

# UV Curable Coatings and Paints Containing Fluorin for Exterior Applications

*Haoya Tan, Lihui Zhou, Wei Che/ Zhuhai Dongcheng Chemical Co. Ltd., Nanshui Chemical District, Zhuhai, Guangdong 529050, P. R. China*

## **Abstract**

A kind of UV curable fluorine-containing acrylate oligomer (FCA) was synthesized based on fluorinated alkyl hydrocarbon modification. The formulations of varnish and pigmented paints were developed using FCA as a main component by selecting different reactive diluents, photoinitiator, pigments and additives. The developed resins were demonstrated to have strong capabilities of weathering resistance, light resistance, chemical resistance and dirt resistance. They have been successfully applied in the areas of interior and exterior architectural coatings on different substrates, such as aluminum-plastic composite panel, plastics and aluminum alloys. Moreover, they are suitable to be applied in the special conditions with high humidity and temperature such as kitchen, bathroom, laboratory, etc.

## **INTRODUCTION**

Due to the worldwide energy deficient and environmental problems, the ‘5E’ rule in coating industries has become more and more important. Recently, radiation curing technology for buildings’ interior and exterior coatings has been widely used because of low energy-consuming, low cost, water resistance, safety, easy renewal and so on.<sup>1</sup> From July 1st, 2007, a new national standard about energy-saving design in public buildings (GB 50189-2005) has been implemented in China. An object of 50% total energy saving in the construction of buildings is proposed.<sup>2</sup> Therefore, there will be a promising increase in the consumption of architectural coatings in China.

There are several kinds of resins for exterior architectural coatings such as pure acrylic resin, urethane acrylic resin, silicon modified acrylic resin and fluorine-containing resin. The pure acrylic resin has a lower capability of weathering and dirt resistance comparing with others, while the general properties of urethane acrylic resin and silicon modified acrylic resin haven’t match the top-grade decorative requirement of exterior walls. As well known, fluorine-containing polymers have enhanced abilities in weathering resistance, chemical resistance, heat resistance, water repellence, oil repellence and so on when compared with hydrocarbon based polymers. Therefore, the fluorine-containing resin applied as top-grade exterior architectural coatings has been concerned specially and become more and more attractively.<sup>3</sup> Fluorine-containing resin has been developed more than 40 years experiencing high temperature melting type, low temperature crosslinking type and organic solvent-borne and water-borne type, respectively. At the present time, the mostly widely used are organic solvent-borne type fluorocarbon resin with a low solid content.<sup>4</sup> However, these organic solvent-borne resins should be replaced due to the increasing environmental concerns and the ongoing legislation to cut the

emissions of volatile organic compounds. Therefore, UV curable fluorine-containing resin will play more important role in future due to its higher solid content, energy saving and efficiency and so on. Up to now, many kinds of UV curable fluorine-containing resins have been developed. For example, a kind of fluorine-containing UV curable urethane acrylate was developed by Solvay Solexis S.p.A.<sup>5</sup>(Italy)

In this study, a kind of fluorine-containing UV curable oligomer was synthesized. Then the applications in formulating UV curable varnish coatings and pigmented coatings were investigated. The cured films are tested and evaluated in details and their applications in different areas are also discussed.

## Experimental

### Materials

Trimethylol propane triacrylate (TMPTA), tripropylene glycol diacrylate (TPGDA), 1,6-hexanediol diacrylate (HDDA) and ethylenediamine modified trimethylol propane triacrylate (NTMPTA) were supplied by Sartomer (USA), Cytec (USA) and Tianjiao Chemical Co. (Tianjing, China). Photoinitiators including TPO , ITX , UV907 , UV1173 and UV184 were obtained from CIBA (The Netherlands) and Changsha NewSun Chemical Co. (Hunan, China). Pigments were purchased from BASF ( Germany). Additives were obtained from BYK Co.(Germany). UV curing systems was purchased from Zhuozhou Lantian Co. (Hebei, China).

### Synthesis of FCA

Two methods were used to synthesize UV curable fluorine-containing acrylate (FCA).<sup>5-10</sup> The fluorous content in FCA could be tunable by changing the feed ratio of monomer in the copolymerization.

### Formulations and Cured Films

The developed formulations of UV Curable fluorine-containing varnish and pigmented coatings based on FCA are shown in Table 1 and Table 2, respectively.

**Table 1. Formulation of Varnish Coatings**

Ingredients	Weight percentage
FCA	50-85
TPGDA	5-15
TMPTA	5-20
UV184	3-5
TPO	0.5-1
BYK 055	0.1-0.3
BYK 306	0.1-0.3



**Table 2. Formulation of Pigmented Coatings**

Ingredients	Weight percentage
FCA	50-85
HDDA	5-10
NTMPTA	3-5
UV1173	2-3
TPO	2-3
ITX	1-2
Pigment	10-15
BYK 163	0.5-1
BYK 055	0.1-0.3
BYK 306	0.1-0.3

## Results and Discussion

The properties of the developed formulations and their cured films are listed in Table 3 as below.

Table 3. Basic Properties of Fluorine-containing Resins and Their Curing Films

Name	DC-SNB0	DC-SNB1	DC-SNB-P	Test Standard
Type	Penetrating agent	filler	pigmented coating	
Appearance	Transparent liquid	Opalescent viscous liquid	Viscous liquid	
Viscosity (TU-4 cup viscometer, 25°C) Second	15±1	150±5	Determined by different color	GB/T 1723-1993
Solid content (%)	≥95	≥95	≥95	
Curing speed, m/min ( 800mJ/cm <sup>2</sup> )		≥20	10-20	
Film appearance		smooth and glossy	smooth and glossy	
Glossness (60°) %			10-95, tunable	GB/T 9754-1988
Pencil hardness			≥2 H	GB/T 6739-1996
Cross-cut test, Grade		≤1	≤1	GB/T 9286-1998
Boiling water resistance			≥48 h	GB/T 1733-1993
Acid resistance			≥168 h	GB/T 9274-1988
Basic resistance			≥168 h	GB/T 9274-1988

Artificial weathering resistance			≥5000 h	GB/T 1865-1997
Neutral salt spray test			≥3000 h	GB/T 1771-1991
Damp heat resistance			≥2000 h	GB/T 1740-1989
Thermal cycling test			≥12 times	JG/T 25
Scrub resistance			≥12000 times	GB/T 9266-1988
Solvent resistance			≥120 times	GB/T 9274-1988
Dirt resistance, %			≤10	GB/T 9257-2001

As the resins according to the formulations in Table 1 and Table 2 exposed to 800mJ/cm<sup>2</sup> medium mercury lamp to irradiate for 5 seconds, the UV cured films with good properties were obtained. Due to be 116 Kcal/mol of F-C bond energy, which is the most strong among organic bonds, the F-C bond is very difficult to be broken under UV and heat irradiation. The cured film has weathering resistance character. After 5000 hours artificially ageing, the gloss still retain over 90%. It is also expected that the duration will be over 20 years.

The volume of fluorine atom in F-C bond is very big. Moreover, the C-C chain is enwrapped tightly by F-C chain, forming helical molecular structure, and strong screen effect. Therefore, F-C polymer films have excellent acid, alkali, solvent-resistance performance. The developed formulations were UV cured to obtain the coatings, which can expose to salt brume for over 3000 h, and be dipped in 5% HCl or 5% NAOH solution for 168 h without damaging adhesion with substrates. The surface tension of coatings is very low, resulting in good scrub-resistance property of over 120,000. The coatings possess both water and oil repellence. After dipped in boiling water for 48 h or in water of 40°C for 240 h the cured film showed no any damage. Moreover, the films have mildew-resistance property except for high adhesion to different substrates and good impact performance.

The comparison results of the developed SNB series of formulations for UV curing F-C paints with traditional solvent-based F-C paint and solvent-based polyurethane acrylate paint are listed in Table 4.

Table 4 Comparisons of UV Curable fluorine-containing coatings with solvent-based F-C pain and solvent-based polyurethane acrylate paint.

property	SNB series UV F-C paint	solvent-based F-C pain (exterior wall)	solvent-based polyurethane acrylate paint
Solid content	≥95%	≤50%	≤50%
Curing time	3-5 s	Exterior dry 20 min , entity dry 24 h	Exterior dry 20 min , entity dry 24 h
Curing temperature	Room temperature	180-250°C	120-150°C
adhesion	Good, special UV F-C soak agent and greasy physicochemical reaction, Cross-Cut Test ≤1 grade	good , Cross-Cut Test ≤1 grade	good , Cross-Cut Test ≤1 grade; after using easy bubbly, chap and peeling
Outdoors duration	Over 20 years , artificial accelerated ageing > 5000 h , scrubbing >12000	15-20 year , artificial accelerated ageing > 4000 h , scrubbing >10000	8-10 year , but after 2-3 year nigrescence , dirty
Corrosion resistance	≥3000 h	≥1500 h	≥500 h
chemical resistance	excellent	good	inferior
Water resistance	> 48 h boiling , or 240 h warm water	3 h boiling	1 h boiling
sully resistance	excellent	excellent	inferior
mildew resistance	excellent	good	inferior

From Table 4, it can be seen that the developed UV Curable fluorine-containing coatings possess high performance-to-price ratio , and have been applied in the areas of interior and exterior architectural coatings on different substrates, such as aluminum-plastic composite panel, plastics and aluminum alloys. Moreover, they are suitable to be applied in the special conditions with high humidity and temperature such as kitchen, bathroom, laboratory, etc..

## Conclusion

Due to high bond energy and special configuration of fluorocarbon materials, Many distinguished advantages such as weathering resistance, chemical resistance, heat resistance, water repellence, oil repellence can be achieved by incorporating fluorine-containing structure into hydrocarbon based polymer. UV curable process is considered to be a clean and green technique and now being increasingly used in various sectors of applications. Combining the above advantages, we have developed a kind of UV curable fluorine-containing varnish and pigmented coatings, which were demonstrated to have strong capabilities of weathering resistance, light resistance, chemical resistance and dirt resistance. Those resins have been successfully applied in the areas of interior and exterior architectural coatings. It also can be used as coatings in kitchen, bathroom and laboratory, etc., though a high humidity and temperature conditions there are.

## Reference

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