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PHOTO-RESPONSIVE AND COLOR CHANGEABLE EMBEDDED IN ALIPHATIC POLYURETHANE

R. Kunanuruksapong[1,*], K. Wongcharee[2], C. Sararuk[2]

[1]Downstream Innovation, PTT Global Chemical Public Company Limited Rayong, Thailand
[2]Department of Chemical Engineering, Faculty of Engineering, Mahanakorn University of Technology Bangkok, Thailand

ABSTRACT

Nowaday, the trend of smart and functional materials is wildly interested as new solutions for modern urban lifestyle. The material that can reversible change its color after inducing with sun light energy is also interesting topic. The light responsive transparent and high abrasive resistance aliphatic polyurethane was successfully prepared by the appropriate combination of rigid polymer, flexible polymers and aliphatic polyisocyanate. The sensitivity (speed of color changing), fatigue resistance and color strength (maximum absorbance) were monitored as evaluation criteria for light responsive efficiency and usable lifetime. The test specimens were prepared by coating the mixed solution on transparent polycarbonate substrate using spinning coat technique. At appropriate ratio between flexible and rigid polymers (0.1 – 0.3) resulted highly transparency film with can suddenly change its color under UV exposure. The fastest sensitivity is shorter than 5 sec. The color cans reversible immediately (shorter than 6 sec) after cut-off UV light source. The color strength and sensitivity of resulting mixed formulations were enhanced by synergistic combination between two species of photochromic color compounds. The light stabilizer additive specie was added in order to extent the usable life time (fatigue resistance) and weathering resistance property of final formulation.

Keywords: Photo-responsive materials, light responsibe materials, color changeable dye, polyurethane

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Author Correspondence, e-mail: Ruksapong.k@pttgcgroup.com

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I. INTRODUCTION

The photo-responsive or light-responsive material is material that can reversible change or respond to the light source or light energy [1]. An example application of light-responsive material is a photochromic lenses that is widely used in daily life. Photochromic lenses are clear (or virtually clear) indoors and automatically turn dark in response to outdoor sunlight. Under stimulates of light energy, a photochromic molecules can change its molecular structure from colorless state to an active state that can effectively absorb the visible light. This active state can be reversed back to colorless state if the light energy source was removed [2]. Recently, the most of commercially available photochromic dye/pigment are Oxazines or Naphthopyrans or the mixture between both families [3-4]. These pigment families are possessed important application in ophthalmic lenses because they exhibit very high performance, fast responsive, attractive cost and long useable lifetime. The most favorite colors in ophthalmic lenses industry are dark black, dark blue, dark velvet and dark orange.

In addition, the efficiency of photochromic dye/pigment relies on a physical changing of the molecular structures and sensitivity or rate of color change is strongly and directly depend on the flexibility of the host matrix. Many experimental results [3-4] supported that the photochromic dyes exhibited high rate of color change when they were embedded into the matrices that have the glass transition temperature (T_g) lower than -10 °C and thus high flexibility. In contrast, the dyes that were embedded into high glass transition temperature matrices (T_g higher than 40 °C) exhibited very slow rate of color change. However, the matrix consisting of only low T_g segment isn’t usable on practical daily use because of a very poor mechanical property, scratch resistance and usable lifetime [5-6]. To overcome this problem, the blending system between high T_g and low T_g polymers had been prepared as main matrix for photochromic application.

In this work, we aimed to develop the photochromic coating layer that can be applied on ophthalmic lenses industry. The blending systems between high T_g polymer or rigid polymers and low T_g polymer or flexible polymers were prepared and mixed with the photochromic pigments and light stabilizer. The effect of matrix types was studied and photochromic efficiency between pigment embedded in non-polyurethane and polyurethane based matrices had been compared. The sensitivity (speed of color changing), fatigue resistance to UV source and color strength were monitored as evaluation criteria for light responsive efficiency and usable lifetime.

II. METHODOLOGY

A. *Raw Materials*

In this work, the selected matrices were divided into two types. The first is non-polyurethane based that prepared from the mixture between high and low T_g polymers. The second type is polyurethane based that prepared from mixture between rigid and flexible polymers but need to add isocyanate crosslinking agent for curing process.

The high T_g or rigid polymer was selected from at least one of polymer type that is tabulated on Table I.

TABLE I. LIST OF HIGH T_G POLYMERS

Name of polymer	***T_g (C)***	***Manufacturer***
(a) Poly(methyl methacrylate), PMMA	105	Polyscience Inc.
(b) Poly(methyl methacrylate-co-butyl methacrylate)	100	Sigma-Aldrich
(c) Poly(benzyl methacrylate)	54	Sigma-Aldrich
(d)Hydroxyl-bearing polyacrylate, Desmophen 870	NA (high rigidity polymer)	Covesto

The low T_g polymer or flexible polymer was selected from at least one of polymer type that is tabulated on Table II.

TABLE II. LIST OF LOW T_G POLYMERS

Name of polymer	***T_g (C)***	***Manufacturer***
(e) Polycaprolactone , PCL	-60	Polyscience INC
(f) Polycaprolactone diol, PCL diol	<-60	Sigma-Aldrich
(g) Poly(octadecyl methacrylate)	-100	Sigma-Aldrich
(h)Poly(2-ethylhexyl methacrylate)	-10	Sigma-Aldrich
(i) lightly branched hydroxyl-bearing polyester, Desmophen 670	NA (high flexibility polymer)	Covesto

In case of polyurethane based that was prepared from the mixture between hydroxyl-bearing polyacrylate (Desmophen 870) and lightly branched hydroxyl-bearing polyester (Desmophen 670), the isocyanate crosslinking agent must be added. The Aliphatic polyisocyanate was selected (Desmodur N 3390, Covesto) on this work because it provides suitable property for coating application.

The photochromic pigments were selected from at least one of Oxazines or Naphthopyrans or the mixture between both families. The photochromic pigments were manufactured by Vivimed Lab. The color shades of photochromic pigments were selected from at least one of Sunflower, Amber, Midnight grey, Mistry grey, Strom purple, Velvet blue, Oxford blue and Volcanic grey.

The solvent that was used for dispersing photochromic pigments and dissolving matrices was selected from at least one of non-polar solvents such as Toluene and Xylene.

The additive specie was added in order to extent the usable life time (fatigue resistance) and weathering property of final formulation. The third additive is light stabilizer that was selected from Hindered amine compound light stabilizer (HALS). The examples of HALS that were used in this work is Tinuvin 144 (bis(1,2,2,6,6-pentamethylpiperidin-4-yl) butyl(3,5-di-tert-butyl-4-hydroxybenzyl)malonate). This additive was manufactured by BASF.

B. *Sample preparation*

B.1 Preparation process of non-polyurethane based matrices

(1) In this step, 0.95 gram of each high T_g polymer (a) or (b) or (c) as mentioned on Table I was dissolved into 4.0 mL of Toluene and stirred at least 24 hrs until completely dissolve.

(2) 0.05 gram of each low T_g polymer (e) or (g) or (h) as mentioned on Table II was dissolved into 1.0 mL of Toluene and stirred at least 24 hrs until completely dissolve.

(3) The photochromic pigment (selected from at least one color shade) was dissolved into 1.0 mL of Toluene and stirred at least 24 hrs until completely dissolve.

(4) The solutions (1), (2) and (3) were mixed together and striped for 90 mins.

(5) The Light stabilizer (HAL) was dissolved into mixed solution (4) and stirred for 30 mins until completely dissolve.

(6) Filtered the mixed solution (5) with a filter that has pore sizes smaller than 0.45 micron.

(7) Applied the mixed solution (6) on polycarbonate substrate by using spin-coating technique. The spinning speed was controlled at 1,000 rpm and dried at 80 °C for 60 mins. The average thickness of coated layer is less than 150 micron.

B.2 Preparation process of polyurethane based matrices

(1) The rigid (d) and PCL diols or flexible polymers (f) and (i) were dissolved into Xylene and mixed together. The mixed solution was stirred for 30 mins after mixing. The photochromic pigments and additives were added into mixed solution and were stirred for 30 mins. The weight ratios between Flexible polymer : PCL diols : Rigid polymer : Crosslinking agent were varied and are tabulated on Table III.

TABLE III. THE WEIGHT RATIOS BETWEEN FLEXIBLE POLYMER : PCL DIOLS : RIGID POLYMER : CROSSLINKING AGENT

Desmophen 670 (d)	***PCL diols (f)***	***Desmophen 870 (i)***	***Desmodur N 3390***	***Ratio between 670/870***
0.070	0.000	0.630	0.300	0.110
0.120	0.000	0.580	0.300	0.210
0.190	0.000	0.510	0.300	0.380
0.190	0.025	0.490	0.295	0.380
0.180	0.050	0.480	0.290	0.380

The dosage of photochromic pigments and additive were fixed at 1.5% and 1.5%, respectively. The weight ratio between pigment and additive was fixed at 1:1.

(2) Filtered the mixed solution (1) with a filter that has pore sizes smaller than 0.45 micron.

(3) Applied the mixed solution (2) on polycarbonate substrate by using spin-coating technique. The spinning speed was controlled at 1,000 rpm and dried at 80 °C for 60 mins. The average thickness of coated layer is less than 150 micron.

C. Characterization and evaluation

C1. Visual evaluation

After applied coating solution on polycarbonate substrate, all specimens had been evaluate by visual check. The obtained specimens must be transparent because it has to be used in ophthalmic lenses industry. High light transmission and clear coating layer are the most important characteristics.

C2. Rate of color change (sensitivity)

Coloring process: In this state, the rate of color change or photochromic sensitivity of prepared specimens was determined and evaluated. The prepared specimens were exposed to UV lamp (UV intensity = 50 W/m^2) for 1, 3, 5, 10, 15, 20 and 30 mins. The color strength

(λ_{max}) of UV excited specimens were measured by using UV-VIS spectrophotometer (Shimadzu, UV-1601).

De-coloring process: In this state, the reversible rate of photochromic samples were measured and evaluated. The UV lamp was removed and the color strength (λ_{max}) of un-excited specimens were measured by using UV-VIS spectrophotometer (Shimadzu, UV-1601) at various times (1, 3, 5, 10, 15, 20 and 30 mins after removing UV source). In this step, the timeline was continuously recorded and was reported as 31, 33, 35, 40, 45, 50 and 60 mins.

C3. Fatigue resistance (useable lifetime)

The usable lifetime or fatigue resistance to UV energy of photochromic specimens was evaluated. The test specimens were exposed to UV light source (UV intensity = 50 W/m^2) continuously until reach 72 hrs. The color strength (λ_{max}) was continuously monitored until end of test at the 72th hour.

III. RESULTS AND DISCUSSION

A. Effect of matrix types on the apperance of photochromic coating layer

A1 Visual evaluation results

Non-polyurethane based

Referred to section *B1* on the previous part, the quality of coating layers (in term of transparency) that were prepared from the combination between high T_g polymers (a, b, c) and low T_g polymers (e, g, h) are reported on Table IV.

TABLE IV. QUALITY OF NON-PU BASED COATING LAYERS

High T_g polymer + Low T_g polymer	***Transparency***
(a) + (e)	Slightly translucent
(b) + (e)	Poor (Very haze)
(c) + (e)	Poor (Very haze)
(a) + (g)	Poor (Very haze)
(b) + (g)	Poor (Very

High T_g polymer + Low T_g polymer	***Transparency***
	haze)
(c) + (g)	Poor (Very haze)
(a) + (h)	Poor (Very haze)
(b) + (h)	Poor (Very haze)
(c) + (h)	Poor (Very haze)

Remark: Ratio between high and low T_g polymers was fixed at 95:5 by weight.

According to the preliminary quality check by visual inspection, all of mixed non-polyurethane based matrices didn't pass and aren't suitable for using as photochromic coating layer on ophthalmic lenses. The poor transparency of mixed polymers causes from the different in the refractive index of each polymer also has a large influence on haze [7]. This effect is very consistent with light scattering theory [7]. Based on this learning, we have to check the compatibility and refractive index of each selected polymer before mixing in order to obtain good transparency blending system.

Because of all non-polyurethane based systems didn't pass the visual inspection and we didn't perform the photochromic sensitivity and fatigue resistance tests on these specimens.

Polyurethane based

The appearances of PU based matrices that were embedded with various kinds of photochromic pigments and light stabilizer additive are shown on Figure I. After visual inspected, all specimens showed good transparency property at normal and excited states (exposed to UV). According these results, we concluded that PU based matrices showed really good compatibility with photochromic pigments and additive. In addition, they have strong interface adhesion with polycarbonate substrate [8].

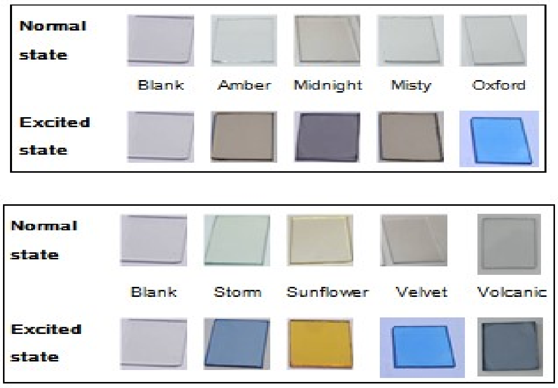

FIGURE I. visual apperances of pu based photochromic system

B. Effect of photochromic pigment types on sensitivity and fatigue resistance

B1. Rate of color change (sensitivity)

Polyurethane based

On this step, the rate of color change or photochromic sensitivity of PU based photochromic system with various kinds of pigments had been performed. The test results are tabulated on Figure II. The Midnight grey and Sunflower pigments exhibited high color strength.

Reverse time or recovery time of the photochromic system is the one of important parameter that can be used for evaluating the pigment performance. Midnight grey reversed from excited state to normal state suddenly (within 3 second after removing UV source) but Sunflower pigment took longer time (more than 2 mins) before reversing back to normal state. Oxford blue and Velvet blue also exhibited really short reverse time (within 3 second). The others pigments (Volcanic grey, Amber, Misty grey and Storm purple) took longer time for reversing back.

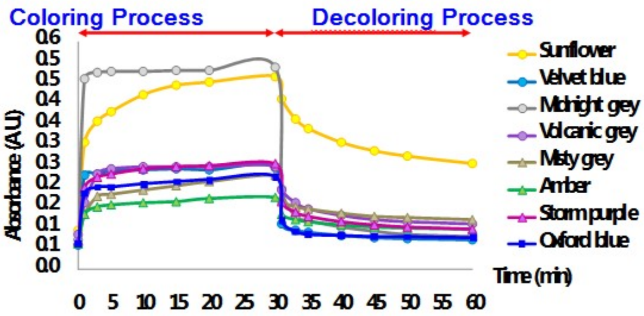

Figure II. Photochromic sensitivity (rate of color change) of PU based photochromic layers

B2. Fatigue resistance of photochromic system (useable lifetime)

The photochromic specimens were exposed to UV light source (UV intensity = 50 W/m2) continuously until reach 72 hrs. The color strength (λ_{max}) was continuously monitored until end of test at the 72th hour and the results are shown on Figure III

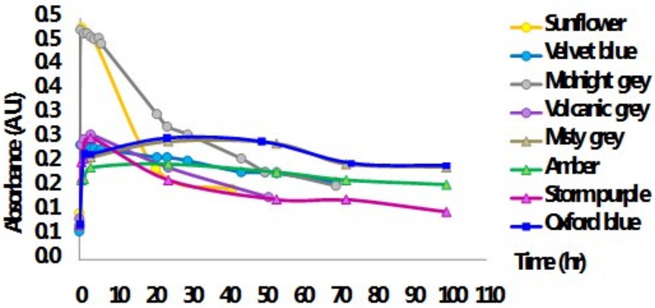

Figure III. Fatigue resistance of PU based photochromic layers

In this test, the maximum absorbance (λ_{max}) of Midnight grey pigment was dramatically decreased by UV light energy and reach the lowest point at the end of test. The Sunflower pigment exhibited the same behavior as Midnight grey but the maximum absorbance (λ_{max}) cannot detect after reach the 40th hr. This phenomenon implies that photochromic efficiency was losing while exposed to UV energy continuously.

On the other hand, Oxford blue and Misty grey exhibited the highest maximum absorbance (λ_{max}) until end of test at 72th hr. In addition, Strom purple and Amber pigments showed the good fatigue resistance too but they have lower maximum absorbance (λ_{max}) than Oxford blue and Misty grey. We extended the testing time to 100 hrs and observed the maximum absorbance of these pigments. At 100th hr, λ_{max} of Oxford blue, Misty grey and Amber slightly changed whereas λ_{max} of Storm purple significantly decreased.

After considered these results (B1 and B2), three types of photochromic pigments (Midnight grey, Oxford blue and Mistry grey) were selected because they have balance property between sensitivity and fatigue resistance.

On the next step, mixtures of pigments were prepared in order to balance the advantages of each pigment type. The results are shown on Figure IV. The combination between Midnight grey and Oxford blue exhibited the highest fatigue resistance over other two systems. According the results, the combination between Midnight grey and Oxford blue was chosen and used on the next section.

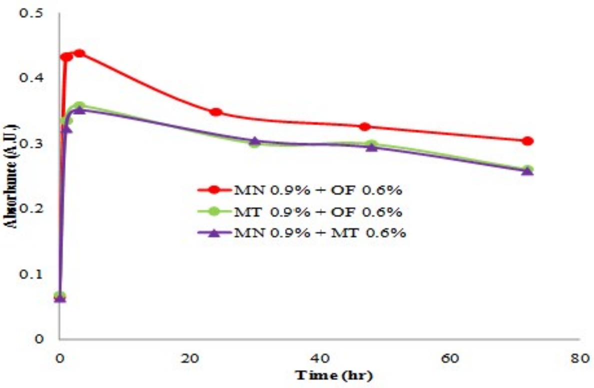

Figure IV. Fatigue resistance of mixed photochromic pigments

C. Effect of ratios between rigid and flexible polymers on PU based photochromic system

On this step, the effect of the dosage ratios between rigid and flexible polymers on the photochromic efficiency of PU based system was investigated. The dosage of photochromic pigment and additive were fixed at 1.5% and 1.5% by weight, respectively. The photochromic pigment was prepared from the combination between Midnight grey and Oxford blue. The photochromic sensitivity and fatigue resistance are chosen as monitoring parameters. The test results are shown on Figure V and VI.

From Figure V, all specimens exhibited photochromic effect suddenly after expose to UV source. The photochromic sensitivity is shorter than 5 sec and less than 3 sec if the ratio between Desmophen 670/Desmophen870 is equal to 0.38. The maximum absorbance (max) increased with increasing ratio of Desmophen 670 upto 0.38 but the fatigue resistance trended to decrease with increasing Desmophen 670. The flexibility of PU matrix is increased with increasing ratio of Desmophen 670. Photochromic pigment is easily excited by UV energy when it was embedded in high flexibility matrix but causes to reduce the usable lifetime.

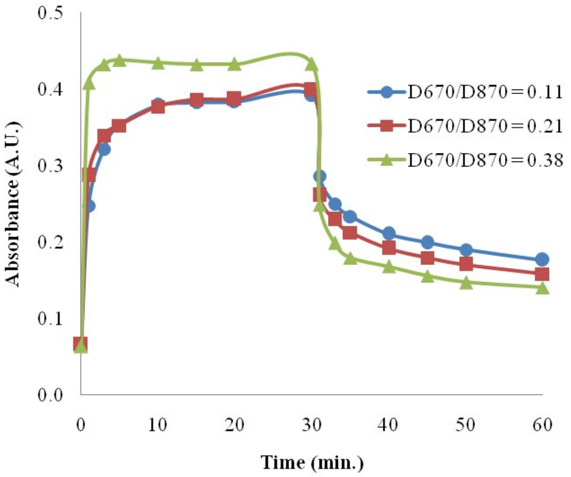

FIGURE V. photochromic sensitivity of pu based matrix

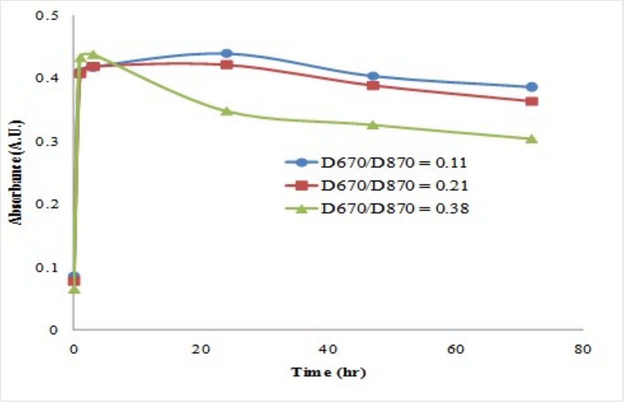

FIGURE VI. Fatigue resistance of pu based matrix

On the next step, low T_g polymer (Polycaprolactone diols, PCL diols) was added into PU based solution because Krishnan et al. [9] reported PCL and PCL diols can enhance flexibility of polyurethane matrix. The selected dosage ratios between flexible polymer : PCL diols : rigid polymer :Crosslinking agent are tabulated on Table III and the results are shown on Figure VII and VIII.

The sensitivity and maximum absorbance (λ_{max}) of photochromic system were increased with increasing PCL diols content because flexibility of PU matrix was increased too. In contrast, the fatigue resistance was decreased as increase PCL diols because the same reason. According to obtained results, flexibility of PU matrix has to be concern because it affects to overall properties of photochromic system [9].

PU based with 2.5% PCL diols was selected as the best formulation because it showed the balance in sensitivity and fatigue resistance.

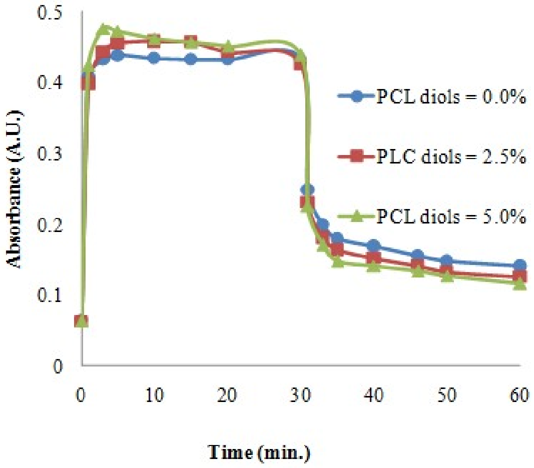

FIGURE VII. Photochromic sensitivity of pcl-diols embeded in pu based matrix

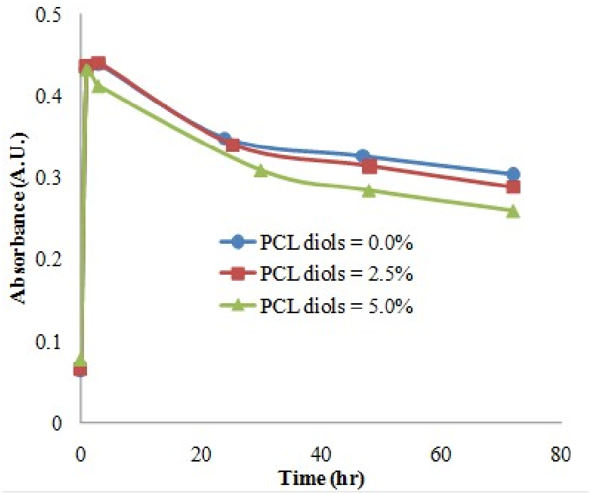

FIGURE VIII. Fatigue resistsnce of pcl-diols embeded in pu based matrix

IV. CONCLUSION

In this work, we succeed to prepare the photochromic system which can exhibit photochromic property and has very short rate of color change (sensitivity). The shortest color change time is less than 3.0 sec when 2.5 wt% of PCL diols was added into PU based system. The appropriated ratio between flexible polymer (Desmophen 670) and rigid polymer (Desmophen 870) is equal to 0.38. In addition, the combination between two types of photochromic pigment provided better fatigue resistance than using single pigment. The composition of the best formulation is shown on Table V. The flexibility of photochromic matrix is strongly affect to sensitivity and useable lifetime of finished product and has to be concerned.

TABLE V. formulation of selected photochromic system

Component	Materials	Wt% of solid content
Photochromic Pigment	Midnight grey and Oxford blue	1.5% (0.9 + 0.6)
Additive	Tinuvin 144	1.5%
Low T_g polymer	Polycapolactone diols	2.5%
Rigid polymer	Desmophen 870	48.0%
Flexible polymer	Desmophen 670	18.0%
Crosslinking agent	Desmodur N 3390	28.5%
Total		**100%**

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