

Antibacterial, Deodorizing, and UV Absorbing Materials Obtained with Zinc Oxide (ZnO) Coated Fabrics

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ABSTRACT: Ultra fine particle zinc oxide from Sumitomo Cement Co. is a multi-functional material with antibacterial, deodorizing, and UV absorbing properties. The company has dispersed ultra fine zinc oxide into various types of vehicles that are classified into water-based and organic solvent-based types.

Fabrics and films that are coated with the dispersion liquids have antibacterial, deodorizing, and UV absorbing properties; furthermore, they have high durability, transparency, and they are safe.

1. INTRODUCTION

IT IS A well known fact that zinc oxide has been used as a white pigment because it possesses the property of UV absorption. It has been used in the field of cosmetics because it has astringent and sterilizing functions.

Sumitomo Cement Co. has developed a transparent zinc oxide that has been deprived of pigment property by a unique process of turning zinc oxide into ultra fine particles—below 150 AU. The zinc oxide developed has a particle diameter much smaller and a surface area larger than that of the conventional type, which provides superior characteristics in transparency, UV absorption, antibacterial/deodorization, and odor removal.

A dispersion liquid has been developed, which uses ultra fine particle zinc oxide. The material, called UFP-ZnO in this paper, is nearly monodispersed; it can be applied in such forms as fabrication agents, printing inks, and paints.

In this paper some actual applications will be described that involve the application of the characteristics of zinc oxide (ultra fine particle) with emphasis on fiber fabrication agents.

2. CHARACTERISTICS OF UFP-ZnO

UFP-ZnO is a voluminous white powder whose primary particle diameter is between 50 and 150 Å, specific surface area is 30 to 70 m²/g, and bulk density is 0.40. UFP-ZnO, being a very fine powder, has the following features that conventional zinc oxides in current use as a white pigment do not provide.

2.1 Transparency and UV Absorption Property

Light that hits a substance can be classified into reflection light, absorption light and transmittance light. For materials to be transparent, it is required that they give little reflection, absorb little light, and create no light scattering in the visible light spectrum. For a substance to be free of light absorption in the visible light spectrum, it is necessary that the short wave absorption edge be in the UV spectrum and that the long wave absorption edge be in the infrared spectrum. The absorption edge on the short wave side is defined by an energy gap between the material's valence band and conduction band and that on the long wave side by plasma frequency. Zinc oxide has an energy gap of 3.2 eV, and it has an absorption point at approximately 380 nm, which means that the UV spectrum area of zinc oxide below 380 nm has an absorption property to make it opaque; the plasma frequency for dielectric materials such as zinc oxide is low and transparent in the visible and infrared spectrum.

It is already known, however, that the light scattering of a substance is affected by the particle diameter of the powder and the wave length of incident light. Powder with a particle diameter of 1/2 that of the wave length of light generally causes the highest level of light scattering; when the particle diameter becomes shorter than the wave length, scattering is substantially reduced at a rate proportional to the sixth power of the particle diameter. The primary particle diameter of UFP-ZnO is short enough compared to its light wave length at 50 to 150 Å to make it possible to realize transparency without causing light scattering.

Usually, when material becomes very fine, its particles tend to be cohesive, which makes dispersion difficult, but UFP-ZnO developed by the company has an excellent dispersion property; it has been developed and is manufactured through a unique production process that prevents cohesion of the particles at the lowest level. The dispersion technology in place at the com-

pany allows dispersion to maintain an average particle dispersion range of 50 to 300 Å, which allows the creation of transparent films of zinc oxide.

Shown in Figure 1 is the transmittance rate when UFP-ZnO is dispersed in acrylic resin and coated in the thickness of about 4 microns; 380 nm is a dividing point, indicating absorption in the UV spectrum and transparency in the visible light spectrum.

2.2 Antibacteria and Deodorization

Metallic ion and metallic compound have some degree of sterilizing effect where it is considered that part of the oxygen in the air or water is turned into active oxygen by way of catalysis by the metallic ion, thereby, dissolving organic substance to create sterilizing effects.

Generally speaking, the sterilizing effect of metallic ion and metallic compounds is not very strong as compared with other sterilizing agents, but UFP-ZnO has a strong sterilizing effect with a very large surface area and an active property; in addition, it has a deodorizing effect resulting from germ growth suppression based on sterilization.

Shown in Table 1 are test results of antibacterial properties of UFP-ZnO. For comparison purposes, the test data of antibacterial properties of ordinary zinc oxide and silver metal type tested at the same time indicate that UFP-ZnO has a very strong sterilizing effect on *Staphylococcus aureus*, *Bacillus*

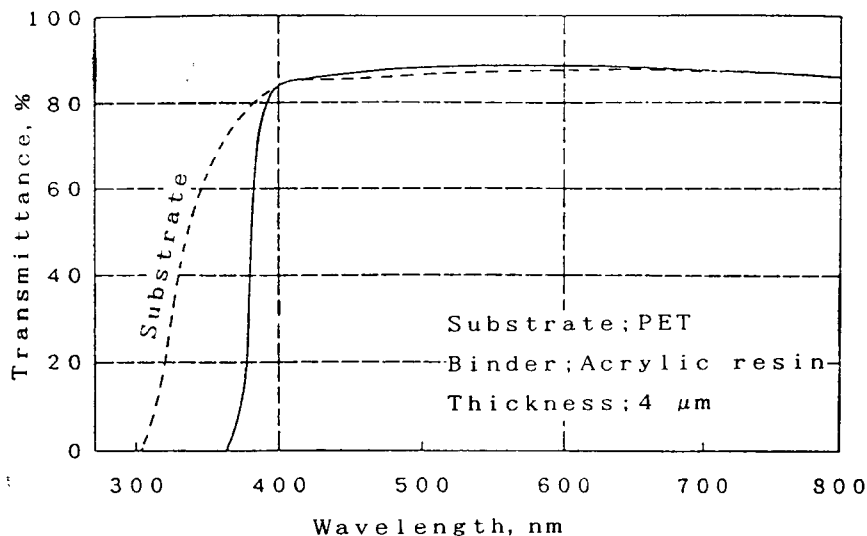


FIGURE 1. Transmittance of UFP-ZnO dispersed in acrylic resin.

Table 1. Test results of antibacterial properties of UFP-ZnO.

	Minimum Interruption Concentration, ppm				
	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>	<i>Escherichia coli</i>	<i>Salmonella typhimurium</i>	<i>Klebsiella pneumoniae</i> MRSA
UFP-ZnO	125	62	500	500	125
Ordinary ZnO	1000	125	>2000	>2000	500
Silver metal	1000	1000	500	500	1000
					160*
					Non-measured
					Non-measured

*Shake-flask method.

subtilis, *Escherichia coli*, *Salmonella typhimurium*, *Klebsiella pneumoniae* and MRSA.

2.3 Deodorization

UFP-ZnO has a large surface area that functions as a strong gas absorbent that absorbs odor ingredients fast and effectively. Zinc oxide is a solid base that shows excellent deodorizing performance for organic acid through not only physical absorption but also chemical absorption functions.

Given in Figure 2 is the deodorizing test result of isovaleric acid (fatty acid believed to cause body odor) [1]. For comparison purposes, granular activated carbon was also tested; UFP-ZnO works faster as a deodorizer.

2.4 Durability

Such organic UV absorbent agents as benzophenone and benzotriazole have been typically used as UV absorbent agents and such antibacterial agents as quaternary ammonium salt compounds, organic acid, and amino acid have been used. All of these agents are organic materials; therefore, they

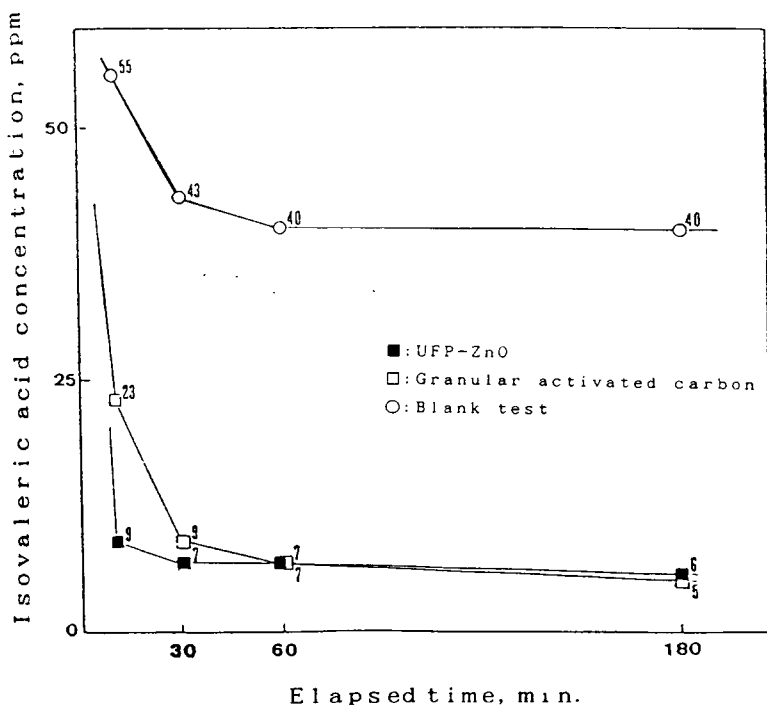


FIGURE 2. Deodorant test of UFP-ZnO for isovaleric acid.

Table 2. Toxicity test.

Acute toxicity*	LD ₅₀ value > 2000 mg/kg in rats for oral administration
Acute toxicity**	LD ₅₀ value > 2000 mg/kg in rats for cutaneous administration
Mutagenicity test*	Negative in Ames test
Cutaneous irritation and corrosion**	Non-irritation and corrosion in rabbits

*Tested at The Japan Food Analysis Center Foundation.
**Tested at EVIC-CEBA (France).

could be easily dissolved by light and heat, which did not allow them to be used for applications in which they become heated or exposed to light on production lines or in usage. Zinc oxide is, however, an inorganic material, which is stable to heat and light making it possible to maintain its functional property almost permanently. There are other types of inorganic antibacterial agents in use that have a silver ion and copper ion added on to zeolite or silica gel, but silver and copper turn black or yellow from oxidation, whereas zinc oxide does not change in color.

2.5 Safety

Zinc oxide is non-toxic to the human body; it has a high level of safety in its use as compared with UV absorbent or antibacterial agents of an organic type.

Given in Table 2 is a toxicity test result. UFP-ZnO has been confirmed for its safety in use by official institutions with regard to acute toxicity in rats, cutaneous irritation and corrosion in rabbits, and mutagenicity test.

3. APPLICATIONS OF UFP-ZnO

UFP-ZnO has been used for sun screen cosmetics as a UV absorbent agent in such a way that it is directly mixed with cosmetics ingredients in its powder form. The other method used involves dispersion of UFP-ZnO into vehicles to form a coating film; this method is more widely used as it permits the ultra fine particle function to be utilized to its fullest degree.

The company has UFP-ZnO dispersed into various types of vehicles and dispersion liquids of 50 to 300 Å in particle diameter for coating applications.

3.1 Varieties and Features of Dispersion Liquids

Dispersion liquids of UFP-ZnO are roughly classified into water-based and organic solvent-based types, which are further broken down into non-binder and binder types; they are shown in Table 3.

The ZR coat liquid has been developed mainly for film coating and printing applications; it is used for UV absorption, prevention of color fading, and improvement in weather resistance.

The ZS coat liquid is a matter that has been deprived of binder from ZR coat liquid; the binder can be added later by users depending on needs in applications, which makes its usage more flexible.

The ZE coat liquid is based on a water-based binder; it is chiefly used for padding and coating in fiber applications.

The ZW coat liquid is a water-dispersed liquid with no binder added; it can be used as an additive and can also be applied to a wider range of water-based binders and emulsion resins.

Shown in Figure 3 is the particle size distribution of ZW-103 as an example of the dispersion property of a dispersion liquid. The liquid, ZW-103, is provided as a dispersion liquid with an average dispersion particle diameter of 113 Å. The dispersion property can be kept unchanged for a long period of time; a test made two months after the last test proved that there was no change in the particle size distribution.

3.2 Applications to Fibers and Fabrics [2]

Surface treatment of fibers and fabrics with these coating materials provides antibacterial, deodorization, and UV absorbing functions. When the coating material is applied to the surface of fabrics with printed patterns, it serves as an agent that prevents color fading.

The water-based ZE coat liquid or the ZW coat liquid should be used for fibers and fabrics. As mentioned before, the ZE coat liquid with binder added can be used as it is, whereas the ZW coating liquid, which does not

Table 3. Varieties of UFP-ZnO dispersion liquids.

Items	Liquid Form	Type	Solvent	Non-Volatile Function %	Viscosity cp
ZR-100	One-liquid	Lacquer	Toluene	40	15-25
ZR-130	One-liquid	Lacquer	Toluene	30	50-100
ZR-133	One-liquid	Lacquer	Toluene	30	50-100
ZR-210	Two-liquid	Thermosetting	Toluene	40	10-20
ZR-213	Two-liquid	Thermosetting	Toluene	40	10-20
ZS-300	One-liquid	Binderless	Toluene	32	1-3
ZS-303	One-liquid	Binderless	Toluene	32	1-3
ZE-110	Two-liquid	Harden agent	Water	30	15-30
ZE-113	Two-liquid	Harden agent	Water	30	15-30
ZW-100	One-liquid	Binderless	Water	30	2-10
ZW-103	One-liquid	Binderless	Water	30	2-10

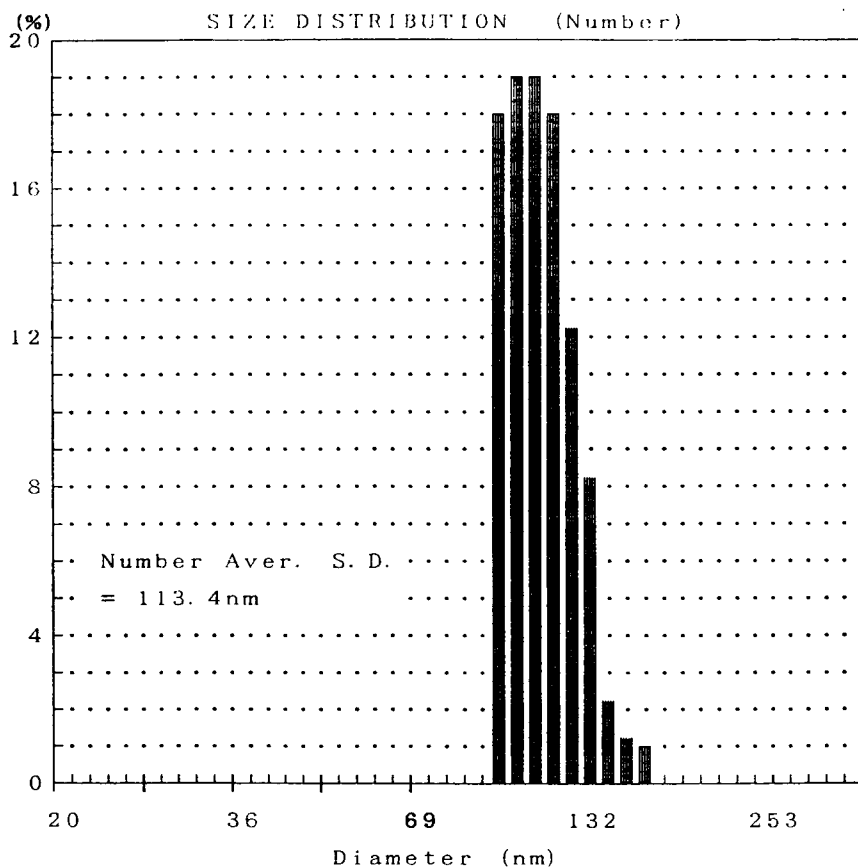


FIGURE 3. Size distribution of ZW-103.

contain binders, is to be used with an appropriate binder added for consideration of laundry resistance and better feelings to the skin. These liquids must be diluted to appropriate levels of density and applied to natural fibers such as cotton, synthetic fibers such as polyester and acrylate, and blended fabrics through the padding method (i.e. resin processing whereby fabrics are soaked in a liquid, the excess liquid is evenly removed, and the fabric is dried), the coating method and the like.

Shown in Table 4 is the antibacterial function of a fabric that is padding treated with ZE-110. The test followed a germ-level test method (based on numbers in which *Staphylococcus aureus* was used) that was specified by The Textile Products Hygienic Fabrication Association; it was conducted at The Japan Spun Product Inspection Institute.

The test data given in Table 4 are a variation difference that is expressed in a difference in the number of germs calculated as a logarithmic value. The value given in Table 4 is a "difference value" that is defined as follows:

$$\text{difference value} = \log \frac{\bar{B}}{\bar{A}} - \log \frac{\bar{C}}{\bar{A}}$$

where \bar{A} is the average number of germs measured immediately after inoculating with germ of non-padded fabrics. \bar{B} is the average number of germs measured after 18 hours cultivation of non-padded fabrics. \bar{C} is the average number of germs measured after 18 hours cultivation of padding treated fabrics. When the difference value is more than 1.6, fabrics are acknowledged germ-resistant by The Textile Products Hygienic Fabrication Association in Japan.

The fabric that is padding treated with ZE-110 at additive rate of 2.5 wt% and 10 wt% gets fewer germ numbers at the level of $1/10^{5.6}$ and $1/10^{3.9}$ as compared with non-treated fabric, which is a good proof of enough antibacterial effect being given. Another test result showed that there was no change in the antibacterial property after ten launderings, which is another proof of good laundry resistance.

In Figure 4, the deodorizing effect on the cotton knit fabric is given, and in the figure it is seen that the ZE liquid coated fabric has an enhanced function of ammonium gas absorption as compared with the non-treated fabric.

Shown in Figure 5 is the spectral transmittance rate of the fabric that is padding treated with the additive rates of ZE-110 varied, which indicates a remarkably improved UV absorbing property as compared with the non-treated fabric. In Figure 6, a post-laundry spectral transmittance rate is given; it is to be noted that UV absorption is not deteriorated by laundering and that durability is kept well.

*Table 4. Antibacterial test of a fabric padding treated with ZE-110.
Germ-level test method based on numbers of Staphylococcus aureus.*

Additive Rate of ZW-110 in Padding Liquid (wt%)	Cotton Knit		Polyester	
	Before Laundry	After Laundry (10 times)	Before Laundry	After Laundry (10 times)
Non-treated	0	—	0	—
2.5	3.9	5.6	4.0	4.3
10.0	5.6	3.9	4.8	5.0

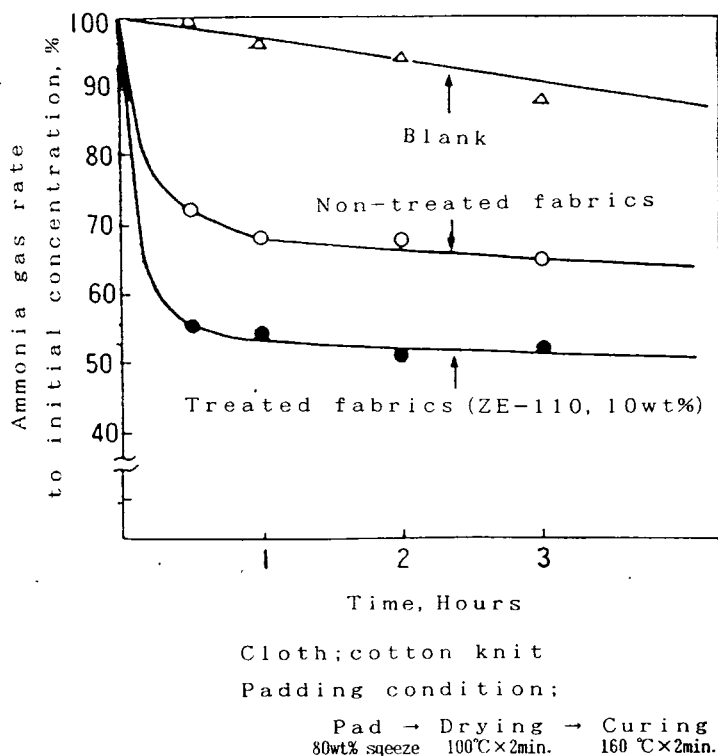


FIGURE 4. Deodorizing effect on cotton knit treated with ZE-110.

3.3 UV Absorbing Film [3]

Coating of the ZR coat liquid on PET film, OPP film, LDPE film, etc., can be made a UV absorbing film.

The spectral transmittance rate of ZR-100 that is coated on PET film on a reverse coater so that its coating thickness will be 4 microns after drying is identical to the one given earlier in Figure 1. As is clearly shown in Figure 1, the PET film coated with ZE-100 has a high level of transparency in the visible light spectrum, but becomes nearly opaque in the UV spectrum of below 380 nm.

Figure 7 shows the difference between the UV transmittance rate and the coating thickness of ZR-100 for UV rays of 380 and 365 nm. There are such organic UV absorbing materials as those linked with benzotriazole, benzophenone, and salicylic acid; however, because those materials do not have a property of good solubility in binders, which makes it difficult to apply a large volume, it is necessary to coat in a thickness of more than 20 microns

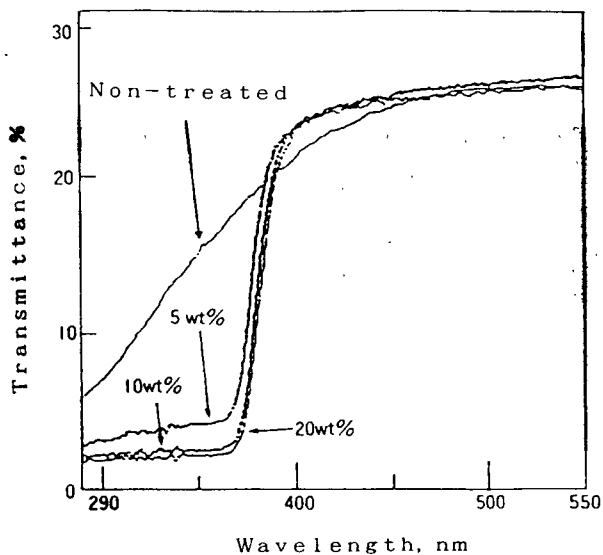
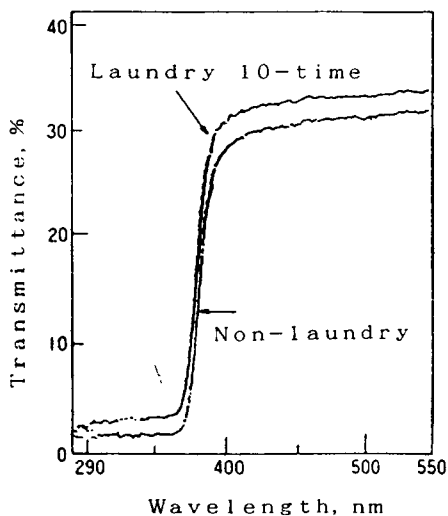


FIGURE 5. Transmittance of fabrics padding treated with ZE-110 at various addition rates of fabric padding.



Padding liquid; Added ZE-110 of 20wt%
 Laundry method; JIS L 0217 103
 Detergent; Monogen-Uni 2g/l content

FIGURE 6. Laundry resistance of fabrics padding treated with ZE-110.

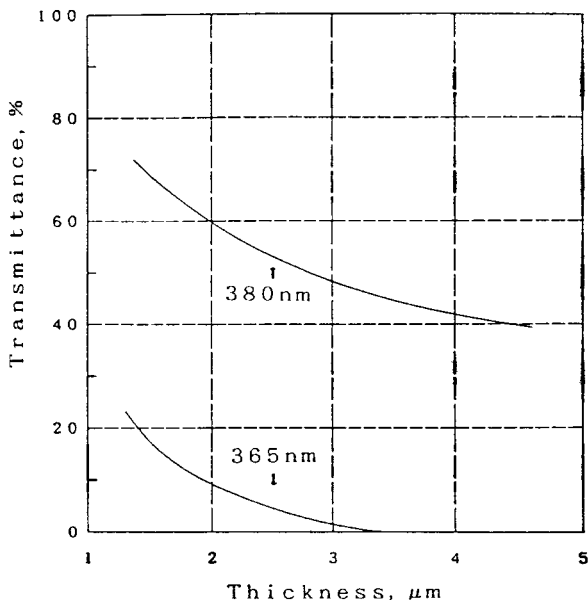


FIGURE 7. Relation of UV transmittance and film thickness of ZR-100.

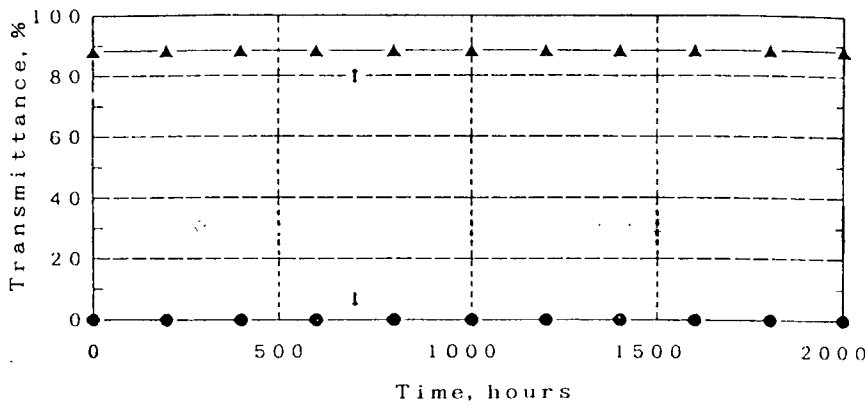
for UV absorption. The ZR coat liquid, on the other hand, performs an effective UV absorption with only a few micron-thick coating; therefore, it is best suited for printing applications such as gravure and reverse coater printing.

The advantages of using the ZR coat liquid include durability and good printability. Organic UV absorbing materials tend to dissolve, deteriorate, and bleed out from the coated layer, thereby, losing the effect. Zinc oxide, which is inorganic, does not deteriorate and its UV absorbing property can be maintained for a longer period of time.

Shown in Figure 8 is a test result of weather resistance by the open-flame sunshine weathermeter, which shows no change in transparency in the visible light spectrum and UV absorption property during a period of 2000 hours.

Coated film has an antibacterial property like fibers mentioned earlier; it can be used as an antibacterial and deodorizing film.

In Table 5, a test result of an antibacterial film is given. The test is made in such a way that a certain size of film sheet is put into a test liquid with a known number of germs and that the number of living germs is measured after a 24-hour preservation at 37°C. It is determined that the antibacterial effect is good at a sterilization rate above 26%. Coated film provided a high



Equipment; Open-flame sunshine carbon-arc type
Coating liquid; ZR-210,
Thickness; 5μm
Substrate; PET

FIGURE 8. Weathering test of UFP-ZnO coating film.

germ killing rate of 84.1% for *Klebsiella pneumoniae* and 68% for *Staphylococcus aureus*.

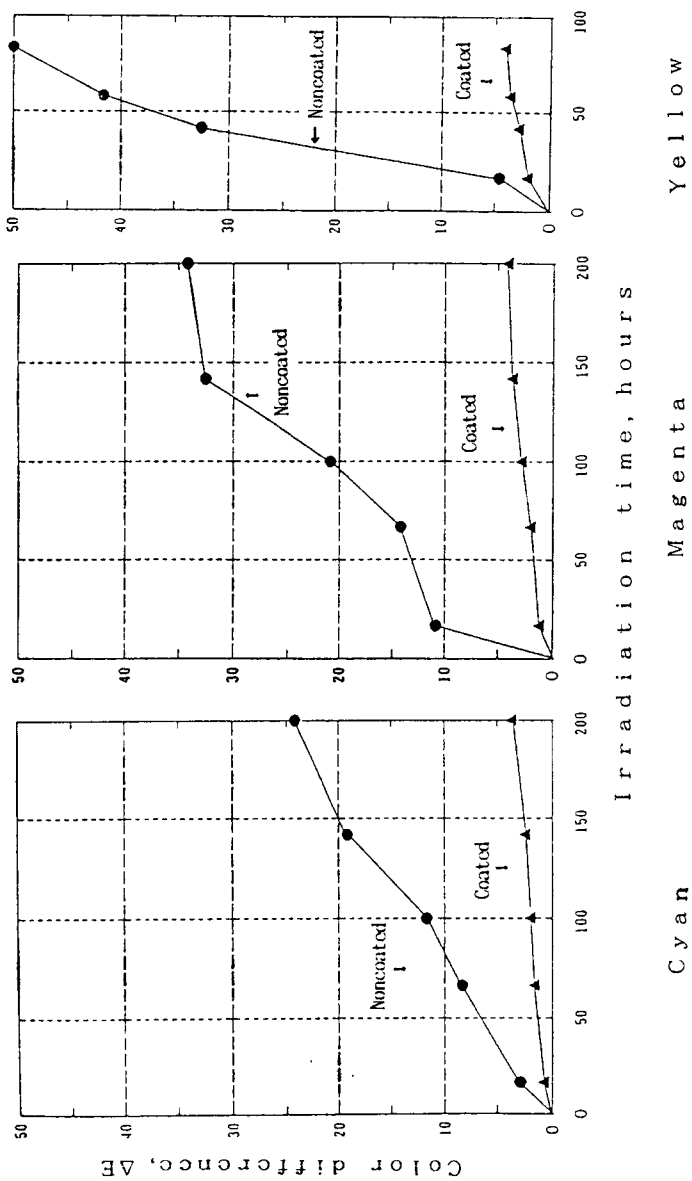
3.4 Overcoating for Color Fade Prevention

Attacking and color fading by UV light can be prevented by overcoating of ZR coat or ZE coat on top of plastics or printed materials; therefore, the liquids are used for prevention of yellowing on polycarbonate and color fading on advertisement and color posters.

In Figure 9, the effect of color fading prevention on cyan, magenta, and yellow is shown. Whereas color fading occurs by visible light and heat, which makes it impossible to control 100%, it is clearly shown that color fading is substantially controlled in comparison with the non-coated materials.

Table 5. Antibacterial test of coated film with ZR-100.

Germ for Test	Testing Film	Number of Living Germs Cell/ml	Germ Killing Rate %
<i>Klebsiella pneumoniae</i>	Non-coated PET	1.97 × 10 ⁶	84.1 <
	Coated PET	10 >	
<i>Staphylococcus aureus</i>	Non-coated PET	1.96 × 10 ⁶	68.0
	Coated PET	1.02 × 10 ²	



Method; JIS K 5400 6.2
Coating liquid; ZR-100
Thickness; 4μm
Substrate; High-quality paper

FIGURE 9. Fade test.

4. CONCLUSION

A description has been given of the material UFP-ZnO and its dispersion liquid as applied to fibers and film in terms of its antibacterial, deodorizing, and absorbing properties. In addition to the above mentioned applications, the following applications can be considered for UFP-ZnO:

- (1) Antibacterial property for non-woven cloth
- (2) Antibacterial and prevention of color fading properties for paper
- (3) Insect-proof film for agricultural applications
- (4) Food packaging film for antibacteria, and odor elimination
- (5) UV absorbing films on glass windows

We would like to take advantage of this opportunity to invite other applications outside of the above mentioned ones or suggestions so that we may expand our R&D activities to meet the needs of others. We look forward to receiving readers' responses.

REFERENCES

1. Saito, K. 1991. *Kakogijutu*, 26:652-655.
2. Saito, K. 1993. *Kakogijutu*, 28:232-235.
3. Saito, K. 1992. *Goseijushikogyo*, 39:83-85.