Ecological Aspects of the Manufacture and Application of Highly Pure Liquid Substances

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ABSTRACT: The action mechanism for aggressive and highly pure media on fluoropolymer constructional elements is assumed to consist of two basic microeffects: destructive changes in the fluoropolymer and contamination of the environment. Our approach to a quantitative estimation of the physicochemical stability is based on logic similar to that of a thermodynamic model of a two-component system. A fluoropolymer and changes in its microstructure are considered the first component of the system. The second component is composed of liquid media contaminated with fluoroorganic compounds extracted from the fluoropolymer. The proposed methods for delivering aggressive and highly pure fluids to consumers allow the exclusion of pollution from working areas with gaseous products through an exception to a number of intermediate stages of product transport. The discussed principles allow the creation of a modern, highly effective, and safe (with respect to the ecology and raw materials) production of aggressive liquid chemicals for consumers. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 906–910, 2002

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INTRODUCTION

Modern technologies for manufacturing highly pure liquid reagents are based, in general, on various types of distillation processes performed in equipment made of fluoropolymers because of aggressive media. Ecological dangers are represented by the emissions of toxic substances (halogens, sulfur oxides, nitrogen oxides, and oxides of other elements) into the atmosphere and wastewater. This pollution penetrates the environment because of reactor infringements and diffusion permeability through walls. This means that manufacturing should be organized toward reducing the amount of wastewater and recycling the wastes.

As we have shown in preliminary results and other researchers have also shown, the creation of ecologically safe manufacturing should be based on solving the following scientific and technical tasks: (1) the quantitative estimations of the physicochemical stability in constructional fluoropolymer/aggressive medium systems, the dependence of the diffusion permeability on the nature of the fluoropolymer and medium, and the technological parameters of the process and (2) the optimization of the washing processes of the internal surfaces of reactors, containers, and

Table I   Increasing Ratio of the Fluoropolymer Value of P_g/P_{g0} with Hydrochloric Acid

Temperature (°C)	Fluoropolymer				
	F-4	F-50	F-4MB	F-2M	F-10
20	1	1	1.2	1.5	2
100	1.8	1.8	2.5	4	100

pipelines with the idea of subsequently recycling washing formulations.

The delivery of highly pure liquid reagents to the consumer is carried out in large containers connected directly to the consumer's working lines. This maintains high product purity and excludes undesirable gaseous emissions of etching agents into the atmosphere. The ideal case is the direct delivery of highly pure reagents through pipelines made from high-proof, low-penetrable fluoropolymers.

QUANTITATIVE ESTIMATION OF PHYSICOCHEMICAL STABILITY IN CONSTRUCTIONAL FLUOROPOLYMER SYSTEMS: HIGHLY PURE AND AGGRESSIVE FLUID

The mechanism of action for aggressive and highly pure media on fluoropolymer constructional elements is assumed to consist of two basic microeffects: destructive changes in the fluoropolymer and contamination of the environment. Our approach to a quantitative estimation of the physicochemical stability is based on logic similar to that of a thermodynamic model of a two-component system. A fluoropolymer and changes in its microstructure are considered the first component of the system. The second component is composed of liquid media contaminated with fluoroorganic compounds extracted from the fluoropolymer.

The degree of structural changes in a constructional fluoropolymer is most fully characterized by an increase in the diffusion permeability coefficient P_g/P_{g0}, where P_{g0} is the diffusion permeability in the beginning of a quasistationary (steady-state) site and P_g is the diffusion permeability at the end of a quasistationary (steady-state) site; structural changes are practically completed. The results of changes in the flu-

oropolymer value of P_g/P_{g0} with hydrochloric acid are given in Table I.

The expression $1/n \sum \lg(C_g/C_{g0})_i$ is taken as a measure of contamination of highly pure media, where n is the amount of controllable types of contamination and i is the index of a type of contamination varying from 1 to n. The contamination of the fluid by impurities of organic and fluoroorganic compounds and microparticles is of the greatest importance. The results of research on increased contamination in acids in contact with fluoropolymers are given in Tables II and III. An increase in the concentration of contaminating impurities is characterized by a ratio of those values at equilibrium (C_g) to the initial concentration of impurities in the highly pure medium (C_{g0}).

The expression of a parameter of physicochemical stability (K_s) can be written as a reciprocal sum: $K_s = [P_g/P_{g0} + 1/n \sum \lg(C_g/C_{g0})_i]^{-1}$. Using this expression for K_s of fluoropolymer/medium systems and browsing the most probable statistical types of the researched systems, we can propose a decreasing sequence of physicochemical stability for constructional fluoropolymers in various aggressive media used in semiconductor and optical engineering at standard temperatures: F-4, F-50, F-4MB, F-2M, and F-10.

Changes in K_s at 20 and 100°C fit into an interval of 0.5–0.3. Accepting the parameter $10K_s$, we obtain, rounding numbers, a rated evaluation of the physicochemical stability.

DIFFUSION PERMEABILITY

Permeability is a one of the basic characteristics determining the ecological safety of plants. Two areas, nonstationary and stationary, characterize the diffusion permeability. The nonstationary area was limited for a number of liquid reagents to 3–4 h for all types of fluoropolymers. Then, the

Table II   Logarithm of the Ratio of the Total Carbon Concentration Increase in Acids After Contact with Fluoropolymers [lg(C_g/C_{g0})]

Fluoropolymer	Acid							
	HNO$_3$		H$_2$SO$_4$		HCl		HF	
	20°C	100°C	20°C	100°C	20°C	100°C	20°C	100°C
F-4	1	1.2	1	1.2	1	1.1	1	1.1
F-50	1	1.3	1	1.3	1	1.1	1	1
F-4MB	1	1.1	1.1	1.2	1	1.1	1	1.1
F-2M	1.5	8	1.5	6	2	20	1	1.1

Contact time = 1 month; experimental error = ±10 wt %.

stationary process was established and was characterized by a constancy of the basic parameters of permeability: permeability and diffusion coefficients and limited electrolyte solubility.

For example, the results of research on halogen hydrides are discussed later. The destruction of azeotrope structures on components (halogen hydride and water) during permeability through a fluoropolymer film has been discovered for the first time. As a result, our research has shown that the diffusion permeability of halogen hydrides is higher than the permeability of water by several orders of magnitude; and we can deal with only the permeability of halogen hydrides. This process in a nonstationary area can be described by Fick's law with modifications depending on the complex (amorphous and crystalline) and partially defective structure of the fluoropolymer.

Average values of diffusion coefficients and limited solubility, proceeding from the ratio $P = DC_s$, were calculated with specially created software. We have confirmed that the diffusion

permeability parameters of the electrolyte components through fluoropolymers depend on the temperature according to the Arrhenius law and that the solubility depends on the hyperbolic dependence of the initial electrolyte concentration.

The dependence of diffusion permeability with a simultaneous change in the electrolyte temperature and concentration can be given by an expression. For example, for hydrofluoric acid,

$$P_i(T, C_x) = P_i(T_0, C_a) \times C_{sa} \times 0.6/(0.95 - C_x)$$
$$\times \exp[1.25E/R \times \Delta 1/T]$$

where $\Delta 1/T = 1/T_0 - 1/T$, C_x is the concentration of an original electrolyte, C_a is the concentration of an azeotrope, C_{sa} is the solubility of an electrolyte in a fluoropolymer at the azeotrope concentration, and E is the activation energy.

Penetration parameters for hydrofluoric acid through fluoropolymer F-4MB at different temperatures and initial concentrations are listed in

Table III   Logarithm of the Ratio of the Fluoride-Ion Concentration Increase in Acids After Contact with Fluoropolymers [lg(C_g/C_{g0})]

Fluoropolymer	Acid					
	HNO$_3$		H$_2$SO$_4$		HCl	
	20°C	100°C	20°C	100°C	20°C	100°C
F-4	1.2	1.5	1.2	1.5	1.1	1.2
F-50	1.1	1.2	1.1	1.2	1.1	1.1
F-4MB	1.1	1.2	1.1	1.2	1.1	1.1
F-2M	3	7	3	20	6	15

Contact time = 1 month; experimental error = ±10 wt %.

Table IV Influence of the Electrolyte Temperature and Concentration on P_i (g/cm s) in the Hydrofluoric Acid/Fluoropolymer F-4MB System

C_{HF} (molar fraction)	23°C $P_i \times 10^{15}$	70°C $P_i \times 10^{14}$	100°C $P_i \times 10^{13}$
0.4	3.0	1.2	2.4
0.5	5.4	1.6	4.2
0.6	6.8	1.7	5.4
0.7	9.7	2.4	6.6
0.8	16.4	4.0	13.0
0.85	24.4	6.3	13.4
0.9	48.8	12.0	14.4

Table IV. Discovered dependencies allow us to propose methods for their practical applications in designing apparatus and tare in the production of highly pure substances.

We have proposed a criterion equation, $\Pi = P_i\tau/C_d \times (V \times l/F)$, for the calculation of ecologically safe processes. Π is a criterion for diffusion semblance; P_i is a coefficient of diffusion permeability in the fluoropolymer/electrolyte system; τ is the contact time of the system's components; $V \times l/F$ comprises dimensional or designed parameters of the equipment, tare, and workspace; and C_d is the concentration of the electrolyte components that have diffused. It should not exceed the limit. In other words, C_d is the upper limit of the concentration.[1]

A magnitude of the criterion (Π) can change limits of 1 to 0.1. This difference, allowing a 10-fold proof of ecological safety, is caused by the inhomogeneity of the construction material, the presence of defects on its surface, variations in the wall thickness, and possible inaccuracy in the determination of C_d.

A technological process is, as a rule, a thermo- and mass-exchange process in an apparatus or the storage and transport of highly pure electrolytes in a fluoropolymer tare or composite container.

A set of dimensional and designed parameters ($V \times l/F$) can have different meanings depending on the goals. Therefore, l, as a rule, is the thickness of the fluoropolymer wall of an apparatus or tare through which an electrolyte diffuses; V is the volume of a coolant in an apparatus or a volume of air in a workspace, storage room, and so forth; and F is the area of diffusion contact in the fluoropolymer/electrolyte system. The logical completion of this research is the creation of software and the calculation of ecologically safe manufacturing of highly pure reagents.

OPTIMIZATION OF WASHING PROCESSES

Our research has shown that the efficiency of washing procedures can be characterized by a kinetic decrease in contamination on the surface (C_F) or by an increase in the impurity concentration in an applied procedure (C_τ):

$$C_\tau = C_0 e^{-m\tau}$$

where C_0 is the impurity concentration in the original washing method and m is the efficiency coefficient of the washing method.

Kinetic curves $[C_\tau = f(\tau)]$ for water and hydrofluoric acid and a universal procedure based on a solution of xenon difluoride in hydrofluoric acid allow us to determine the required time for completion of the washing process by the aforementioned methods and to quantitatively evaluate the efficiency of that or another washing procedure. The test conditions were standard ($t = 20°C$); the velocity of fluid flow was optimal.

Experimental work has revealed that the average concentration of inorganic substances for medium-contaminated surfaces of fluoropolymers under fourth-grade purity is $C_{F0} = 1–5 \times 10^{-6}$ g/cm^2. This value is an average of the 10 most present elemental impurities: Fe, Al, Mg, Ca, Na, Cr, S, Ni, Mn, and Si. The washing process is considered complete when 90% of the impurities on a surface are washed off.

For the determination of the efficiency coefficient m, several experimental points have to generate the dependence $\ln(C_F/C_{F0})$. The calculation of m is described in detail in another article.[2]

m is correlationally dependent on the wetting value of the fluoropolymer through a liquid reagent:

$$\Psi = K(1 + \cos\theta_a)/(1 + \cos\theta_w)$$

where θ_a and θ_w are the wetting angles of the fluoropolymer surface for an acid and water, respectively.

The proposed washing optimization of fluoropolymer surfaces is expedient for calculation with the criterion equation, $K_w = C_F F/C_1 N(\tau_{\min}$

$+ \Delta\tau$), where K_w is the criterion of washing optimization; $C_F F$ (g) is the amount of contamination that has been washed off from a fluoropolymer surface; C_l (g/cm^3) is the concentration limit of an impurity in a washing fluid ($C_l \leq 10C_s$); C_s is the average concentration for the 10 most widespread impurities in the washing fluid, according to the state standard; N (L/h) is the productivity of the pump; and $\tau_{min} + \Delta\tau$ is the optimum washing time under real conditions.

There is a limiting quantity for the washing fluid; exceeding it does not result in increased process efficiency. For washing methods using hydrofluoric acid, this quantity is 30 L on 1 m^2 of surface. These data are used for a choice of productivity of the pump.

The value of the criterion K_w is within the limits of 1–0.3 and is connected to the degree of washing fluid purity, the amount of contamination not taken into account, and experimental error.

Developed and proposed washing methods for fluoropolymer surfaces are regenerated with a maximum return of the basic products to the technological process. This allows the creation of a combined, ecologically safe process of washing and regeneration. The practical calculations involving the use of K_w were performed with specially developed software.

BASIC PRINCIPLES OF APPLYING HIGHLY PURE LIQUID REAGENTS

The proposed ways of delivering aggressive and highly pure fluids to the consumer allow us to exclude pollution from the working area with gaseous products through the exception of a number of intermediate stages of the product transport. The basic principle is the installation of an apparatus for final purification and equipment for the regeneration of wastes by the manufacturing area of the consumer. This allows us to reduce transportation and improve ecological safety in the use of toxic products. The second major principle is the separate selection of used chemicals (without mixing) and their regeneration. All this has allowed us to create a modern, highly effective, and safe (with respect to the ecology and raw materials) production of aggressive liquid chemicals in regions of the consumer.

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