COMPARISON OF STRENGTH RETENTION OF NOVOLAC VINYL ESTER JOINTS IN HOT HCL*

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ABSTRACT

HCl users could have lower installation costs by using FRP piping with adhesively bonded pipe joints, but have concerns that the adhesive may be more readily attacked in hot HCl service. An experiment was undertaken to provide comparative data on the performance of adhesive joints with butt & wrap joints in HCl.

Keywords: FRP, Fiberglass, pipe, HCl, adhesive, joints, butt & wrap

INTRODUCTION

Hydrochloric acid is a versatile processing chemical used extensively in mining, pulp and paper, and many other industries. The corrosive nature that makes HCl so effective also makes it very difficult to handle, process, store and, transport. Since its introduction in the early 1960's, FRP or Fiberglass has proven to be one of the most effective and economical solutions to storing and transporting HCl. Today, hundreds of tanks and miles of piping safely handle HCl. The fabrication of fiberglass tanks and piping follows accepted industry practices. However, with piping, fabricators and end-users need to address the added complexity of joining numerous pipe and fitting segments. The basic methods of joining fiberglass pipe and fittings are summarized below.

FIBERGLASS PIPE JOINTS

Fiberglass pipe is fabricated by impregnating glass fibers with thermosetting resins such as polyesters and vinyl esters. The piping is generally constructed using either a hand lay-up technique where layers of reinforcement are applied by hand to a mold, or by filament winding where numerous glass strands are applied to a rotating mold. The initial method used to join pipe and fittings was an extension of the hand lay-up technique where layers of reinforcement would be applied over the joint area of sufficient thickness to withstand axial and circumferential loads, and of sufficient length to withstand shear loads. This became known as the "butt & strap" or "butt & wrap" joint.

Butt & Wrap Joint: (refer to Figure 1)

1. The pipe and/or fittings ends are prepared by sanding or removing any wax coatings or contaminants on the surface.

2. The ends of the pipe are butted together and held in place. The crevice between each section is filled with a thickened resin known as putty or paste. This is allowed to cure.

3. Layers of reinforcing material (typically chopped strand mat and woven roving) are "wet-out", or saturated with resin, and applied over the joint. The resin will have a "working life" based on the resin type and curing system, and will give-off heat or "exotherm" as it cures. Only those layers that can be applied with a non-damaging exotherm are put on the pipe at on time.

4. The applied reinforcement is "rolled-out" to remove entrapped air and compact the layers

5. Once the necessary reinforcement has been applied, cured, and allowed to cool: the entire area is covered with a wax and resin mixture known as topcoat or brushcoat.

6. The finished joint blends the two segments together with the peak of the "hump" indicating the center of the joint.

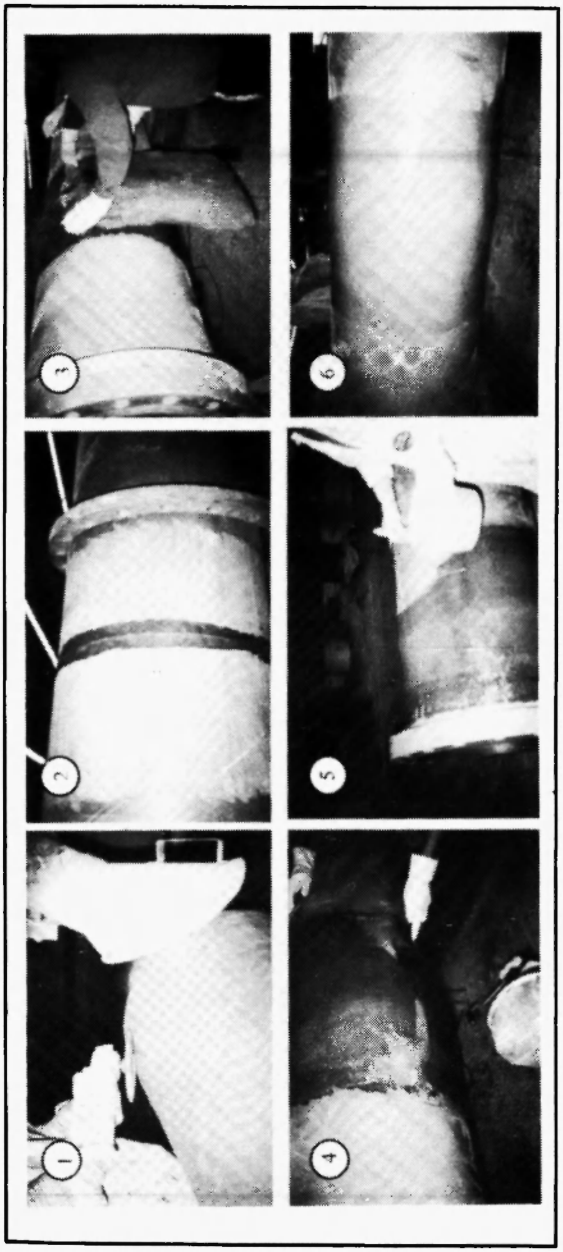

Fig. 1: Butt & Wrap Joint

An alternative to the straight butt joint is the "tapered butt joint" where each pipe (or fitting) end is tapered down to the corrosion liner before the ends are butted together. This provides less opportunity for chemicals to penetrate into the structural layers of the piping and a stronger joint.

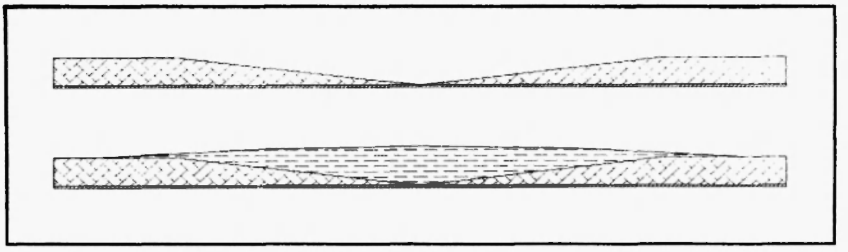

Fig. 2: Tapered Butt & Wrap Joint

A further alternative to the straight butt joint is the use of edge-capping; where the ends of the pipe or fitting are covered or capped with surfacing veil or a total corrosion barrier. Although time consuming, the edge-cap seals the ends of the pipe or fitting thereby greatly reducing the potential for chemicals to penetrate into the structural layers. Due to the increased labour costs associated with edge-capping, this is generally only specified in severe service conditions.

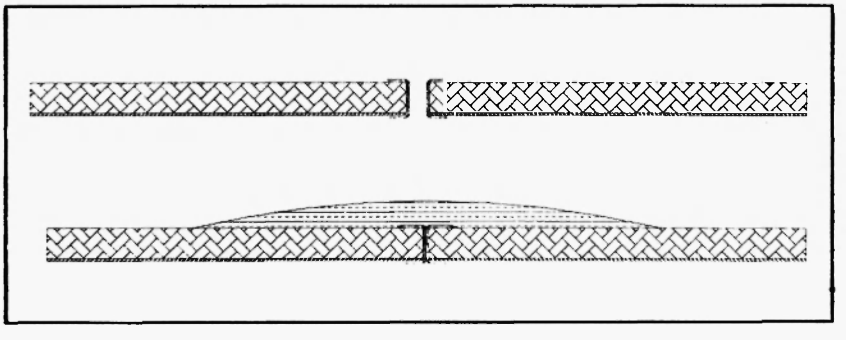

Fig. 3: Butt & Wrap Joint with Edge-cap

As fabricating methods improved, and manufacturers and end users looked for faster ways of joining fiberglass pipe and fittings, adhesive bonded joints were developed. These joints are generally divided into two basic types; namely, socket adhesive joints and tapered adhesive joints. The socket style joint utilizes a straight bell or female end designed to loosely accept a straight spigot or male end. The tapered adhesive system utilizes a tapered bell or female end designed to tightly match the tapered spigot or male end.

Socket Adhesive Joint:

1. The male (spigot) and female (bell) ends are prepared by lightly sanding or removing the protective wrap.

2. Adhesive is applied to both the male and female ends.

3. The arrangement is slid together and held in place.

4. Excess adhesive is removed from the outside, forming a neat fillet. A "pig" (rag) is generally pulled through the ID to remove and smooth excess adhesive on the interior. The thick layer of adhesive in the joint may be cured using a heating blanket.

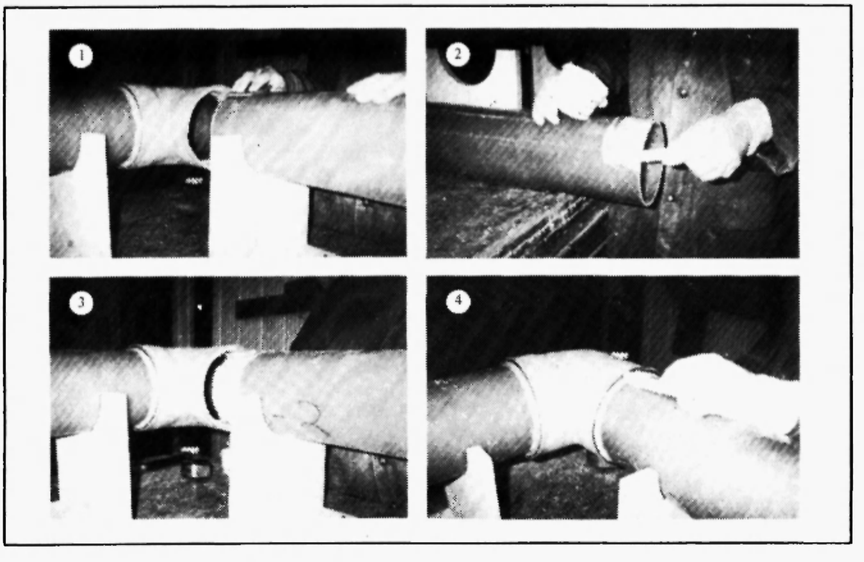

Fig. 4: Socket Joint

Tapered Adhesive Joint:

1. The male or spigot end is prepared by grinding a specified taper on the OD; the female or bell is prepared by lightly sanding the ID.

2. The adhesive used to join the segments is catalyzed and thoroughly mixed.

3. Adhesive is applied to the bell end.

4. Adhesive is applied to the spigot.

5. The arrangement is slid together. Excess adhesive on the OD is removed forming a neat fillet. A pig (rag) may be pulled through the ID to remove and smooth excess adhesive on the inside.

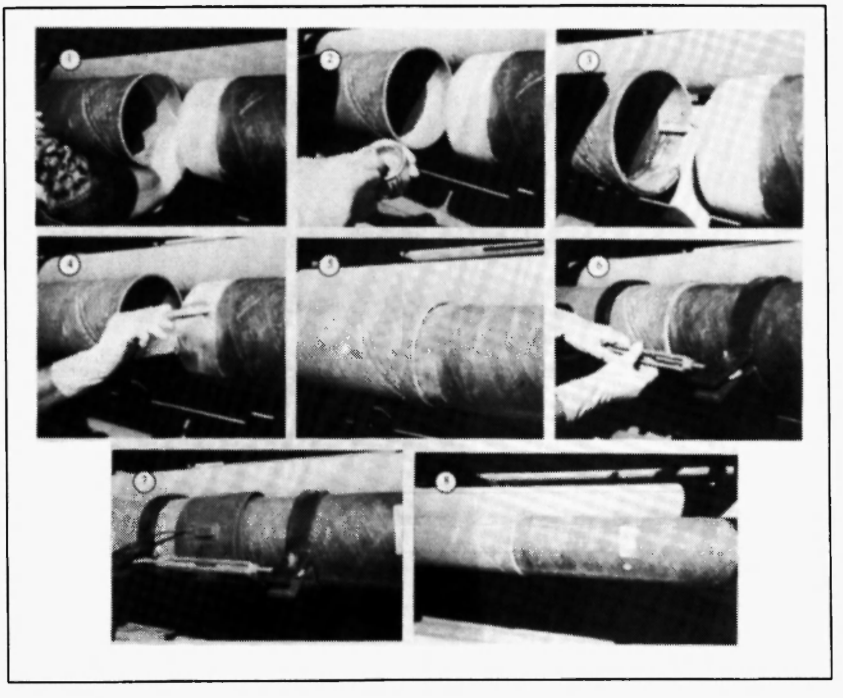

Fig. 5: Tapered Adhesive Joint

6. The joint is held in place (excess movement of the joint may draw air into the joint).

7. The thin layer of adhesive is usually cured using a heating blanket.

8. The finished joint is ready to be tested or put into service.

CORROSION RESISTANCE

Since the advent of the adhesive joint, there has been a long-standing debate over the corrosion resistance of the adhesive style joint versus the traditional butt & wrap joint. Proponents of the adhesive style joint argue that the butt & wrap joint is vulnerable to attack at the edges when the filler paste cracks. Proponents of the butt & wrap joint system argue that the fillers used to make the adhesive workable and crack resistant are vulnerable to chemical attack.

The following are common methods used to measure chemical attack:

- Swelling, indicating permeation of chemical media into the laminate
- Blistering, indicating permeation of chemical media into the laminate
- Softening, indicating attack of the laminate matrix by the chemical media
- Discoloration, indicating attack of the laminate matrix by the chemical media
- Exposed fibers, indicating total attack of the resin matrix
- Decrease in mechanical properties, indicating attack of the resin/glass matrix

An experiment comparing the chemical resistance performance of a tapered adhesive style joint to a traditional butt & wrap joint in hot HCl is summarized below.

DESCRIPTION OF EXPERIMENT

To compare the chemical resistance of a tapered adhesive joint versus a tapered style butt & wrap joint in HCl service, three type of flat panels were fabricated:

- Hand Lay-up Laminate with no joint
- Hand Lay-up Laminate with tapered butt & wrap style joint
- Hand Lay-up Laminate with tapered adhesive style joint

The construction of all the panels was identical consisting of:

Resin:	Epoxy Novolac Vinyl ester
Cure System:	0.3% Cobalt Naphthanate (6% active) 0.05% N,N-Dimethylanaline (100% active) 0.10% Wetting agent and foam suppressant 1.5% Cumene hydroperoxide (catalyst)
Room Temp Cure:	24 hours
Post Cure:	2 hours @ 176°F. (80°C.) followed by 4 hours @ 230°F. (110°C.) (after joining)
Reinforcement:	1 Layer Synthetic Surfacing Veil 10 Layers chopped strand mat ECR glass 1 Layer Synthetic Surfacing Veil
Edge Protection:	Epoxy Novolac Vinyl ester Resin paste (applied at lab)
Adhesive:	Epoxy Novolac Vinyl ester resin with glass fibers and inorganic oxides thixotropes. BPO/Analine curing system
Measurements:	Thickness 0.40” (+/- 0.1”) Resin Content 68% (+/- 1%) Tg (using DSC) 284°F. (140°C.) Residual Styrene < 1% (estimated from Tg value)

Tapered Butt & Wrap Joint Coupons:

The tapered butt & wrap joint coupons were constructed as follows:

- Cut the coupons to the required length (1/2 the finished length + 1/2 the overlay length)
- Machine the end (across the panel) at a 7° angle leaving a 1/32" feather edge
- Apply: 1 layer of Synthetic Veil
  10 layers chopped strand mat
  1 layer of synthetic veil
- Cover lay-up with mylar and press to correct thickness
- Total Joint length 2.81" to 3.25" (3.03" average)

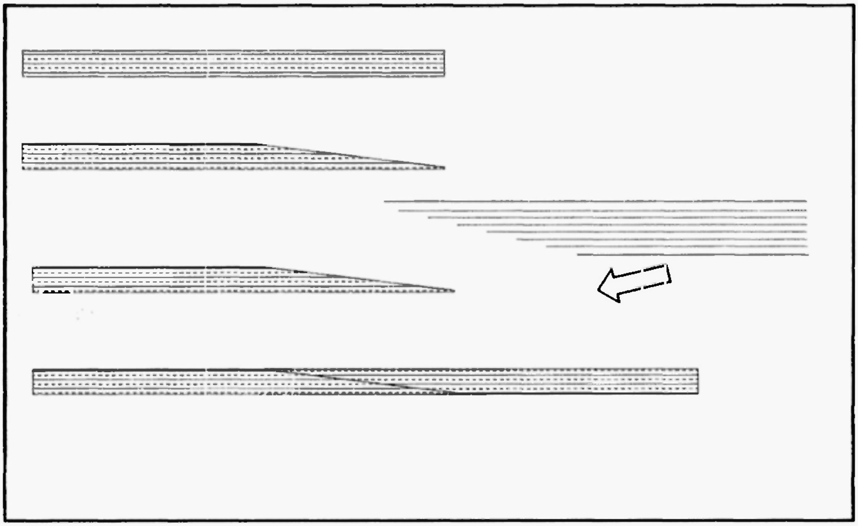

Fig. 6: Fabricating Butt & Wrap Coupon

Tapered Adhesive Joint Coupons:

The tapered adhesive joint coupons were constructed as follows:

- Cut the coupons in two equal halves
- Machine the ends (across the panel) at a 7° angle leaving a 1/32" feather edge
- Apply Epoxy Novolac Vinyl ester Resin Adhesive to each face

- Press to two halves together forming a glue line of ≈ 0.01"
- Total joint length 2.43" to 2.53" (2.48" average)

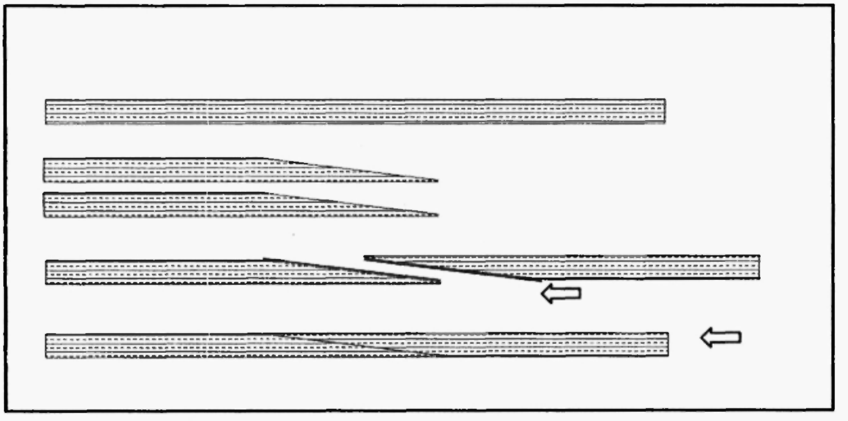

Fig. 7: Fabricating Tapered Adhesive Joint Coupons

CHEMICAL MEDIA

The panels described above were immersed for two-sided exposure in HCl at the following temperatures and concentrations:

- 37% HCl at 150°F. (65.6°C.)
- 30% HCl at 180°F. (82.2°C.)
- 20% HCl at 210°F. (98.8°C.)

Acid in the bath was replaced monthly and coupons with no exposure were initially tested as controls.

PHYSICAL TESTING

To evaluate the effect of the HCl on the joint, the coupons were removed from the bath at various time intervals, examined for appearance, and tensilely tested per ASTM D638; modified as noted. The chemical immersions and physical testing were all conducted at the DOW Chemical Company's testing facility in Freeport Texas.

Modifications to ASTM D638:

- The coupons were thicker than standard to accommodate two-sided exposure while still replicating the service conditions.

- Coupons were cut straight rather than the "dog bone" shape required in the standard as machining of the acid soaked coupons was difficult.

TEST RESULTS

Tensile Strength:

The tensile strength of the laminates was measured and is summarized in the figures below.

- After 12 months exposure to 20% HCl at 210°F. (98.8°C.), the tapered adhesive joint coupons lost 19% tensile strength, while the straight and butt & wrap joint coupons lost 29% and 45% respectively.

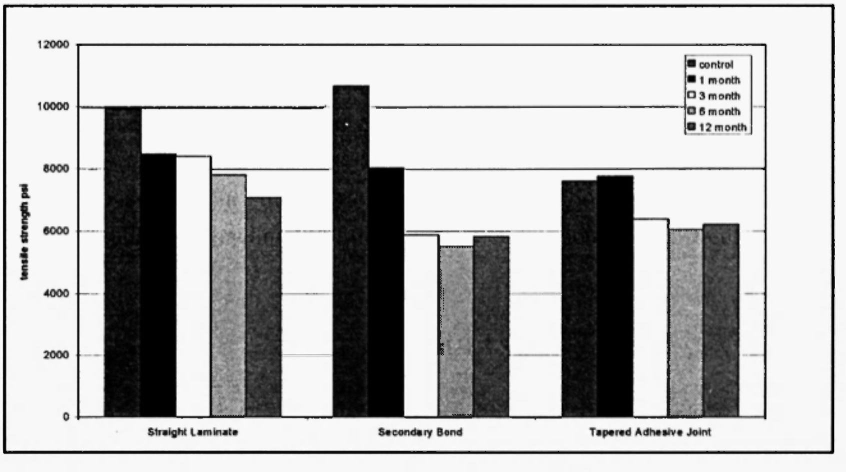

Fig. 8: Tensile Strength of Coupons Exposed to 20% HCl @ 98.8°C.

• After 12 months exposure to 30% HCl at 180°F. (82.2°C.), the tapered adhesive joint coupons lost 15% tensile strength, while the straight and butt & wrap joint coupons 18% and 30% respectively.

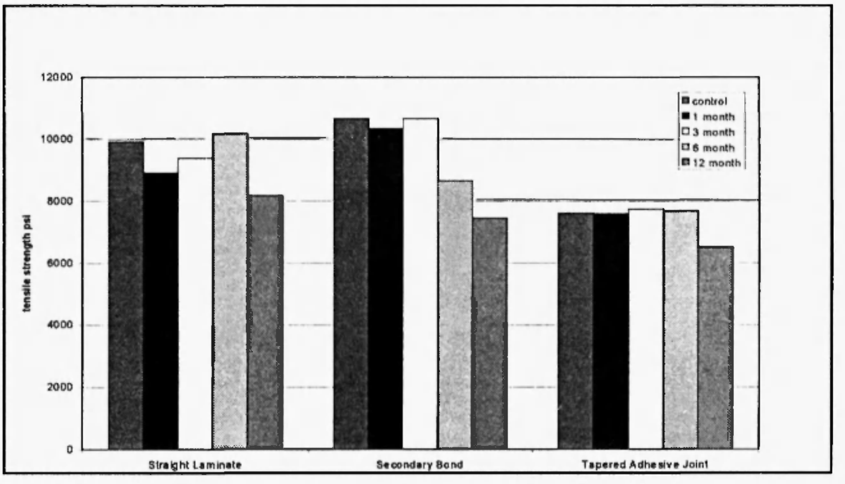

Fig. 9: Tensile Strength of Coupons Exposed to 30% HCl @ 82.2°C.

• After 12 months of exposure to 37% HCl at 150°F. (65.6°C.), the tapered adhesive joint coupons retained all tensile strength, while the straight and butt & wrap joint coupons lost 23% and 16% respectively.

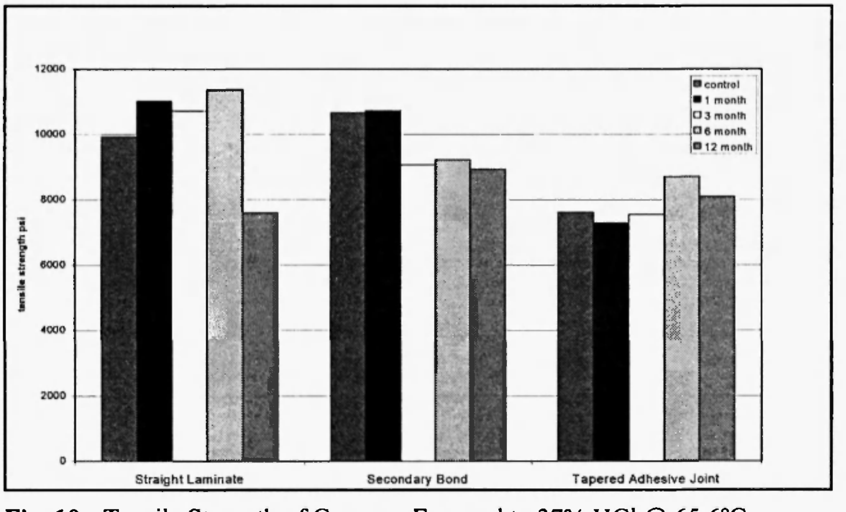

Fig. 10: Tensile Strength of Coupons Exposed to 37% HCl @ 65.6°C.

Tensile Testing Comments:

Initial examination of the tensile test results indicates that the tapered adhesive style joint displayed a lower ultimate tensile strength than the straight laminate or the secondary bond joint. However, this is related to the fact that the shear length of the adhesive joint was approximately 18% ((3.03-2.48)/3.03) less than with the secondary bond joint, resulting in an initial ultimate strength which was also approximately 18% lower. Had the shear length of the tapered adhesive style joint been the same as the secondary bond joint, it is assumed that the initial ultimate strength would have been governed by the laminate and thus would be similar in strength to the secondary bond joint.

The strength of the straight laminate and secondary bond laminates degraded as the laminates were attacked by the acid over time. The strength of the adhesive joint laminates was initially governed by the shear length of the adhesive joint itself. However, as the acid attacked the laminate, failures began to occur in the laminate itself rather than in the joint. This indicates that the adhesive was not attacked over the course of the study.

Visual Effects:

The coupons in 37% HCl at 150°F. (65.6°C.) exhibited a darkening of the liner and slight greenish tinge after 1 month. At 6 months, the surfacing veil was mid brown, but distinctly visible with a noticeable greenish attack on the cobalt under the surfacing veil between 0.03" and 0.05"and penetrating 5/16" from the edges along the glass layers. At 12 months, the surfacing veil was mid brown and still distinctly visible with the attack of the cobalt extending 0.03" to 0.06" into the laminate, and penetrating 1/4" from the edges. The interior was opaquely dark brown.

The coupons in 30% HCl at 180°F. (82.2°C.) exhibited little change from the original appearance after 1 month. At 6 months, the surfacing veil was yellow-brown, but distinctly visible with a whitish/greenish attack on the cobalt under the surfacing veil penetrating approximately 1/4" from the edges along the glass layers. The interior was a redish-amber opaque color. At 12 months, the surfacing veil was light orange-brown with the patter distinctly visible with the attack of the cobalt 3/8" on from the edges. The interior was dark brown.

The coupons in 20% HCl at 210°F (98.8°C) exhibited a slight darkening of the liner after 1 month. At 6 months, the surfacing veil was still light brown and distinctly visible with a greenish attack on the cobalt under the surfacing veil penetrating approximately 3/8" from the edges along the glass layers. At 12 months, the surfacing veil was dark brown with the pattern almost undetectable. The attack of the cobalt penetrated approximately 0.03" to 0.05" and extended 1/2" on from the edges. The interior was dark amber.

The visual effects noted above appear to be consistent with the pattern of attack noted in laboratory testing and industrial case studies, and are presented to validate the test data.

CONCLUSIONS

From the mechanical testing and visual examination conducted in this experiment, it can be concluded that a properly fabricated FRP laminate; utilizing an epoxy novolac vinyl ester resin with a synthetic surfacing veil; will perform well in hot HCl environments, including concentrated HCl (37%) at 65.6°C. (150°F.) and 20% HCl at 98.8°C. (210°F.). This conclusion is consistent with case histories demonstrating the success of straight FRP in similar environments for 10+ years.

From the mechanical testing and visual examination, it is it also evident that the tensile property performance of the tapered adhesive style joint is equivalent to the secondary bond joint and the straight laminate itself when immersed in hot HCl. This information provides confidence that a properly designed tapered adhesive style joint system will work well in hot HCl environments. Given the harshness of this environment, a properly designed tapered adhesive joint system would be expected to offer chemical resistance comparable to a traditional butt & wrap joint design, for most corrosive environments.

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