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AQUAZOL STABILIZED HYDROGEN PEROXIDE:

AN INNOVATIVE COMBINATION

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Aquazol Stabilized Hydrogen Peroxide: An Innovative Combination

Abstract

Hydrogen peroxide is a reagent used in many industries and this usage is growing especially where it is replacing reagents known or suspected of causing cancer and other long-term health problems. Hydrogen peroxide is an effective chlorine-free bleaching agent and is FDA generally recognized as safe (GRAS) as an antimicrobial. Aquazol is a water-soluble, non-hazardous, non-toxic, and biocompatible polymer. Much of Aquazol's unique chemistry is due to the amide linkage and the exceptional hydrogen bonding acceptor capabilities. Aquazol is a superior stabilizer of hydrogen peroxide in aqueous solution. Hydrogen peroxide and Aquazol are currently used in many of the same industries. This innovative combination is ripe for research and growth.

H_2O_2 & AQUAZOL: HIGHLIGHTS AND COMMON INDUSTRIES

Hydrogen Peroxide

Air
Quality treatment
Dry mist disinfectant of hospital, dental,& long term care ventilation

Analytical reagent

Antiseptic, cleaning & disinfectant
Agriculture
Barn
Food handling & packaging
Dairy
Dental & surgical instrument
Medical devices
Contact lenses
Produce post-harvest
Soil

Aseptic packaging

Bleaching
Paper, pulp, deinking,
Fiber & fabric
Taxidermy

Cleaning & etching circuit boards

Water
Combating microbes in cooling towers
Dechlorinization of water
Disinfectant of water lines in medical, dental, & hospital settings
Drinking water treatment
Wastewater treatment
Algal bloom treatment

Free radical source

Fuel in compact form
Rocket / Missile
Submarine

Personal care
Hair & Dental treatment

Pickling of Metals

Application or Industry

ELECTRONIC
AIR
PAPER
MEDICAL
WATER
PACKAGING
FABRIC
FIBER
PERSONAL CARE
METAL

Aquazol

Printing
3-D Printing
Photo quality printing

Paper
Paper coatings

Metal treatment
Steel quench

Films & coatings
Paints
Inks

Ceramics
Binders

Water Treatment
Membranes
Filtration
Wastewater treatment

Air treatment
Filters

Electronics

Medical
Medical devices

Personal Care
Cosmetics
Dental treatment
Hair care

Adhesives
Hot melts
Glue

Fibers
Textiles, Glass & Carbon

Surface care
Polishing

Figure 1. Industries mutually common to Aquazol, poly (2-ethyl-2-oxazoline), and hydrogen peroxide

HYDROGEN PEROXIDE INTRODUCTION AND HISTORY

As a clean, environmentally-friendly reagent, the industrial usage of hydrogen peroxide is growing. Hydrogen peroxide can act as a bleach, a disinfectant, a cleaning agent, or as a fuel, among other uses. With its non-polluting decomposition products of water and molecular oxygen, hydrogen peroxide is increasingly attractive to a variety of industries. According to Transparency Market Research, the hydrogen peroxide market is expected to increase to $3.68 billion US Dollars by 2025.[1]

A strong oxidizing agent, hydrogen peroxide, as shown in Figure 2,was discovered over 200 years ago. In July 1818, Louis-Jacques Thenard reported in the Paris Academy of Sciences his method of producing what he called “oxidized water.” His further studies of this oxidized water led him to realize he had an entirely new compound. His investigations showed a “novel form of chemical combinations, and, it could decompose vigorously”[2] Commercial manufacturing of hydrogen peroxide began in the 1870’s, and by 1901, 10,000 tons were being produced per year in Europe.[2]

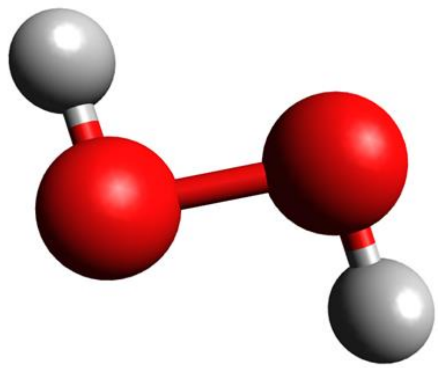


FIGURE 2. BALL AND STICK FIGURE OF HYDROGEN PEROXIDE SHOWING THE NON-LINEAR STRUCTURE OF THE LOWEST ENERGY

AQUAZOL INTRODUCTION AND HISTORY

A water-soluble, biocompatible, non-toxic polymer poly(2-ethyl-2-oxazoline), sometimes called PEOX or POX, in literature, is an innovative and superior alternative to other water-soluble polymers. Poly(2-ethyl-2-oxazoline) is an excellent film former and adhesion promotor, and is stable to 380 °C, is shear stable, UV stable, and readily hydrogen-bonds.

Poly(2-ethyl-2-oxazoline), which is sold commercially as Aquazol, by Polymer Chemistry Innovations (PCI), was discovered in 1966 by Kagiya el all.[3,4,5,6] Within the span of a year, four groups published on the synthesis and properties of poly(2-ethyl-2-oxazoline). Dow manufactured this polymer in the 1980’s.[7] In 1990, Dr. Bernard Gordon, III, founded PCI, which is the sole global source of Aquazol.

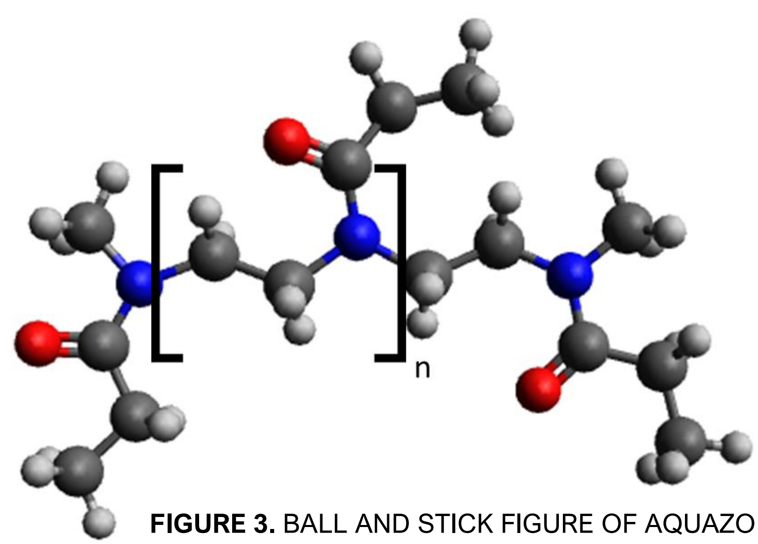


FIGURE 3. BALL AND STICK FIGURE OF AQUAZOL, POLY(2-ETHYL-2-OXAZOLINE), SHOWING THE NITROGEN IN BLUE AND OXYGEN IN RED.

PROPERTIES OF H_2O_2

BOILING POINT[8]
(DECOMPOSES) 150.2 °C

MELTING POINT[8]
-0.43 °C

DENSITY[8]
1.44 AT 25 °C

DIELECTRIC CONSTANT[9]
73.2 at 20 °C (water is 80.4)
Dielectric constant 65% solution 120

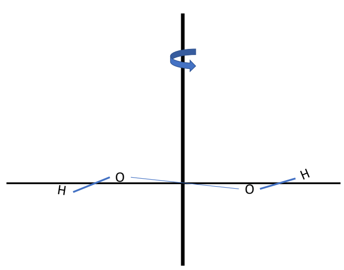
CAS
7722-84-1

CHEMICAL FORMULA
H_2O_2

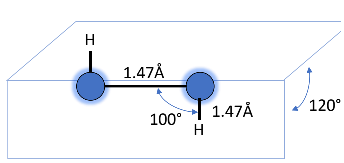
SOLUBILITY IN WATER[4]
MISCIBLE

MOLAR MASS
34.0147 G/MOL

C_2 Symmetry[8]



Gas phase hydrogen peroxide



HYDROGEN PEROXIDE CHEMICAL PROPERTIES and CHEMISTRY

Neat, or pure, hydrogen peroxide, H_2O_2, is a clear pale blue to colorless liquid with low odor. The simplest form of peroxide, hydrogen peroxide is composed of four atoms, H–O–O–H, arranged in a non-planar C_2 symmetry. The oxygen atoms in hydrogen peroxide are two-coordinate, the most common stereochemistry of oxygen, where each oxygen atom is bonded by a single bond to two other atoms, hydrogen atoms in this case. The oxygen-oxygen bond is formally assigned to be a single bond with a high rotation barrier due to the electron pair repulsion between the two oxygen atoms present in liquid or aqueous solution of hydrogen peroxide.[8]

STABILITY

In theory the boiling point of hydrogen peroxide is 150.2 °C, but in practice hydrogen peroxide will undergo a potentially explosive rapid thermal decomposition before it reaches a boil at standard atmospheric pressure. Hydrogen peroxide prepared, purified, and meticulously kept pure is stable. Although it is stable, great care must be taken in storage as hydrogen peroxide decomposes slowly in light but readily decomposes catalytically if certain trace metals are present or if the surface of the storage container is not sufficiently smooth. Hydrogen peroxide is very reactive to metals, metals salts and metal oxides. Homogeneous decomposition can occur in the presence of many metals including, vanadium, iron, ruthenium, chromium, molybdenum, tungsten, nickel, lead, mercury, copper, silver, gold, platinum or palladium. Hydrogen peroxide will decompose slowly when exposed to a broad spectrum of light. Rapid decomposition occurs in alkali conditions over a pH of 6.5. Heterogeneous decomposition can occur when hydrogen peroxide is exposed to insoluble solids and decomposes at varying rates when in contact with any surface. A fine powder in the presence of hydrogen peroxide can cause a rapid decomposition due to a high surface area, whereas a smooth polyethylene storage container that is clean and suitably prepared limits decomposition to a slow pace. Hydrogen peroxide decomposition to water and oxygen:

$$2H_2O_2 \longrightarrow 2H_2O + O_2 + 99\ \text{kJ mol}^{-1}\ \text{of}\ H_2O_2$$

In addition to decomposition, hydrogen peroxide can undergo several different reaction types depending upon conditions such as oxidation, reduction or as an agent forming various compounds.

AQUAZOL CHEMICAL PROPERTIES and CHEMISTRY

Aquazol, poly(2-ethyl-2-oxazoline), is an amorphous, non-toxic, neutral, non-ionic polymer with a tertiary aliphatic amide in the repeat unit. The repeat unit formula of $(C_5H_9NO)_n$ features the nitrogen of the amide as part of the structure of the backbone while the acyl group is attached to the nitrogen, placing the carbonyl in the dangling side chain. Amides are neutral, highly stable, and irreversibly bound under typical ambient conditions. The amide linkage is far less reactive than that of the similar groups of esters, acid anhydrides and acid chlorides.[9] The amide functional group with the nitrogen in the backbone gives Aquazol better stability under higher temperature, shear, and UV exposure than other similar water-soluble polymers. Aquazol can undergo hydrolysis to form polyethyleneimine or will partially hydrolyze to form copolymer.

STABILITY

Aquazol is a water-soluble thermoplastic polymer of "exceedingly good stability."[10] Aqueous solution shear tests demonstrate constant fluid properties and stable viscosity over a duration of time without decomposition of the polymer with a shear rate of up to 10^5 sec^{-1}.[16] One test ran an aqueous solution of the polymer through a high-shear Vicker's vane pump for 260 hours and the solution retained "three quarters of its initial viscosity."[14] Thermogravimetric analysis (TGA) probing the thermal stability of Aquazol indicates it can be stored for short periods of time at 320 °C without any decomposition or formation of plasticizing species.[17]

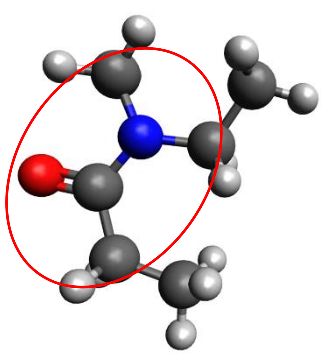


FIGURE 4. BALL AND STICK FIGURE OF THE AMIDE. THIS FUNCTIONAL GROUP IS THE PRIMARY BUILDING BLOCK FOR PROTEINS.

This stability can be explained by the amide repeat unit in the polymer backbone shown in the red oval in Figure 4. Amides are composed of a nitrogen bound to a carbonyl carbon. Nitrogen requires three bonds to complete its octet. The carbonyl-carbon – (C=O) in the amide is bound to the nitrogen with the electron lone pair of the nitrogen delocalizing to the carbonyl-carbon giving this bond double-bond character. Oxygen requires two bonds to complete its octet. The electronegativity of the oxygen and the pi-bonding configuration of the oxygen electrons give the carbon-oxygen double-bond a stronger dipole than the nitrogen-carbon bond. Both dipoles allow the amide to function as hydrogen-bond acceptors. Each repeat unit amide in Aquazol has two sites where an acidic proton under the right conditions can accept a hydrogen-bond, the nitrogen and the carbonyl oxygen.[18] The tertiary amide structure does not allow for the nitrogen act as a hydrogen-bond donator.

PROPERTIES OF AQUAZOL

CHEMICAL NAME
Poly(2-ethyl-2-oxazoline)

REACH REGISTERED
01-2120773935-39-0000

T_g[10] 69 – 71 °C

VICAT SOFTENING [11]
70°C

DEGRADATION[14]
380 – 390 °C in air

FORMULA
-$[C_5H_9NO]$-

MONOMER
2-ethyl-2-oxazoline

REFRACTIVE INDEX[6]
1.52

DENSITY[14] 1.14

SOLUBLE[12,13,14]
Water (< 60 °C)
Methanol
Dioxane
dimethylformamide

LCST
66 °C

BIOCOMPATIBLE
Yes

SOLUBILITY PARAMETER[15]
25.73

DIELECTRIC CONSTANT[15]
3.68

AUTO IGNITION
>400°C

HANSEN SOLUBILITY[26]
~26 $J^{1/2}$ $cm^{-3/2}$

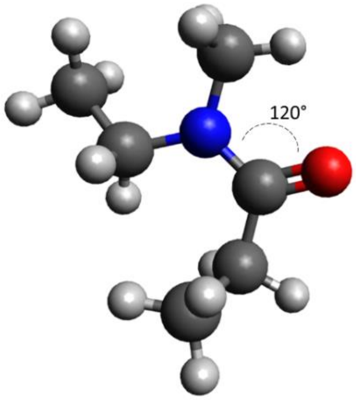


FIGURE 5. TRIGONAL PLANAR GEOMETRY OF THE AMIDE HAS 120 ° BOND ANGLES.

Using valence bond theory to describe the bonding of the amide functional group, the carbonyl-carbon has a single bond to the nitrogen, a single bond to the ethyl group carbon, and a double bond to the carbonyl oxygen. This geometry is sp^2 hybridized and the geometry around the carbonyl carbon is trigonal planar with bond angles around the carbonyl-carbon at approximately 120°. This is as expected by valence bond theory for a carbon with four bonds that includes a double bond. The nitrogen has a lone electron pair and bonds to three carbons. Two of the carbon atoms bound to the nitrogen are in the backbone of the polymer and the third carbon atom is the carbonyl carbon.

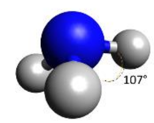


FIGURE 6. AMMONIA SHOWS THE TYPICAL GEOMETRY OF THE NITROGEN BOUND TO THREE ATOMS WITH 107 ° BOND ANGLES.

While typically a nitrogen with three bonds and a lone pair, such as is observed in ammonia, has a tetrahedral geometry of sp^3 hybridization, the amide functional group exhibits a geometry of trigonal planar, which is consistent with sp^2 hybridization. The nitrogen, carbonyl carbon, and oxygen are arranged in the same plane. This coplanar configuration and sp^2 hybridization of the nitrogen and carbon allow for resonance delocalization of the nitrogen's lone electron pair.[4] The overlap of the *p*-orbitals allow for these electrons to delocalize over the N–C–O atoms, lowering the potential energy and adding to the stability of the system. This delocalization of the electrons makes the amide less susceptible to a nucleophilic attack.

HYDROGEN BONDING OF AQUAZOL

A key benefit of Aquazol is this polymer's hydrogen-bond acceptor properties. Intermolecular hydrogen-bonding is the molecular origin for Aquazol's solubility in many solvents and compatibility with polymers that contain hydrogen-donating groups.[12, 17, 18, 19] Aquazol is miscible in water at temperatures below 60 °C.[13, 14, 17] Above 60 °C, Aquazol shows inverse solubility and undergoes a liquid-liquid phase separation in an aqueous solution. This is its lower critical solution temperature (LCST)[13, 18, 20, 21] In an aqueous solution, the hydrogen-bond acceptor properties of Aquazol are affected by temperature, pH, and whether added salts or other solubility modifiers are present.[12, 19, 21] The specific hydrogen-bond interactions give opportunities to selectively tune the solubility properties of the polymer for specific purposes.

AQUAZOL STABILIZATION OF HYDROGEN PEROXIDE

Aquazol is particularly attractive as a hydrogen-peroxide, H_2O_2, stabilizer. Hydrogen peroxide has a pK_a of 11.65 while water has a pK_a of 15.7. The lower the pK_a, the stronger the acid. The more acidic protons of hydrogen peroxide will form a stronger hydrogen-bond with the carbonyl oxygen in the polymer and will preferentially hydrogen bond with the polymer in an aqueous solution.[22] In his patents, S. Jensen notes that poly(2-ethyl-2-oxazoline) is superior to other polymers used to stabilize hydrogen peroxide. "Experience has shown that a 30% hydrogen peroxide gel made with poly(2-ethyl-2-oxazoline) stays a gel during six month's storage at room temperature. Poly(2-ethyl-2-oxazoline) is a superior polymer in an oxidizing peroxide environment to current thickening polymers."[23, 24]

AQUAZOL + H_2O_2

One of several intriguing possibilities is the use of hydrogen peroxide and Aquazol together in an industry where both are already used, and where the combined performance may be of an enhancement to a process. Some of these areas of overlap were highlighted in Figure 1 on page 2 of this white paper.

RECYCLED PAPER

One example of an unexplored area is the use of Aquazol-stabilized hydrogen peroxide in the bleaching of recycled fibers in sustainable paper production. In the US, 80% of paper mills utilize recycled fiber to some degree in production and recycled fiber makes up 36% of the total fiber used in paper production.[25]

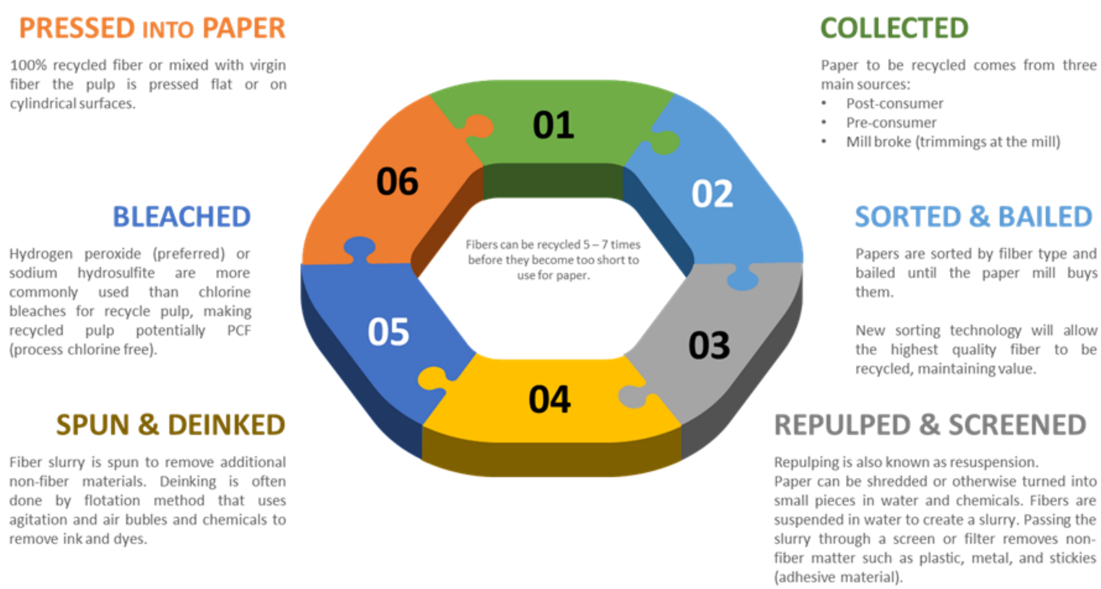


FIGURE 7. STEPS IN RECYCLING PAPER WASTE INTO NEW PAPER PRODUCTS.

The recycled fiber market is strong globally, even after China banned nearly all recyclables starting January 2021. The US recycled fiber export market is showing slight growth overall as US exports to countries such as India, Thailand, Mexico, and other countries. Greater growth is found in the US exporting pulp made from recycled fiber to China (83%) and Canada (12%).[27]

Products made from recycled fiber can be of the same or lesser quality as the fiber that they are originally from. Mixed paper typically has a mixture of recycled fibers that are often used in containerboard, paperboard and tissue.[28] However, with targeted community education and better sorting technologies, the value of high-quality recycled fibers is an area of potential growth.[28] Even with existing conditions, there is room for growth in containerboard, paperboard, and tissues with room for an additional “463, 21, and 257 thousand short tons” each.[28]

Currently, 60% of the world’s production of hydrogen peroxide is used in pulp & paper bleaching.[1] Hydrogen peroxide is used in one or more of the steps of the pulp bleaching process and is a preferred bleaching agent for recycled pulp, [29, 30, 31] as the only byproducts are oxygen and water, making it non-polluting and total chlorine-free. Aquazol is used in various areas of paper processing and is an excellent fiber sizing agent.[32,33]

It is postulated by this author that with its hydrogen bonding properties, stability, and known benefits, that using Aquazol-stabilized hydrogen peroxide in the pulp bleaching stage of recycled paper processing, that this would add to the chemical efficiency of the process and yield a superior product. Aquazol's presence in this formulation will add strength to the finished paper, as leaving a residual amount of Aquazol acts as a sizing agent to the fibers.[32] Aquazol aides in the fibers bonding together forming a stronger paper.[33] Better bonding properties allow for a greater percentage of recycled fiber in the product.[33]

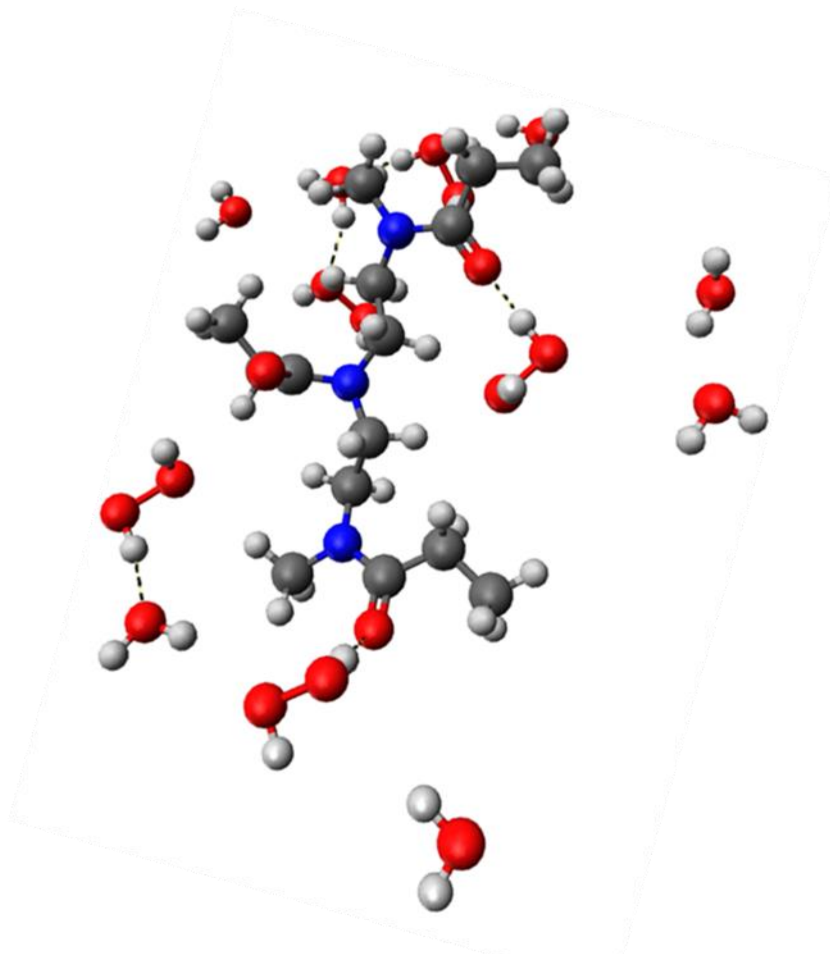


FIGURE 8. HYDROGEN PEROXIDE AND AQUAZOL IN AQUEOUS SOLUTION WITH THE HYDROGEN BONDS HIGHLIGHTED.

In addition to the stabilizing of hydrogen peroxide and fiber bonding aid benefits, Aquazol has two other notable benefits. Aquazol is non-hazardous and FDA approved as a non-contact food additive under 21 CRF175.105, making it an attractive processing aid in food packaging application. Using Aquazol-stabilized hydrogen peroxide is in alignment with the goals of the American Forest & Paper Products Association *Better Practice Better Planned Initiative 2020* goals,[35] specifically, clean water and sanitation. Aquazol is readily recovered from water through its inverse solubility properties.

Hydrogen peroxide stabilized by Aquazol has potential applications in multiple industries, particularly those industries where both materials are already used. This white paper describes the molecular basis for Aquazol stabilizing hydrogen peroxide and offers an example where this innovative combination may add benefit and efficiency.

Summary

Aquazol is an excellent polymer stabilizer of hydrogen peroxide that is not broken down or decomposed by hydrogen peroxide.

Nine or more industries already use both Aquazol and hydrogen peroxide separately in production processes.

Both reagents are environmentally friendly.

Aquazol stabilized hydrogen peroxide is an innovative combination that may add benefit and value to the final product.

For more information visit www.polychemistry.com or email info@polychemistry.com.

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