derakane™ signia™ resins

improved shop efficiency

introduction

Introduced in 1965 to combat corrosion in hot, wet chlorine environments, Derakane™ epoxy vinyl ester resins have become the industry standard for corrosion-resistant fiber reinforced polymer (FRP) equipment. High performing derivatives have been introduced over the years to allow vinyl ester solutions for expanded chemical environments, high temperature performance and areas requiring improved toughness. With the introduction of Derakane™ Signia™, Ashland has leveraged new production capabilities to modernize resin features including improved environmental performance, better workability, increased workplace conditions and worker satisfaction.

features

Derakane™ Signia™ resins provide significant advantages for fabricators, designing engineers and owner / end users of corrosion-resistant FRP equipment.

in the shop

- low styrene emission
- improved shop efficiency
- longer shelf life

in the field

- unchanged polymer backbone
- identifiable resin system

In this paper we will expand on how Signia™ resins improve shop efficiency. Derakane™ Signia™ 411 bisphenol-A epoxy vinyl ester resin is used in key examples from shop trials to demonstrate how Signia™ technology provides a cleaner, more efficient shop environment.

Today many fabricators are challenged with finding qualified and experienced operators to meet current order demands. Anticipating these needs, Signia™ resins were designed to deliver improved processing characteristics to drive faster laminate consolidation, lower foaming, and greatly reduced sanding for application of secondary laminations. These features, combined with reduced styrene emissions, reduced odor from finished parts, and cure packages that can eliminate production steps when making thick parts lead to greatly improved shop efficiency and cleanliness resulting in a much more desirable workplace.

improved laminating

reduced foaming

Reduced foaming in Signia™ resins leads to less entrapped gas bubbles and faster consolidation of reinforcement layers. In Figure 1 the foaming of Derakane™ Signia™ 411 (left) is compared to Derakane™ Momentum 411-350 (right) 1 minute 30 seconds after adding Norox®[1] 925H MEKP. Much less foaming is seen in the Signia™ resin. This feature leads to laminates with fewer voids. In this study Derakane™ Signia™ 411 was promoted with 0.2 parts per hundred (pph) Cobalt Naphthenate 6% and 0.05 pph Dimethylaniline (DMA) and Derakane™ Momentum 411-350 was promoted with 0.2 pph Cobalt Naphthenate 6%. Both were initiated with 1 phr of high dimer Norox® 925H MEKP for a 15 minute gel time.

Figure 1: Comparison of foaming in promoted and initiated Derakane™ Signia™ 411 (left) and Derakane™ Momentum 411 (right) resin 1 minute and 30 seconds after initiation.

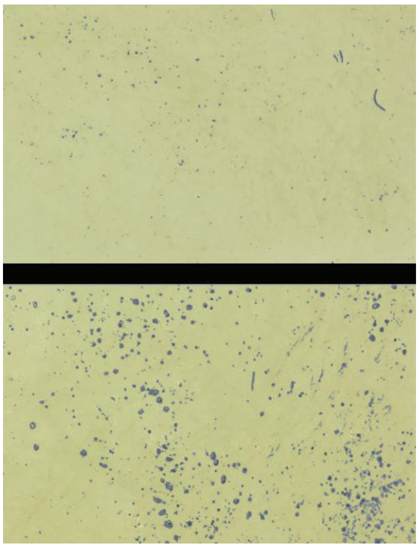

Figure 2: Backlit images of Derakane™ Signia™ 411 (top) and Derakane™ Momentum 411 (bottom) laminates used in image analysis for void content analysis.

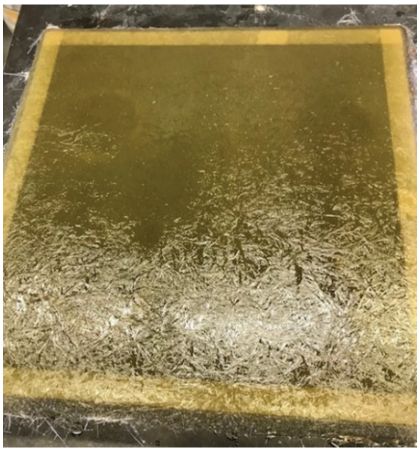

Figure 3. Picture of a completed secondary bonding test laminate with border tape separating the edge of the first and secondary layers.

fewer entrapped voids

In shop trials with Derakane™ Signia™ 411, operators consistently noted that wet-out and air release is significantly improved compared to Derakane™ Momentum 411-350 and Hetron™ 922. To demonstrate this improvement, experiments were conducted where 2 plies of 450 g/m^2 (1.5 oz/ft^2) chopped strand glass mat were made where only 10 passes of a serrated roller was allowed to consolidate the plies and eliminate bubbles. The resin to glass content for these experiments was controlled at 65% resin to 35% glass. Figure 2 shows typical images of laminates from this experiment. Note the appearance of fewer voids in the Signia™ resin laminate (top) compared to the Momentum laminate (bottom). Cured laminate images were analyzed using an in-house image analysis tool to quantify the number of voids in each picture. Signia™ laminates were shown to have only 0.008 to 0.01 percent voids compared to 0.04 to 0.06 percent entrapped voids in the Momentum laminates.

easy surface preparation

Reduction of steps in fabrication is one of the shortest paths to improving shop efficiency. Reducing the amount of preparation needed to apply secondary layups of FRP is a key benefit of Signia™ resins. We used two methods to confirm good secondary bonding for Signia™ 411 – qualitative analysis through fiber tear evaluation and quantitative shear strengths values through ASME RTP-1-2017 Appendix M5 bonding test standard[2].

secondary bonding test laminate preparation – fiber tear evaluation

Fiberglass-reinforced laminates were prepared for fiber tear evaluation using standard hand lay-up preparation methods. The laminates were prepared in the Ashland Corrosion Science Center (Dublin, Ohio) and at various customer locations. Several resin cure schedules based on MEKP, Cobalt Naphthenate, and Dimethylaniline were used. To understand the effect of reactive mass on cure and secondary bonding fiber tear, thick and thin laminates were prepared. Primary laminates were fabricated as a representative FRP substrate, aged, subjected to surface preparation by sanding/grinding or no preparation performed, and finally a secondary lamination was applied to the primary laminate. The final laminate constructions were split at the interface between the primary and secondary layers using a wedge. The degree of fiber tear due to the failure of the secondary bond was evaluated according to an established scale.

thick laminate preparation

Primary substrate laminates were constructed using 7 plies of 450 g/m^2 (1.5 oz/ft^2) chopped strand mat and promoted and initiated epoxy vinyl ester resin. The primary laminates were cured at ambient conditions for 24 hours. In some cases, primary laminates were post-cured for 4 hours at 82 °C (180 °F) to simulate extended aging. A secondary layup of 7 plies of 450 g/m^2 (1.5 oz/ft^2) chopped strand mat and promoted and initiated epoxy vinyl ester resin was applied on top of the primary laminate. For ease of driving the wedge between the primary and secondary layers, a one-inch border of tape was applied to the primary laminate before application of the secondary layer (see Figure 3). The laminates were cured at ambient conditions, 17 °C to 26 °C (63 °F to 79 °F), for a minimum of 72 hours, followed by separation of the primary and secondary layers to evaluate bond peel resistance and fiber tear. A completed secondary bonding laminate is shown in Figure 3.

thin laminate preparation

Thin laminates were prepared as described above in the Thick Laminate Preparation section, but 3 plies of 450 g/m² (1.5 oz/ft²) chopped strand mat were used in place of 7 plies.

secondary bonding fiber tear

Secondary bonding by wedge or peel test is difficult to evaluate as it is largely based on subjective observations of the observer/operator. A wedge test standard was developed by Ashland Technical Service for previous secondary bonding studies. Figure 4 shows the relative level of fiber tear at 20, 60 and 100%.

The top picture in Figure 5 shows the general setup of the test apparatus, with the wedge placed into the taped split initiation area of the upper laminate. In Figure 5 at the bottom are pictured examples of tested specimens. The tested specimens shown in Figure 5 gave excellent fiber tear and are representative of the typical fiber tear witnessed from specimens made in Signia™ trial fabrication shops and in Ashland labs. In Figure 5 the bottom fiber tear specimen was post cured for 4 hours at 82 °C (180 °F) before application of the second layer where the fiber tear specimen above had no post-cure applied.

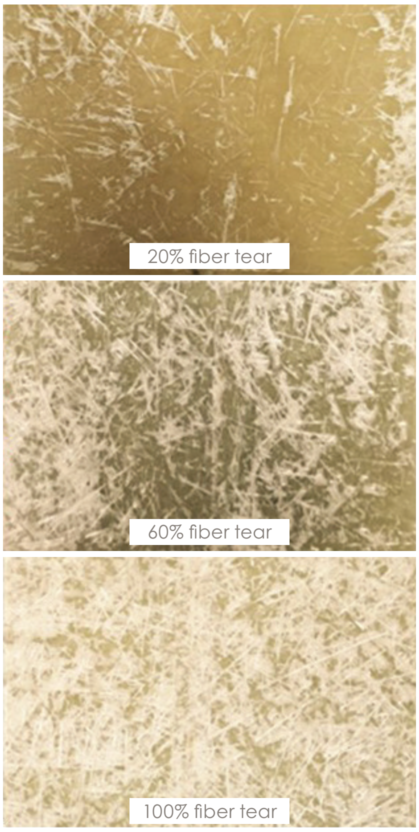

Figure 4. Secondary Bonding Wedge Test example scale.

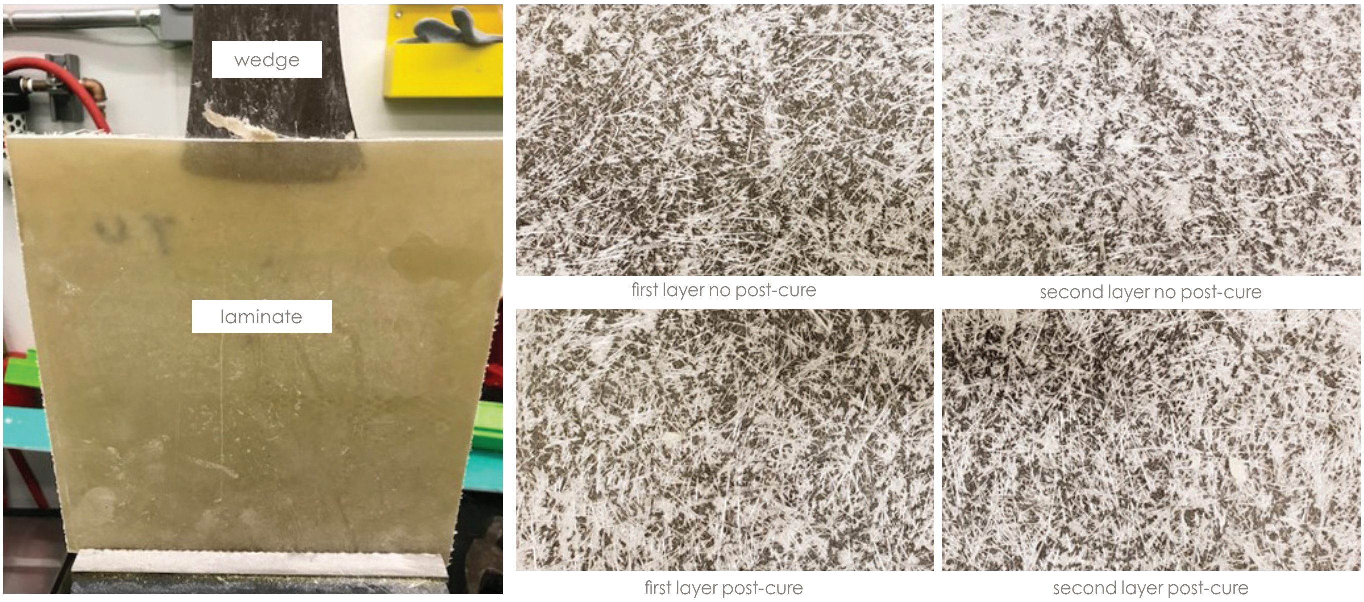

Figure 5. Secondary bonding wedge test setup (top) and tested secondary bonding laminates with no surface preparation by sanding of the primary layer (bottom).

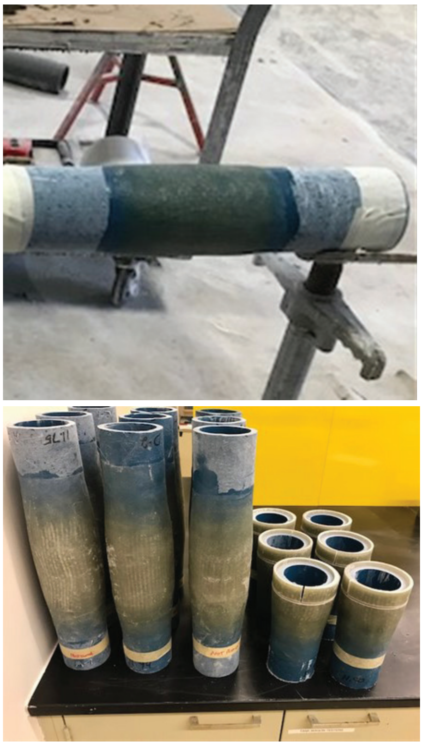

Figure 6. Preparation of M5 test specimens in a customer's shop (top) and precut and machined M5 test specimens (bottom).

In tests conducted on laminates where the corrosion barrier was the interface with the secondary layer we typically found poor secondary bonding. Upon evaluation it was found that dis-bonding occurred due to a lack of reinforcement at the interface. Because the corrosion barrier is resin-rich, the bond is only as strong as the resin. When trying to bond against the surfaces that had cured against the mold, we found residual mold release also caused clean dis-bonding with no fiber tear. Another impediment we found to secondary bonding was with filament wound laminates where there was no chopped strand glass or intimate contact of glass between the primary and secondary layers. Based on these observations, in cases where there is a continuous resin rich layer some type of surface prep or application of chopped strand glass should be applied to prevent dis-bonding.

When constructing equipment to a manufacturing standard such as RTP-1 or an end user specific specification where sanding is mandated between secondary overlays, these protocols should be followed and surface preparation should be performed as directed by the standard or specification. In these cases, it was observed by fabricators that the Derakane™ Signia™ resin did not gum up sanding disks the same way as current resins. This performance was attributed to the improved surface cure driven by the kinetics of the Signia™ cure and presence of the styrene suppression film preventing air inhibition of cure at the resin surface. In secondary bonding studies and in full scale equipment fabrication trials, it was found that Signia™ resins typically developed a higher Barcol in a shorter period of time – typically, greater than 30 in 1.5 hours. Further studies on this capability are being conducted and will be presented in the near future.

ASME RTP-1-2017 appendix M5 secondary bond test specimen construction and testing

The ability to quantify secondary bonding in a way that is meaningful to fabricators was identified in the ASME RTP-1-2017 Appendix M5 Secondary Bonding test standard. Following the procedures defined in Appendix M5, a FRP pipe section was produced using Derakane™ Signia™ 411. A 15 minute promotion and initiation schedule was used for pipe and secondary layup of the M5 test specimens. The pipe was allowed to cure for a minimum of 72 hours between 21 °C (70 °F) and 27 °C (80 °F) before the secondary lamination was applied. The application of the secondary layup can be observed on prefabricated pipe in the top picture of Figure 6. Note the pipe is pigmented blue so the pipe laminate can be distinguished from the secondary laminate for test specimen machining. Machined specimens can be seen in the bottom picture of Figure 6. ASME RTP-1-2017 Section 4-320 and Appendix M5 specify that the pipe surface should be prepared by sanding before application of the secondary bonded laminate. The goal of the testing described here is to evaluate the ability of Derakane™ Signia™ 411 to bond to prepared and unprepared surfaces; therefore, in some cases during these tests there was no preparation of the pipe surface by sanding.

Machining and testing of specimens was conducted by Fiberglass Engineering Mechanics (FEMech) Testing Lab, in Harrison, AR, as well as the Ashland Physical Testing Lab (APTL) in Dublin, OH. The top picture in Figure 7 shows a close-up view of the M5 test specimen after machining. The picture on the bottom in Figure 7 shows a closeup view of the M5 test specimen in the Instron™ compression fixture.

Using the ASME RTP-1-2017 Appendix M5 test standard a shear strength value can be calculated to evaluate how well a secondary bond is made by a fabricator. To pass, the specimen must reach a minimum shear strength value of 13.79 MPa (2000 psi). Test samples were prepared in two RTP-1 certified shops by Appendix M5 certified fabricators. Samples made with sanded and un-sanded pipe were sent to Ashland's Physical Testing Lab (an ISO9001 independently certified lab) and to Fiberglass Mechanics.

Figure 8 presents data for RTP-1 Appendix M5 test specimens for sanded and un-sanded pipe. This data clearly shows that shear values for sanded (Prep) and non-sanded (No-Prep) pipe are similar, and in all cases bonding exceeded the minimum M5 shear strength requirement of 13.79 MPa.

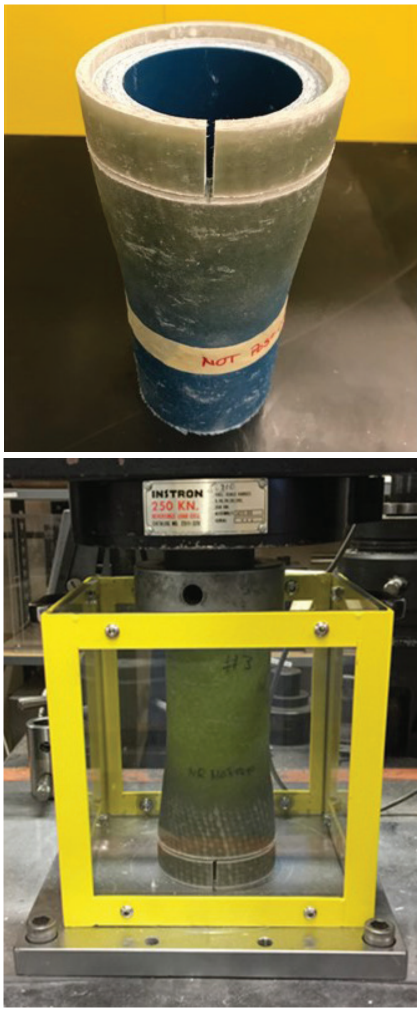

Figure 7. Machined M5 test specimen after machining (top) and M5 test specimen mounted in the Instron compression fixture (bottom).

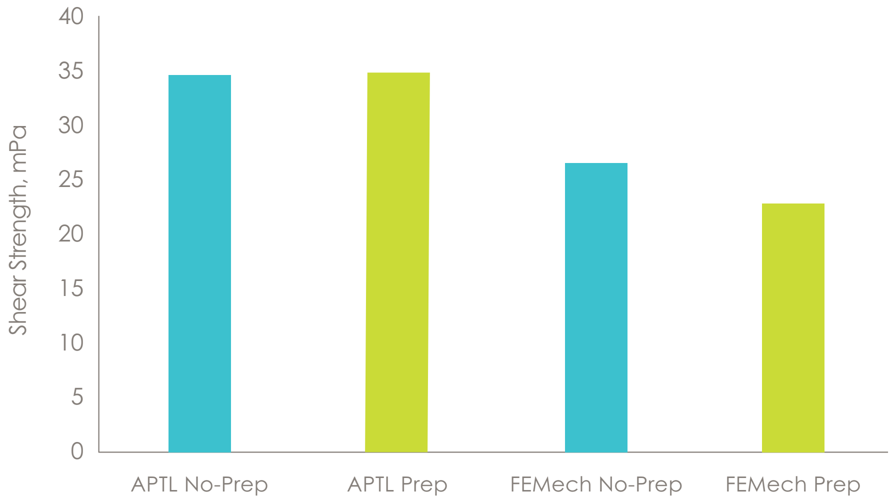

Figure 8. ASME RTP-1 Appendix M5 secondary bonding shear strength values for sanded (Prep) and un-sanded (No-Prep) test specimens.

Figure 9: Measurement of thick filament wound tank section made in a single continuous step with Derakane™ Signia™ 411 resin.

faster fabrication

The cure and processing characteristics of Derakane™ Signia™ 411 resin makes it possible to reduce the number of steps required to make thick part such as a hand laid-up flange or filament wound vessel. Signia™ is not sensitive to air inhibition which leads to excellent Barcol development and surface cure allowing fabricators to begin secondary layups sooner than with previous resin systems used. This is useful in flange attachment layups and application of repad for construction of headers, columns and tanks. Signia™ resin technology has been shown to make thick parts without warping and scorching related to heat development. In several customer trials very thick parts were made without issue related to heat development.

filament winding of thick tank sections

The vessel wall pictured in Figure 9 was produced in one continuous winding process using a common MEKP / Cobalt Naphthenate cure to a thickness of 27 mm (2 in) with a high glass content (~65%). When building vessels by filament winding the fabricator can build the corrosion barrier by hand layup and chopper gun and then take advantage of Signia™ 411's excellent secondary bonding by not having to sand the surface before starting the winding process. It's important to note that the best practice is to apply a layer of resin and chopped strand for a bedding layer between the cured corrosion barrier and the layers of glass filament roving. This practice is common when laying up on a sanded surface.

hand lay-up of thick laminates

When building large manway flanges it commonly takes a fabricator three to four steps to lay up the complete sequence corrosion barrier and structural layer reinforcements. It is common for there to be 26 to 36 layers of alternating 450 g/m² (1.5 oz/ft²) chopped strand mat and 680 g (24 oz) woven roving. Typically, MEKP/CHP initiator blends are required to achieve long gel times to provide the desired working time and minimize high heat build-up upon cure. With Signia™ 411, Copper Naphthenate (CuNap) has been successfully used to reduce the peak exotherm and extend the gel-to-peak exotherm with minimal effect on gel time. This gives fabricators the time needed to lay up the full reinforcement sequence for the flange, while preventing high heat development that can scorch the upper layers of resin and reinforcement. In Table 1 the effect of Copper Naphthenate can be seen in standard 100 gram cup gel time studies. It can be seen in this data that high hydrogen peroxide (H_2O_2) containing MEKP initiators like Luperox®[3] DDM-9 have a larger reduction of peak exotherm when using Copper Naphthenate. The effect is not as large for high dimer MEKP initiators like Norox® 925H.

resin temperature, °F	75	75	75	75
derakane™ signia™ 411 resin, pph	100	100	100	100
6% cobalt, pph	0.15	0.15	0.15	0.15
10% cunap 8%, pph	0	0.25	0	0.25
high dimer MEKP, pph	1	1	—	—
high H_2O_2 MEKP, pph	—	—	1	1
GT, min	28	28	27	33
G-PE, min	20	41	23	54
PE °F	325	275	310	110

Table 1: Effect of Copper Naphthenate in parts per hundred (pph) on and MEKP choice on gel time (GT), gel-to-peak exotherm (G-PE) and peak exotherm (PE) in 100 gram T-Cam cup gels.

In a recent trial a fabricator was able to make 36" ID manway with a ¾ inch (20 mm) thick flange in one layup, significantly reducing the amount of needed to make this part. In addition to producing a good quality laminate in the flange and next of the manway the amount of drawback of the is critical to if the part is acceptable or not. In Figure 10 it can be seen the drawback on the flange is minimal and consistent with existing flanges made by a multi-step process. Using Derakane™ Signia™ 411 with CuNap allowed the customer to reduce fabrication time from a multi-step production process that took 2–3 days to complete from start to demolding to a 6 hour process from start to demolding.

summary

The chemistry of epoxy vinyl ester resins makes them highly reactive and when first invented they were unstable and difficult to use because of this. Introduction of better production capabilities improved their stability and allowed them to become a material of choice for corrosion applications where alloy cannot perform. In Derakane™ Signia™ resins Ashland has combined the best technological features of the Derakane™ and Hetron™ lineage with additional new learnings to introduce a leap forward in stability and usability compared to previous generations of epoxy vinyl ester resins.

The experiments described in this paper demonstrate Derakane™ Signia™ resin technology is capable of improving shop efficiency through less surface preparation, faster Barcol development, less waiting time between the application of additional laminates, and the ability to make thicker parts. This results in improved labor efficiency through a reduction or removal of entire fabrication steps, improved shop cleanliness and overall faster processing of high quality FRP parts. Since Ashland's introduction of Derakane™ Signia™ resin technology it has been widely embraced by shop fabricators and owners for the landmark improvements and value it brings.

Figure 10: Derakane™ Signia™ 411 with CuNap manway on mold (top) and measure of flange drawback or curl after cure (bottom).

[1] *Norox® is a registered trademark of United Initiators.*

[2] *ASME Standard RTP-1-2017, Appendix M5, Qualification of Laminators and Secondary Bonders, The American Society of Mechanical Engineers, Two Park Avenue, New York, NY 10016-5990, 2017.*

[3] *Luperox® is a registered trademark of Arkema Inc.*

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