Where water repellent layers and film remain, RETRO's surfactant complex is quick to establish sites for adsorption of water molecules – resulting in a return of uniform patterns of infiltration, improved percolation, retention and favorable wetting patterns.

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Treating the Symptoms of Water Repellency

The use of RETRO poses no additional management resources than those associated with surfactant applications used to treat symptoms of water repellency in soils. When used on a monthly basis, it's best-in-class non-ionic surfactants will overcome hydrophobic conditions and promote a consistent and effective pattern of hydration and re-hydration of the soil profile. Following its use in a well-designed rootzone management program, turfgrass managers should expect:

- Relief from localized dry spots and water repellent soils
- Uniform movement of water through the rootzone
- Improved drainage
- Healthier roots and increased stress tolerance
- Enhanced water use efficiency

Addressing the Cause of Water Repellency

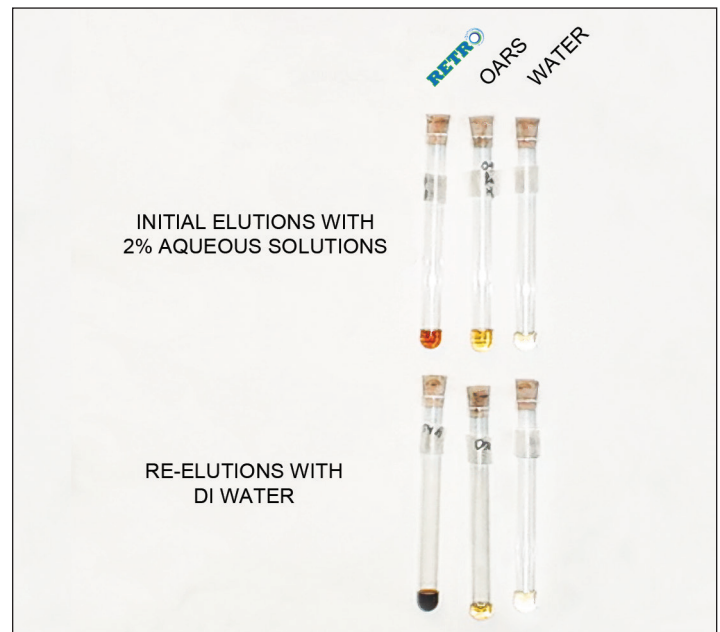
It is well documented that natural organic matter in soils interacts with surfaces of inorganic materials, primarily aluminosilicates or clay minerals, to form a strongly associated organo-mineral composites that can become hydrophobic. It takes less than 10% of hydrophobic materials in the soil matrix to promote non-wetting conditions in the soil profile.

Water-repellent "films" or layers of hydrophobic films will accumulate on the soil particle surface, resulting in water-repellent conditions that exacerbate with time. Use of soil surfactants will successfully address the symptoms of the hydrophobic conditions, but do little to correct the problem.

RETRO also contains a proprietary blend of organic substance removal agents that have been shown to be very successful in disrupting key bonds that bind the hydrophobic organic substances to soil particle and other hydrophobic substances (layer-on-layer deposition). In addition to promoting separation of these materials from the soil particle surface, they increase the negative charge of the humic substance molecules that reduces the hydrophobic nature of the molecules. The negative charge on the humic substance attracts water molecules that improves hydration of the soil particle surface and also aids in separating the humic substance coatings from the surface.

The non-ionic, "block" surfactants found in RETRO have been chosen specifically for their use in organic matter removal applications due to their ability to enhance solubilization of humic substances rendered accessible by RETRO's organic coating removal agents. It appears that their solubility is correlated to the length of their hydrocarbon chain and their attraction to humic substances.

Humic Substance Removal Trial May - 2014



Picture above shows elutant collection of 2% solutions of RETRO compared to OARS and water (control). Color difference is result of humic substance contaminant removal from the soil.

USE DIRECTIONS

Apply RETRO at 4 to 6 oz. (120 ml to 180 ml) per 1000 sq. ft. (100 meters squared) in 2 gallons (8 liters) of water. For best results, apply monthly throughout the growing season. No watering is required when used at recommended rates.

RETRO

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