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# The Boundary Dynamic

*The performance of a polymeric adhesive depends on the properties and composition of its surface. Now a scientist at the General Motors Research Laboratories has developed and validated a theory that describes the coupled effects of diffusion and chemical reaction on the changing surfaces not only of adhesives, but of chemically reacting surfactant systems in general.*
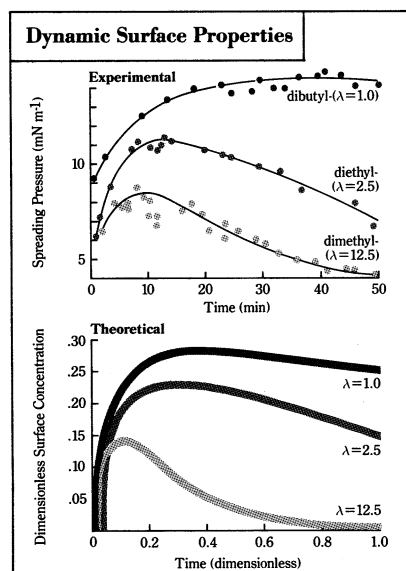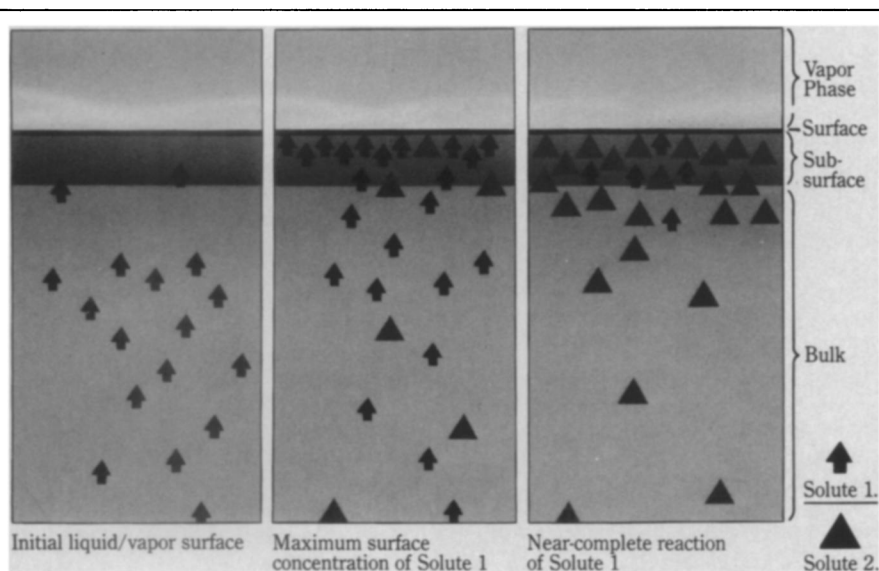


Figure 1: Experimental measurements of spreading pressure v. time for dialkylaminopropyl-amines with various Damköhler numbers ($\lambda$), and corresponding theoretical calculations of surface concentrations.

*Figure 2: Evolution of an adhesive surface: Surface-active Solute 1 reacts with host resin to form surface active Solute 2.*

T HE USE OF adhesives in the production of an automobile promises to make both the product and the process more efficient. Both weight and operations can be reduced. In practice, however, steel and other metallic surfaces are often contaminated by process lubricants. A durable bond depends on the ability of an adhesive to displace contaminants and to wet the substrate.

Assuring intimate contact between adhesive and substrate requires detailed knowledge of adhesive surface tension, since it is this property that controls displacement of contaminants and wetting. Up to now the surface tension of an adhesive has typically been assumed constant. In reality, though, surface-active components in the adhesive collect preferentially at the interface and also react, so that the surface composition varies with time, giving rise to dynamic surface tension. Variations can be large enough to significantly affect adhesive performance.

The understanding of time-dependent surface tension has been advanced by the work of Dr. Robert Foister, a scientist at the General Motors Research Laboratories. Investigation of dynamic surface properties of thermosetting adhesives led him to develop a general theory of adsorption kinetics in binary, chemically reacting surfactant systems. The significance of this theory is that it includes the coupled effects of surfactant diffusion and chemical reaction, making it possible for the first time to describe quantitatively the changing surfaces of such systems.

In a typical adhesive that polymerizes, or "cures," by chemical reaction (Figure 2), a surface-active curing agent (Solute 1) reacts with the host resin to form a second surface-active species (Solute 2) that is also reactive. Both solutes migrate to the surface, lowering the surface tension. Diffusion to the surface is driven by a potential energy gradient between the surface and the bulk, with the solute molecules experiencing a lower energy at the surface.

Dr. Foister derived appropriate transport equations to describe diffusion and chemical reaction in the bulk, in a subsurface region, and at the surface itself. The transport equations can be solved analytically if the chemical rate equations are assumed to be first order in the concentrations of reacting species, and if the subsurface and surface concentrations can be related to one another by a linear adsorption isotherm. For more complicated isotherms, a set of coupled, non-linear integral equations is generated.



Initial liquid/vapor surface    Maximum surface concentration of Solute 1    Near-complete reaction of Solute 1

These must be solved numerically.

Analytical solution for the special case of the linear isotherm indicated that the change with time in surface concentration (and consequently in surface tension) is composed of two terms: first the diffusive flux of Solute 1 into the subsurface from the bulk, and second the depletion of this solute due to chemical reaction. Hence, the surface concentration of Solute 1 exhibits a maximum with time (Figure 2). This maximum in surface concentration corresponds to a minimum in surface tension.

MODIFYING the transport equations to include binary adsorption isotherms allowed for consideration of competitive adsorption of the two reacting and diffusing solutes. By solving these equations numerically and conducting dimensional analysis, Dr. Foister identified various dimensionless parameters as predictors of system behavior. The most important of these parameters was a dimensionless number ($\lambda$), of the Damköhler type, involving terms representative of reaction, diffusion, and adsorption.

$$\lambda = \frac{k\,(\Gamma_m\,a)^2}{4D}$$

Here $k$ is the reaction rate constant of Solute 1, $D$ its diffusivity, $\Gamma_m$ its "surface capacity" (the maximum number of molecules absorbed per unit surface area), and $a$ its "surface affinity" (a measure of its energy of adsorption). For an adhesive, lowering $\lambda$ by reducing $k$ (the reactivity of the curing agent), for example, would prolong the time to maximum, and would increase the value of the surface concentration at the maximum (see Figure 1, Theoretical). As a practical consequence, this would improve wetting by minimizing the surface tension.

In experiments using a series of dialkylaminopropylamine curing agents (dimethyl-, diethyl-, and dibutyl-) in a host epoxy resin matrix, good agreement has been demonstrated between theoretical predictions for surface concentration and the measured dynamic spreading pressure, which is the change in adhesive system surface tension due to the curing agent (Figure 1, Experimental).

"I expect," says Dr. Foister, "that the physical insights gained from this analysis can be applied to other reactive surfactant systems by using specifically tailored isotherms and chemical reaction schemes. Predicting surface behavior can certainly help us design better adhesives for specific applications, but it is also pertinent to the performance of anti-oxidants and anti-ozonants in synthetic rubber, for example. And applied to interfaces in biological systems, a suitably modified theory may prove valuable in understanding the phenomenon of enzyme activity."

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**General Motors**

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MARK OF EXCELLENCE

## THE MAN BEHIND THE WORK

Dr. Foister is a Staff Research Scientist in the Polymers Department at the General Motors Research Laboratories.

Dr. Foister received his undergraduate degree from Guilford College, and holds a Ph.D. in Physical Chemistry from the University of North Carolina at Chapel Hill. His thesis dealt with the role of liquid inertia in the intrinsic viscosities of rod-like polymers.

He did post-doctoral work in Canada as a Fellow at McGill University in Montreal, and in the Applied Chemistry Division of the Pulp and Paper Research Institute of Canada, working on the microrheology of colloidal dispersions.

Dr. Foister joined General Motors in 1980. He is the leader of the Structural Adhesives Group in the GMR Polymers Department. His current research interests center on surface chemistry and adhesion.