



**ACTON
TECHNOLOGIES**

The Etching of Fluoropolymers

in Preparation for Bonding and Metalization

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THE TREATMENT OF PTFE FOR BONDING

INTRODUCTION

In order to achieve some perspective, any discussion of the treatment of fluorocarbon polymers for bonding should include at least a few comments on methods that have been tried in the past. The need to render the surface of these polymers wettable, and therefore bondable, arose almost as soon as their extremely low coefficient of friction was realized. The most common fluoropolymer is PTFE and its most easily identified property is its lubricity. The universal recognition of this attribute is due in large measure to the early introduction of Teflon®¹ coated frying pans to the mass market.

But fluoropolymers have come into use in numerous and diverse industries for many of their other properties. For the purpose of this discussion, we will use “PTFE” to describe all of the subsequently developed fluoropolymers like FEP, PFA, PVDF, etc. Although this is chemically incorrect, PTFE is the prevalent fluoropolymer in industry today and many of these polymers are used interchangeably in many applications with the difference being one of degree rather than of basic physical property.

Its chemical resistance has made PTFE very useful in the chemical process industry as linings for vessels and piping. The biomedical industry has found PTFE to be biocompatible and so has used it in the human body in the form of both implantable parts and devices with which to perform diagnostic and therapeutic procedures. In many applications, asbestos has been replaced by PTFE as a high-temperature wire coating. Automotive and aircraft bearings and seals are now commonly made of PTFE.

As you know, the dielectric property of this unique polymer has given rise to an entirely new technology in printed circuit board design. This concept is responsible for the very latest in high-speed, high-frequency radar and communications found in our newest defense systems as well as in the next generation of ultra high-speed computers. The list of applications goes on and on.

In order to take advantage of any of the other remarkable properties of PTFE, it sometimes has to sacrifice its lubricity in order to be bonded to another material. The applications mentioned above all require PTFE to be etched to some degree to enable bonding.

PTFE film and sheet is etched on one side to bond it to the inside of steel tanks and piping. The OD of small diameter, thin wall PTFE tubing is etched to bond to an over-extrusion resulting in a PTFE lined guide catheter. PTFE jacketed high-temperature wire is etched to allow the printing of a color stripe or other legend such as the gauge of the wire and/or the name of the

¹ Teflon is a registered trademark of DuPont.

manufacturer. PTFE based printed circuit boards require etching to permit the metallization of through-holes creating conductive vertical paths between both sides of a double sided board or connecting several circuits in a multilayer configuration.

The first commercially viable processes were chemical in nature and involved the reaction between sodium and the fluorine of the polymer. In general, some quite toxic and very dangerous substances were involved such as Tetrahydrofuran (THF), anhydrous ammonia and of course the raw sodium itself.

In time, some of the chemistry was changed to make the process less potentially explosive and hazardous but the essential ingredient—sodium—remains the most reliable, readily available chemical ‘abrasive’ for members of the fluoropolymer family.

WET PROCESSING OF PTFE

For many years, sodium was carried into the reaction by Tetrahydrofuran or liquid ammonia. ‘Home brews’ were concocted to achieve the desired wetability, hence bondability of these slippery surfaces.

An etchant made with sodium ammonia is not portable and is very difficult to store and handle because its boiling point is approximately -25° F). This, in conjunction with its odor and the hazardous nature of both the free sodium and the ammonia, is why it was never adopted as the etchant of choice with which to carry out this procedure.

On the other hand, THF being somewhat stable at room temperature (although highly flammable), came into prevalent use where PTFE etching needed to be done. It was usually conducted ‘out in the alley’ or in a shed well away from the normal process areas of the factory.

By the late 1950’s, another group of solvents, the Glycol Diethers, was being developed and they would eventually be successful in replacing both liquid ammonia and THF as the carriers for sodium in most in-house etching operations. Also, what was thought at the time to be a much safer way of handling sodium evolved—that of mixing the sodium with naphthalene or ‘moth balls’. These factors greatly furthered the premixed etchant business and enabled PTFE users to process their parts with much greater ease and safety.

THE “NEW CHEMISTRIES

The development of the Glycol Diethers did much for many industries. Various members of this family of chemicals found their way into lithium battery production; pharmaceutical production as stabilizers; refrigeration; paint, pesticide, detergent and propellant production, just to name a few. Some other, quite diverse applications include gold purification, uranium extraction and the production of colorfast and no-iron fabrics.

Three of these Glymes, as they are called, came in to use in the manufacture of etchants for Teflon:

1. Ethylene Glycol Dimethyl Ether or **MONOGLYME**
2. Diethylene Glycol Dimethyl Ether or **DIGLYME**
3. Tetraethylene Glycol Dimethyl Ether or **TETRAGLYME**

MONOGLYME, being the simplest of the three, has the greatest affinity for sodium and, therefore, is the easiest solvent with which to complex sodium naphthalene. The solubility of sodium naphthalene in Monoglyme is quite high so the resulting etchant is very sodium rich but also very viscous, sometimes needing to be thinned for particular applications.

The closed cup flash point of this solvent is approximately 30° F, which makes it a flammable material and a considerable hazard. A third factor regarding etchants made with Monoglyme is their thermal stability. At temperatures above 32° F, these etchants begin a spontaneous reaction, consuming their active ingredient—sodium—in the process and giving off methyl vinyl ether. It usually is recommended to store these etchants under refrigeration in order to limit this deterioration.

DIGLYME, while it dissolves less sodium naphthalene in complex, has a much higher flash point (134° F which classifies it as a combustible) and makes an etchant with the viscosity of about that of water. Diglyme is very stable at room temperatures and above and does not exhibit the same spontaneous decomposition as Monoglyme at temperatures up through its flash point. Also, the evolution of methyl vinyl ether is about one-tenth that of Monoglyme.

TETRAGLYME, the most complex of the three solvents, has a very high flash point (around 230° F). However, an etchant made with this solvent yields poor bond strengths because the complexity of the solvent inhibits the release of the active ingredient—sodium—to the etching process.

ELEVATED TEMPERATURE ETCHING

So we have this relationship among these "glymes," in the ascending order of their complexity that bears directly on the efficacy of the etchants made with them.

Monoglyme, as the simplest solvent, dissolves sodium naphthalene the easiest and gives it up the most readily in reactions with fluorine when etching PTFE. Diglyme, having a more complex molecule, dissolves sodium naphthalene less easily and does not give it up as rapidly in these reactions. And Tetraglyme, being the most complex of the glymes, presents the least amount of active sodium to the etching process.

In 1987, in an attempt to release more active sodium from a diglyme-based etchant, the first elevated temperature experiments were done using a diglyme-sodium naphthalene etchant. The purpose was to determine the degree of the catalytic effect of heat on the reaction and the results were very favorable.

Several tests conducted at Lehigh University showed that etching at approximately 125° F increases the bond strengths between 50% and 75% over room temperature etching. This same elevated-temperature process was compared to parts etched with sodium ammonia and found to yield bond strengths over 25% higher than those etched by the sodium ammonia process.

The mechanism here seems to be simply that of the catalytic effect, which is where molecules that are predisposed—by a heat-induced higher level of molecular activity—to react faster and more completely with each other. Corroborating this, it was found that, along with using a heated etchant, heating the parts to the same temperature further enhances the effect. This phenomenon proves helpful when re-etching must be done. It is not recommended to heat monoglyme based etchants because of their very low flash point. Another distinct advantage to the elevated temperature process is the change in the viscosity of the etchant. Diglyme etchants, at room temperature, have approximately one-half the viscosity of monoglyme and tetraglyme etchants. When heated, a diglyme etchant drops to about one-half of its room temperature consistency (which is around that of water) rendering it in the range of 25% as viscous as etchants made with the other two solvents. This is an important factor when trying to etch confined areas such as in small-diameter, high aspect ratio through-holes in printed circuit boards or tightly woven Teflon fabrics. Viscosity is a particularly important factor in the etching of fluoropolymer films where the fluid dynamics of a thinner etchant contribute considerably to a very uniform chemical reaction over large surface areas.

The recent development of the first wettable, bondable PTFE whisker—Aclon²—was greatly facilitated by the low viscosity of a diglyme-based etchant.

² Aclon is a registered trademark of Acton Technologies Inc.

THE SHELF LIFE OF ETCHED SURFACES

There has been a great deal of concern over just how long an etched fluoropolymer surface will retain its original bond strengths. There are specifications that call for wrapping the etched parts in black plastic, storing them in humidity- and temperature-controlled environments, and completing the bonding within eight hours of etching!

While it is true that temperature, humidity and UV light do have a detrimental effect on the etched surface, the deterioration of bondability is much slower than is commonly believed. Tests have shown that etched PTFE parts exposed to 250° F for 14 days exhibit bond strengths approximately 40% weaker than those done on the day they were etched.

Another interesting fact revealed in two other independent studies is that the bond strength actually **increases**, at room temperature, over the first 24 hours after etching.

We have not studied the impact of humidity and UV light on the etched surface in depth, but empirically we can say that those factors take a very long time to affect bondability. The deterioration occurs over a period of weeks and perhaps months as opposed to hours or days, which seems to be the prevailing belief.

All of this suggests that the sodium etching process creates a very active layer on the surface of fluoropolymers. The rate of that activity changes over time—at first, fairly rapid as the fluorine is replaced by hydrogen and oxygen, forming hydroxyl groups with the carbon chain—and then more slowly as the surface becomes more satiated and stable.

Another factor that is of concern in this process is that of the depth of the etched layer. The sodium reaction with fluorine is a self-limiting one and it has been shown to take place to a depth of only a few hundred Angstroms (not microns as had been believed). It is thought that, due to the amorphous nature of these polymers, a rotational migration occurs over time; accelerated by environmental factors—especially heat—that re-exposes more of the original C₂F₄ molecule at the surface resulting in a lower coefficient of friction.

A much better understanding of these phenomena will be possible only when technology allows us to look at these surfaces at the atomic level. The scanning-tunneling and atomic force microscopes are doing just that for conductive materials today. The hope is that it will be only a matter of time before we will have a computer-generated photomicrograph of a fluoropolymer surface showing its topography, atom by atom, at which time we will be able to answer some of these lingering questions much more definitively.

EXHIBIT I

Selected Comparisons in the Chemistry of Some Glycol Diethers

ETCHANT	MONOGLYME	DIGLYME	TETRAGLYME
FLASH POXNT °C Closed cup	-6	57	141
VOLATILITY nButylacetate = 100	499	36	0.1
VAPOR PRESSURE mm Hg/20° C	54	2	0.01
EMPIRICAL FORMULA	C ₄ H ₁₀ O ₂	C ₆ H ₁₄ O ₃	C ₁₀ H ₂₂ O ₅

EXHIBIT II

Oven Aging vs. Bond Strength

ETCHANT	AGING CONDITIONS	BOND STRENGTH CONTROL	BOND STRENGTH AGED
Glyme-based	72 hrs 50° C	17.1	9.7
Diglyme-based	2 wks 100° C	16.7	5.3
Diglyme-based	1 wk 100° C	21.5	15.0
Diglyme-based	1 wk 100° C	21.5	11.9

EXHIBIT III

Total Sodium, Active Sodium and Bond Strengths

ETCHANT	MONOGLYME	DIGLYME	TETRAGLYME
Total Sodium: (titration with HCL)	2.6%	1.8%	2.7%
Active Sodium: (titration with 1-butanol)	1.1%	1.2%	2.2%
Bond Strength: (lbs/linear inch)	14.3%	13.7	1.4

EXHIBIT IV

The Effect of Etch Time on Bond Strength and Depth of Etch

Etch Time (min)	Total Wt. Loss (%)	Bleaching Wt. Loss	Bond Strength
0.25	0.314	0.126	6.0
0.50	0.327	0.140	8.8
1.00	0.362	0.169	11.5
2.00	0.375	0.159	11.0
3.00	0.414	0.202	10.5
5.00	0.465	0.188	10.0
10.00	0.484	0.234	10.0
60.00	1.281	0.526	10.0



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