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Sodium Etching of Fluoropolymers

In order to provide some perspective, any discussion of the treatment of fluorocarbon polymers for bonding or fastening 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® 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 article, 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 co-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 using devices such as angioplast catheters. In many applications, asbestos has been replaced by PTFE as a high-temperature wire coating.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.

The dielectric property of this unique polymer has also given rise to a whole new technology in printed circuit board design. This concept is responsible for the very latest in high-speed, high-frequency microwave integrated circuits controlling radar, communications and military weapons 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 with or laminated to another material. The applications mentioned above all require PTFE to be etched to some degree, sometimes selectively, on one side or all over.

PTFE film and sheet are etched on one side to bond it to the inside of steel tanks and piping; 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 metal 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 - metallic 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 -32° 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, sodium, naphthalene and THF as the carrier solvent came into prevalent use where PTFE etching needed to be done. It was usually conducted 'out in the alley' or in a shed or bunker located well away from the normal process areas of the factory due to THF's high toxicity and low flash point.

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. Some 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 is usually 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 there is 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 also 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 could increase the bond strength between 50% and 75% over room temperature etching.

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 phenomena proves helpful when re-etching must be done. It can often eliminate the need to bleach the defectively etched parts before re-etching. It is not recommended to heat monoglyme-based etchants because of their very low flash point.

Another aspect of 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. Viscosity is also beneficial when etching fluoropolymer films where the fluid dynamics of a thinner etchant contribute to a uniform chemical reaction over large surface areas.

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. 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. It is now commonly held that the deterioration occurs over a period of weeks and perhaps months as opposed to hours or days which was the prevailing belief.

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).

Resources

If you would like more information on the etching of fluoropolymers, contact Acton Technologies and Goodrich Corporation, Porter Process. They offer two different processes to address your etching needs.

ACTON Technologies uses a sodium naphthalene etching process that provides a

uniform etch both in the machine direction and across the web of film materials. They have the ability to etch sheet, tubing, molded shapes and machined parts. Their plants in North America and Europe are both ISO 9000 certified for quality and ISO 14000 certified for being environmentally harmless. Their process also meets or exceeds every commercial or military specification for the surface modification of all Fluorine containing polymers.

ACTON also offers a portable etchant, FluoroEtch®, that allows customers to etch in-house. ACTON's customer service engineers provide their customers with advice and training and will also build application specific equipment for Fluoroetch® users.

Goodrich Corporation, Porter Process offers a sodium ammonia etching service that provides customers with a uniform aggressive etch on tape, sheet, tubing, molded shapes, and machined parts of any configuration. Their etch complies with applicable commercial, military and Federal specifications for the surface treatment of fluoropolymers. Goodrich Corporation, Porter Process has demonstrated that its quality system is in compliance with: ISO 9002-1994

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For more information, contact Bill Scott, Acton Technologies, Inc., P.O. Box 726, 100 Thompson Street, Pittston, PA 18640, 800-654-0612, Fax: 570-654-2810, E-mail: bscott@actontech.com, Web: www.actontech.com.

Also contact Bruce Baker, Goodrich Corporation, Porter Process, 1600 Industry Road, Hatfield, PA 19440, 800-618-4701, 215-855-9916, Fax: 800-618-4717, 215-855-3570, E-mail: bruce.baker@goodrich.com.

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Phone: (708) 588-1845
Fax: (708) 588-1846
[Email Us](#)