The Progress of Newly Developed Fluoro-polymer Topcoat Systems

－Weathering performance and track records since the 1980's－

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ABSTRACT

Coating systems with ambient cure fluoro-polymer topcoats were developed in 1982 and have been applied to numerous steel structures since then. They have been demonstrated to give the best weathering performance among other commonly used topcoats. To confirm this, outdoor tests and accelerated weathering tests have been carried out. Gloss retention during exposure was measured, the surface appearance of each sample observed by SEM, and surface degradation analyzed by FT-IR spectroscopy. In addition, the extent of coating degradation by chalking was measured. It was observed that chalking of fluoro-polymer was much lower compared with that of coating systems such as polyurethanes, which means the fluoro-polymer coating retains its initial coating film thickness. Fluoro-polymer coatings have been applied to many steel and concrete structures, for example to high rise buildings and bridges where it is not easy to do maintenance. The results showed that the protective performance of the fluoro-polymer coating system was superior to other topcoats such as the polyurethane coating. Track records of fluoro-polymer topcoats were also studied and compared with laboratory testing.

Key words: Weather-ability, Protective performance, Fluoro-polymer coating
Surface observations, maintenance, Life cycle cost

INTRODUCTION

Several different types of coating systems have been used for steel and concrete in Japan, e.g. bridges.

Generally speaking, fluoropolymer coatings are superior to other coatings in properties such as heat resistance, weather-ability and chemical resistance. These characteristics arise from the strong chemical bonds between carbon and fluorine atoms in the polymer structure. Fluoropolymer coatings are also highly resistant to ultraviolet light from the sun.

Coating systems with fluoropolymer topcoats have been applied to steel and concrete structures both offshore and onshore, and the protective capability and weather-ability of the coating system have been examined.[1, 2]

Both outdoor and accelerated weathering tests have been carried out. Especially outdoor exposure tests have now passed over 20 years resulting in truly excellent weather-ability. The result in decrease of film thickness of fluoro-polymer top coat was less one micron after 18 years outdoor exposure test we feel highly significant. Gloss retention during exposure was measured; the surface of the each sample was observed by SEM, and analyzed by FT-IR spectroscopy to investigate surface degradation. The results of these tests for an ambient cured fluoropolymer topcoat are discussed below.

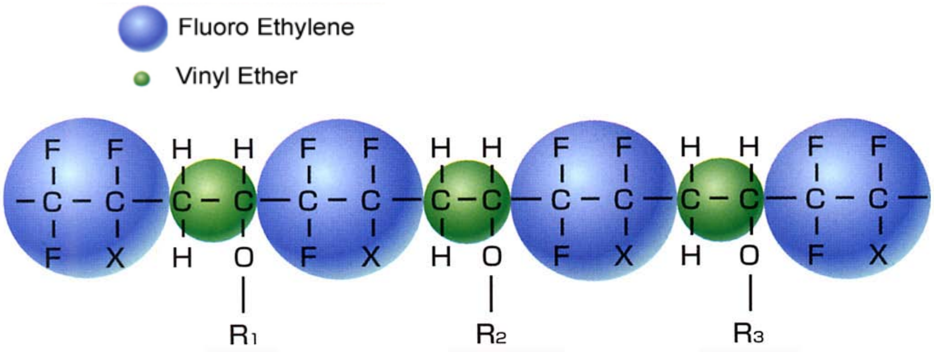
FLUORO-POLYMER COATINGS

Composition of Ambient Curing Fluoro-polymer

Fluoro-olefin vinyl ether copolymers, abbreviated FEVE, were developed as highly durable polymers for coatings. These solvent soluble, ambient cure fluorinated copolymers were introduced in 1982.

The polymer structure of the FEVE resin is shown in Figure1. The FEVE polymer structure consists almost entirely of regularly alternating fluoro-ethylene and vinyl ether segments. While FEVE resins derive durability from the strong C-F bonds, this regularly alternating sequence is the main reason for the high level of durability compared with conventional polymers like acrylics.

FEVE paints have for some time been used as solvent borne, ambient curable coating raw materials cross-linked with isocyanate hardener. They can also be cured at high temperatures with blocked isocyanate or melamine hardeners. So FEVE paints can be used both as field applied coatings and for factory coatings.



Fluoro ethylene Segment	Vinyl Ether Segments
Weather ability, durability,	R1=Clarity, gloss, hardness
chemical resistance	R2=Flexibility
	R3=Cross linking site (-OH)

Figure1: Structure of fluoro-polymer [3]

Fundamental Chemistry of Fluoro-polymer

Table 1 shows bond energies of Fluoro-compound compared with commodity compounds. The bond energies found in the alternating copolymer of the FEVE resin are higher than the energy in natural UV light. This makes the fluoro-polymer difficult to decompose by natural UV radiation. When UV radiation decomposes a chemical bond, free radicals are formed. These free radicals can initiate degradation of other coating components, including the reacted resin, pigments, and other additives. It is very difficult to generate these free radicals in the FEVE resin. Therefore, the degradation of the crosslinked FEVE coating, which contains several types of chemical bonds, is more difficult than in common polymers like standard polyurethanes and acrylics.

Table 1

Bond energy of Fluoro-Chemicals and Commodity-Chemicals [4]

Resin	C-C Chain	KJ/mol	C-F. C-H	KJ/mol
Fluoro-Compound	C**F**3-CF3	**414**	**F-**CF2-CH3	**523**
	C**F**3**-**CH3	**424**	C**F**3CH2**-H**	**447**
Commodity	CH3**-**CH3	379	CH3CH2**-H**	411

Natural strongest UV energy in the outdoor: 411KJ/mol (290nm)

Results of Molecular Weight Change of Fluoro-polymer Compared with Polyurethane

Coated panels were attached to a bridge in a marine environment and exposed to the atmosphere for 3 years. The initial and final molecular weight of the coatings was determined by dissolving the cured films in tetra-hydro-furan (THF) and analyzing by gel permeation chromatography. Table 2 shows the molecular weight change in a fluoro-polymer coating compared to that of a polyurethane coating after outdoor exposure test. The fluoro-polymer showed no change in molecular weight, but the polyurethane binder was drastically decomposed during the course of the test.

Table 2

Change of mol wt on Fluoro-polymer and Polyurethane paint

Over sea Exposure	Binder Resins			
	Fluoro-polymer		Polyurethane	
Exposed period (years)	0	3	0	3
Mn	9,000	8,400	3,600	600

LABORATORY INVESTIGATION OF FLUORO-POLYMER TOPCOAT AS PART OF A COATING SYSTEM

General Performance

The four different coating systems given in Table 3 are either in use currently or have been used in the recent past as typical protective coatings in Japan. Due to good results in performance testing, the fluoropolymer topcoat system has been adopted as a guideline by a transportation authority in Japan for use on bridges.[5, 6, 7] The fluoro-polymer was adopted as one of the generic types in ISO12944-5.

Table 4 shows the performance of fluoro-polymer topcoat in several liquid chemical environments. The film appearance was observed and degree of rusting, blistering and cracking were assessed.

The protective performance of fluoro-polymer coating system was superior to other coating systems not only in accelerated laboratory testing but also during field service in a marine environment after more than 10 year exposure. [5, 6, 7]

Table 3

Coating systems used for the outdoor exposure test

Topcoat / System	Fluoro-polymer	Polyurethane	Chlorinated rubber	Alkyd
Substrate	steel panel			
Primer	zinc-rich primer			Wash primer
Undercoat	Epoxy resin	Epoxy resin	Chlorinated rubber	Anti corrosive Undercoating
Intermediate Coat	Epoxy resin	Epoxy resin	Chlorinated rubber	Alkyd
Top coat	Fluoro-polymer	Polyurethane	Chlorinated rubber	Alkyd
Total Film thickness(μm)	255	255	245	170

Table 4

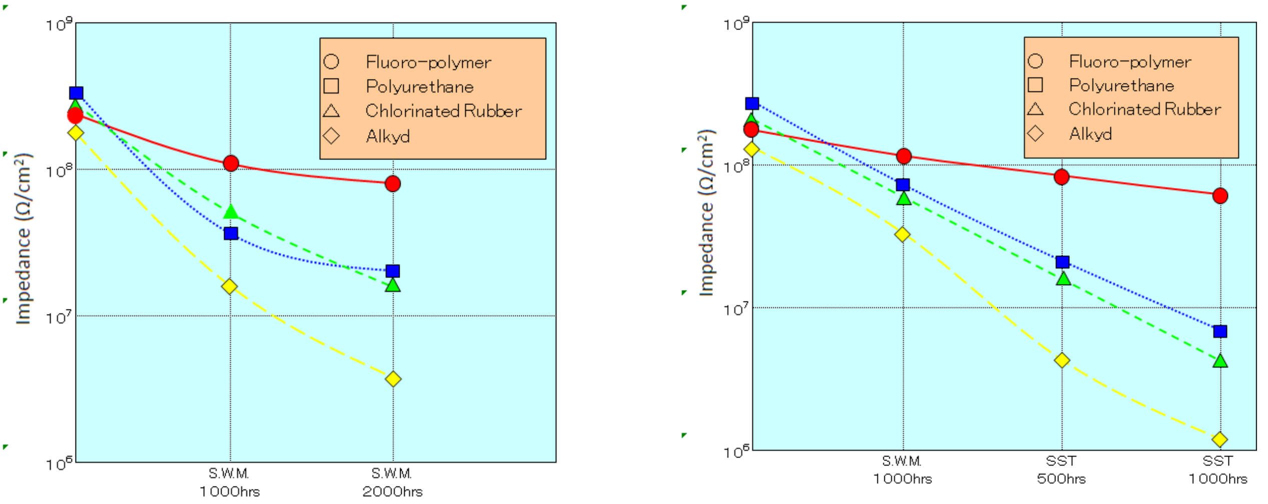
Performance of Fluoro-polymer Topcoats in coating systems

Test items	Test contents	Test result
Gloss	60°	80%
Adhesion	2mm cross cut	25/25
Bend	10mm	No defect
Shock resistance	Du Pont 300gx50cmx1/2in.	Excellent
Hardness	Pencil hardness	H
Chemical resistance	5%NaOH Soln./six months.	＞6 months
	5%HCl Soln./six months.	＞6 months
Protective performance	3%NaCl Immersion	＞12 months
	Salt Spray/1000h.	＞10,000 hrs.
Weathering performance	Sunshine Weather Meter, 4000h.	Gloss Retention 90%

Test specimen: OZRP/75 μ m + Epoxy/120 μ m +Fluoro-polymer/55 μ m

Corrosion Protective Performance of Fluoro-polymer Coatings

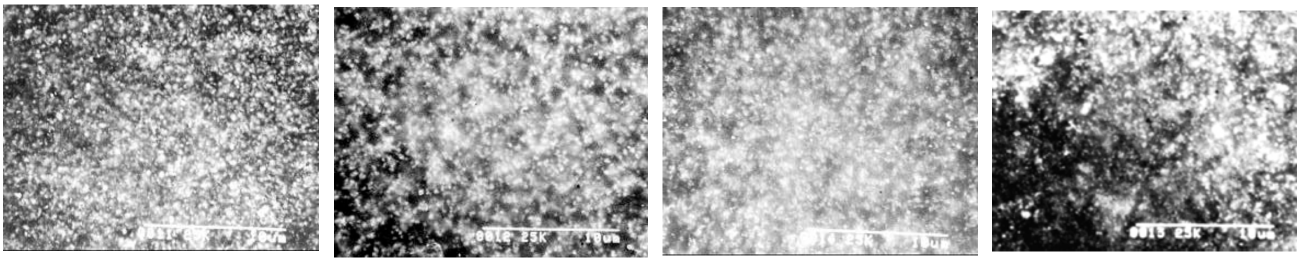
Each top coat system in Table 3 was tested by an electrochemical impedance measurement before and after accelerated testing, in the “sun-shine-weather meter ”(SWM) and in the salt spray test (35℃,5％NaCl). The smaller the change in impedance is, the better the corrosion protection imparted by the coating system. Test results are shown in Figure 2. The impedance reduction of the fluoro-polymer topcoat is the smallest in each system. There is a substantial difference in impedance change between the fluoro-polymer system and the polyurethane system even though only the top coat is different. This is caused by the difference in the degradation level of the coating surfaces. The polyurethane film has no binder layer on the surface after testing; only pigments were observed by SEM. Corrosive materials such as chloride ion and water are believed to be able to penetrate to the inner coats of the polyurethane film, initiating further coating degradation. The degradation of chlorinated rubber and alkyd system is observed with large cracking of the alkyd and the chlorinated rubber, more than polyurethane. Table 5 shows time period ratio of corrosion protection for each coating system calculated from each gradient of the slope in Figure 2. The fluoro-polymer system has more than doubles the corrosion protection time of the polyurethane system even though the coating systems differ only in the topcoat. This indicates that the fluoropolymer topcoat is far more effective than the polyurethane topcoat in preventing corrosion initiation.



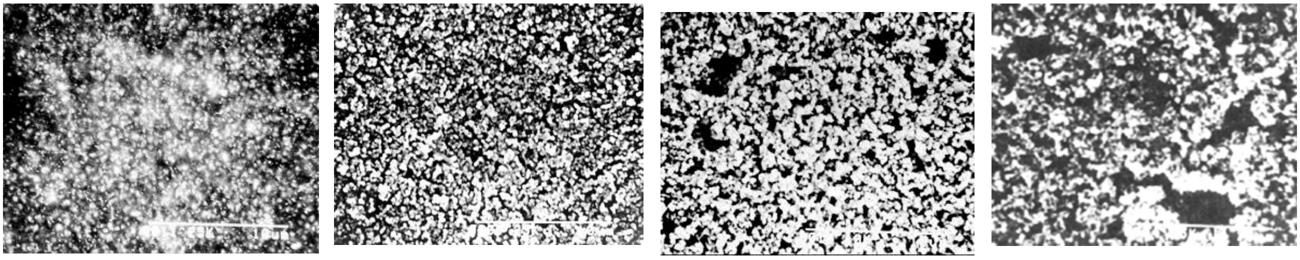
a) Sunshine WM 2000 hrs b) Sunshine WM 1000 hrs + Salt spray test 1000

Figure 2: Impedance reduction for each Top coat system after accelerated testing

Initial surface: 0 hrs



Exposure surface with SWM after 2000hrs



Fluoro-polymer Polyurethane Chlorinated rubber Alkyd

10μm

Figure 3: SEM observation of surface for each coating system

Table 5

Time period ratio of corrosion protection for each coating system

Top coat system	tan θ from slope in Fig 2 a)	The period ratio of Protection
Fluoro-polymer	5.7	2.2
Polyurethane	2.6	1.0
Chlorinated Rubber	1.8	0.75
Alkyd	1.3	0.5

After the 4-year outdoor exposure test at Miyakojima in Okinawa, the retention of adhesive strength and electrochemical resistance were measured. The film resistance of each coating system is shown in Figure 4. [9] The degradation of the dielectric property of fluoropolymer topcoat system was lower than the polyurethane topcoat system and chlorinated rubber coating system after 4 years. The change in adhesive strength with time for each of the three coating systems is shown in Figure5. [9] The change in adhesive strength retention of fluoropolymer topcoat system was lower than the polyurethane topcoat system and chlorinated rubber coating system.

The test results suggest that a UV resistant fluoropolymer topcoat system may provide better adhesion and dielectric property retention after long term service.

Table 2 (above, p. 4) shows the performance of fluoropolymer topcoat in several liquid chemical environments. The film appearance was observed and degree of rusting, blistering and cracking were assessed.

The protective performance of the fluoro-polymer coating system was superior to other coating systems not only in accelerated laboratory test but also during field service in a marine environment after 10 year exposure. [8, 9, 10]

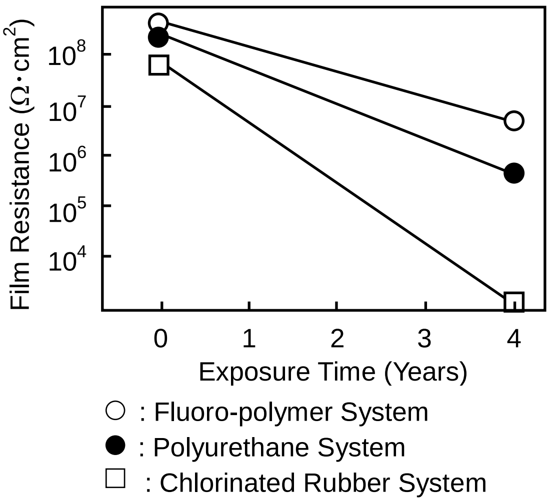


Figure 4: Film resistance after outdoor Exposure test (Miyakojima) [9]

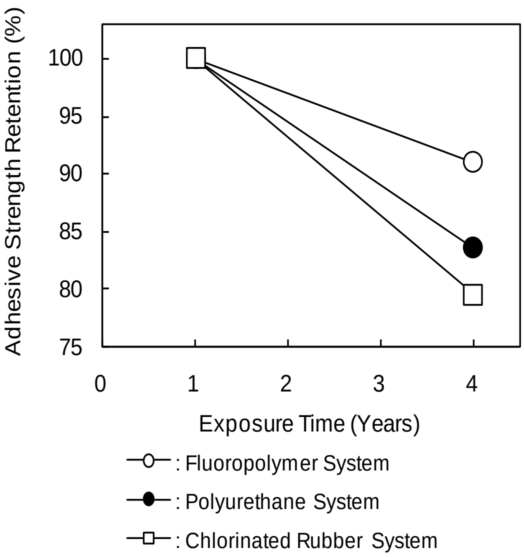
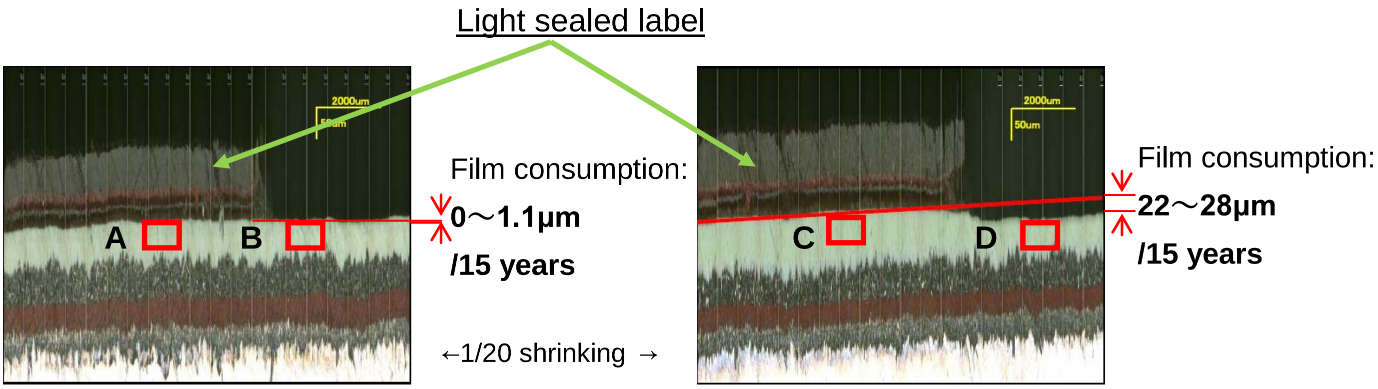


Figure 5: Adhesive Strength Retention after Exposure Test (Miyakojima)

The degradation starts from the top coating surface with the 1 µm resin layer at the coating surface disappearing. Chalking may appear and pigments are also degraded. As a result, water more easily penetrates through the film and under the film so corrosion of metal occurred. If the water penetration rate of the top coating is very low, weather-ability may be slow, and this will lead to the corrosion of metal occurring only slowly. Hence the corrosion protective performance may be affected by the weather-ability of the topcoat.

Weather-ability of Fluoro-polymer Coating

Fig.6 shows film consumption for the fluoro-polymer coating and polyurethane coating in cross section after 15 year exposed (horizontal scale:1/20 shrinking). A portion of the coating was covered with tape and thus was not exposed to sunlight. Under the tape the film was not damaged. The film thickness of each topcoat after 15 years outdoor exposure could be compared to the original film thickness under the tape. After 15 years, the fluoro-polymer topcoat has lost about 1.1μm total, about 0.1 μm/year), while the polyurethane topcoat has lost 22-28μm , about 2μm/year).



A, B, C, D area were for Imaging IR measurement as below (Figure 7)

a) Fluoro-polymer b) Polyurethane

Figure 6 : Consumption of topcoat in film thickness after15 year exposure (Cross section)

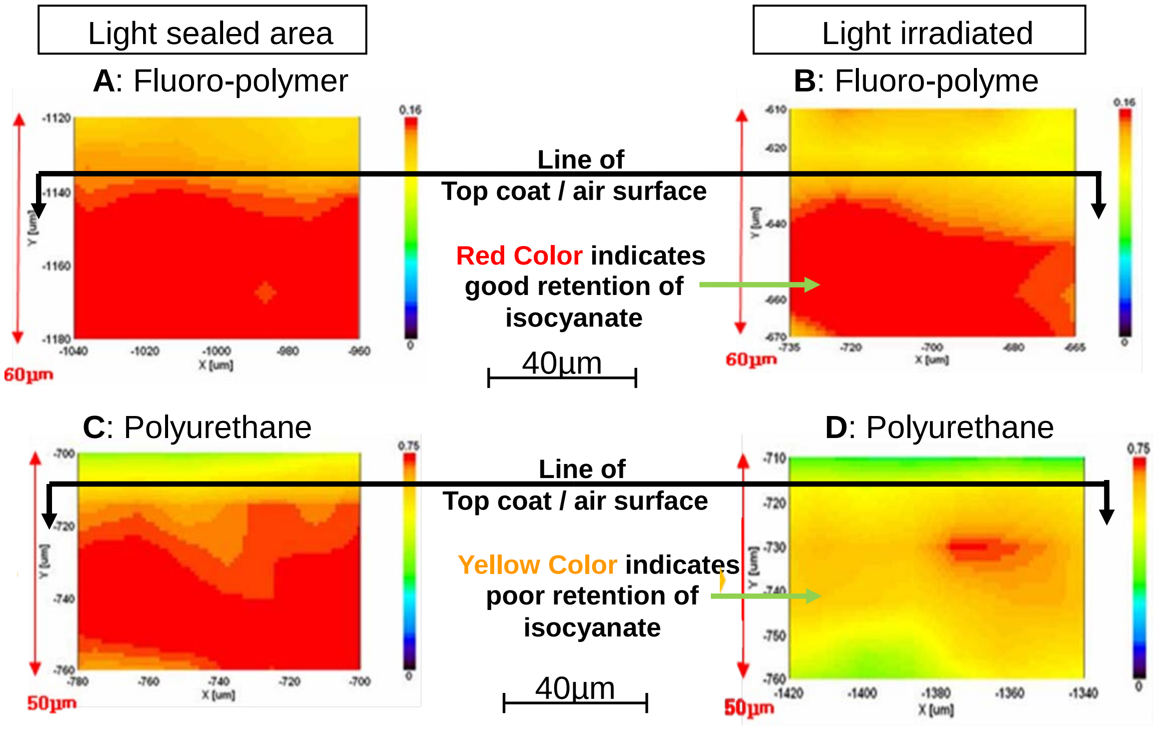


Figure 7: Isocyanates retention of each cross section of coats about mild light seal or irradiated surface area

In Figure 6, four points of Marked □ are measured area by Imaging IR (IRT-7000(1)). That measurement can trace amide (II) absorbance as distribution for cross-section area comparing with C-H band or C-F band. In Figure 7, the isocyanates in the protected area of each coating are shown in red. The portion of the polyurethane coating exposed to UV light shows the isocyanate decomposition in the polyurethane paint in the UV irradiated area in yellow. The decomposed area is seen even at 20μm depth from the surface. The fluoro-polymer coating shows no decomposition of the isocyanate.

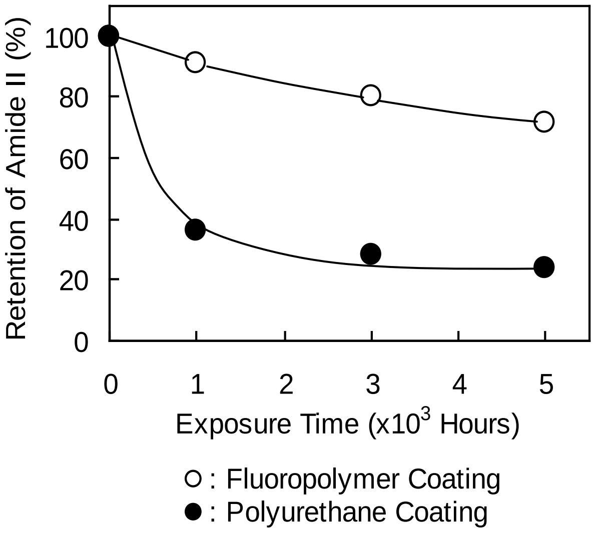


Figure 8: Change in Amide II Retention (QUV)

The amide (II) (1530cm^{-1}) retention ratio is shown in Figure 8 after 1000 hours of fluorescent UV-condensation cycle testing.[1] Surface degradation of the polyurethane coating was progressing steadily. On the other hand the fluoropolymer coating showed little or no surface degradation. The reason why the fluoropolymer coating did not show degradation was thought to be because fluorine atoms develop a structure with strong chemical bonding which makes it difficult to produce the free radicals which cause coating decomposition.

SUMMARY OF TRACK RECORDS OF USE OF FLUORO-POLYMER TOP COAT SYSTEM IN THE FIELD

Now that fluoro-polymer topcoats have been exposed for twenty six years. we review what has been learnt about them during the process. Two of the first applications of fluoro-polymer topcoats were for an oil tank in 1982 and for a power transmission tower in 1983.

The first patents on the use of fluoropolymer topcoats in highly weatherable coating systems were filed in 1985. [10]

Figure 9: Marine test station
In service since 1983

In Japan, the Public Works Research Institute and Ministry of Construction began the research project on “the technology of durability advancement for ocean structures by protective coatings for steel and concrete materials”, and a marine test station was build for this purpose in 1983.[11] In this research, fluoro-polymer topcoat systems were tested alongside other coating systems. The marine station was built 250 meters away from the coast in Suruga Bay. This station is one of 47 exposure sites throughout the world which are used in ISO9223. In order to establish the best protective coating system in an ocean atmosphere, an investigative project was started in 1984. One of the aims of the project was to find coating systems that have durability of more than 20 years. Fluoro-polymer and polyurethane coated panels were tested on the deck of the marine station. The change in gloss after 20 years of service is shown in Figure 10.[12], while the chalking rating after 20 years is shown in Figure11.[12] The gloss retention of polyurethane coating declined immediately after only 2 years of service, and the rating number for chalking was very low after 2 years . On the other hand, the gloss retention of the fluoro-polymer coating was higher than that of the polyurethane coating after 20 years. Chalking was not observed in the fluoropolymer coating. In summary the weatherability of fluoropolymer coating was still excellent after 20 years of service.

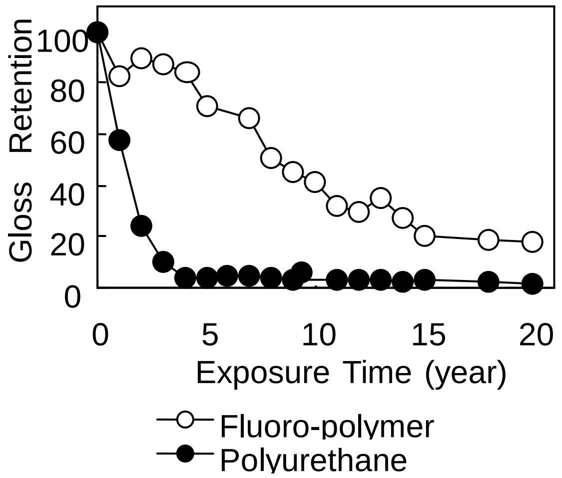


Figure 10: Outdoor Exposure Test[12]

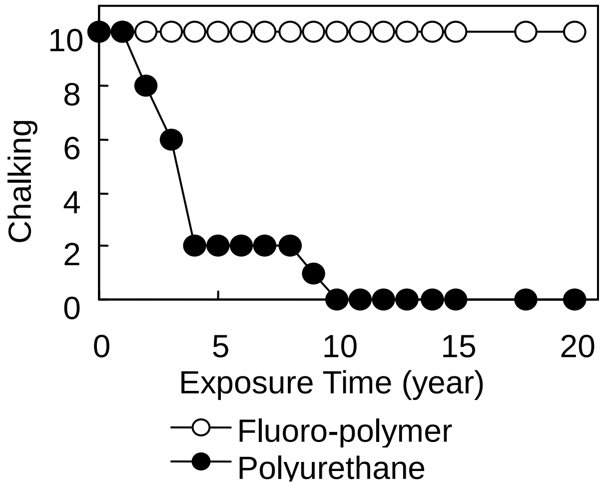


Figure11: Rating Number of Chalking[12]

The project of the collaborative research for lifetime improvement of off-shore structures organized by government institute started in 1983 in which fluoro-polymer topcoat systems were included with other coating systems. Now that twenty six years passed since then, we review the significance of fluoro-polymer topcoat we have learnt during the process. The total number of structures with applied protective coating system using fluoro-polymer topcoats has become about one thousand and their total area has been increasing to about three million square meters. Among them are Akashi Strait Bridge, 3991m in length in 1998 and Tokyo Aqua Bay Bridge 15Km in length in 1889.

Table 6

Gloss retention and color change after 20 years

	Wiped with wet cloth	Un wiped
Gloss retention (%)	100	92
Color difference ΔE	2.8	3.2

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(1) Jusco Corporation: 2967-5 Ishikawam-machi Hachioji-city Tokyo Japan

Figure 12: Tokiwa Bridge
after 20 years Photo in 2008

The bridge is shown in Figure 12 is the Tokiwa Bridge, Hiroshima, Japan. Table 6 shows gloss retention and color difference, those are almost unchanged after 20 years. Chlorinated rubber topcoat had been applied 8 years before the fluoro-resin system was adopted as repainting system 20 years ago. The durability and life cycle cost (LCC) of both systems is shown in Table 7. The initial total cost of the fluoro-polymer coating system was 1.5 times that of the chlorinated rubber system. The durability of fluoro-polymer paint has been more than 20 years, which is almost 3 times as long as the chlorinated rubber. Consequently the LCC (=Cost of one years : Life Cycle Cost) of the fluoro-polymer paint at present is lower than 1/2.6, or 58%, of the cost of the chlorinated rubber system.

Table 7

Durability and LCC comparison of Fluoro-polymer paint and C

System	Fluoro-polymer	Chlorinated rubber	Cost Ratio
Top coat ($)	502	101	5.0
Paint cost ($)	1,724	278	6.2
Manpower cost ($)	3,696	2,796	1.3
Scaffolding cost ($)	3,957	3,297	1.2
Total repaint cost ($)	9,377	6,371	1.5
Durability (years)	>20	8	>2.6(durability)
LCC: cost($) / year	469	796	<0.58

Some applications of fluoro-polymer coatings for bridges are shown in Figure 13, which are expected to keep good condition for many years. So it is estimated that Life Cycle Cost for the fluoro-polymer coatings will be lower than others.

Akashi Straits Bridge* (12 years)　Hirado Bridge (10 years)　Gateway Bridge; Nashville, TN

*Longest Suspension Bridge in the world.

Figure 13: Some of applications for bridges

Advanced　Application

High raised tower, “The Tokyo Sky Tree®”, 634m in height is under construction as a landmark structure in Dec. 2011 to be completed.[13] Regarding the advanced use of fluoro-polymer, a new coating system is shown in Table 8. The advantage of using the fluoro-polymer topcoat is the workability, that is, saving the number of coats, which means dry film thickness of 55 μm per a coat.

Table 8

A new coating system applied to structures

Coating system	Name of coating	DFT
Primer	Organic or Inorganic zinc rich primer	75μm
Intermediate coat	Epoxy	120μm
Top coat	Fluoro-polymer	55μm

Surface preparation for new work: ISO Sa2.5

Figure 14: “The Tokyo Sky Tree®” rendering (2),(3)

FURTHER DEVELOPMENTS

An important area is to make coatings more environmentally friendly i.e. reduce their VOC. To this end a weak solvent type consisting of mineral spirits that has a small MIR VOC value (i.e. generation of g-ozone/1g solution) has been developed for repainting top coat system. Water borne paint of fluoro-polymer has been also developed with hardener as 2K system as protection top coat for many steel structures.

SUMMARY

The durability of fluoro-polymer coating was investigated through the outdoor exposure tests and accelerated tests. The fluoro-polymer topcoat was extremely superior to other topcoats such as polyurethane, chlorinated rubber and alkyd in weather-ability. The decrease of film thickness by surface degradation after 18 years outdoor exposure was surprisingly less one micron. Protective performance of fluoro-polymer topcoat system was evaluated at a marine testing station. Degradation, such as rust, blistering, and chalking, were not obvious after 20 years. The degradation manner of top coating was found. The protective performance was affected by the weather-ability of top coating. Fluoro-polymer coating was excellent in weather-ability and its top coated coating system showed much better protective performance compared with polyurethane top coated coating system. Life cycle cost is expected to be reduced by adopting the fluoro-polymer. We suggest we should focus on the importance of top coat durability in coating systems.

(2) TOBU RAILWAY Co., LTD. : 2-18-12, Oshiage, Sumida-Ward, Tokyo, Japan
(3) TOBU TOWER SKY TREE Co., LTD. : 1-33-12, Mukozima, Sumida-Ward, Tokyo, Japan

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