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Investigation of Antifouling Paints for Vessel in Tropical Seawater of North Jakarta in Indonesia

G. Priyotomo^{*}^a, S. Prifiharni^a, A. Nikitasari^a, S. Musabikha^a, R. Kusumastuti^a, L. Nuraini^a, J. Triwardono^a, H. Nugraha^a, A. Budi Prasetyo^a, H. Julistiono^b

^a Research Center for Metallurgy, National Research and Innovation Agency, Bld.720, Serpong, Tangerang Selatan, Banten, Indonesia ^b Research Center for Applied Microbiology, National Research and Innovation Agency, Jakarta-Bogor No.KM 46, Pakansari, Cibinong, Bogor, Jawa Barat, Indonesia

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ABSTRACT

The copper-based biocide is mostly used as primary additive of Antifouling (AF) paint in Indonesia especially on vessels. The evaluation for the efficacy of AF paint was conducted where anti corrosion (AC) paint was also as a reference. The panels with both paints were exposed to various sea depths of up to 3 meters until 12 months of exposures. The measurement of parameters of seawater consisting of water conductivity, pH, temperature, dissolved oxygen and salinity were carried out. There was no or less attached marine biofouling on AF-painted panels but not on AC-painted panels up to 12-months of field exposure in various sea depths. There was no difference between the properties of AF paints before and after exposure to various sea depths. The inhibitive performance of AF paint depends on the existence of AF layer containing Cu₂O biocide where the thickness of that layer decreases in increase of time exposure.

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1. INTRODUCTION

The existence of marine biofouling have potency of major issues for the physical and mechanical degradation of submerged offshore structures particularly metal and alloys (1). The growth and settlement of biofouling have a detrimental effect on submerged structure (2-4). The metabolism of biofouling organisms may cause a decrease in corrosion resistance, an increase in drag, and a reduction in the frequency of drydocking operations for ships (5-8). The presence of corrosion could induce mechanical properties and operational time on existing structures (9, 10). In addition, the safety issues have been taken an essential part of consideration when the decrease of structure stability due to the growth and settlement of marine biofouling (11, 12). The biological metabolism of marine biofouling is mainly affected by seawater factors such as salinity, pH, water flow, dissolved oxygen, water temperature and surface

temperature (13, 14). Furthermore, the increased growth rate of biofouling organisms frequently occurs aggressively as a result of the warmer seawater temperature and higher salinity in tropical zones compared to those in temperate zones. Indonesia is one of several tropical countries with a hot and humid climate. Due to the warm surface water temperature and high salinity in the marine environment, the seasonal change is comparatively consistent every year. Additionally, Indonesia's ocean waters are home to a variety of marine species and ecosystems in both deep water and along the coast. Therefore, in Indonesia, marine biofouling continues to grow and settle without interruption, but not in subtropical countries. The usage of antifouling (AF) paint on marine submerged structures is a frequent mitigation strategy for the severity of associated marine biofouling. Biocide is typically the added chemical that makes up the majority of AF paints. The biocide of copper (Cu²⁺) being released from the

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^{*}Corresponding Author Email: gadangp@gmail.com (G. Priyotomo)

bulk of AF paint has the advantage of preventing biofouling from adhering to the structure (3).

Moreover, the poisonous property of copper compounds serves to inhibit the growth of some microand macroorganisms, including mollusks, algae, bacteria, and other organisms (15, 16). The usage of AF paint is the most proven method of mitigation up to now (17). Commonly AF paints comprise three types such as hard AF paint, ablative AF paint and self-polishing copolymer (SPC) AF paint. In Indonesia, SPC-AF paint is used at ship and boat due to the longer operational time service compared to other AF paints for the last 15 years. In addition, the other justification for using SPC-AF paint is the improved management of the discharge of copper compound or cuprous oxide (Cu₂O), which act as the primary biocides (12). Due to the negative impacts of tributyltin (TBT) compound as prior biocides, tin-free self-polishing copolymers (tin-free SPC) AF paint has now been used as AF paint incorporating copper biocide. Generally, generic SPC-AF paint comprises resin, solvent, pigment, biocide, co-biocide, anti-settling agent, extender and soon on.

In preceding investigation, few researchers had reported the efficacy of SPC-AF paint in North Jakarta and Madura strait, Indonesia within a month after field exposure (4, 18). However, there is no comprehensive investigation the efficacy of SPC-AF paint perfomance for a longer exposure in Indonesia in North Jakarta especially the relationship amongs the depth of seawater level, intrinsic properties of SPC-AF and seawater parameters againts tropical marine biofouling particulary a binder of silyl acrylate. Therefore, this research aims to clarify the effectiveness of performance on SPC-AF paint compared to anticorrosion paint as reference material for a longer exposure up to 12 months in North Coastal of Jakarta District, Indonesia.

2. MATERIALS AND METHODS

2. 1. The Preparation of Specimens A plate of low carbon steel was cut (length: 25 cm, width: 20 cm and thickness: 0.03 cm) for a coating metal substrate. By using a portable sandblaster, all metal substrates were sanded in accordance with ISO 8501-1 Sa 2.5. According to that ISO standard, stains, streaks, and rust should only cover 5% of the steel substrate's surface. In addition, SPC-AF paints is classified as a top coat which define as a final layer of multiple paint layers over intermediate layer and primer layer. SPC-AF paints are essentially a three-layer system made up of an epoxy primer base coat, an epoxy intermediate base coat, and an epoxy top coat. There were two commercial SPC-AF paints used in this current work (AFP-A and AFP-B). On other hand, as controlled paint, anticorrosion (AC) paint also was applied over epoxy primer coating. In addition, both AF paints were received from two distinct Indonesian companies that specialize in tin-free self-polishing copolymers (SPC). Those companies produced the generic type of AF paint using the certain chemical formulas as well as that in preceeding work (19).

In early September, during the tropical rainy season, each test rack of both samples of AF paint and AC paint was positioned on submerged piles of Muara Baru sea port in North Jakarta (6°05'46.0"S 106°48'01.0"E), as shown in Figure 1. In addition, Geographically, Jakarta is located in an alluvial plain that is low and flat, with an average elevation of 8 meters (26 feet) above sea level with historically large swampy areas. North Jakarta region is a suitable field area to represent the environmental parameters and the growth of tropical biological fouling. In this field work, the exposure time was carried out by 2, 3, 6 and 12 months. In addition, during operational times, the maximum lifespan of SPC-AF paints is approximately 36 months where the recent evaluation of those paints efficacy was conducted before that lifespan. The evaluation of potential damage to those paints before the maximum operational time is needed in this work, especially in tropical countries like Indonesia. Following a period of exposure, the specimen was retrieved from the water and kept in storage until further characterization and analytical steps, as shown in Figure 2.

Furthermore, the settlement of marine biofouling on structure is affected by the water parameters such as water conductivity, salinity, pH, water temperature and dissolved oxygen (1, 4, 18). Those water parameters could be considered to be carried out in this present work where were measured by using HACH HQ40d Advanced Portable meter during operational service.

2. 2. Evaluation of AF Paint Properties In this work, paint testing was conducted to evaluate physical and mechanical properties of paints before and after field test. Paint was tested for hardness using the Elcometer 501 pencil hardness tester in accordance with American Standard Testing and Material (ASTM) D-3363. The evaluation pencil hardness was valued through the ranges



Figure 1. Location of specimen placement in Muara Baru, Jakarta, Indonesia



Figure 2. An activity of paint specimen retrievement at certain time of exposure in Muara Baru Sea port, North Coastal of Jakarta

from 6B (softest) up to 9H (hardest). The adhesion strength of paint was carried out using Elcometer 510 Automatic Pull-Off Adhesion Gauge according to ASTM D-4541. Adhesive strength refers to the ability of a paint to stick to surface of metal subtract and bond two surfaces together. Horiba Gloss Checker IG-331 was also used to perform properties of glossy at a 60-degree angle (ASTM D-523). In order to maintain the accuracy of the results, the tests were also run five times. The specimens are visually examined to check for the presence and distribution of biofouling. A JEOL JSM-6390 series scanning electron microscope was used to observe the cross-sectional morphology of samples.

3.RESULTS AND DISCUSSION

3. 1. The Paint Properties and Seawater **Parameters after Exposure** The gloss properties of AFP-A and AFP-B following field exposure in various depths of saltwater are shown in Figures 3, respectively. The value of AFP-A and AFP-B gloss are 7.0 and 3.0 in the field test before exposure, respectively. The cause of gloss values difference in both AF paints is due to the lesser solid content of Paint A compared to Paint B. On the basis of result, the magnitudes of AFP-A gloss were almost the same each exposure time as well as those of AFP-B gloss. Low gloss AF paint is defined as having values of less than 10 Gross Units (GU), which were achieved by both AF paints. On the basis of results, the magnitudes of gloss paint are almost the same in both certain exposure times and different sea depths. It was found that both AFP-A and AFP-B had nearly the same gloss properties both before and after exposure.

Furthermore, both AFP-A and AFP-B are classified as tin-free self-polishing copolymers that have self polishing mechanism in paint matrix during service in marine environment. That mechanism can make surface of AF paint smooth until no more outer AF coating layer



Figure 3. (a) Glossiness of the AFP-A as a function of sea depth and (b) Glossiness of the AFP-B as a function of sea depth

on primary coating during service (19). In addition, the roughness of paint surface is attributed with gloss degree of coating (20). Before and after field exposure, the pencil hardness values of both AFP-A and AFP-B were classified in B scale. In addition, during field exposure, the pencil hardness values of AFP-A and AFP-B are the same.

Figure 4 shows that adhesion strength for AFP-A and AFP-B as function of depth levels of the sea after exposure. In varying levels of sea depth, the adhesion strengths of the paints were almost the same. There is no significant alteration of adhesion strengths in both two type of antifouling paints in different sea depth. The category of coating failures refers to 100% cohesion pattern, where both AFP-A and AFP-B occurred failure in a layer of antifouling coating as shown in Figure 5. Cohesive failure is in the coating itself due to internal crack (21) where that crack caused by abrasion process and dissolving additive in coating matrix. Main factors include water temperature, salinity, pH, dissolved oxygen, and others cause biological fouling to settle (19, 22). Most marine biofouling organisms suitably grow and settle in the environment with pH 7.5-8.0 and temperature of more than 20oC (23). Furthermore, North Jakarta bay is distinguished by its shallow water, 13 rivers flowing into it, and connections to the Java Sea which has been impacted by tropical seawater parameters. On the basis of results, the temperatures and pH of

seawater has the appropriate growth and settlement for marine organism where there are no or less shift alteration for those parameters in various depths of sea and different exposure times as shown in Table 1.

The dissolved salt concentration of bodily water is referred to as salinity, and the typical average saltwater salinity is around 35 ppt (24). The Muara Baru area of Jakarta Bay has salinity levels less than 35 ppt. North coastal of Jakarta has many estuaries near coastline which is lower salinity value in the range of 24-33.5 ppt (25) as well as the present results. Furthermore, the solubility of dissolved oxygen (DO) commonly increases in decreasing water temperature and vice versa (26) where DO concentration decreased with increasing seawater depth (27).





Figure 4. Adhesion strength for (a). AFP-A and (b). AFP-B as function of depth levels of the sea after exposure



Figure 5. An illustration of AF paint adhesion failure after exposure

Exposure time (months)	Depth (meter)	Temperature (°C)	рН	Salinity (ppt)	DO (mg/L)	Conductivity (mS/cm)
	0	30.9	8.2	28.1	5.58	48.7
2	1	30.7	8.3	28.2	5.44	48.7
2	2	30.6	8.3	28.2	5.2	48.6
	3	30.6	8.3	28.1	5.25	48.5
	0	30.45	8.35	28.15	5.06	48.45
2	1	30.35	8.38	28.15	4.937	48.38
5	2	30.25	8.41	28.15	4.814	48.31
	3	30.15	8.44	28.15	4.691	48.24
	0	30.05	8.47	28.15	4.568	48.17
E	1	29.95	8.5	28.15	4.445	48.1
0	2	29.85	8.53	28.15	4.322	48.03
	3	29.75	8.56	28.15	4.199	47.96
	0	30.7	7.79	29.9	1.89	51.4
12	1	30.7	7.79	30.1	1.6	51.7
12	2	30.7	7.8	30.5	1.05	52.4
	3	30.7	7.81	31.1	0.03	53.3

TABLE 1. Seawater parameter during field exposure at Muara Baru, North Jakarta

The level of DO is practically the same concentration at different depths below sea level up to a depth of three meters. The lowest magnitude of DO took place in 12 months of exposure. The authors presume that the significant decrease of DO concentration each depth of sea is caused by anthropogenic activity nearby Muara Baru, North Jakarta in 12 months of exposure. In addition, the euphotic zone is defined as the area with a maximum sea depth of 3 meters as well as this work. The penetration of the radiation of sunlight occurs intensively (27) where the active photosynthesis process supplies oxygen level in water (28). Moreover, Table 1 presents that water conductivity is nearly the same magnitude at different sea depths. Sea water commonly has average conductivity of approximately 55 mS/cm (29). However, in the present results, the values of conductivity each interval exposure is lower than 55 mS/cm.

When considering the effectiveness of antifouling paint, temperature, pH variations, DO and saltwater salinity are all essential factors. The solubility of biocides took place in small changes in the alkaline behavior of seawater, whether due to the production of hydrosulfide (pH decrease) or an increase in pH due to a decrease in CO_2 caused by the presence of algae. The effectiveness of antifouling paint is constrained by the rate of chemical and enzymatic reactions, which accelerate the slow stages of cell growth and the rate of polymeric coating crystallization in moderate temperatures. The higher salinity has impact to speed up the dissolution process of cuprous oxide (Cu₂O), a common binder in soluble antifouling paints where the performance of antifouling paints is more efficient in seawater compared to that in estuary water.

3. 2. Visual Examination of Exposed Specimens The usage of anticorrosion and antifouling paints A and B as primary specimens in preceding research [19] is also utilized in the present research. All of the paints A and B specimens after being exposed to seawater are shown in images in Tables 2, 3, 4, and 5. The use of both AFP-A and AFP-B, compared to both AC paint A and AC paint B, could reduce the growth and settlement of marine biofouling organisms for up to 12 months.

Table 6 shows biofouling percentage on antifouling paint surface after certain field exposure. On the basis of results, the percentage of adherent biofouling increased gradually with the exposure time up to 12 months for both antifouling paints. The attachment of biofouling occurs at 6 months of exposure. The percentage of biofouling type A antifouling paint is less than type B antifouling paint.



Depth of the sea (m)	AC paint A	AF paint A	Depth of the sea (m)	AC paint B	AF Paint B
0	S COL	• • • • • • • • • • • • • • • • • • •	0	5.00	5 cm
1		20 0 - 5 cm	1	<u>5 em</u>	7922 - Mb
2	5 cm	4 13 cm	2	3 on	5 cm
3			3	÷ cm	<u>5 cm</u>

TABLE 3. Visual observation of samples after three months of exposure

TABLE 4. After six months of exposure, the visual examination of representative specimens



In the present research, tubeworms and barnacles are apparently some of the most significant and visible marine biofouling organisms on both AC paints during exposure. Mature barnacle species started appearing on both AC paints in 6 months of exposure. There is no or less different of marine biofouling growth distribution on both type of AC paints in different depth of the sea and various exposure times. The homogeneity of biofouling distribution on the samples of AC paint is caused by the installment of field test racks in euphotic zone where seawater quality parameters were almost the same in that zone. Furthermore, the existence of barnacles and tube worms as most attached biofouling organisms are categorized as calcareous macrofouling (30). Moreover,

Depth of the sea (m)	AC paint A	AF paint A	Depth of the sea (m)	AC paint B	AF Paint B
0		.5 cm	0		5 cm
1		Sem	1		

TABLE 5. After twelve months of exposure, the visual examination of representative specimens

TABLE 6. Biofouling percentage on antifouling paint surface after certain field exposure

Depth of the sea (m) AC AF Paint A Paint (%) A (%)	Depth t of the P) sea (m) 0	AC AF Paint B Paint (%) B(%)				
	0					
0 100 0		100 0				
1 100 0	1	100 0				
2 100 0	2	100 0				
3 100 0	3	100 0				
3 months of exposure						
Depth of the sea (m) AC AF Paint A Paint A Paint A (%)	Depth t of the P) sea (m)	AC AF Paint B Paint (%) B(%)				
0 100 0	0	90 0				
1 90 0	1	90 0				
2 70 0	2	85 0				
3 100 0	3	100 0				
6 months of exposure						
Depth of the sea (m) AC AF Paint A Paint A Paint A (%)	Depth t of the P) sea (m)	AC AF Paint B Paint (%) B(%)				
1 100 5	1	100 35				
2 100 5	2	100 10				
12 months of exposure						
Depth of Paint A Paint A Paint A (%)	Depth t of the P) sea (m)	AC AF Paint B Paint (%) B(%)				
0 90 5	0	90 40				
1 90 5	1	80 35				

numerous different bacterial colonies are typically discovered on AC paints during the initial stages of biofouling growth, and these colonies serve as the principal nutrition for the growth of macroorganisms after few days to many weeks of exposure. Due to the ideal habitat of seawater, it can be assumed that marine biofouling will continue to grow and mature over month of exposure as well as the present results.

3.3. The Inhibitive Mechanism of Antifouling Paint against Marine Biofouling Figures 6 and 7 show cross sections of both AF paints, each of which has a three-layer coating consisting of a primer coating (the first layer), an intermediate coating (the second layer), and a top coating (AF layer). Before exposure, the average AF layer thickness of the two multiple systems of AFP-A and AFP-B was 226 µm and 116 µm, respectively. On the basis of the results, AF coating layer thickness decreased for both AFP-A and AFP-B during field exposure up to 12 months. In Figures 8 and 9, the AF coating layer thickness reduction on AFP-A is less than that on AFP-B after exposure. AF layer is not present in AFP-B after 12 months of exposure compared to AFP-A after 12 months of exposure. The difference in thickness loss of both AF paints after exposure is presumed due to the different initial thickness of AF coating layers. Moreover, the initial thickness of coating value prior to exposure is used to estimate the service life of AF paints (19, 31, 32) as well as recent study. It suggests that the initial thickness of the AF coating layer up to 12 months of field exposure determines the service life of the AF paint system.

In recent work, both of AFP-A and AFP-B is classified as tin-free-polishing copolymer (tin-free SPC) which based on silyl acrylate (SA) as primary binder according their technical data sheet. The efficacy of tin-free SPC AF paints is related to the ability of that paint which inhibit the growth and settlement of biofouling in controlled



Figure 6. Prior to exposure, a cross-section picture of Paint A



Figure 7. Prior to exposure, a cross-section picture of Paint B



Figure 8. Cross-sectional pictures of Paint A that are representative after (a) 3 months of exposure, and (b) 12 months of exposure to seawater at a depth of 1 m

release rate of binder matrix. That ability could make to control the loss rate of AF paints thickness during field service compared to other type of AF paints such as hard AF paint and ablative paint. The inhibitive mechanism of SPC-AF paint against the settlement and growth of marine biofouling, the ingress of seawater takes place into the



Figure 9. Cross-sectional pictures of Paint B that are representative after (a) 3 months of exposure, and (b) 12 months of exposure to seawater at a depth of 1 m

paint matrix, dissolve gradually all additives such as primary biocide, co-biocides and others to environment. That process takes place simultaneously and repeatedly which create a thin leached layer of AF coating without main dissolved additives such as Cu₂O and ZnO. The absence of soluble primary biocide, such as Cu₂O, results in pores being left in the matrix paint, which can be defined as a leached layer.

Furthermore, the leaching process of SPC AF paint comprises two sections such as initial leaching and steadystate leaching. When a freshly painted surface comes into touch with seawater environment and a biocide additive begins to dissolve at the top layer of AF paint, the leaching process for the painted structure begins immediately. The main ingredients used to formulate AF paints: solvent, binder, biocide, booster biocide, extenders, pigments, and miscellaneous additives (19). Generic Cu₂O is used as the primary inorganic biocide in both types of AF paints A and B, with co-biocides like ZnO additive also added to enhance the suppression of micro- and macro-algae growth and settlement. The presence of CuPt compound is necessary to boost the performance of primary biocide. Moreover, the following chemical Equation 1 is the proposed mechanism of the primary biocide of Cu₂O dissolving in seawater:

$$Cu_{2}O(s) + 2H^{+}(aq) + 4Cl(aq) \rightarrow 2CuCl^{-}(aq) + H_{2}O$$
(1)

The presence of a high concentration of chloride ions, which increases the rate at which Cu_2O dissolves, is

correlated with salinity levels of a high magnitude. In initial stage, when Cu₂O additive firstly contacts with sea water, that process yields soluble hydrated Cu(I) chloride complexes. That complexes compound is rapidly oxidized to Cu^{2+} ion as the main biocidal species against biofouling. The mechanisms of controlled release rate of biocides and co-biocides such as diffusion and chemical reactions where binder reaction, seawater water soluble pigments dissolution and polishing processes take place concurrently. In addition, those mechanisms could govern the magnitude of thin leached layer thickness for SPC AF paint. It is presumed that the disappearance of mostly biocide and co-biocide additives in silyl acrylate matrix creates many small pores in that matrix and enhances the magnitude of total wetted area on top surface of AF paint. During operational service, the wettability of the binder changes from hydrophobic to hydrophilic, causing the hydrolysis reaction to occur through the layer of AF coating that has been leached. Because partially reacted binder tends to be eroded by the motion of seawater and exposed at a less reacted AF layer surface, the AF coating has a self-polishing action. Biocides and co-biocides enriched matrix are present in the less-reacted AF coated surface or no leached layer zone, which inhibits the growth of marine biofouling. After completing the initial stage of leaching process, the steady-state leaching process starts simultaneously. In steady-state conditions, the rate of AF binder erosion caused by mechanical activity such as saltwater tide, current, and vessel movement is equal to the diffusion of ions from seawater bulk through the leached AF layer. The rate of biocide release from paint matrix is affected by seawater current, where leached AF layer can be eroded of polished easily. The role of seawater current rate is essential for the reduction of AF coating layer during service. The crucial function of the tidal current is its ability to easily wear or erode a leached layer of the AF layer, producing a fresh surface of the biocide-enriched layer. The simultaneous AF layer leaching process continues until there is no AF layer present during service. Therefore. It is pressumed that the thickness factor of SPC-AF paint can increase its lifespan during operational services at coastal aquifers of North Jakarta

4. CONCLUSIONS

The performance of both self-polishing copolymer (SPC) antifouling paints A and B showed remarkable efficacy compared to anticorrosion paints A and B in North Sea of Jakarta, Indonesia against the settlement of marine biofouling especially tubeworm and barnacle species. During operational service, the physical and mechanical properties of the AF paints are not significantly affected by variations in sea level up to 3 meters of depth and certain period of exposure such as pencil hardness, gloss

and adhesion strength. In both AF paints A and B, the presence of a primary biocide like Cu_2O may minimize the growth and establishment of marine biofouling at coastal aquifers of North Jakarta. The seawater parameter such as salinity, water temperature, sea current and pH has a greater impact on the gradual lossed thickness for AF paints due to the dissolution of Cu_2O and other additives to seawater. The dissolution of Cu_2O took place in both initial and steady-state leachings of SPC-AF paint during service.

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بیوساید مبتنی بر مس بیشتر به عنوان افزودنی اولیه رنگ ضد رسوب (AF) در اندونزی به ویژه در مخازن استفاده می شود. ارزیابی کارایی رنگ AF در جایی انجام شد که رنگ ضد خوردگی (AC) نیز به عنوان مرجع بود. پانل ها با هر دو رنگ تا دوازده ماه در معرض اعماق دریاهای مختلف تا سه متر قرار گرفتند. اندازه گیری پارامترهای آب دریا شامل هدایت آب، pH، دما، اکسیژن محلول و شوری انجام شد. بر روی پانل های رنگ آمیزی شده با AF، رسوب زیستی دریایی چسبیده یا کمتری وجود نداشت، اما در پانل های رنگ شده با AT تا دوازده ماه قرار گرفتن در معرض میدان در اعماق مختلف دریا وجود نداشت. هیچ تفاوتی بین خواص رنگ های AF قبل و بعد از قرار گرفتن در اعماق رنگ شده با AT تا دوازده ماه قرار گرفتن در معرض میدان در اعماق مختلف دریا وجود نداشت. هیچ تفاوتی بین خواص رنگ های AF مختلف دریا وجود نداشت. عملکرد بازدارنده رنگ AF به وجود لایه AF حاوی بیوسید Cu₂O بستگی دارد که در آن ضخامت آن لایه با افزایش زمان قرار گرفتن در معرض کاهش می بابد.

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