ThreeBond
TECHNICAL NEWS

Three Bond Technical News
Issued January 1, 2004
62

Titanium-Oxide Photocatalyst

Introduction

Newspapers and other media often announce reports of various types of serious damage that are caused by bacteria in the medical and food fields. Most of those problems could be prevented if clean environments were maintained. The hygienic effect of washing hands and bed-bath in order to maintain environmental cleanliness has been stressed in research papers and reports, and the importance of personal hygiene is attracting a great deal of attention as a prerequisite for ensuring sanitary environments in many fields.

Three Bond has developed the ThreeBond 6731 (hereinafter abbreviates as TB6731) for the maintenance of clean environments, and it is expected to provide superb functions in various applications requiring the strict control of bacteria, such as in medical institutions where many people are coming and going, and in food factories where advanced quality control is required.

Contents

1. Mechanism of titanium-oxide photocatalytic reactions

1-1. Band structure of semiconductors and band gap energy[1)]

If the nucleus of an atom were the sun in our solar system, the electrons revolving around the nucleus would be the orbiting planets. The path that an electron travels is referred to as an "orbit." There is a limit to the number of electrons that can occupy one orbit. Electrons in the outermost orbit are referred to as "valence electrons." Valence electrons are responsible for the bonding of atoms.

When there are few atoms, the energy values of electrons in orbits are scattered. However, when the number of bonded atoms increases, the values become continuous within a certain range, rather than being scattered. This range is referred to as an "energy band." The area between two energy bands, where there is no electron energy, is referred to as a "forbidden band."

Among the bands filled with electrons, the one with the highest energy level (the electron orbit farthest from the nucleus) is referred to as the "valence band," and the band outside of this is referred to as the "conduction band." The energy width of the forbidden band between the valence band and the conduction band is referred to as the "band gap."

The band gap is like a wall that electrons must jump over in order to become free. The amount of energy required to jump over the wall is referred to as the "band-gap energy." Only electrons that jump over the wall and enter the conduction band (which are referred to as "conduction electrons") can move around freely. In the case of silicon, the band gap energy is approximately 1.1 eV, which is equal to approximately 1100 nm when converted to the wavelength of light. When rutile type titanium oxide and anatase type titanium oxide are irradiated with light of 413 nm or lower, or 388 nm or lower, respectively, valence band electrons move up to the conduction band. At the same time, as many positive holes as the number of electrons that have jumped to the conduction band are created.

1-2. Energy structure of titanium oxide and photoeffect[1)]

In a compound semiconductor consisting of different atoms, the valence band and conduction band formation processes are complicated, but the principles involved are the same. For example, it is known that the valence band of titanium oxide is comprised of the 2p orbital of oxygen (O), while the conduction band is made up of the 3d orbital of titanium (Ti). In a semiconductor with a large band gap, electrons in the valence band cannot jump up to the conduction band. However, if energy is applied externally, electrons in the valence band can rise (this is referred to as "excitation") to the conduction band. Consequently, as many electron holes (holes left behind by the electrons moving up to the conduction band) as the number of excited electrons are created in the valence band. This is equivalent to the movement of electrons from the bonding orbital to the antibonding orbital. In other words, the photoexcited state of a semiconductor is generally unstable and can easily break down. Titanium oxide, on the other hand, remains stable even when it is photoexcited. This is one of the reasons that titanium oxide makes an excellent photocatalyst.

The following three factors pertaining to the band structure of semiconductors have the greatest effect on photocatalytic reactions:

(1) Band gap energy
(2) Position of the lowest point in the conduction band
(3) Position of the highest point in the valence band

In photocatalytic reactions, the band gap energy principally determines which light wavelength is most effective, and the position of the highest point in the valence band is the main determinant of oxidative decomposing power of photocatalyst.

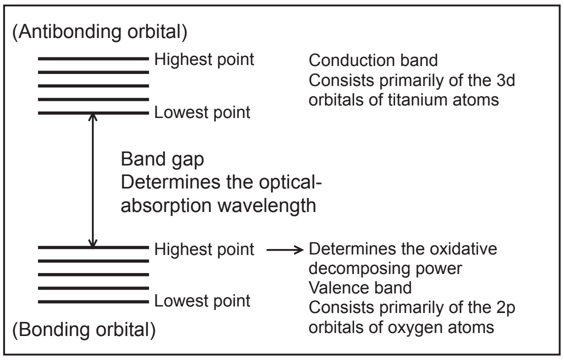

Fig. 1 Titanium-oxide Band Structure[1)]

1-3. Crystal structures and photocatalytic activity of titanium oxide[1)]

There are three types of crystal structures in natural titanium oxide: the rutile type, the anatase type, and the brookite type. All three of these types are expressed using the same chemical formula (TiO_2); however, their crystal structures are different. Titanium oxide absorbs light having an energy level higher than that of the band gap, and causes electrons to jump to the conduction band to create positive holes in the valence band. Despite the fact that the band gap value is 3.0 eV for the rutile type and 3.2 eV for the anatase type, they both absorb only ultraviolet rays. However, the rutile type can absorb the rays that are slightly closer to visible light rays.

As the rutile type can absorb light of a wider range, it seems logical to assume that the rutile type is more suitable for use as a photocatalyst. However, in reality, the anatase type exhibits higher photocatalytic activity. One of the reasons for this is the difference in the energy structure between the two types. In both types, the position of the valence band is deep, and the resulting positive holes show sufficient oxidative power. However, the conduction band is positioned near the oxidation-reduction potential of the hydrogen, indicating that both types are relatively weak in terms of reducing power. It is known that the conduction band in the anatase type is closer to the negative position than in the rutile type; therefore, the reducing power of the anatase type is stronger than that of the rutile type. Due to the difference in the position of the conduction band, the anatase type exhibits higher overall photocatalytic activity than the rutile type.

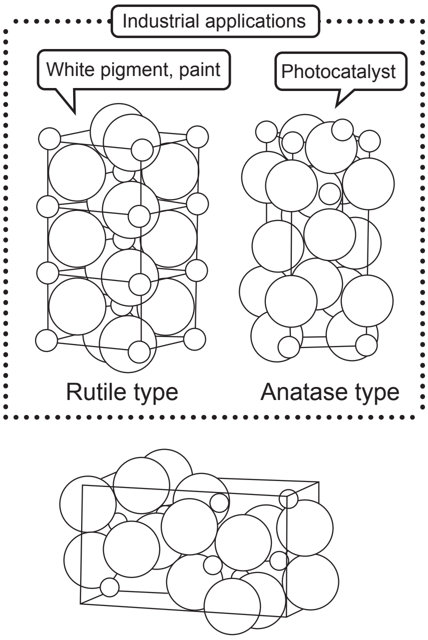

Fig. 2 Crystal Structures of Titanium Oxide

1-4. Effect of ultraviolet rays in activating titanium oxide[1)]

The band gap of anatase type titanium oxide is 3.2 eV, which is equivalent to a wavelength of 388 nm. The absorption of ultraviolet rays shorter than this wavelength promotes reactions. These ultraviolet rays are near-ultraviolet rays contained in the sunlight reaching the earth and emitted by room lights, and they have a very limited range of weak light throughout the spectrums of sunlight and room lights.

The development of a visible-light photocatalyst may be considered as a solution, but no substance superior to titanium oxide as a material for photocatalysts has yet been discovered. One major reason for this is that a semiconductor with a smaller band gap than that of titanium oxide results in autolysis if it receives light in the presence of water. In titanium oxide, the absorption of ultraviolet rays with a wavelength of 388 nm or shorter promotes reactions; however, it is known that 254-nm rays having a greater energy level, which are used in germicidal lamps, are absorbed by the DNA of living organisms and form pyrimidine dimers, thereby damaging the DNA.

Titanium oxide photocatalyst does not require ultraviolet rays that have an energy level as high as 254 nm and are hazardous to humans. It also allows reactions to be initiated by the near-ultraviolet rays with relatively long wavelengths contained in sunlight and emitted by fluorescent lamps.

Table 1 Ultraviolet Rays in Ordinary Surroundings

measurement location		intensity of ultraviolet rays	remarks
outdoors	under direct sunlight	4 to 5mw/cm^2	fair weather
		2 to 2.5mw/cm^2	slightly overcast
		0.7 to 0.8mw/cm^2	cloudy
inside vehicle	through rear window glass	150 to 350μw/cm^2	fair weather - slightly overcast
	through side window glass	90 to 300μw/cm^2	
	through front glass	0.5 to 2.0μw/cm^2	
	rear seat in shade	10 to 30μw/cm^2	
	ceiling surface	2 to 4 μw/cm^2	
inside of house	immediately below the fluorescent lamp	2 to 3 μw/cm^2	

Illuminance meter: TOPCON UVR-2 manufactured by Topcon Corporation

1-5. Decomposing power of titanium oxide photocatalyst1)

When light is absorbed by titanium oxide, two carriers -- electrons (e-) and positive holes (h+) -- are formed. In ordinary substances, electrons and positive holes recombine quickly; however, in titanium oxide photocatalyst they recombine more slowly. The percentage of carrier recombination has a major effect on the photocatalytic efficiency.

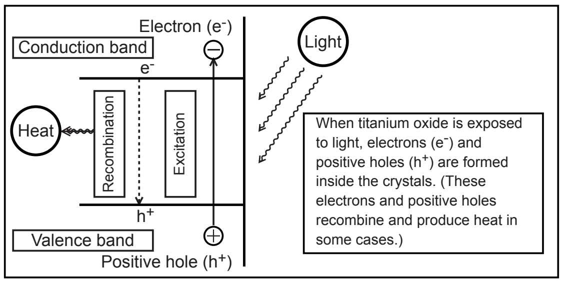

Fig. 3 Electron structure of titanium oxide[1)]

One of the notable features of titanium oxide is the strong oxidative decomposing power of positive holes, which is greater than the reducing power of electrons excited to the conduction band. The surface of a photocatalyst contains water, which is referred to as "absorbed water." When this water is oxidized by positive holes, hydroxy radicals (• OH), which have strong oxidative decomposing power, are formed. Then, the hydroxy radicals react with organic matter. If oxygen is present when this process takes place, the intermediate radicals in the organic compounds and oxygen molecules can undergo radical chain reactions and consume oxygen in some cases. In such a case, the organic matter eventually decomposes, ultimately becoming carbon dioxide and water. Under some conditions, organic compounds can react directly with the positive holes, resulting in oxidative decomposition.

Meanwhile, the reduction of oxygen contained in the air occurs as a pairing reaction. As oxygen is an easily reducible substance, if oxygen is present, the reduction of oxygen takes place instead of hydrogen generation. The reduction of oxygen results in the generation of superoxide anions (• O_2^-). Superoxide anions attach to the intermediate product in the oxidative reaction, forming peroxide or changing to hydrogen peroxide and then to water.

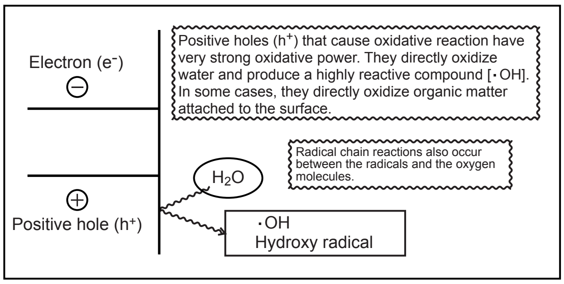

Fig. 4 Oxidation mechanism[1)]

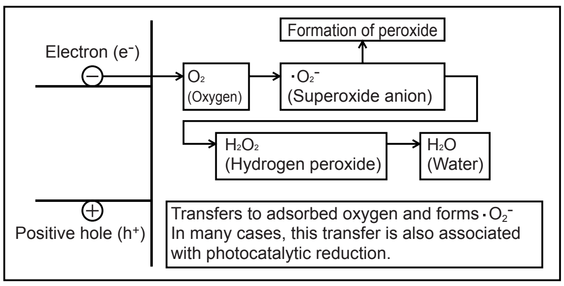

Fig. 5 Reduction mechanism[1)]

As reduction tends to occur more easily in organic matter than in water, when the concentration of organic matter becomes high, the possibility of positive holes being used in the oxidative reactions with organic matter increases, thus reducing the rate of carrier recombination. It is believed that, under conditions in which positive holes are sufficiently consumed, the process of electrons transferring to oxygen molecules on the reduction side determines the reaction speed of the entire photocatalytic reaction. In other words, by enabling easier transfer of electrons to oxygen molecules, the efficiency of photocatalytic reactions can be improved. This can be achieved by allowing titanium oxide to carry a metal as a support.

2. Titanium oxide photocatalyst TB 6731

2-1. Structure of TB 6731

The titanium oxide powder used in the TB 6731 consists of extremely small nanosize particles with a very large specific surface area. In addition, by incorporating silver as a support, it inhibits the recombination of carriers and improves the photocatalytic efficiency. By incorporating silver as a support, the silver's intrinsic antibacterial characteristic can be added to the titanium oxide powder, thus providing an antibacterial effect even without light.

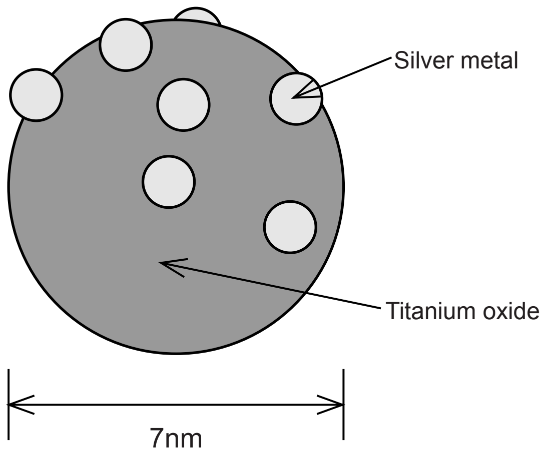

Fig. 6 Structure of TB 6731[3)]

2-2. Oxidation potentials of various oxidants

Table 2 shows the oxidation potentials of commonly used oxidants. The higher the oxidation potential, the greater the decomposing capability of the material.

Table 2 Oxidation potentials of various oxidants

Oxidants	Oxidation potential (V)
• OH (hydroxy radical)	2.80
O_3 (ozone)	2.07
H_2O_2 (hydrogen peroxide)	1.77
ClO_2 (hypochlorous acid)	1.49
Cl (chlorine)	1.36

2-3. Features of TB 6731

(1) As the surfaces of photocatalytic particles are allowed to carry silver metal as a support, higher photocatalytic action is achieved. When a

photocatalyst is exposed to ultraviolet rays, electrons and positive holes are produced and generate catalytic action; however, electrons and positive holes can recombine very easily. When photocatalytic particles are allowed to carry silver, electrons are drawn to the silver. This inhibits the recombination of electrons and positive holes, thereby ensuring the stable formation for emitting radicals more effectively than a photocatalyst without silver.

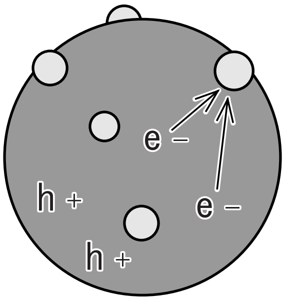

Fig. 7 Electron transfer model of TB 7631

(2) The synergetic effect of photocatalyst and silver produces various additional functions.

1) Antibacterial action and detoxication action

While titanium oxide has a photocatalytic effect only when it is irradiated with ultraviolet rays, the TB 6731 has excellent antibacterial effects even without ultraviolet rays due to the function of the silver. Furthermore, when ultraviolet rays are irradiated, the TB 6731 can decompose the remains of dead bacteria.

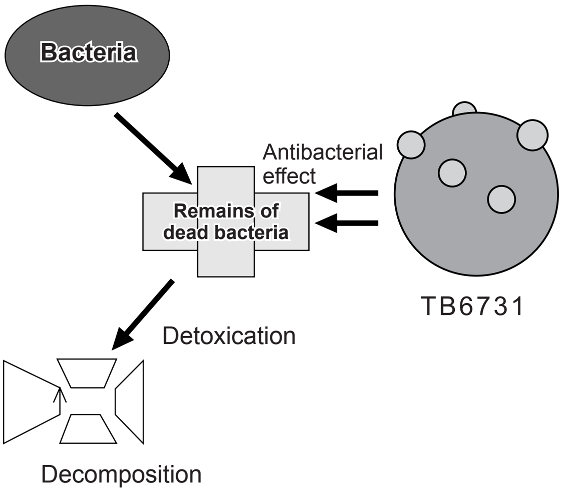

Fig. 8 Antibacterial action and detoxication action

2) Excellent deodorizing effect

Due to the silver-carrying titanium oxide, the TB 6731 inhibits the recombination of electrons and positive holes, thus providing an enhanced photocatalytic effect. It also produces a noticeable difference in deodorizing performance compared to titanium oxide without silver.

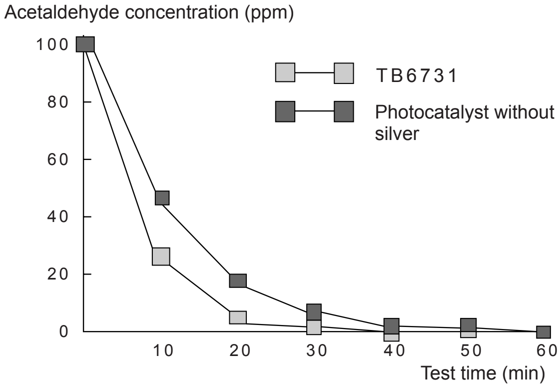

Fig. 9 Deodorizing Effect of TB 6731[3)]

Test conditions

Each photocatalyst powder sample weighing 0.1 g was spread on a 90-mm-diameter petri dish and placed in a container with a capacity of 5 L. The samples were irradiated with a 1 mW/cm^2 black light, and the concentration of acetaldehyde in each sample was measured using a gas chromatograph at predetermined time intervals.

3. Antibacterial effect of TB 6731

The TB 6731's antibacterial performance is confirmed against representative bacteria that are causing concern in the medical and food fields, as well as against tubercle bacillus and influenza virus, which cause droplet infection.

3-1. Effect against bacteria

If the measured Minimum Inhibitory Concentration (MIC), which is the antibacterial performance standard established by the Society of Industrial Technology for Antimicrobial Articles (SIAA) in Japan, is 800 μg/ml or less, the material is certified to have an antibacterial effect, which means antibacterial agent. The measured MIC values for representative bacteria are shown in Table 3.

Table 3 Minimum Inhibitory Concentration (MIC) for bacteria[3)]

Sample bacteria	MIC	Testing organizations
Staphylococcus aureus MCMR9901	200	*1
Preudomonas aeruginosa NEPA0015	200	*1
Pseudomonas putida	100	*1
Burkholderia cepacia NEPC0001	200	*1
Serratia marcescens NESM0002	200	*1
Echerichia coli ENEC001	100	*1
Salmonella typhimurium	100	*1
Listeria monocytogenes VTU206	200	*2

Testing organizations
*1: Microbiology Laboratory, Faculty of Pharmacy, Meijo University
*2: Japan Food Research Laboratories

3-2. Effect against fungi

The TB 6731's effect against fungi is shown in Table 4.

Table 4 Minimum Inhibitory Concentration (MIC) of Fungi[3)]

Sample fungus	MIC	Testing organizations
Candida albicans	12.5	*1
Aspergillus fumigatus	100	*1
Aspergillus flavus	100	*1
Aspergillus niger	50	*1
Penicillium citrinum IFO6352	100	*2
Cladosporium cladosporiodes IFO6348	100	*2
Chaetomium globosum IFO6347	100	*2

Testing organizations
*1: Microbiology Laboratory, Faculty of Pharmacy, Meijo University
*2: Japan Food Research Laboratories

About the Minimum Inhibitory Concentration (MIC)

This method is used for evaluation of the antibacterial performance of inorganic and organic antibacterial agents that do not dissolve easily. The cultured-bacteria count is adjusted between 1.0 x 10^4/ml and 5.0 × 10^4/ml. To a culture medium sterilized by high-pressure steam, a bacterial sample, the reference amount of which is set as 100 μg/ml, is gradually added in an amount either twice or one-half of the reference amount. Then, 0.1 ml of inoculum organism broth is added to the prepared culture medium. After 24 hours of culturing, the growth of the test bacteria is checked with the naked eye, and the minimum concentration of the sample with no recognizable bacterial growth is determined as the minimum inhibitory concentration.

3-3. Effect against tubercle bacillus

The tubercle bacillus has a thick cell membrane, so strong agents or ultraviolet rays are normally used for disinfection and sterilization. The tests conducted at The Research Institute of Tuberculosis verified that the TB 6731 was also effective against tubercle bacillus while being gentle to the human body.

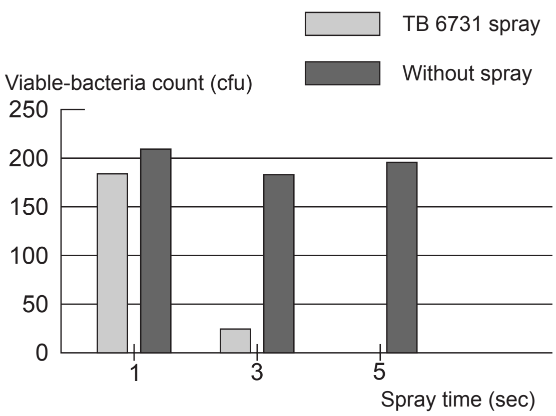

Fig. 10 Effect against H37Rv[3)]

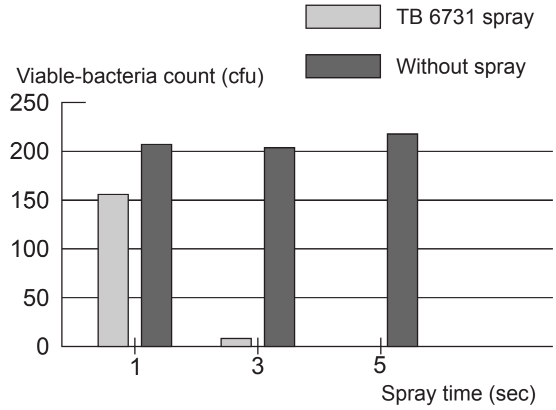

Fig. 11 Effect against M. Avium[3)]

Test method

Each culture medium was sprayed with the TB 6731 for a specified time, and the developing colony was counted after three weeks.

* cfu (colony forming unit) = units of colonies formed in a 1-ml sample
Report presented at the 47th meeting of The Japan Society of Clinical Pathology held on November 4, 2000
Testing organization: The Research Institute of Tuberculosis, Japan Anti-Tuberculosis Association

3-4. Effect against influenza viruses

The TB 6731 was originally found to be effective in inactivating influenza virus by the Kitasato Research Center of Environmental Sciences.

Table 5 Effect against Influenza Viruses[3)]

	Treated with TB 6731			Untreated		
No	1	2	3	1	2	3
HA value	*	*	*	1280	1280	1280

The numerical values are HA values (n = 3) measured after 24 hours of contact.

* mark: Indicates that hemagglutination (agglutination of red blood cells) was not observed.
Sample virus: Influenza virus AOPR8
Testing organization: Kitasato Research Center of Environmental Sciences
Test report (No. 130168-04)

Test method

The amount of antibodies in normal blood uninfected by viruses is approximately 2 μg/ml, which was defined as "HA value = 2." When blood is infected by a virus, hemagglutination occurs, causing antibodies to increase in number. The HA value of 1280 for the untreated samples means that the virus caused hemagglutination and increased the number of antibodies by 640 times. On the other hand, the samples treated with the TB 6731 inhibited hemagglutination by destroying the virus. The fact that the HA value remained the same as that of uninfected blood indicates that the TB 6731 has an influenza-virus inhibiting effect.

4. Representative antibacterial agents

Thus far, the TB 6731's antibacterial effect has been explained. The following describes representative antibacterial agents used in our daily lives.

4-1. Alcohols (ethanol)[2)]

"Alcohol" is a generic term used to refer to any compound in which hydrogen in the carbon hydride is replaced by (-OH). The antibacterial effect of alcohol becomes higher as the carbon number increases, but the number of carbon chains that exhibit the highest activity varies depending on the target bacterial strain.

The principle of the sterilizing and growth-inhibiting mechanism is the same in all alcohols. Alcohols prevent microbial bacteria growth by promoting albuminoid degeneration, dissolving fat and inhibiting enzymatic activity. The bactericidal action of alcohols is affected by water. Ethanol provides the highest bactericidal effect when it is a 70% to 80% aqueous solution. The bactericidal action of 100% ethanol becomes lower.

When the ethanol concentration exceeds 1%, bacterial growth is hindered. When the concentration is approximately 8%, the growth of microorganisms other than yeast is inhibited. When it exceeds 30%, a bactericidal effect is exhibited.

Table 6 Alcohols' bactericidal strengths against food-poisoning bacteria and various microorganisms[2)]

Sensitivity	High (30%)	Slightly high (40%)	Moderate (50%)	Low (70% and up)	None
Food - poisoning bacteria	Vibrio parahaemolyticus, salmonella, Escherichia coli, campyrobacter	Staphylococcus aureus			Spores (Bacillus cereus, botulinus bacillus, Welch bacillus Clostridium perfringen)
Other micro-organisms	Lipophilic (AIDS, herpes, vaccination, etc.), gram-negative bacteria	Gram-positive bacteria (listeria, lactic-acid bacilli, etc.), barm, algae	adenovirus, rotavirus, fungus spores	Hydrophilic viruses, picornavirus (polio, rhinovirus), parvovirus	Viroid, prion

Ethanol has a high bactericidal effect against gram-negative bacteria, but has no effect on spores. Ethanol has the following drawbacks for use as an antibacterial agent.

(a) Being volatile, it evaporates quickly. Therefore, the effect does not last for an extended period.
(b) Ethanol's bactericidal effect decreases at low temperatures.

4-2. Stabilized chlorine dioxide[2)]

Chlorine dioxide is a yellowish or reddish-yellowish vapor with a pungent odor similar to that of chlorine or ozone at normal temperature. Although chlorine dioxide has high oxidative power, it is difficult to store. Because chlorine dioxide is thermally unstable, explosive, and corrosive, its applications have been limited. The bactericidal action of chlorine dioxide is approximately the same as that of chlorine, but chlorine dioxide is less effective against spores. Chlorine dioxide is suitable for treating wastewater with a high quantity of organic substances.

Stabilized chlorine dioxide is made by stabilizing a large amount (50 to 150 g/l) of chlorine dioxide, which is highly active due to its high oxidative power, in pure water. It has been developed for safe, small-quantity use in diverse array of applications.

Stabilized chlorine dioxide provides its bactericidal effect in the following way. Chlorine oxide that breaks free from the stabilized chlorine dioxide reacts with organic matter such as bacteria, and produces hypochlorous molecules and oxygen ions. The hypochlorous molecules penetrate the cell membranes of bacteria and react with metabolic enzymes, while the oxygen ions trigger albuminoid degeneration in bacteria.

Table 7 Bactericidal rates of stabilized chlorine dioxide for various organisms[2)]

Chlorine dioxide concentration		50ppm		400ppm	4000ppm
Microorganism	Exposure time	1 min	60 min	1 min	1 min
Salmonella typhimurium		None	Effectiveness observed	99.998	99.998
Escherichia coli		Effectiveness observed	99.999	99.998	99.998
Pseudomonas aeruginosa		Effectiveness observed	99.999	99.999	99.999
Staphylococcus aureus		None	98.95	99.998	99.998
Streptococcus		98.54	98.988	99.51	99.998
Bacillosis bacillus		98.21	98.06	99.10	-
Clostridium		Effectiveness observed	Effectiveness observed	99.83	99.99
Mold		None	97.00	98.10	99.87

4-3. Hinokitiol[2)]

Hinokitiol is a rare natural tropolone with a seven-membered ring, and is also called β-thujaplicin. Hinokitiol easily forms complexes with metal ions. The tendency to form complexes with iron ions is particularly high. Depending on the ratio of concentration, the color of the substance varies widely, from pale yellow to green and auburn.

Hinokitiol's bactericidal spectrum is very wide, extending beyond that of ordinary bacteria strains to include spirochaeta, fungi, and basidiomycete. It is particularly effective against fungi and basidiomycete, and develops virtually no resistant strains. Hinokitiol's bactericidal activity is not dependent on the pH level. Although the details of its antibacterial mechanism are not yet clear, hinokitiol's action is believed to center on the modification of protein in bacteria. In addition, as hinokitiol easily forms inner complex salt with metal ions, it is believed that it has strong effect on oxidation-reduction enzymes having a metal group, such as cytochrome. Hinokitiol's powerful inhibitory action against protease is also recognized, and is suspected to be a factor contributing to hinokitiol's bactericidal characteristics. Table 8 shows the results of an antibacterial characteristic test on hinokitiol.

Table 8 Results of the hinokitiol antibacterial characteristic test[2)]

Bacterial strain	MIC	Bacterial strain	MIC
Micrococcus		Fungus	
Staphylococcus aureus	100	Yeast	12.5
Streptococcus faecalis	100	Asoergillus oryzae	25
Bacillus		Helicobasidium monpa	50
Escherichia coli	100	Valsa ceratosperma	50
Pseudomonas aeruginosa	200	Botrytis cimerea	100
Serratia marcescens	100	Basidiomycete	
Proteus mirabilis	100	Tyromyces palustris	25
Klebsiella pneumoniae	100	Coriolus versicolar	25
Bacillus subtilis	50		
Welch bacillus Clostridium perfringen	100		

4-4. Silver-containing inorganic antibacterial agents[2)]

Most silver-containing bactericidal agents do not use silver metal directly, but rather use inorganic carriers incorporated silver as a support. Commonly used carriers are inorganic compounds such as zeolite, silica gel, glass, apatite, titania, and zirconium phosphate. Silver-containing inorganic antibacterial agents do no provide an instant bactericidal effect as in the case of organic chemicals, and the effect is not seen for several hours. Although the bactericidal mechanism is not clearly understood, one theory speculates that a very small quantity of silver ions enters bacteria to inhibit microorganisms' respiratory system, electron transport system, and enzymes, while another theory is that silver ions change oxygen or dissolved oxygen in water to active oxygen in order to achieve a bactericidal effect.

5. Conclusion

Due to its wide range of functions, titanium oxide photocatalyst is rapidly finding applications in various fields. Titanium oxide photocatalyst is used in deodorizers and antibacterial agents as described in this article, as well as in products featuring anti-stain, hydrophilic, anti-fog, and harmful substance removal functions. Titanium oxide photocatalyst is expected to be used in various products primarily to increase their environmental friendliness. It is our hope that the TB 6731's superb performance will contribute to environmental preservation.

Referenced Documents

1) Mechanism of photocatalyst
(Published by Nippon Jitsugyo Publishing Co., Ltd.)
2) New development of sterilization and antibacterial technologies
(Published by Toray Research Center)
3) Technical Document: TB6731

Sakae Amemiya
External Products Development Division
Development Department

Research Laboratory
Three Bond Co., Ltd.

ThreeBond TECHNICAL NEWS
THREE BOND CO., LTD.
1456 Hazama-cho, Hachioji-shi, Tokyo 193-8533, Japan
Tel: 81-426-61-1333