JOURNAL OF APPLIED POLYMER SCIENCE VOL. 19, 3201-3210 (1975)

Quantitative Explanation of the Mechanism of Corrosion of Poly(tetrafluoroethylene) Caused by Active Alkali Metals

J. JANSTA, F. P. DOUSEK, and J. ŘIHA, *J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 102 00 Praha, Czechoslovakia*

Synopsis

The known method of surface treatment of poly(tetrafluoroethylene) (Teflon) by alkali metals was studied quantitatively. It was shown that the reaction proceeds by an electrochemical mechanism in solid phase. The alkali metal acts as anode and Teflon as a cathodic active material of a typical galvanic corrosion cell. A relation describing the rate of the penetration of this reaction into the depth of Teflon was derived.

INTRODUCTION

Often, it has not been possible to make use of the extraordinary chemical, electrical, and mechanical properties of poly(tetrafluoroethylene) (PTFE) due to the impossibility to bind it to other construction materials. The bonding is difficult owing to an almost universal chemical inertness of PTFE. It is attacked only by unusual chemicals such as molten alkali metals, sodium in an activated state (e.g., dissolved in liquid ammonia or in naphthalene complexes), chlorine trifluoride, and fluorine at elevated temperatures and pressures.[1] A vast effort has been devoted to adapting the PTFE surface to bonding. Aside from drastic surface treatment by flame,[2] special adhesives[3,4] were looked for or experiments were made with a modification of the polymer itself.[5] Later, research succeeded in finding such chemical methods of surface treatment that ordinary adhesives could exhibit good bonds between PTFE and other substances. The method works with solutions of metal sodium or other alkali metals in anhydrous liquid ammonia and makes itself apparent by turning the color of PTFE surface grayish-brown or brown-black.[6-10] It has been stated that this is due to carbon left behind when the sodium-ammonia complex has extracted fluorine atoms from the polymer. The fact that, after the reaction, fluorine ions were detected in the bath supported this mechanism.[7] It was shown that the same kind of attack of the PTFE surface could be caused using solutions containing solvated complexes of alkali metal ions, namely, sodium and lithium, and aromatic ion radicals. Such complexes can be formed between any of the alkali metals and many aromatic hydrocarbons, or some aromatic nitro compounds dissolved in certain ethers or tertiary amines, e.g., Na or Li+ naphthalene, phenanthrene, and anthracene in tetrahydrofuran.[10-12] For all practical purposes, the bond strength in tension and shear of treated PTFE was independent of the treatment time in the range of 0.5 min to 24 hr when Na-containing baths were used. A satisfactory bond strength was achieved as a result of treatment with a solution of Na+ naphthalene in tetrahydrofuran after times as short as 2 or 3 sec. When cut edges of the treated samples were examined microscopically, the depth of attack by the treating agent was found to be less than 1 μm (ref. 11) in all mentioned cases.

The present paper reveals evidence of an electrochemical mechanism of the PTFE surface reaction with active alkali metals; some physicochemical relationships describing the reaction are mentioned.

EXPERIMENTAL

The lithium metal employed contained 0.7 wt-% Na and 0.01 wt-% K. The Li content in the sodium metal was below 5×10^{-4} wt-%. Potassium metal used for preparing the amalgam contained 0.6 wt-% Na and less than 3×10^{-4} wt-% Li. The series of amalgams employed was of a uniform equivalence concentration, its value 1.138 at-% being limited by the low solubility of lithium in mercury[13] (0.047 wt-% at 20°C). Amalgams of 0.040 wt-% Li, 0.133 wt-% Na, and 0.225 wt-% K were prepared by dissolving a surplus of alkali metals in redistilled mercury, filtering through a glass capillary, and, after analysis, diluting to the required concentration. All operations were performed in vacuo. A detailed description of the equipment employed has already been given.[14]

PTFE foils were imported commercial products of unknown origin obtained by continually cutting off the surface of a cylinder of 100 mm diameter and height. The cylinder was prepared by pressing and sintering the powdered polymer. Slight longitudinal scars were left by the knife on the surface of the foils. A part of the foil was cut off, degreased by boiling in a solution of 50 g/l. Na_3PO_4 and 20 g/l. NaOH, rinsed with distilled water, and heated in an electric oven to 340°C to remove mechanical tension. Around this temperature, PTFE becomes glassy, and the foil gains transparency and plasticity (crystalline melting point[1] 327°C). The cooling rate was 2°C/min. The foil was then cut into plates of the required size and placed into evacuated glass ampoules with amalgam. Prior to putting the plates into the ampoules, they were measured and weighed for precise determining their surface area. The ampoules were of an inner diameter of 12 mm and of a length of 150 mm, and in about one third of the length they were tapered to a diameter of 5 mm. To prevent the foil from coming out of the amalgam owing to its low specific weight, it was placed into the shorter part of the ampoule, the volume of the amalgam being always larger than that of the shorter part of the ampoule. After filling, the ampoules were kept upright in a liquid bath thermostat. Once every 24 hr, the amalgams were agitated by turning the ampoules upside down several times. By varying the surface area of the foil or by varying the volume of the amalgam, the final amalgam concentration was prevented from falling below one half of its initial value.

After finishing the experiment, the ampoule was taken out of the bath, its longer end was cut off, and the amalgam was poured out. Both parts of the ampoule were then quantitatively rinsed with water. The remainder of the alkali metal in the amalgam was determined by acidimetry and the mercury was dried and weighed. The decrease of the alkali metal content corrected[15] by a factor 0.91 was expressed with the aid of eq. (1) in the weight of PTFE consumed in the reaction. Using the specific gravity of our PTFE foils ($s = 2.174\ g/cm^3$) and from the known surface area of the plates, the thickness of the reacted layer of PTFE was determined. The accuracy of the determination was 0.5 μm. Blank experiments were made at equal conditions without PTFE foil. Microscopic measurements of the thickness of the black layer of reaction products created on the white PTFE base were made by preparing a ground section of the foil in an acrylic resin.

RESULTS AND DISCUSSION

The papers to the present describing the heterogeneous reaction between PTFE and an alkali metal have shown that the reaction occurs only in the case of a high purity and activity of the metal surface. When studying the decomposition of propylene carbonate in contact with lithium and sodium, we found that passive, quite unreactive metal surface could be activated by amalgamation, which disclosed the thermodynamic instability of this chemical system.[16] The assumption was, therefore, made that alkali metals in amalgams could react with PTFE in the same way as in the bath described in the introduction. Although free energy of the metal is naturally lowered by the value of amalgamation energy ($\Delta E = \Delta G/nF \doteq 1\ V$), the assumption was experimentally confirmed.

The moment the alkali metal amalgam comes into contact with PTFE, the surface of the foil starts blackening even at ambient temperature. The rate of the coloring decreases in the order Li → Na → K amalgam, the difference being apparent at first sight. The forming layer was dull black, nonporous, and adhered firmly to the PTFE base. The original relief of the surface was not affected by the reaction. Thicker layers of reaction products exhibited some properties reminding one of ceramic materials, e.g., when touched or cut. During the reaction, the weight of the foil increased by the weight of the alkali metal removed from the amalgam. The volume of reaction products was larger than that of PTFE taking part in the reaction. By determining the quantity of the alkali metal remaining in the amalgam and by qualitative analysis of the resulting black layer the following overall reaction was found to have taken place:

$$-\!\!(CF_2)_n\!- + 2n\mathrm{MeHg}_x \longrightarrow n\mathrm{C} + 2n\mathrm{MeF} + 2xn\mathrm{Hg} \qquad (1)$$

It was observed that, with time, reaction (1) penetrated into the depth of PTFE although no mercury was found in the thick, black layer of reaction products. This, therefore, excludes the mechanism of amalgam penetrating through the formed layer to PTFE surface, because reaction (1) would have to stop after a film, as thin as several Å, of the reaction products impenetrable for the amalgam has been formed between the amalgam and the PTFE surface.

Figure 1 gives the quantitative dependence of the thickness l' of the layer of PTFE consumed in reaction (1) on time at varying temperatures and concentrations of $LiHg_x$; it appears that reaction (1) keeps penetrating into

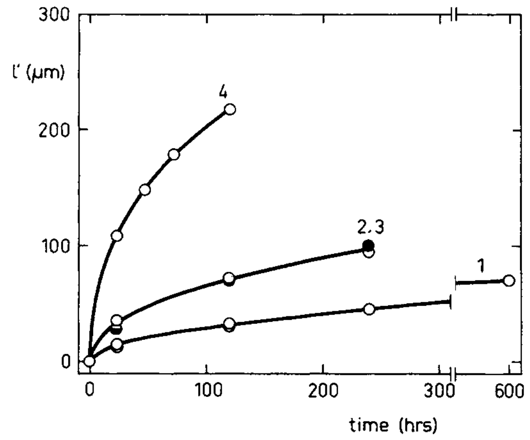


Fig. 1. Dependence of thickness l' of the PTFE layer consumed in the reaction with $LiHg_x$ on time: (1) 25°C, 1.138 at-% Li; (2) 50°C, 1.138 at-% Li; (3) 50°C, 0.569 at-% Li; (4) 100°C, 1.138 at-% Li.

depth of PTFE even though the rate of penetration slows down with time. The thickness of the black layer of reduction products l was determined simultaneously by measuring ground section of the same sample. This method turned out to be less accurate than titration, which yielded an ideal mean value of the thickness over the whole area. A substantial difference between the hardness of PTFE and that of the reaction products made good-quality ground section a difficult affair. A satisfactory agreement, however, has been obtained, deviations not exceeding 20% of values, determined by titration.

Cross sections of the PTFE foils covered with the black layer exhibited a sharply defined boundary without any signs of gradual changes between the black layer and the unreacted PTFE. The black layer was homogeneous and had a uniform thickness all over the foil surface. Its fracture had pearly brightness. It appears that reaction (1) gives rise to a highly dispersed mixture of C + 2LiF with a structure related to the original arrangement of the polymer molecule $\text{+}CF_2\text{)}_n$. With excess of Li amalgam, the reaction proceeds until the foil (0.2 mm thick) falls apart to yield two separate sheets equal in weight and thickness within 0.5% (see Fig. 2). Evidently, the reaction starts at either side of the foil and proceeds until the reaction heads meet. Carbon atoms originally bound in polymer chains are rearranged obviously in a new structure, and there are no conditions for uninterrupted structural connection in the plane of the encounter of both reaction heads. The fact that in a given time the reaction reaches the same depth over a considerably large area suggests that the rate of penetration of the reaction into the depth must be controlled by a strictly defined and dominating factor. Another explanation of such a spontaneous separation of both halves of the plate seems impossible. Homogeneity of the original PTFE is, of course, necessary.

If the layer of the reaction products adhering to PTFE is freed of the alkali fluoride by extraction with water, which is very easy especially with KF and NaF due to their high solubility, the carbon skeleton is found to be rather loose (it can easily be rubbed off with fingers).

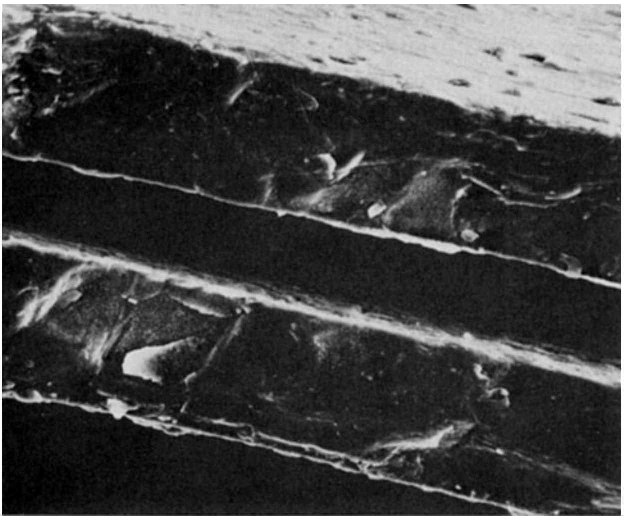
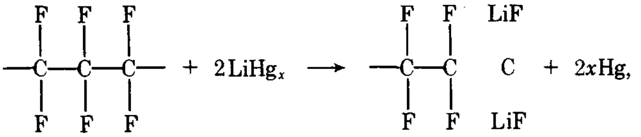


Fig. 2. PTFE foil originally 0.2 mm thick separating spontaneously into two halves owing to complete corrosion by lithium amalgam (view of fracture, scanning microscope Jeol, Japan).

The penetration of reaction (1) into the depth of PTFE may be explained by the following electrochemical mechanism: First a surface chemical reaction takes place:

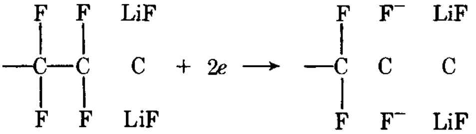


$$-\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{C}}}- + 2\mathrm{LiHg}_x \longrightarrow -\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{C}}}\quad \overset{\mathrm{LiF}}{\underset{\mathrm{LiF}}{\mathrm{C}}} + 2x\mathrm{Hg}, \tag{2a}$$

whereby the electrochemical decomposition of PTFE is initiated. The reaction leads to the formation of a several-Å-thick film of reaction products. The resulting layer of C + 2LiF functions as a mechanical separator of both reaction partners, but at the same time it has the nature of a solid electrolyte and an electron conductor. From this moment on, Li amalgam can behave as anode of a galvanic cell supplying electrons and Li^+ ions:

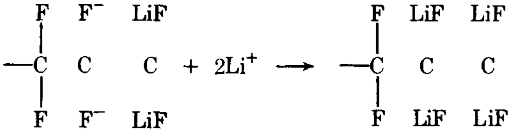
$$\mathrm{LiHg}_x \longrightarrow \mathrm{Li}^+ + e + x\mathrm{Hg}. \tag{2b}$$

PTFE as a cathodic depolarizer takes up electrons:



$$-\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{C}}}\quad \overset{\mathrm{LiF}}{\underset{\mathrm{LiF}}{\mathrm{C}}} + 2e \longrightarrow -\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{C}}}\quad \overset{\mathrm{F}^-}{\underset{\mathrm{F}^-}{\mathrm{C}}}\quad \overset{\mathrm{LiF}}{\underset{\mathrm{LiF}}{\mathrm{C}}} \tag{2c}$$

and Li^+ ions



$$-\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{C}}}\quad \overset{\mathrm{F}^-}{\underset{\mathrm{F}^-}{\mathrm{C}}}\quad \overset{\mathrm{LiF}}{\underset{\mathrm{LiF}}{\mathrm{C}}} + 2\mathrm{Li}^+ \longrightarrow -\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{C}}}\quad \overset{\mathrm{LiF}}{\underset{\mathrm{LiF}}{\mathrm{C}}}\quad \overset{\mathrm{LiF}}{\underset{\mathrm{LiF}}{\mathrm{C}}} \tag{2d}$$

Electrons generated by reaction (2b) are carried in (2c) to a subsequent group CF_2 in the polymer chain through the carbon set free by reaction (2a). This carbon thus represents the cathode of the galvanic cell but at the same time forms a conductive skeleton closing up the cell circuit. Such a closing up which cannot be interrupted is typical for electrochemical corrosion processes (local corrosion cells on metal surface).

The ionic current between the amalgam anode and C–PTFE cathode must be transferred exclusively by Li^+ cations in a solid phase (solid electrolyte) which forms between both electrodes in a continuously growing layer through reactions (2c) and (2d). If the ionic current were carried also by F^- anions, a white LiF layer would appear in the boundary between the amalgam and the carbon containing layer; this layer would easily be detected on the black background. Such a layer, though not necessarily preventing the passage of the ionic current, would definitely cut off the corrosion cell circuit and reaction (1) would stop as step (2c) would be impossible.

It is known from the literature[17,18] that LiF crystals are cationic conductors with a transference number $t_{Li^+} = 1$ at temperatures of 250–842°C (melting point). Their specific conductivity at 250°C is about 10^{-8} (ohm·cm)$^{-1}$. The transfer of cations is made possible by lattice defects, the conductivity of an ideal crystal being zero. At room temperature, the conductivity of LiF is negligibly small and is due to lattice defects generated by impurity ions of different valence (e.g., Mg^{2+}). It, therefore, follows that at 25°C, Li^+ ions in pure LiF crystals are immobile in the electric field. However, the conditions in the C + 2LiF mixture, formed during reaction (1), apparently make the motion of Li^+ possible. It is not probable that a LiF crystal lattice would be formed during the reaction with regard to the intercalation of LiF and C particles, as they seem to be dispersed on a molecular scale. This was suggested also by the liberation of carbon particles after the dissolution of fluoride, mentioned above. X-Ray diffraction patterns of the mixture C + 2LiF prepared at 25°, 50°, and 100° showed the presence of low, diffuse LiF peaks, which, in comparison with the sharp peaks of pure crystalline LiF, suggest that the structure of LiF in the mixture under study is characterized by a very low degree of arrangement. No characteristic graphite lines were found.

Even if a crystal lattice were formed in the mixture by several neighboring LiF molecules, it would be perfect, and hence nonconductive. We, therefore, assume the ionic conduction in the mixture C + 2LiF to be due to migration of small Li^+ cations accelerated by the electric field of F^- anions formed by reaction (2c) in the boundary between PTFE and the carbon-containing layer, the F^- being too big to be able to move across the given solid-phase structure. The space necessary for Li^+ transport could be formed in the mixture of reaction products by rearrangement of C atoms after splitting of the bonds in the PTFE molecule chain. This hypothesis is supported by the fact that the considerably larger ions of Na^+ and K^+ move more slowly through the mixture C + 2NaF or C + 2KF than do Li^+ ions through the mixture C + 2LiF as may be seen from Table I. Tabulated values K/a stand for the thickness of the layer of the PTFE consumed within the first hour (see further details below).

To verify the stoichiometry of reaction (1), a stated quantity of PTFE was made to react fully at 25° and 100°C in the presence of an excess of lithium

TABLE I

Values of K/a as a Function of Temperature, Concentration, and Time for the Reaction of PTFE with Various Alkali Metal Amalgams

Initial concentration of metal, at-%	$(K/a) \times 10^4$, cm·h$^{-1/2}$, for			
	25°C	50°C	100°C	Time, hr
Li 1.138	2.97	6.78	22.2	24
	—	—	21.5	48
	—	—	20.9	72
	2.76	6.55	19.7	120
	2.86	6.20	—	240
	2.80	—	—	600
Li 0.569	—	6.64	—	24
	—	6.48	—	120
	—	6.52	—	240
Na 1.138	0.16	0.22	1.0	240
K 1.138	—	—	0.22	240

amalgam; in these cases a consumption of Li amounting to on an average 110% of the theory of reaction (1) was observed. The increased consumption of Li was found in three samples of PTFE of different make and thickness. The reaction of glass vessel walls with Li was excluded by blank experiments (i.e., without PTFE).

By short rinsing with water, a small residue of the alkali metal amalgam could be completely removed from the surface of the reacted foil of PTFE. When the black foil was subsequently treated with an excess of water, lithium fluoride dissolved and the carbon skeleton disintegrated into very small carbon particles. In this suspension, the quantity of the base corresponding to the excess Li consumed from the amalgam was found by potentiometric titration. This means that the excess of Li was present in a form yielding LiOH by reaction with water. In the system under study, only some as yet undefined compounds of lithium and carbon can be considered. Lithium in the metallic form could only be present as amalgam, but, as already mentioned, no mercury was found in the reaction products.

The formation of Li_2C_2 by a direct reaction of the elements at an undefined elevated temperature was mentioned before.[19] But neither in the water suspension nor in the gas phase was acetylene found by gas chromatography or by a reaction with Ag^+ in an ammonium complex solution. The quantity of acetylene calculated from the excess of lithium could not have remained unobserved. Of the gaseous hydrocarbons only ethylene was detected by gas chromatography, but the determined quantity amounted only to 1% of the calculated volume. In the reaction products, the existence of compounds of the type C_xLi_y with a higher number of C atoms has to be supposed, which decompose with water to C_xH_y and LiOH. Under unusual conditions of our reaction arrangement (reduction in solid phase under complete exclusion of water and air atmosphere), the existence of unusual carbonaceous radicals can be expected. These radicals could arise from the highly reactive C atoms, in "statu nascendi" set free by reduction of the polymer chain. The radicals, for example, C_x^-, fixed in the structure of the forming solid phase could react with Li^+ ions moving into the depth of the layer.

Assuming that the system under study forms a corrosion galvanic cell $MeHg_x/C,2MeF/C\text{-}PTFE$, the sum of the electron and ionic conductivities of the mixture C + 2MeF could be the dominating factor controlling the rate of penetration of the corrosion reaction into the depth of PTFE foil. For this case, the following relationship between the thickness of the reacted layer of PTFE (l' in cm) and time (t in hr) was derived[15]:

$$l' = (K/a)t^{1/2} \tag{3}$$

where a = const. = l/l', and l is the thickness of the layer of the formed reaction products thus taking into account the volume change during the reaction. The constant ratio

$$K/a = (EM/\rho n s F a)^{1/2},$$

where E is the voltage of the galvanic cell $MeHg_x/C\text{-}PTFE$, M is the sum of atomic weights in the CF_2 group, ρ is the specific resistance of the mixture C + 2MeF, n is the number of electrons in reaction (2c), s is the specific weight of PTFE, and F is the Faraday constant.

Table I shows values of K/a for three different temperatures and for various times, verifying the relationship (3) experimentally. In the range of 25–100°C and within experimental error, these values may be considered constant. At 100°C, a slight decrease in K/a may be observed with time, i.e., with an increase in the thickness of the layer of PTFE consumed in the reaction. A slight implication of this phenomenon may be observed at lower temperatures as well. It is not possible to elucidate this phenomenon on the basis of experiments made to date. Equation (3) apparently does not describe the corrosion of PTFE in its whole complexity. Deviations may be due to several reasons. For instance, it must be admitted that the resistance of the layer C + 2LiF may not be constant as was assumed in the derivations, that it can vary a little with time and especially at elevated temperature, e.g., as a consequence of the rearrangement of particles in the layer of reaction products. Or, the decrease in the influence of electrostatic field taking place with increasing distance of anodic and cathodic processes could also be of importance.

In all events, however, Table I shows that experiments confirm to a great extent the validity of relation (3). The agreement of theory with experiment also confirmed the assumption that the resistance of the layer of reaction products represents the limiting step in the rate of the layer growth, and consequently the PTFE corrosion with alkali metal amalgams. A further proof of the dominating influence of the electric resistance and thus of the fact that the reaction mechanism is an electrochemical one is that the K/a value undergoes no significant change after cutting down the initial concentration of Li amalgam from 1.139 at-% to one half (see Table I and Fig. 1, curves 2 and 3). Even when the experiment was made in such a way to make the concentration of Li in the amalgam fall to 16% of the initial value, the value of K/a remained constant. From the point of view of chemical reaction kinetics, such a change in concentrations would be considered high. In terms of electrochemistry, such a concentration change will cause a decrease in potential and open circuit voltage of only several tens of mV which represents only 3–4 hundredths of the assumed voltage of the $LiHg_x$/C-PTFE cell. For the same reason, agitation done by periodically turning the ampoules, which from the chemical kinetics point of view was insufficient, had no unfavorable effect either.

Equation (3) is formally consistent with the so-called parabolic law derived by Wagner[20,21] for surface oxidation of metals in a dry gas medium at increased temperatures if compact solid oxide layers of the order of magnitude of 1 μm or more are formed. For corrosion reactions of metals under these conditions, electrochemical mechanisms were also proposed and confirmed by experiment. This analogy is an added support for the evidence of the electrochemical mechanism of corrosion of PTFE.

The observation mentioned above[11] that a 24-hr etching in a solution of Na attacks PTFE into a depth of less than 1 μm is in very good agreement with relation (3). Taking $K/a = 0.16$ (from Table I for Na amalgam), we obtain $l' = 0.8$ μm. Our value refers to the reaction with the amalgam, but if the anode were made of the metal instead of the amalgam, the value of the cell voltage E would rise from about 3 to 4 V, and the numerical value of the constant would rise by the factor $\sqrt{4/3}$, i.e., 1.15 times only.

It has also been shown that satisfactory bond strengths can be obtained after 2 or 3 sec. of etching.[11] In this case, it may be calculated from reaction (3) that for the change of the surface properties of PTFE, a layer of reaction products 40–50 Å thick is sufficient.

Alkali metals are known to dissolve in liquid ammonia forming a blue solution of metal ions and solvated free electrons.[22] Even an aprotic solvent, hexamethylphosphoramide, has recently been shown to form a blue solution of metal sodium showing strongly reducing properties. Papers on metal-aromatic hydrocarbons[23–25] indicate that these are solvated complexes of metal ions and aromatic ion radicals in a mole ratio of 1:1. Such ionic radicals are also strong reducing agents and, therefore, may function as electron donors for the electrochemical reduction of PTFE with electrolytic potentials more negative than those of alkali metal amalgams. The fact that fluoride ions were found in the bath after etching PTFE with the solution of sodium in liquid ammonia[7] proves only that NaF is soluble in this bath.

It may be stated that all conditions are fulfilled for the mechanism of the reduction of PTFE to be of electrochemical nature even when using the baths or molten alkali metals mentioned above. The reaction of molten lithium with PTFE may occur explosively owing to the relatively high melting point of the former and also owing to the above-mentioned high reactivity of Li toward PTFE. The course of the reaction between molten alkali metals and PTFE will very probably follow the parabolic law discussed in this paper up to the point of thermal decomposition of PTFE.

References

1. *Encyclopedia of Polymer Science and Technology*, Vol. 13, H. F. Mark and N. G. Gaylord, Eds., Wiley, New York, 1964–1972, p. 637.
2. M. F. Kritchever, U.S. Pat. 2,648,097 (1953).
3. British Thompson-Houston Co., Ltd., Brit. Pat. 659,439 (1951).

4. J. Hochberger, U.S. Pat. 2,710,226 (1955).
5. M. A. Rudner, U.S. Pat. 2,728,698 (1955).
6. E. I. Du Pont De Nemours and Co., Belg. Pat. 548,516 (1957).
7. Minnesota Mining and Mfg. Co., Brit. Pat. 765,284 (1957).
8. R. J. Purvis and W. R. Beck, U.S. Pat. 2,789,063 (1957).
9. E. I. Du Pont De Nemours and Co., Brit. Pat. 793,731 (1958).
10. R. C. Doban, U.S. Pat. 2,871,144 (1959).
11. E. R. Nelson, T. J. Kilduff, and A. A. Benderly, *Ind. Eng. Chem.*, **50**, 329 (1958).
12. G. Rappaport, U.S. Pat. 2,809,130 (1957).
13. M. T. Kozlovskij, A. I. Zebreva, and V. P. Gladyshev, *Amalgamy i ich primenenie,* Nauka, Alma-Ata (U.S.S.R., 1971, p. 23, in Russian.
14. J. Jansta, F. P. Dousek, and J. Řiha, *J. Electroanal. Chem.*, **38**, 445 (1972).
15. F. P. Dousek and J. Jansta, *Electrochim. Acta,* **20**, 1 (1975).
16. F. P. Dousek, J. Jansta, and J. Řiha, *J. Electroanal. Chem.*, **46**, 281 (1973).
17. H. H. Landolt and R. L. Börnstein, *Zahlenwerte und Funktionen,* Vol. 2, Springer, Berlin, 1959, Pt. 6, p. 230.
18. A. B. Lidiard, in *Handbuch der Physik,* Vol. 20, S. Flügge, Ed., Springer, Berlin, 1957, p. 246.
19. H. Remy, *Lehrbuch der anorganischen Chemie,* Vol. I, Akademische Verl aggesellschaft Geest & Portig, Leipzig, 1954, p. 56.
20. C. Wagner, *Z. Phys. Chem.* (B), **21**, 25 (1933).
21. C. Wagner, *Z. Phys. Chem.* (B), **32**, 447 (1936).
22. D. C. Walker, *Quart. Rev.*, **21**, 79 (1967).
23. W. A. Holmes-Walker and A. R. Ubbelohde, *J. Chem. Soc.*, 720 (1954).
24. D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956).
25. T. L. Chu and S. C. Yu, *J. Amer. Chem. Soc.*, **76**, 3367 (1954).

Received January 3, 1975
Revised March 31, 1975