Effects of Tinuvin 292 on ageing-resistance properties of electromagnetic transparent coating

Vu Quang Hung, Pham Minh Tuan, Dang Tran Thiem,
Pham Nhu Hoan, Nguyen Viet Long, Duong Van San, Pham Xuan Thao*

Institute of Chemistry and Material, Academy of Military Science and Technology.
*Corresponding author: thaovn1987@gmail.com
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ABSTRACT

The coating for the radar must satisfy the requirements of resistance to severe weather conditions while allowing electromagnetic waves to transfer almost completely. UV protection agents are added during the coating manufacturing process to limit the effects of ultraviolet rays in sunlight, improve colour fastness, and ensure the mechanical properties of the coating. In this paper, the author presents the results of a study to evaluate the effectiveness of the amine-based UV protection agent Tinuvin 292 under test conditions of colour difference ΔE (ASTM 2244), gloss loss (TCVN 2101: 2016) on samples of electromagnetic transparent coating (ETC) based on ester epoxy alkyd resin (EEA). Electromagnetic transparent coating with 2% Tinuvin 292 additive improves ageing resistance and weather resistance, ΔE = 2.15, gloss loss reached 12.1% at an angle of 60° while ensuring durability requirements mechanics, electrical properties, and electromagnetic transparency of coating film.

Keywords: UV protection agent; Transparent electromagnetic; Tinuvin 292; Ageing resistance; Weather resistance.

1. INTRODUCTION

Electromagnetic transparent coating (ETC) made by the Institute of Chemistry-Materials based on ester epoxy alkyd resin (EEA) [1], cured by diethylene glycol urethane (DGU), with better mechanical strength and electrical properties than coating EP-255 electromagnetic transparency for radar and some components in Russian missiles. This ester combines the advantages: high adhesion to many materials, chemical resistance,... of epoxy resins and flexibility, ability to be cured by air oxygen, etc. of alkyd resins. Although the epoxy has been modified to open the epoxy ring with vegetable oil fatty acids, which has partially overcome the disadvantages of epoxy, in the circuit of the epoxy ester film-forming agent, there is still an aromatic ring; this is the link easily broken, allowing UV rays to attack. UV-B light strongly influences breaking bonds in polymers with energies of 290 ÷ 460 kJ/mol to break unstable bonds in polymers and generate free radicals [2].

To improve the weathering resistance of the outdoor coatings, in addition to selecting the main components, such as resins and pigments with high weathering durability, organic and inorganic light stabilizing additives are usually added to the paint formulation. Previously published works showed that organic light stabilizers (such as Tinuvin 384, Tinuvin 1130, Tinuvin 292) exhibited an excellent light stabilizing efficiency. Adding these additives at appropriate content could increase the weathering durability of the polymer coatings by 2 - 3 times [3]. S. Amrollahi et al. use 0.4% Tinuvin 292 and 0.6% Tinuvin 1130 to decrease UV absorption at 250 - 400 nm while increasing reflectivity and improving weather resistance of an acrylic/melamine clearcoat [4]. Research by RP Singh et al. to investigate the change in yellow index (YI) of polyurethane coating film for anti-UV agents with 400 hours of irradiation, Tinuvin 292 0.5% by weight, reaching the lowest yellow index 70.12 compared to Tinuvin P, Irganox 1010, Tinuvin 9000 [5]. However, it seems that no research has evaluated the effects of Tinuvin 292 on ageing resistance and mechanical strength durability of coating films based on ester epoxy alkyd resins. Tinuvin 292 is a liquid-hindered amine light stabiliser (HALS) especially developed for colour-sensitive coating applications. It is a very pure mixture of Bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate and 1-(methyl)-8-(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate is widely used in coating products, Tinuvin 292 content from 0.5 - 3% mass of film-forming agent, which helps to prevent UV rays and increase colour fastness for coating, increase gloss for coating, reduce cracking. The tetramethyl piperidyl group stabilises the effect, acting mainly as a free radical scavenger, especially with peroxy radicals [6].

The research investigated the effect of Tinuvin 292 with content from 0.5 to 3% on ageing resistance properties while ensuring durability, mechanics, and electromagnetic transparency of coating film to find the optimal ratio.

2. EXPERIMENTAL

2.1. Chemicals, equipment

2.1.1. Chemicals

Ester epoxy alkyd resin (EEA), synthesised from linseed oil, phthalic anhydride and epoxy E-40 at the Institute of Chemistry-Materials [1], 60% dry matter content, acid values: 2.5-3.0 mg KOH/g); Diethylene glycol urethane 70% in cyclohexanone (DGU 70%), di-isocyanate, NCO group content: 24-28%, Russia; Pigment TiO_2, pigment G.7, pigment Y.83, pigment R.170, Japan; Nanosilica modified PDMS by sol-gel method at Institute of Chemistry-Materials [7], organic matter content 10-15%, particle size 10-20 nm; n-hexane, toluene, xylene industrial products, China; Tinuvin 292, BASF, USA; Electromagnetic transparent coating EP-255, Russia.

2.1.2. Instruments, equipments

The equipment used included Vibra 3-digit analytical balance, U.S Stoneware 2-stage coating crushers, a 5L porcelain ball mill, Erichsen impact test equipment, a pendulum device for measuring film hardness, an Elcometer coating film thickness measuring instrument, equipment for measuring flexural strength, a transmission loss measuring device an ultrasonic material dispersion machine, a centrifuge, a compressor, and a paint gun.

2.2. Sample preparation

2.2.1. Fabrication of electromagnetic transparent coating using additive Tinuvin 292

Accurately weigh 500 g of EEA film-forming agent solution (60% solution in xylene) and 6 g of nano silica-PDMS for 15 minutes [7]. The mixture, after sonication, is put into a 2-litre ball mill, and then add 90g TiO_2, 60g pigment G.7, 72g pigment Y.83, 22g pigment R.170 and 244g xylene. The mixture was incubated for 4h, then the ball mill was rotated on a machine at 600 rpm for 8h. The semi-finished coating obtained after grinding is mixed with 180 g of DGU curing [7]. Tinuvin 292 was added 0.5%, 1%, 1.5%, 2%, 2.5%, and 3% mass of the EEA to measure ageing resistance and mechanical strength to find the optimal ratio. In addition, Russia's EP-255 electromagnetic transparent coating sample is used to evaluate and compare ageing resistance. Research sample size: 100g.

2.2.2. Preparation of coating samples

The CT3 steel sample with dimensions of 75 x 150 x 0.8 mm, according to TCVN 5670:2007, was coated with the spray method with a coating film thickness of 60-80 µm.

2.3. Research methods

The surface morphological structure of the coating is analysed by scanning electron microscope (SEM), and standards test the mechanical strength of the coating film: TCVN 2098: 2013, TCVN 2099: 2013, TCVN 2100-1: 2013; Coating samples for accelerated aging test were exposured on the Atlas UVCON chamber (model UC-327-2) equipped with UVA-340 fluorescent lamps, according to the ASTM D 4587-05 standard (1 cycle consists 8 h of UV irradiation at 60 °C and 4 h of CON at 50 °C); colour difference delta E according to ASTM 2244, gloss loss according to TCVN 2101: 2016; dielectric constant and dielectric loss evaluated according to ASTM D150, breakdown voltage according to ASTM D149; electromagnetic transparency assessed according to TCQS 71: 2016/VKHCNQS.

3. RESULTS AND DISCUSSION

3.1. Effect of Tinuvin 292 on ageing resistance properties of ETC

3.1.1. Effect of Tinuvin292 on colour difference delta E and surface structure of coating film

According to the comparison formula through Delta E of materials after the ageing process, samples with ΔE < 3: are considered to have insignificant colour changes that are difficult for the naked eye to perceive, 3 < ΔE < 5: there is a clear difference between two colours, ΔE > 5: two different colours [8]. The results of the effect of Tinuvin 292 on colour difference delta E are presented in figure 1 and table 1.

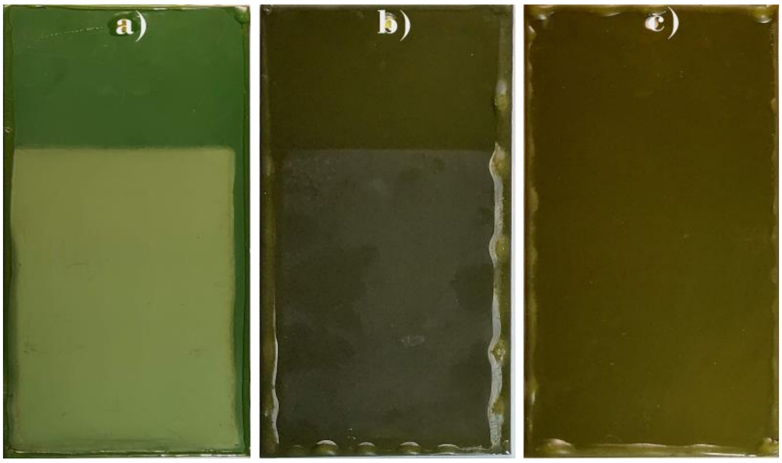

Figure 1. *Sample: (a) EP-255, (b) ETC-UV0, (c) ETC-UV2 after 1000 h of humid heat UV irradiation.*

Table 1. *Effect of Tinuvin292 on colour difference delta E.*

Entry	Sample	Tinuvin-292 (%)	ΔE
1	ETC-UV0	0	8.27
2	ETC -UV0.5	0.5	4.65
3	ETC -UV1	1.0	3.78
4	ETC -UV1.5	1.5	2.96
5	ETC -UV2	2.0	2.15
6	ETC -UV3	3.0	2.04
7	EP-255	-	17.24

After 1000 h of humid heat UV irradiation, the sample EP-255 (figure 1a) had apparent colour difference and chalking (ΔE = 17.24) due to the nature of epoxy film-forming agent of EP-255 coating, which is easily damaged by UV rays. Colour difference ΔE decreases with increasing content of anti-UV additive (table 1). Sample without UV protection agent ETC-UV0 with a film-forming system derived from epoxy-alkyd esters of vegetable oil has partially overcome the inherent disadvantage of epoxy resin, which is poor weather resistance; however, a phenomenon of fading and chalking after 1000 hours of humid UV irradiation can still be easily seen with the naked eye (ΔE = 8.27 > 5). Adding tiny Tinuvin 292 (0.5% to 3%) markedly improved anti-ageing ability. Samples ETC-UV0.5 and ETC-UV1 still had colour differences, but the level decreased gradually compared to ETC-UV0. Samples ETC-UV2 (figure 1c) and ETC-UV3 have very little colour difference ($\Delta E = 2.15$ and $\Delta E = 2.04 < 3$), almost unchanged from the original.

Under the influence of UV rays, most fillers are almost unaffected due to their main component being SiO_2, a relatively inert and stable compound. Therefore, the change in colour and gloss of the coating film will depend on the changes in the film-forming substance [9]. Degradation mechanism of the esters epoxy alkyd film-forming can be found in the literature [10]. During the accelerated ageing, the coatings might be simultaneously affected by various factors, including ultraviolet radiation, heat, moisture and oxygen. The ultraviolet radiation may cause the polymer chain scission, and then, with the presence of active oxygen, the photooxidation of polymer would take place. Besides, the coating might also be deteriorated by moisture and water via the hydrolysis reaction of the hydrophilic ester in polymer chains. High temperatures might accelerate this process [3].

The polymer substrate was protected by radical scavenging of HALS Tinuvin 292 according to a mechanism: the original 2,2,6,6-tetramethyl piperidine group is converted into a nitroxide radical under the influence of oxygen and light. The next step is the formation of an aminoether by recombination of radicals. The aminoether reacts with peroxy radicals, which again leads to the formation of nitroxide radicals. The destruction of the peroxy radicals results in the formation of alcohols or carbonyl groups. The formation of nitroxide radicals significantly reduces the concentration of peroxy radicals in the coating [3].

**Morphology coating's surface*

Investigating the influence of UV rays on the coating's surface, research analysed SEM images on samples EP-255, ETC-UV0 and ETC-UV2 after 1000 hours of humid heat UV irradiation (figure 2).

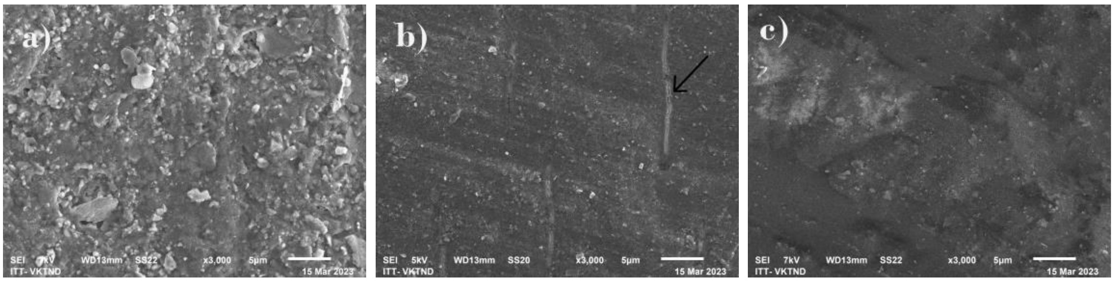

Figure 2. *SEM images: a) EP-255 sample; b) ETC-UV0 sample; c) ETC-UV2 sample.*

SEM images of samples after 1000 h of humid heat UV irradiation have proven the effectiveness of Tinuvin 292. When adding 2% Tinuvin 292 to ETC coating (figure 2c), surface quality was improved, smoother than sample EP-255 (figure 2a), and no cracks appeared on surface of sample ETC-UV0 (figure 2b).

The use of HALS-type UV stabilisers has limited the breaking of chemical bonds in the molecular chain of film-forming substances, thereby slowing down the transformation process on the surface of coating [11], limiting the destruction of chemical bonds in film-forming substances that reduce the density of gaps in material structures [12].

3.1.2. Effect of Tinuvin 292 on coating film gloss

Gloss loss of the coating film decreased with increasing anti-UV additive content, presenting effectiveness of Tinuvin 292 in film gloss (table 2).

At a 60° angle, the gloss loss of sample ETC-UV0.5 decreased by up to 16.5%, much lower than that of the EP-255 (97.01%) and was significantly improved when the content of Tinuvin 292 was increased to 1.5%.

Table 2. *Effect of Tinuvin 292 content on coating film gloss.*

Entry	Sample	Unit	Gloss loss
1	ETC-UV0	%	24.3
2	ETC -UV0.5	%	16.5
3	ETC -UV1	%	15.1
4	ETC -UV1.5	%	13.5
5	ETC -UV2	%	12.1
6	ETC -UV3	%	10.2
7	EP-255	%	97.01

It is worth noting that the incorporation of UV-absorbed leads not only to slow down the gloss of coating but also changes the mechanism of gloss loss. Our assumption is that, during the first stage of degradation, the photodegradation is relatively low and then accelerates for further degradation to generate low molecular weight by chain scission. The latter is then removed by water during the condensation cycle reducing gloss and increasing surface rugosity of coating. In the stabilized coating, this degradation is obstructed, especially in preparation step, by its free radical and hydrogen peroxide scavenging capacity [13].

3.2. Effect of Tinuvin 292 on the mechanical strength of ETC

When the content of UV additives increases, the ability to absorb UV rays increases, and the anti-ageing power lasts longer; however, a large amount will affect and reduce the mechanical strength of the coating film. To find the optimal ratio of Tinuvin 292, mechanical strength parameter measurement methods were applied (table 3).

Table 3. *Effect of Tinuvin 292 content on mechanical strength of coating film.*

Sample	Unit	ETC-UV0	ETC-UV0.5	ETC-UV1	ETC-UV1.5	ETC-UV2	ETC-UV3
Tinuvin 292 content	%	0	0.5	1.0	1.5	2	3
Impact resistance	kG.cm	200	200	200	200	200	180
Flexural strength	mm	2	2	2	2	2	2
Hardness		0.45	0.44	0.44	0.45	0.45	0.41

Mechanical strength parameters of samples proved the presence of anti-UV additive particles affected the impact resistance and hardness of the ETC film. The film-forming of ETC is a polyurethane based on an epoxy alkyd ester resin cured with DGU for a coating film with high physical and mechanical durability. Tinuvin 292 does not participate in the process of curing the polyurethane between EEA and DGU, with the content of 0.5-2% of Tinuvin 292 is not enough to affect the physical and mechanical properties of the coating film: impact resistance 200 kG.cm, flexural strength 2 mm and hardness 0.45. However, excess additive content (3% Tinuvin 292) can cause phase separation, decrease polymer chain crosslink density, and reduce the mechanical properties of coating film: impact resistance 180 kG.cm, and hardness 0.41.

3.3. Effect of Tinuvin 292 on electromagnetic transparency of ETC

Interaction between electromagnetic waves and matter depends on the polarity of the bonds in the material structure. Electric field loss (dielectric constant, dielectric loss) is proportional to the polarisation of the material. In the low-frequency region, the polarising dielectric's energy loss is small, but this loss increases rapidly at high frequencies [14].

Sample ETC-UV2 was filmed 70 µm thick and measured for electromagnetic transparency in the S-band, C-band, and X-band. Measurement results are shown in table 5 and figure 3.

The results of electrical properties measurement, including the following parameters:

dielectric constant, dielectric loss, and breakdown voltage (table 4), show that the coating film satisfies the requirements for the properties of an insulating. Adding a small amount of 2% Tinuvin 292, a less polar organic compound, does not change the electrical properties of the coating film. ETC coating is made from a film-forming agent with less polar structure, long alkyl chains, uniform structure than EP-255 coating, dielectric constant, and small dielectric loss. However, after a working time, due to the harmful effects of UV rays, they destroy the circuit structure of the film-forming agent, create free radicals that cause a dielectric constant, and the dielectric loss of the coating film increases. Therefore, the faster the material ages, the more dielectric loss increases. Ageing resistance is very important for electromagnetically transparent material systems [14]. Sample ETC-UV2 containing 2% Tinuvin 292 transmits electromagnetic waves almost completely (over 99%) higher than EP-255 coating Russia (according to GOST 23599-79) based on the epoxy resin achieves an average electromagnetic transparency over the S, C, and X bands of 96.4%.

Table 4. *Electrical properties of ETC coating film.*

	Electrical parameters	**Unit**	ETC-UV2	ETC-UV0	EP-255
1	The dielectric constant, 1 MHz	-	2.63	2.63	4.671
2	Dielectric loss factor, 1 MHz	-	0.022	0.023	0.0306
3	Breakdown voltage	kV/mm	68	68	60

Table 5. *Electromagnetic transparency of ETC coating film.*

Entry	**Band**	**Frequency range (GHz)**	**Electromagnetic transparency (%)**
01	S	3.9 ÷ 4.2	> 99
02	C	4 ÷ 8	> 99
03	X	8 ÷ 12	> 99

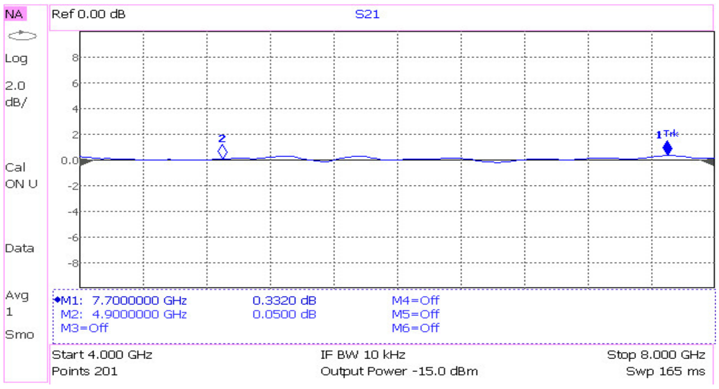

Figure 3. *Electromagnetic transparency of the coating film at 4 - 8 GHz frequency range.*

4. CONCLUSIONS

Investigation of the amount of Tinuvin 292 amine-based UV protection agent on ETC shows an apparent effect in reducing material ageing and weather resistance while ensuring mechanical strength properties and electromagnetic transparency. The following results were achieved with 2% Tinuvin 292 content: colour difference ΔE = 2.15 < 3, gloss loss at 60° angle was 12.1% after 1000h of humid heat UV irradiation, impact resistance reached 200 kG.cm, hardness reached 0.45, and electromagnetic transparency reached over 99%. With 2% Tinuvin 292 content, the coating film's ability to protect and resist the environment has been significantly improved, from which it can be applied to protect radars in coastal and marine areas and islands. Research results can be applied to make some durable coating in oceanic climates to protect steel truss frames and equipment.

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TÓM TẮT

Ảnh hưởng của Tinuvin 292 đến khả năng chống lão hóa của lớp phủ trong suốt điện từ

Sơn cho ra đa phải đáp ứng yêu cầu chống chịu được trong các điều kiện thời tiết khắc nghiệt, đồng thời đảm bảo sóng điện từ truyền gần như qua hoàn toàn. Chất chống tia UV được thêm vào trong quá trình sản xuất sơn nhằm hạn chế các tác động của tia cực tím có trong ánh sáng mặt trời, nâng cao độ bền màu và đảm bảo cơ tính của sản phẩm. Trong bài báo này, tác giả đưa ra kết quả nghiên cứu đánh giá hiệu quả của chất phụ gia chống tia UV gốc amin đơn phân (Hindered Amines Light Stabilizers-HALS) Tinuvin 292 trong điều kiện thử nghiệm suy giảm màu ΔE (ASTM 2244), suy giảm độ bóng (TCVN 2101: 2016) trên mẫu sơn trong suốt điện từ (ETC) với nhựa nền ester epoxy alkyd. Sơn trong suốt điện từ với 2% phụ gia Tinuvin 292 cải thiện độ bền lão hóa, bền thời tiết với ΔE = 2.15, độ bóng suy giảm 12.1% tại góc 60° đồng thời đảm bảo các yêu cầu độ bền cơ lý, tính chất điện và độ trong suốt điện từ.

Từ khoá: Chống tia UV; Trong suốt điện từ; Tinuvin 292; Bền lão hóa; Bền thời tiết.