Light Emitting Diode

Hermetically Sealed LEDs and VOCs

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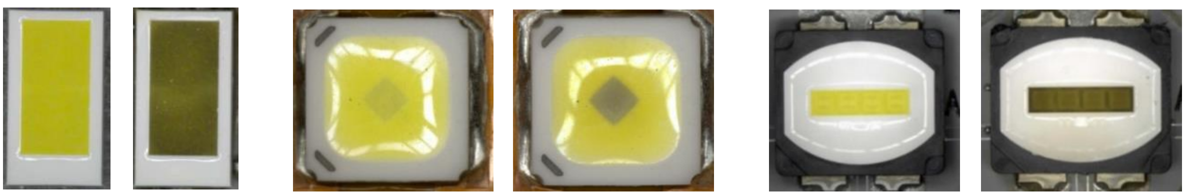
1. Overview

In outdoor light fixtures such as headlamps, street lights, and floodlights, there are cases where the fixture is hermetically-sealed in order to protect it from moisture/dust. Light fixture materials used around LEDs (surrounding materials) may outgas volatile components when they are exposed to heat and light, and if the LED is used in an environment where the light fixture is hermetically-sealed, the concentration of the outgassed components may become high and the LED can be adversely affected by the components. Some components outgassed from materials may contain volatile organic compounds (VOCs), some of which can react and discolor under the exposure to heat and light energy.

Figure 1 shows abnormal LEDs caused by the discoloration of VOCs. VOCs are more likely to affect an LED if the air circulation around the LED is poor inside the light fixture, especially when it is hermetically sealed. Thus, considerations are required when designing a hermetically-sealed light fixture.

This application note explains some adverse effects of VOCs on LEDs and how VOCs can affect them as well as preventive measures.



Part No. NC2W170B　　Part No. NFSW172　　Part No. NK4W093

Figure 1. Adverse Effect of VOCs on LEDs (Left: Before Discoloration; Right: After Discoloration)

2. VOCs

2.1 What are VOCs?

Volatile organic compounds (VOCs) are organic chemicals that can easily volatilize and turn into gas in the air. VOCs are generally found in glues, paints, and organic solvents (e.g. cleaning agents). As they can also be contained in additives in molded resins such as housings and gaskets etc., VOCs can be outgassed from solid materials as well.

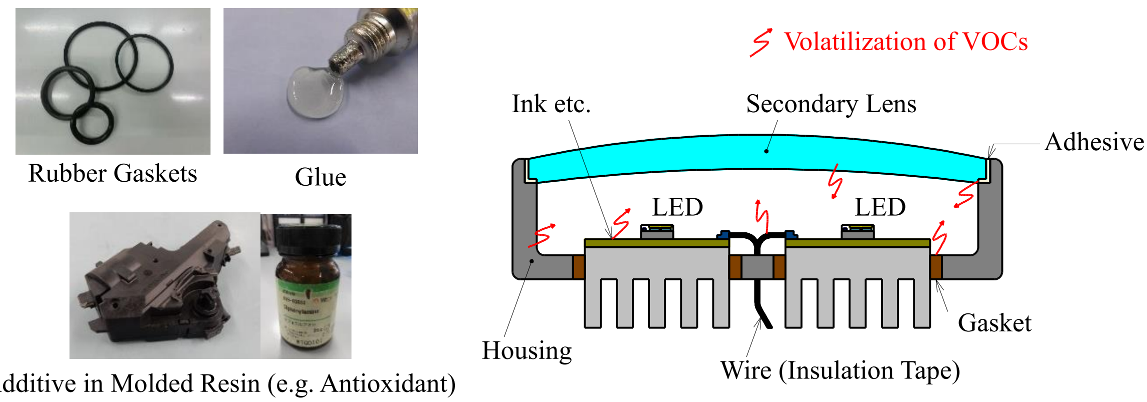


Figure 2. Examples of Surrounding Materials that may Release VOCs

VOCs can be classified as shown in Table 1 below. Note that VOCs in this document encompass all types of VOCs below.

Table 1. VOC Classification by Boiling Points

Abbreviation	Description	Boiling Point Range	Example Compounds
VVOC	Very Volatile Organic Compounds	<50°C	Acetaldehyde(C_2H_4O), Dichloromethane(CH_2Cl_2), Methane(CH_4), Formaldehyde(CH_2O)
VOC	Volatile Organic Compounds	50°C to 260°C	Ethanol(C_2H_5OH), Benzene(C_6H_6), Toluene(C_7H_8), Xylene(C_8H_{10})
SVOC	Semi Volatile Organic Compounds	260°C to 400°C	Diphenylamine($C_{12}H_{11}N$), Chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$),
POM	Particulate Organic Matter	≥400°C	PCB($C_{12}H_{10}$-nClN), Benzo[a]pyrene($C_{20}H_{12}$)

2.2 VOC Effects on LEDs

There are two reasons why VOCs have adverse effects on LEDs:

- -VOCs can permeate the inside of an LED and remain there.
- -VOCs can discolor when they are exposed to heat and light energy.

There are no direct changes in LED's components themselves in these phenomena; however, VOCs may change (discolor) after they enter an LED and can eventually have adverse effects on the LED's performance.

2.3 Permeation of VOCs into an LED and Remaining

Nichia uses materials suitable for intended applications/purposes in our LEDs. For LEDs' encapsulating resin, epoxy resin and silicone resin etc. are used.
In the case of LEDs intended for outdoor applications in which LEDs can be exposed to the outside air, epoxy resin is often used to prioritize gas barrier performance and mechanical strength; whereas for LEDs used in light fixtures/electronic devices where LEDs will not be exposed to the outside air, silicone resin is often used to prioritize LED's characteristics under high temperature and longer lifetime.
Silicone resin has good resistance to heat, photochemical reactions, and moisture; however, due to its gas permeability, it is more likely to allow outgassed components to permeate into an LED. Hence, VOCs that are volatilized from surrounding materials and turn into gas can pass through the silicone encapsulating resin and permeate the inside of an LED and remain (adhere) there.

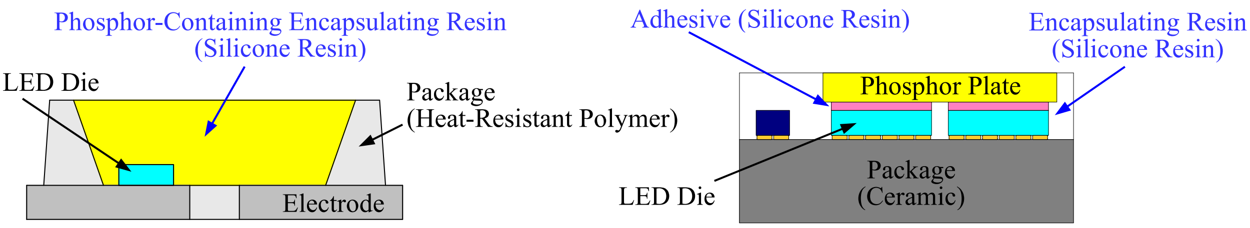


Figure 3. Examples of Silicone Resins Used in LED

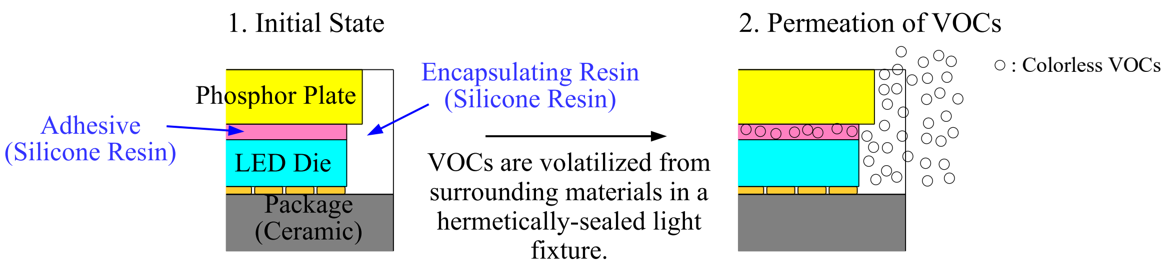


Figure 4. VOC Permeation

2.4 Discoloration of VOCs

When a VOC is exposed to light energy, photochemical reaction occurs in the VOC and the chemical bonds (molecule structure) change. Due to the change in the chemical bonds, the absorption spectrum also changes. Most organic compounds have their absorption spectra in the ultraviolet region and are colorless. However, once the chemical bonds change and hence the compound absorbs light in the visible region, the VOC will be colored and the transparency will decrease.

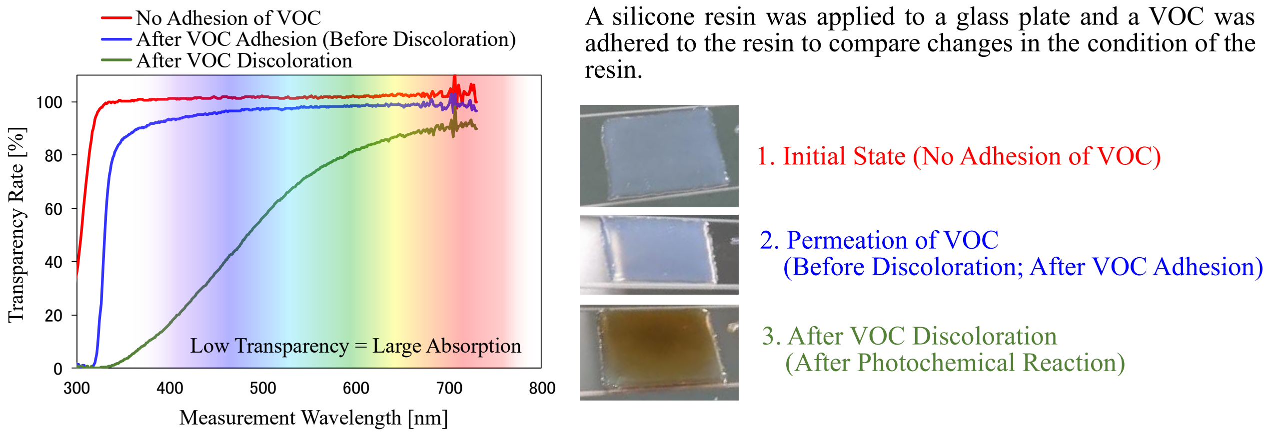


Figure 5. Transparency Change due to VOC Adhesion and Discoloration

If VOCs permeate the silicone resin and remain around the light emission area of the LED, they will be intensely exposed to light energy emitted from the LED die and discolor. As a result, it appears as if the light emission area is discolored, causing a decrease in the luminous flux and color shift in the LED.

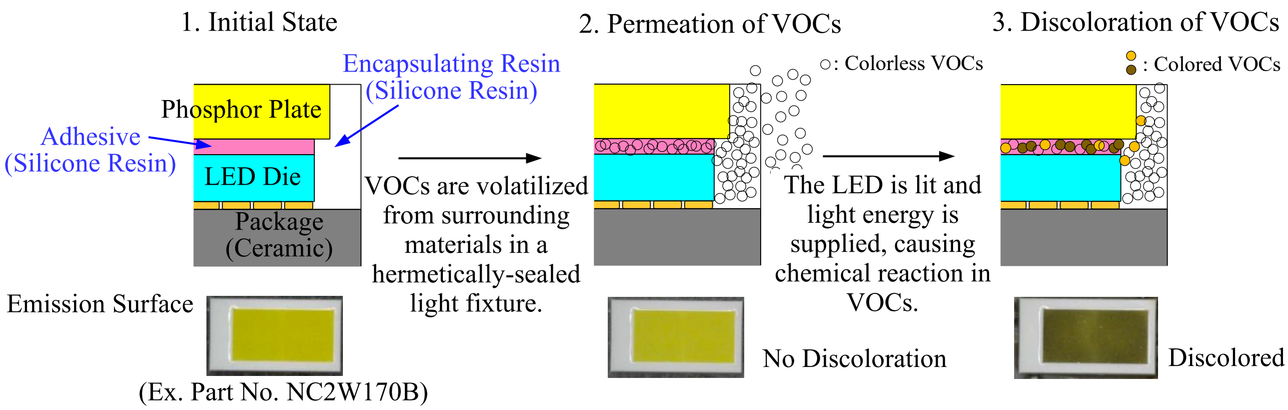


Figure 6. VOC Discoloration

3. Measures against VOCs

As an effective measure against VOCs, decreasing the VOC concentration around the LED is suggested.

3.1 Improve Air Circulation around the LED

One of the effective measures is to improve air circulation around the LED by creating air vent(s) near the LED to avoid a complete hermetic sealing of the light fixture. The larger the vent is, the better the air circulation becomes. If the air circulation is improved, the VOC concentration around the LED decreases, which creates an environment where discoloration of VOCs is less likely to occur. Note that even if the light fixture has air vent(s), there is a case where the VOC concentration around the LED does not decrease depending on the air flow inside the fixture. Thus, when the vent(s) is located near the LED, it is expected to be more effective.

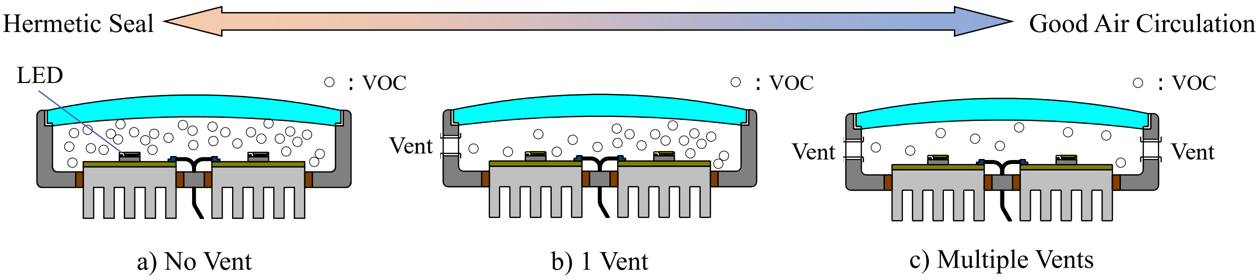


Figure7. Example of Preventive Measure (Ventilation)

3.2 Increase the Volume of the Light Fixture

It is more effective to have a large volume of a light fixture in order to decrease the VOC concentration around the LED. If the VOC concentration is low, the discoloration of VOCs is less likely to affect the LED (see Figure 13).

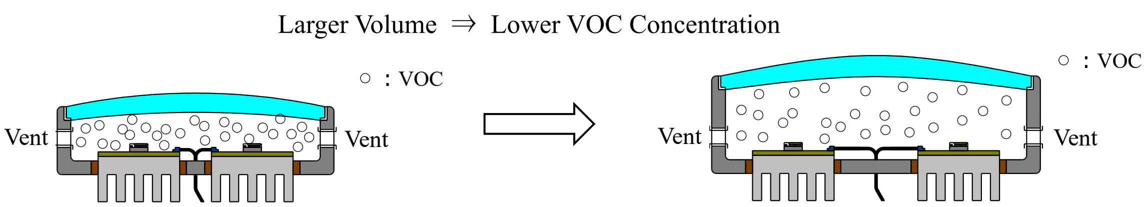


Figure 8. Preventive Measure (Increase the Volume of the Light Fixture)

3.3 Avoid Materials Susceptible to VOC Discoloration

Some materials used around LEDs may be susceptible to VOC discoloration.

-Rubber materials (synthetic, natural)
-Adhesive of Tapes, Glues
-Additives in the Resin (Antioxidants, Flame Retardants etc.)
-Cable Insulations (Sheaths)

There have been cases where an antioxidant and a flame retardant in molded resins caused discoloration. Thus, cautions are required for solid materials as well. How much the discoloration of VOCs from each material will affect LEDs can be examined by carrying out a comparison test. See the next chapter 4. Test Method to Examine VOC Discoloration for reference.

Tables 2 and 3 show the examples of substances tested at Nichia to examine VOC discoloration. The effects of VOC discoloration can vary depending on the VOC concentration; thus, there may be no effect even if the substance with the test result of “discolored” is contained in the material to be used in the light fixture. However, Nichia recommends avoiding materials containing these substances to reduce potential risks.

It should be noted that this document does not identify or present all materials that may affect LEDs. Besides those listed in the tables, there are substances that can outgas VOCs and be the source of VOC discoloration. When selecting/changing materials of a light fixture, please optimize the materials by choosing those that are less likely to outgas VOCs and confirm that they will not affect the LED’s characteristics prior to use. Note that the information provided in the tables is merely Nichia’s test results and does not guarantee that the same results will be obtained, as these substances may affect an LED when combined with different substance(s) etc.

Table 2. List of Substances with which VOC Discoloration was Confirmed (Additives in Resin)

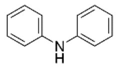
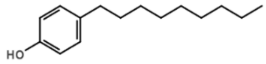
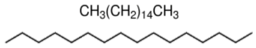
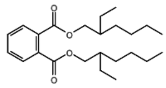
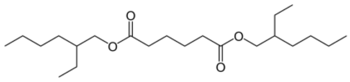
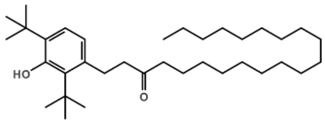
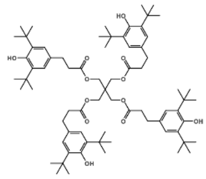
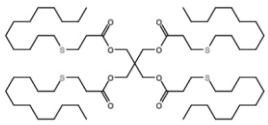
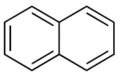
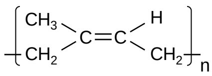
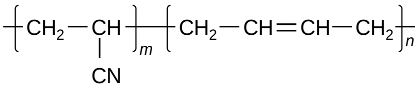
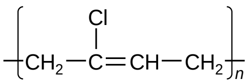
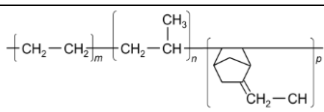
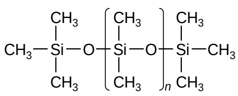
Substance	Common Application	Formula	Chemical Composition	Boiling Point	Test Result
Diphenylamine	Antioxidant	$C_{12}H_{11}N$		302°C	Discolored
Nonylphenol	Antioxidant	$C_{15}H_{24}O$		295°C	Discolored
Hexadecane	Glidant	$C_{16}H_{34}$		287°C	Discolored
DOP Bis(2-ethylhexyl) phthalate	Plasticizer	$C_{24}H_{38}O_4$		385°C	No Effect Observed
DOA Bis(2-ethylhexyl) adipate	Plasticizer	$C_{22}H_{42}O_4$		335°C	No Effect Observed
Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate	Antioxidant	$C_{35}H_{62}O_3$		323°C	Discolored
Pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]	Antioxidant	$C_{73}H_{108}O_{12}$		779.1°C	No Effect Observed
2,2-Bis{[3-(dodecylthio) -1-oxopropoxy]methyl} propane-1,3-diyl bis[3-(dodecylthio)propinate]	Antioxidant	$C_{65}H_{124}O_8S_4$		323°C	No Effect Observed
Naphtalene	Dye Intermediate, Raw Material of Synthetic Resin	$C_{10}H_8$		218°C	Discolored

Table 3. List of Substances with which VOC Discoloration was Confirmed (Rubber Materials)

Substance	Category	Chemical Composition	Test Result
Isoprene rubber (IR)	Synthetic Rubber		Discolored
Nitrile rubber (NBR)	Synthetic Rubber		Discolored
Chloroprene rubber (CR-70)	Synthetic Rubber		Discolored
Ethylene propylene rubber (EPDM)	Synthetic Rubber		Discolored
Silicone rubber	Silicone Rubber		No Effect Observed

4. Test Method to Examine VOC Discoloration

It is difficult to reproduce the exact environment where an LED is actually used when examining VOC discoloration. It should be noted that the test described below is an example of VOC discoloration test and cannot be used as a test to determine if VOCs will discolor in customers' light fixtures. This test is solely to check whether the discoloration of VOCs from test materials is severe or not.

4.1 Example of Test Method

Test LED: Part No. NC2W170B
Test Specimen (Material Confirmed to Release VOCs): Polypropylene 60mg
Glass Dome Volume: 0.9ml
Adhesive: EA 0151 Manufactured by LOCTITE
Illuminance Meter: CL-70F Manufactured by Konica Minolta
Others: PCB, Heat Sink, DC Power Supply
Ambient Temp.: 25°C
I_F: 1000mA

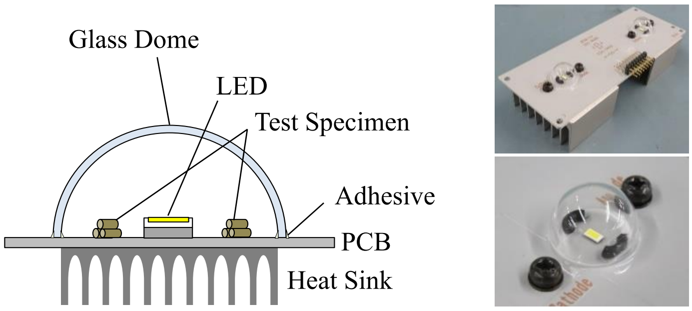


Figure 9. Example of Test Apparatus for VOC Discoloration Test

In this test, the test LED and specimen are hermetically sealed so that the VOC concentration remains the same to check for discoloration of VOCs. A glass dome or a glass beaker that does not release VOCs is used for hermetic sealing. The adhesive and PCB, also used for hermetic sealing, should be checked prior to the test without placing the test specimen inside the dome to confirm that the VOCs that may be outgassed from them do not affect the LED. Since VOCs are more likely to be outgassed if the ambient temperature is high, the adhesive used for hermetic sealing may affect test results depending on the temperature condition. Considering the possibility of the adhesive outgassing a slight amount of VOCs, a reference sample without the test specimen should be also prepared for comparison purposes to check the difference in the degree of effects.

Prepare two (or more) sets of an LED mounted on a PCB and a glass dome and use one of the sets as a reference sample without placing the test specimen inside the glass dome. For the other set, place the test specimen in the dome. As shown in Figure 13 in the next chapter, VOC effects are more likely to appear with the higher VOC concentration. Thus, the effects can be observed more easily if the test is carried out with more than ten times as high a concentration as that in the actual use environment (the ratio of the volume of the test specimen to the volume of the glass dome or the ratio of the surface area of the test specimen to the volume of the glass dome).

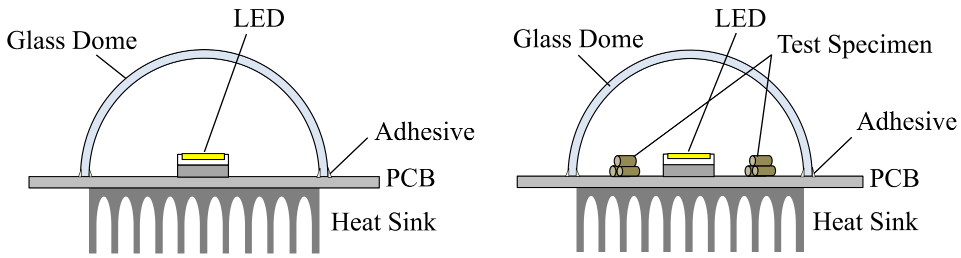


Figure 10. Test Method Examples (Left: Reference; Right: Apparatus with Test Specimen)

The adhesive should be applied in a way there is no gap between the glass dome and PCB. Apply the adhesive to the glass attachment area and then place the glass dome onto it. Slightly rotate the glass dome as you push it down to eliminate gaps. If a gap is still found, use a spatula etc. to fill the gap. Leave approximately 24 hours to completely cure the adhesive before lighting up the LED to start the test.

The illuminance meter should be used at a fixed position directly above the LED to measure the luminous intensity (arbitrary illuminance) and color at the initial state. The measurement device does not have to be an illuminance meter as long as the luminous intensity relative to the initial state can be determined. If no luminous intensity measurement device is available, visually compare the discoloration of VOCs that appears in the LEDs by lighting the LED in the reference sample (without the test specimen) and the LED with the test specimen for the same period of time to determine if they are affected by the VOCs. In the case of visual comparison, ensure that the LEDs are turned off before observing the emission surfaces to avoid directly viewing intense light.

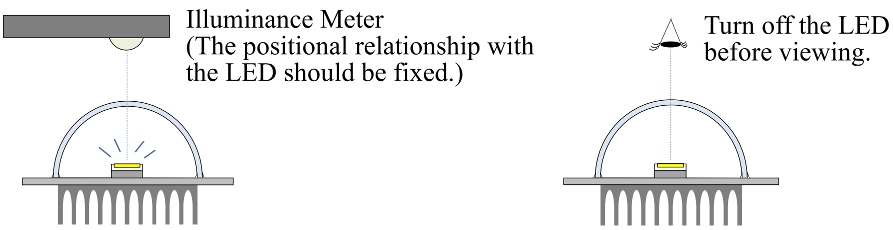
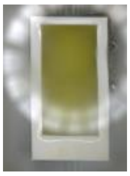
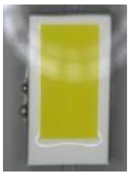


Figure 11. How to Check Luminous Intensity and Discoloration

The discoloration of VOCs progresses if they are exposed to light energy. Hence, the test results should be evaluated based on the total time of light emission regardless of whether the emission was continuous or intermittent. How fast the effects will emerge depends on the VOCs and their concentrations. Some may be discolored in approximately 10 hours if early. If discoloration is found in an LED, the material tested with the LED is likely to give adverse effects of VOCs on LEDs and thus, should be avoided. It is difficult to reproduce the exact environment where the end product is used by performing a simplified test like this one. Therefore, other measures (e.g. ventilation) should be taken in addition to the test.
Table 4 shows the results of the VOC discoloration test. The test was originally scheduled for 500 hours, however, since discoloration was detected in 60 hours, it was discontinued after 60 hours.

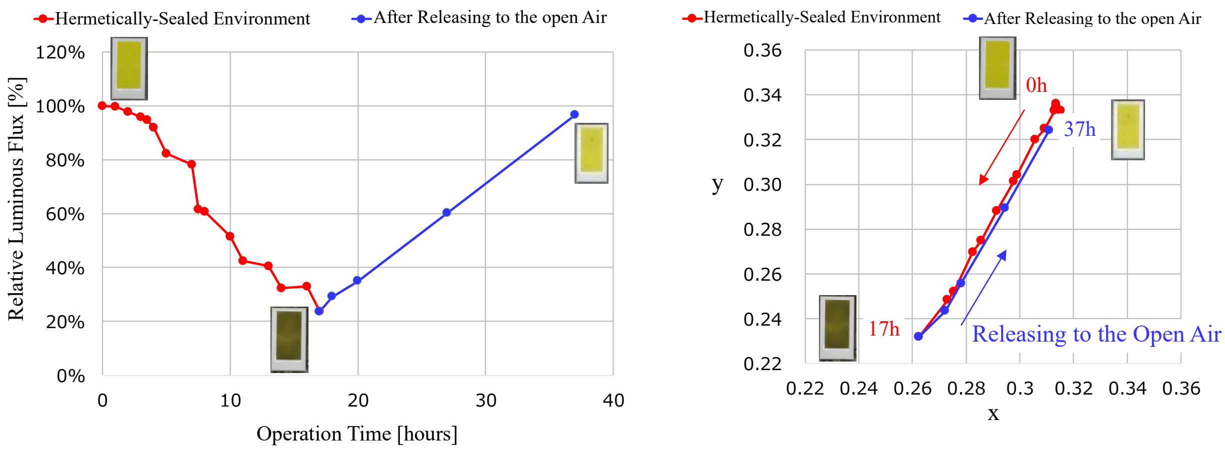
Table 4. VOC Discoloration Test Results (Example)

Lighting Duration	0hrs.	10hrs.	20hrs.	40hrs.	60hrs.
Material A (Polypropylene)					 Discolored
Material B (Polypropylene)		 Discolored	 Discolored	 Discolored	 Discolored
Reference (W/O Specimen)					 No Effect Observed

5. Examples of VOC Effects

5.1 Effects of VOC Discoloration on LEDs

In an environment where the LED is hermetically sealed or the air circulation around the LED is poor, VOCs may permeate the LED, and they may discolor when exposed to heat and light energy, which can cause a decrease in the light output or color shift of the LED. Even if discoloration occurs, the decreased light output and color shift tend to be improved by having better air circulation.
Note that even in a hermetically-sealed environment, if substances that cause discoloration (e.g. VOCs) are not present, the environment does not have adverse effects on the luminous flux/color of the LED.



a) Luminous Flux Transition

b) Color Transition

Figure 12. Discoloration of VOCs and Reduction in the Discoloration
(Verification by Accelerated Test Under High VOC Concentration)

Figure 12 shows the discoloration as a result of LED operation in a hermetically-sealed environment and the reduction in the discoloration after operating the LED in an open air. Since the test was an accelerated test under a high VOC concentration in a hermetically-sealed space, discoloration occurred in several hours in this test. Depending on the components/concentration of VOCs and/or light energy intensity, time required for discoloration may vary; in some cases, discoloration may be observed after a long period of time (e.g. after 100 hours or longer).

5.2 Effect of VOC Concentration

Figure 13 shows an effect of VOC concentration using different amounts of VOC source (diphenylamine) that causes discoloration under a hermetically-sealed environment.

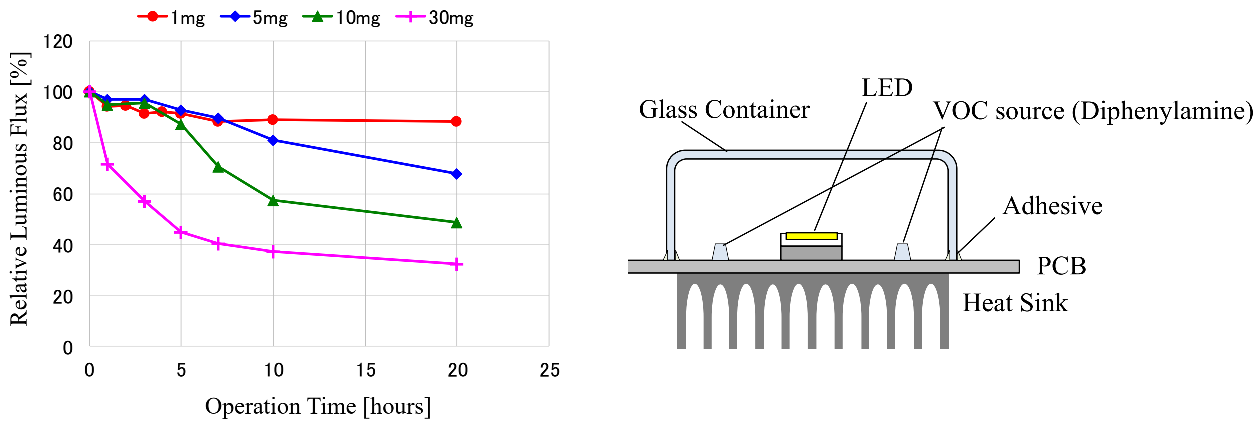


Figure 13. Diphenylamine Amount vs. Decrease in the Luminous Flux in a Hermetically-Sealed Environment

5.3 Repetition of On and Off

The progression of discoloration is accelerated when the LED is turned on and off repeatedly rather than being operated continuously without interruption.

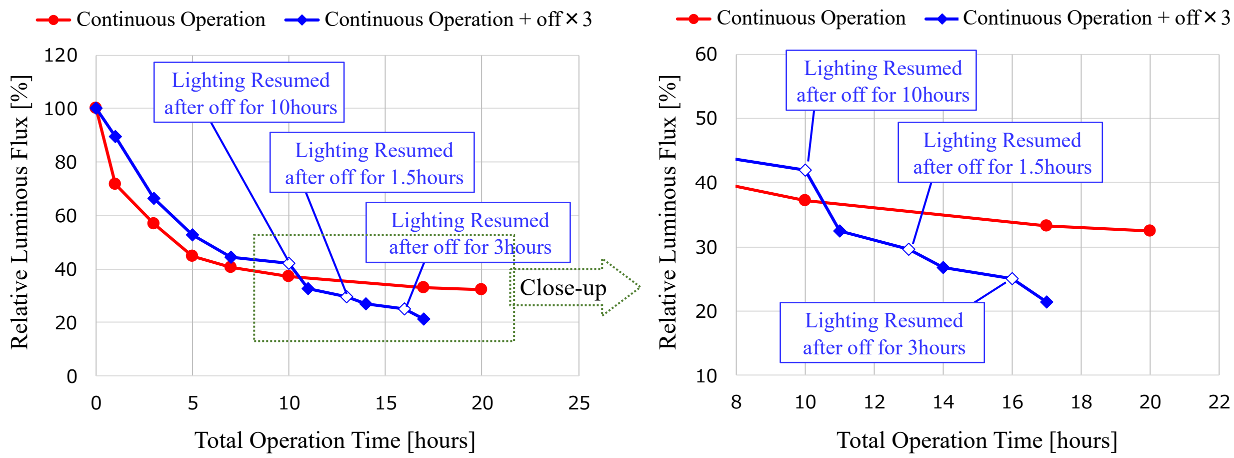


Figure 14. Comparison of Continuous Operation and On/Off Operation

VOCs are more likely to remain (adhere) inside the silicone resin in low temperature than in high temperature. Thus, if the LED is turned off for a certain period of time, the temperature of the LED (silicone resin) decreases and adhesion progresses. As a result, the VOC concentration inside the LED becomes higher than that in the continuous operation without interruption and the progression of discoloration is accelerated.

6. Summary

Volatile organic compounds (VOCs) can be outgassed from various materials used around LEDs. If VOCs permeate the inside of an LED and remain there, chemical reaction may occur due to heat and light energy and the VOCs may discolor. The discoloration of VOCs can cause a decrease in the luminous flux or color shift of the LED, the degree of which may vary depending on the volatilized VOCs and the VOC concentration.

The VOC discoloration is more likely to occur if the concentration of the VOCs is high; thus, improving air circulation around the LED is suggested as an effective measure. When designing a light fixture, measures such as ventilation are recommended to have better air circulation around the LED. If the LED is used in a hermetically-sealed environment, please check for the effects of VOCs on the LED and perform verification prior to use to ensure that there are no issues with the LED performance.

It is difficult to perform a reproduction test of VOC release and discoloration for all materials used around LEDs or all environments where the LEDs are used. This document does not identify or present all the materials that may affect LEDs. It is important to take the effects of VOCs described in this document into consideration when selecting/changing materials.

Disclaimer

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