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Treatment of Teflon to Promote Bondability

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Introduction

Three and a half years ago, chemists at the Diamond Ordnance Fuze Laboratories (DOFL) published the first article dealing with the sodium treatment of Teflon (polytetrafluoroethylene) for the purpose of rendering it bondable with adhesives.[1] At about the same time, patents were granted to several companies for different versions of sodium treatment of polyfluorocarbons.[2,3] Since then, new Teflon treatment processes have been developed, each offering certain advantages. However, none has displaced the sodium treatment which apparently retains sufficient advantages to be the most commonly used method to date.

Teflon exhibits certain extraordinary characteristics that cause it to be used in many engineering applications. A drawback during its first dozen years of availability was the difficulty of attaching it to other materials or to itself.

Early attempts at making a bondable Teflon included surface roughening or the incorporation of salt which was subsequently leached out; both techniques aimed at producing surfaces to which adhesives might bond or key mechanically. An alternate approach involved the use of specially formulated, pressure-sensitive adhesives, none of which, however, yielded strong bonds.

The first truly useful method whereby Teflon might be modified so that ordinary adhesives could achieve good bonds was disclosed in a patent issued in 1957 and assigned to the Minnesota Mining and Manufacturing Co.[2] This method employs a solution of sodium metal in liquid anhydrous ammonia, the effect of which is to extract fluorine from the fluoro-polymer and leave a carbonaceous surface to which adhesives can readily bond. This bath releases ammonia fumes, therefore requiring an exhaust system. However, because an immersion time of only a few seconds yields a bondable Teflon surface, this process is widely employed in large-scale continuous operations.

Sodium-Naphthalene System

In 1956, an organic reaction being carried out at DOFL was noted to attack and darken the surface of a Teflon stirrer. This led to the development of a treatment bath consisting of a 1:1 molar complex of sodium and naphthalene solvated by an excess of tetrahydrofuran. Concurrently, work at the General Motors Corp. resulted in a patent centered on the use of sodium and naphthalene in a dimethyl glycol ether, an operative but less effective method than that employing tetrahydrofuran.

It has been shown[1] that the sodium-naphthalene-tetrahydrofuran bath requires a few minutes to render Teflon bondable to the same extent as that achieved by the sodium-ammonia system in a few seconds. On the other hand, the naphthalene bath is stable when protected from exposure to air and requires no exhaust system. It therefore lends itself to small-scale or laboratory operations in which a variety of parts or shapes are treated, or where the service is intermittent. Figure 1 shows a set of stainless steel tanks wherein Teflon and other polyfluorocarbon parts are treated with the sodium-naphthalene bath and rinsed in acetone.

In the original work at DOFL, a bath was prepared by reacting 23 g. of metallic sodium in lump form with 128 g. of naphthalene flakes dissolved in a liter of tetrahydrofuran. The preparation time can be reduced appreciably by the use of a dispersion of sodium in naphthalene, now commercially available. This proportioned dispersion is a solid and is safe to ship and handle. Treatment is achieved simply by immersing the Teflon part in the bath for a few minutes and then rinsing it successively in acetone and water. When dry, the treated surface is receptive to the application of any common adhesive. Some characteristics of the sodium-naphthalene-tetrahydrofuran bath are: bath preparation: approx. 5 min.; shelf-life of bath: 60 days (in closed container); Teflon treatment time: 1-5 min.; bond strength in tension

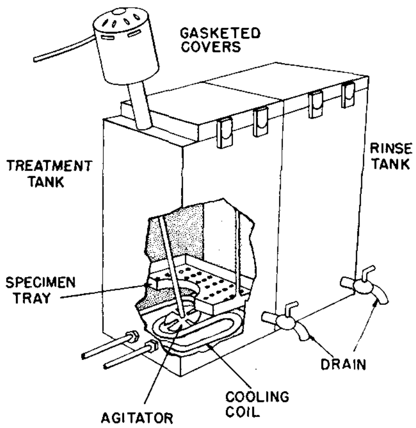

Fig. 1. Stainless steel tanks for treatment of polyfluorocarbons.

using epoxy adhesives: 1000–2000 psi; change in dielectric properties of Teflon due to treatment: not detectable.

The broad range of bond strengths includes the results of the butt-tensile, disc-tensile, and lap-shear tests illustrated in Figure 2.

Other polyfluorocarbons susceptible to sodium treatment include FEP-Teflon (copolymer of tetrafluoroethylene and hexafluoropropylene) and KEL-F (polychlorotrifluoroethylene).

Three main objections have been raised to the sodium treatment process: (*1*) the resulting dark surface on the polymer obscures any intentionally introduced coloring, such as that commonly used to color-code wire coating; (*2*) at high humidities, the surface resistivity of treated Teflon is substantially lower than that of the untreated polymer; and (*3*) prolonged exposure to sunlight reduces the bondability of the treated surface.

Sodium-treated Teflon has found its way into numerous military items. Examples include fiber-filled Teflon radomes in the Jupiter nose cone (see Fig. 3) and inexpensive, Teflon film, microwave windows in the electronics of several missiles (see Figs. 4 and 5).[7]

Some interesting work is in progress at DOFL and elsewhere on the direct plating of metals on sodium-treated Teflon. Early results indicate the possibility of achieving interfacial bond strengths approaching the tensile strength of the Teflon itself without the use of any intermediate adhesive.

In the past year or two, several alternate methods for treating polyfluorocarbons have come to light. These purport to cope successfully with one or more of the deficiencies of sodium treatment.

Radiation-Induced Grafting

Perhaps the best known of these alternate methods employs radiation-induced graft polymerization.[4] In this method, the Teflon part is exposed to radiation from a cobalt source or from an electron generator while in the presence of some dissimilar monomer. This monomer polymerizes onto the base Teflon thereby producing a foreign, and if properly selected, transparent, bondable coating. Teflon film, rod, wire insulation, and irregular shapes have been commercially treated in this manner with an undisclosed grafting monomer.

An epoxy bond to a commercial, radiation-grafted surface on Teflon was found to be 25% weaker in tension than a similar bond to a sodium-treated surface.

Electrical measurement at 95% relative humidity showed radiation-grafted Teflon to have a surface resistivity greater than 10^{16} ohms, a value indistinguishable from that of untreated Teflon. Sodium-treated Teflon, measured at the same humidity, had a surface resistivity of 5×10^{13} ohms.

It is obvious that radiation sources are not commonplace tools; therefore, Teflon parts must be shipped to a special facility in order to be subjected to surface treatment by irradiation.

Fluorinated Alkyl-Titanate-Polymer Treatment

Treatment methods which avoid the use of radiation have been developed for the wire-coating industry. A patent[5] assigned to Hitemp Wires Co. discloses a technique whereby a virtually colorless polymer containing perfluorinated sidechains is caused to form on and adhere to the surface of Teflon. A typical treatment bath consists of a solution of tetrabutyltitanate, perfluorooctanoic acid and other agents. The Teflon-insulated wire is passed through this solution which, in the presence of a small amount of water, yields a coating of a polymer consisting of an alkyl-titanium-oxygen structure with perfluorinated sidechains as illustrated in Figure 6.

The adhesion of the fluorinated titanate polymer to the Teflon is increased by heating the treated wire coating to 600°F. The surface activity of the coated Teflon may be further increased by a second coating of finely divided silica which, in turn, may be covered with a resin such as epoxy or methacrylate. A Teflon-coated wire, treated with a combination of these steps, approaches the degree of bondability exhibited by sodium-treated Teflon.

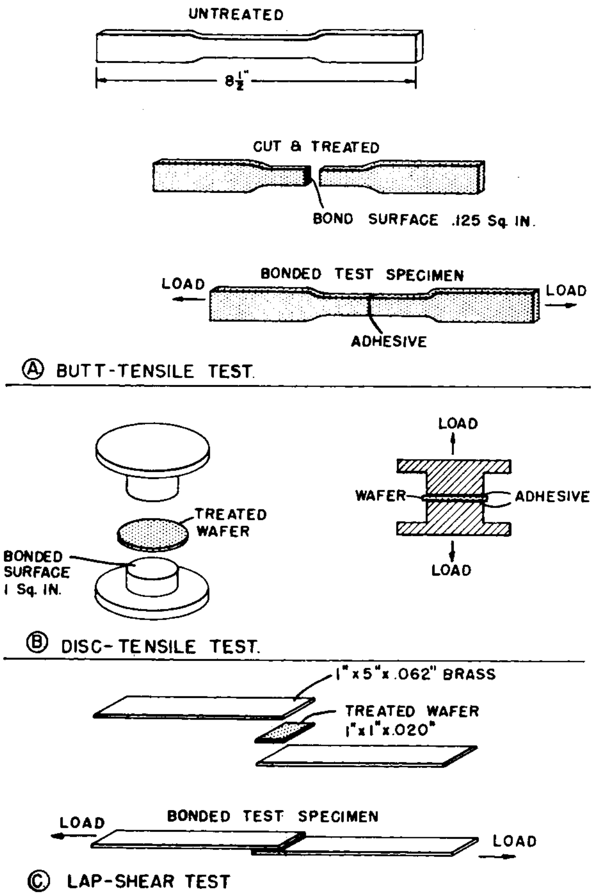

Fig. 2. Test specimens for determination of bondability of treated Teflon.

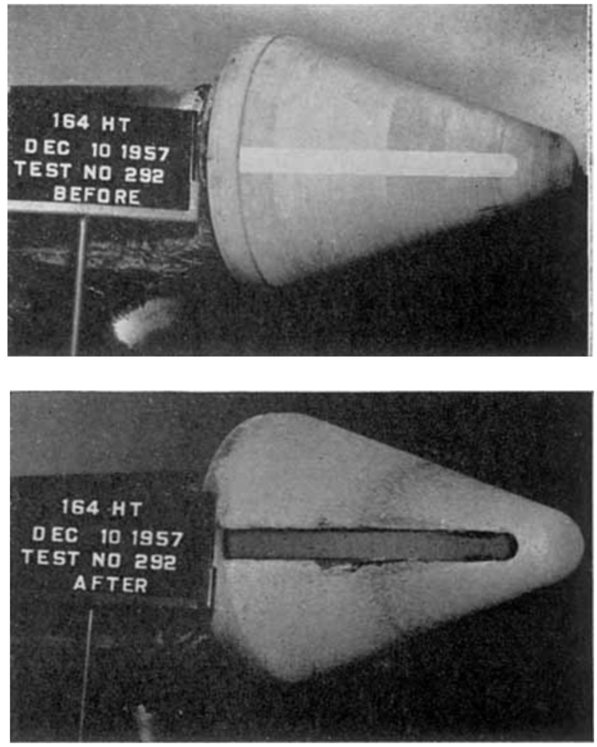

Fig. 3. Jupiter nose cone with ceramic-fiber-filled Teflon radome insert before and after simulated re-entry heating.

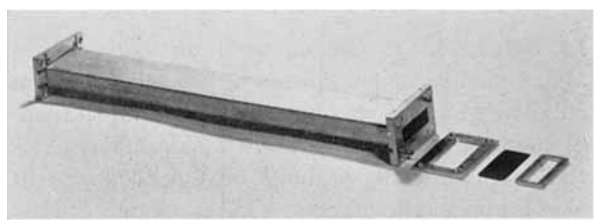

Fig. 4. Exploded view of Teflon window assembly at flange end of a section of wave guide (courtesy of the *Microwave Journal*).

Corona Bombardment

A third method[6] for the treatment of coated wire was evolved by du Pont and is effective on FEP-Teflon copolymer only. In this method the insulated wire is exposed to a corona discharge produced by high-frequency high-voltage alternating current. The bombardment produces free radicals on the surface of the copolymer. These free radicals are capable of forming bonds with a variety of substances. One such substance is oxygen and, therefore, the corona bombardment is carried out under nitrogen. It is claimed that if the oxygen concentration is kept as low as 10 ppm during corona treatment bond strengths equivalent to those resulting from sodium treatment can be obtained.

A new type of cementable FEP-Teflon film is now available. One surface of this film has been precoated with a thin layer of epoxy resin which is an integral part of the film. This epoxy surface can be readily bonded to other surfaces with common adhesives.

The manner in which the FEP-Teflon film was first rendered coatable by the applied epoxy resin is not disclosed by the manufacturer. However, bearing in mind the recent work on FEP-Teflon wire insulation, it is perhaps not unreasonable to suspect that the film has also been subjected to corona bombardment. In any case, the treatment allows the films to remain transparent. This form of cementable film, like its sodium-treated counterpart, is susceptible to bond weakening as a result of exposure to air and sunlight. The surface resistivity of the treated and coated side would, of course, be expected to be like that of a typical epoxy surface.

Fig. 5. Teflon window across feed end of the microwave antenna of a guided missile (courtesy of the *Microwave Journal*).

Conclusions

1. Treatment of Teflon, with virtually no resultant change of color, can be accomplished by radiation grafting or by coating with a titanate polymer that has perfluorinated sidechains. Corona bombardment, without resultant change in color, is applicable to Teflon-FEP copolymer only.

2. Radiation grafting of a suitable monomer onto Teflon results in a surface whose resistivity at high humidity is indistinguishable from that of the untreated polymer. Bond strengths to this surface are approximately 25% weaker in tension than those to sodium-treated Teflon.

3. The titanate-polymer method of treatment is especially applicable to insulated wire; it involves a combination of several coatings and a high temperature bake. The bondability of the resultant Teflon surface approaches that of sodium-treated Teflon.

4. Corona bombardment of FEP-Teflon copolymer yields bond strengths like those resulting from sodium treatment if the bombardment is carried out in an inert atmosphere.

5. Treatment of Teflon, with a resultant darkening of the surface, can be accomplished with such alkaline baths as sodium-ammonia and sodium-naphthalene. The treated surface has a lowered electrical resistivity at high humidity, and a susceptibility to partial deterioration in sunlight. In coping with these disadvantages, it should be borne in mind that Teflon can be treated selectively on only those areas that are to be bonded.

6. The sodium-ammonia treatment is effective after a few seconds and is therefore the most prevalent commercial process. It requires an extensive exhaust system, but no afterbake.

7. The sodium-naphthalene system offers the advantages of versatility in the treatment of complex shapes of FEP- and ordinary Teflon as well as of Kel-F. The bath can be stored and used intermittently without exhaust hoods or inert atmospheres. No high temperature afterbake is required. The bond strengths are at least as great as those resulting from any other treatment.

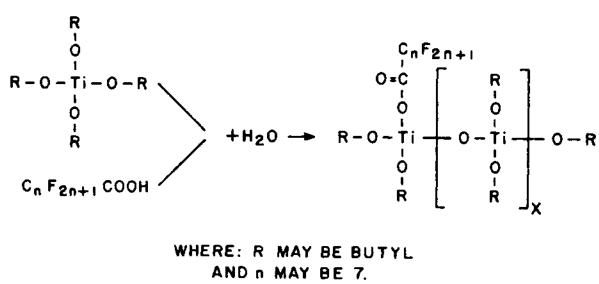

Fig. 6. Formation of a fluorinated, alkyl-titanate-polymer from an alkyl titanate and a perfluorinated aliphatic acid.

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Synopsis

Various methods are reviewed whereby Teflon and other polyfluorocarbon resins can be surface treated in order to enhance their bondability with ordinary adhesives. The features of these methods are compared and some conclusions are drawn as to their relative usefulness. Particular emphasis is placed on the sodium-naphthalene-tetrahydrofuran treatment system and reference is made to a few military applications wherein sodium-treated Teflon has been employed.

Résumé

Différentes méthodes pour traiter superficiellement le Teflon et autres résines fluorocarbonées afin d'améliorer leur capacité de liaison avec les adhésifs ordinaires, sont passées en revue. Les particularités de chacune de ces méthodes sont comparées entr'elles et certaines conclusions en sont tirées quant à leur utilité relative. Une particulière attention est consacrée au traitement sodium-naphtalène-tétrahydrofuranne, et quelques applications militaires sont données, dans lesquelles le Teflon traité au sodium est employé.

Zusammenfassung

Verschiedene Methoden zur Oberflächenbehandlung von Teflon und anderen Polyfluorkohlenstoffharzen zur Erhöhung ihrer Bindungsfähigkeit mit gewöhnlichen Klebstoffen werden besprochen. Die Grundzüge dieser Methoden werden verglichen und einige Schlüsse über ihre relative Brauchbarkeit gezogen. Besonderer Nachdruck wird auf die Behandlung mit dem Naphthalinnatrium-Tetrahydrofuransystem gelegt und einige militärische Anwendungen von natrium-behandelten Teflon erwähnt.