Robert F. Brady, Jr.

Dr. Brady attended the University of Virginia, earning B.S. and Ph.D. Degrees in Chemistry. He joined the Naval Research Laboratory in 1982 after previous positions at the National Bureau of Standards (now the National Institute for Standards and Technology), the U.S. Customs Service, and the General Services Administration.

At the Naval Research Laboratory, Dr. Brady has formulated, patented, and introduced to the fleet a wide range of high performance marine coatings. Among these are nonskid coatings for aircraft carrier flight and hangar decks, fluorinated polyurethane coatings for submarine antennas, epoxy linings to eliminate corrosion/erosion in copper-alloy piping, low solar absorbance (LSA) haze-gray exterior topcoats, and LSA light-gray gelcoats for composite components used in electronics. His present interests include high-solids epoxy and urethane coatings, and nontoxic coatings based on silicone and fluorinated resins which limit or prevent the attachment of marine fouling.

For one year from July 1990, Dr. Brady was a visiting scientist at the Defense Aeronautical and Maritime Research Laboratories in Melbourne, Australia, where he collaborated with defense scientists on problems of mutual interest. Since 1993 he has been U.S. National Leader of Technical Panel 6 on Polymers, Adhesives, and Coatings of The Technical Cooperation Program, an organization which coordinates the defense research efforts of Australia, Canada, New Zealand, the United Kingdom, and the United States.

Dr. Brady has received a Roon Award from the Federation of Societies for Coatings Technology (first place, 1992) and the Gordon Award from the Chemical Society of Washington (1993). He has also received the Meritorious Civilian Service Award (1997), Technology Transfer Award (1996), NRL—Sigma Xi Award for Applied Research (1994) and an Alan Berman Research Publication Award (1986) from the Naval Research Laboratory. He has published more than 300 papers and reports of chemical research, holds seven patents, and speaks frequently on coatings science and technology.

Dr. Brady is a member of the Baltimore Society. He was Technical Editor of the JOURNAL OF COATINGS TECHNOLOGY from 1992 to 1997, and a member of its Editorial Review Board from 1985 to the present, serving as Chairman from 1992-97. He was also a member of the Program Committee for the 1990 Annual Meeting, and the Publications Committee from 1991 to 1997, serving as Vice-Chairman in 1991-92 and as Chairman from 1992 to 1995. Dr. Brady was Chairman of the 1999 Gordon Conference on Coatings and Films. He was also a contributing editor of the Journal of Protective Coatings and Linings (1986-90) and a member of ASTM Committee D-1 on Paints and Related Materials for many years, serving on the D-1 Executive Committee from 1980 to 1985.

Dr. Brady is a member of the American Chemical Society, Alpha Chi Sigma, Sigma Xi, SSPC: The Society for Protective Coatings, and the Washington Paint Technical Group, and a Fellow of the Royal Society of Chemistry (London).

❋ *1999 Mattiello Memorial Lecture* ❋

Clean Hulls Without Poisons: Devising and Testing Nontoxic Marine Coatings

Robert F. Brady, Jr.—Naval Research Laboratory*

There is an old curse: "May you live in interesting times." Joseph J. Mattiello lived in interesting times, and so do we. Joe Mattiello was faced with opportunities that offered uncertainty, risk, and reward, and so are we. Among the many virtues he demonstrated during his regrettably short life, there are three that particularly speak to me. I want to draw special attention to them, for I consider these attributes to be enduring values, as indispensable today as they were 50 years ago.

Joe Mattiello was a patriot and a leader. Leadership is always difficult, unrewarding, and subject to misinterpretation, but none of that deterred Dr. Mattiello. He stepped forward when his country needed him, and he responded to the national and international paint communities when they needed him. In each case he paid an enormous price, but the benefits were enormous as well. This Lecture, and the technical organizations he founded, led, and supported, endure some 50 years after his passing. But more than that, his devotion to something bigger than one's self and his spirit of selfless service to his country and to our industry illuminate and motivate us today.

Because this paper marks 50 years since the first Mattiello Memorial Lecture, it begins with a remembrance of the man in whose honor we meet and an appreciation of his character and his contributions to the coatings industry. The body of the paper is concerned with the coating used on a hull of a ship to prevent the accumulation of barnacles and other fouling. The most effective antifouling paint now being used contains toxins and will be forbidden by international regulations within eight years. The ideal replacement will be a nontoxic material that resists the attachment of marine life and encourages the organisms to fall off the ship. This paper describes laboratory and field work during the past 18 years on a variety of fluorinated coatings and silicone coatings with these properties and criteria for formulating successful nontoxic coatings. Silicone and fluorinated coatings frustrate fouling by different mechanisms, and thus the criteria for a successful coating are distinct in important ways.

Joe Mattiello was thoroughly convinced that research and development play a fundamental and indispensable role in the coatings industry. I think Joe Mattiello would be genuinely disappointed to find the lack of emphasis on research that pervades the coatings industry today. I think he would believe that the industry has defaulted on its responsibilities for research, leaving this role largely to the universities. Now don't get me wrong—universities have a fundamental role in giving students the broadest possible education and preparing them for productive work in the coatings industry, and for performing the pre-competitive research that underlies, supports, and advances our technical knowledge, and they do a fine job of this. But universities don't know our plants, don't know our customers, and don't own the proprietary knowledge base that has come to each company at great cost and is one of its most important intangible assets. Bringing aboard graduates to enlarge and deepen this knowledge, and to invent and validate new products is the lifeblood of our industry, the source of new products, and the mainspring of executive talent. If Joe Mattiello were at the helm of Hilo Varnish Corporation today, you can bet he would devote an important part of their resources to the creation and diffusion of new knowledge and new coatings, and to the development of the leaders our industry will certainly need in the 21st century. And you can bet he would exhort his contemporaries to do the same. He would organize meetings

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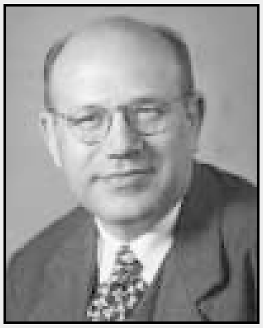
*Chemistry Div., Washington, D.C. 20375-5342.

Joseph J. Mattiello

1900-1948

This year we celebrate a landmark in the history of the Mattiello Memorial Lecture. Fifty years ago the first Mattiello Memorial Lecture was presented to the Federation at its meeting in Atlantic City, NJ.[1] Thus it is fitting to spend a few moments recalling the man in whose honor we meet. Regrettably, there are few remaining among us who knew this remarkable person, and his reputation and his accomplishments are in danger of fading from our view.



Joseph J. Mattiello[2,3] was born in New York City on February 28, 1900 and orphaned before he was 12 years old. He enlisted in the New York National Guard at the age of 16 and served on the Mexican border. He fought in World War I from October 1917 until March 1919, serving as an infantry sergeant with the American Expeditionary Forces in France, and he fought in the battles of Champagne-Marne and Aisne-Marne. On October 17, 1918, he was wounded in both legs and his right arm, and suffered the loss of his right leg. He was awarded the Regimental Citation and the Order of the Purple Heart.

Returning to the United States, he earned Bachelor's and Master's Degrees from the Polytechnic Institute of Brooklyn (now Polytechnic University) in 1925 and 1931, and a doctorate from Columbia University in 1936. In 1925 he joined the Hilo Varnish Corporation, where he became noted for his research and publications in all of the areas that were consequential at that time, especially linseed oil, fatty acids, pigments, fish oils, resins, and performance properties of organic coatings. Ultimately he attained the position of Vice President, Technical Director, and member of the Board of Directors at Hilo Varnish Corporation. Dr. Mattiello was a member of the New York Society, serving as Technical Committee Chairman in 1936, Secretary-Treasurer in 1937, Vice President in 1938, and President in 1939. He was President of the Federation for one year beginning in 1943.

During the Second World War, Dr. Mattiello served as a civilian chemical expert assigned to the U.S. Army Quartermaster Corps. He led a committee which prepared military specifications for the rapid and economical procurement of a host of specialized paints, lacquers, and coatings for the Armed Services. He also conducted fundamental studies of the infrared properties of paints and pigments, and used this information in the design of camouflage paints, for it is the infrared properties of these coatings that give them their special usefulness. At Hilo Varnish Corporation, he developed and manufactured special coatings required by the Allied Forces. The War Department presented him the Meritorious Civilian Service Award for his efforts. All of this work added to his international stature.

Dr. Mattiello had a fine sense of humor. He once remarked to his specification-writing colleagues that "we are sticking our necks out on some of these specs." He also suggested that "all of us who are sticking out our necks band together for mutual fun and protection and form a club." This was the birth, in 1943, of the Gallows Birds.[4] Dr. Mattiello was immediately chosen the Permanent Most High Gallows Bird, an office that he held until his death and has held posthumously ever since. To quote from their constitution, the membership is restricted to "those misguided beings who, thinking to benefit the human race, have laid themselves open to and have received public and private denunciation by instigating and abetting federal government specifications for paints, varnish and protective coatings, thereby bringing themselves under the shadow of the gallows and making themselves the most miserable of men." The first official "hanging" took place on May 8, 1943 in Cincinnati during a symposium sponsored by the Federation.

Dr. Mattiello represented the Federation in Paris at the first International Congress of Paint Technologists in 1947, and at that meeting, representatives of France, Great Britain, and North America (Canada and the United States) formed the "Tri-Alliance," with Dr. Mattiello taking a leading role. While in France for this conference, the French government presented him with the Legion of Honor in recognition of his outstanding services in both World Wars. Dr. Mattiello had traveled to France against the advice of his doctors, who had told him to curtail his activities. Henry Payne, in his Mattiello Memorial Lecture[5] of 1960, recalled that he asked Dr. Mattiello before the journey "if he considered the results to be accomplished would be worth the price. With hardly a moment's hesitation, Joe replied, 'Henry, I'm going.'" The exertion of the journey proved to be overwhelming, and he died of a heart attack at his home in Brooklyn on May 16, 1948.

Some years earlier, as Chairman of the Federation's Technical Program Committee, Dr. Mattiello had started the practice of having a special speaker address each Annual Meeting. After his death, the New York Society recommended to the Federation that this address be named the Joseph J. Mattiello Memorial Lecture, to commemorate his memory and his contributions to the Federation and to the science of paint technology. The suggestion was embraced immediately, and the first Mattiello Lecture was given in October 1949, 18 months after his death.[1]

Earlier in 1949 the Federation of Paint Technical Societies of Western Europe was organized, modeled after our Federation. Before his death, Dr. Mattiello had encouraged his many European friends to create such an organization. They were very explicit that it was his encouragement that led this concept to fruition.

—Robert F. Brady, Jr.

where technical information is exchanged, and he would come away from those meetings knowing he had received value for the effort and time invested.

Joe Mattiello reached out to the international community of paint professionals and was instrumental in establishing those international relationships that underpin the modern industry. Today, we are an international Federation, with Societies in Canada, Mexico, the United Kingdom, and the United States, and members from all the corners of the earth. Many of us now work for corporations organized outside the United States. We buy raw materials and sell products far from our factories, and as our customers expand internationally, we follow them or risk losing their business. We conform to the laws of the nations where we do business, we are concerned on a daily basis with the environmental, worker safety, and transportation laws of many countries, and we manufacture our products with a spectrum of international specifications and test methods in mind. Our international involvement becomes wider and deeper each day. Today more than ever we must understand and participate in the events that are shaping international coatings research and marketing, in order to ensure the growth and prosperity of our individual firms and our industry.

In the paint and coatings industry today, we have women and men of character, accomplishment, and vision all around us. For the continuing vitality of our industry, each of us needs to remember and emulate Joe Mattiello. We may never equal his valor in combat or his scientific achievements, but all of us can work together for the common good of all, emphasize the importance of leadership in the coatings community, give a portion of our time to sustain the Federation and other organizations devoted to technical innovation, and inspire and support others to do the same.

NEED FOR FOULING RELEASE COATINGS

Our work concerns antifouling paints for ship's hulls and is an example of research driven by international regulations. Antifouling coatings prevent the growth of marine organisms on hulls, for this growth decreases the speed, maneuverability, and range of ships, and raises propulsive fuel consumption by as much as 30%. Ultimately ships must be taken from the water and mechanically cleaned to remove fouling.

Throughout history sailors have used poisons to keep these creatures off of their hulls. For example, copper sheathing was first used on British Naval ships in 1779.[6,7] Such poisons as arsenic, cadmium, lead, and mercury have long been prohibited by most nations, but copper- and tin-containing toxins continue to be used. Antifouling paints containing organotins are widely used around the world because they are effective at low concentrations against most forms of fouling. However, these compounds persist in the water, cause deformations in some kinds of sea life, and perhaps enter the food chain. The Marine Environmental Protection Committee (MEPC) of the International Maritime Organization (IMO), a unit of the United Nations, has recently approved a draft resolution to phase out and eventually prohibit the use of toxic organotin derivatives in antifouling paints.[8] The draft resolution, which were presented to the IMO Assembly for their approval in November 1999, includes a deadline of January 1, 2003 for the application of organotins acting as biocides in antifouling systems on ships, and a second deadline of January 1, 2008 for the complete prohibition of antifouling paints containing organotins. Some countries, such as Japan, have already banned organotins in antifouling paints for most ships.

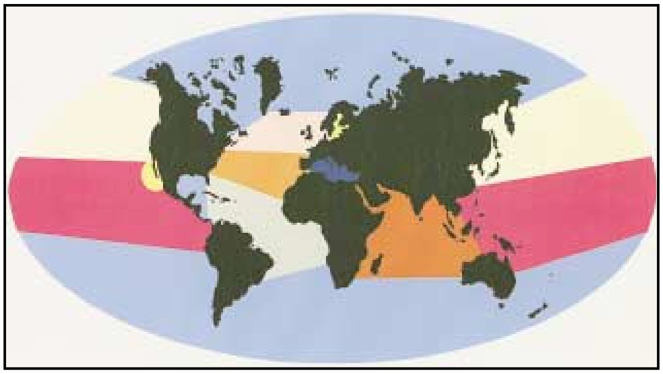


Figure 1—The 12 distinct fouling zones in the oceans of the world.

The successor to toxic antifouling paints has been a subject of intense laboratory and field studies for some 25 years now. These coatings, called "fouling-release" to differentiate them from their poisonous precursors, ideally would prevent the attachment of fouling, but in practice they significantly limit the strength of the bond between fouling and hull, making the bond so weak that it can be broken by the weight of the fouling or by the motion of the ship through the water.

There are 12 well-defined zones in the oceans of the world (*Figure* 1) that differ in temperature, salinity, clarity, the nature and amount of micronutrients, and other factors. Thus, the types and numbers of native fouling organisms differ from zone to zone. Shell fouling (barnacles, mussels, bryozoans) and soft fouling (tunicates, algae, hydroides, slime, diatoms, bacteria) occur in many forms, and the adhesives used by these organisms are equally varied. For example, barnacles excrete a hydrophobic protein adhesive having a molecular weight of 39,000 Daltons which crosslinks through cysteine linkages.[9] On the other hand, mussels fashion byssus threads from their foot to the surface; these threads consist principally of collagen, but contain a hydrophillic polyphenolic adhesive protein that crosslinks in an oxidation-reduction reaction involving a polyphenoloxidase catalyst.[10] Diatoms attach by producing neutral or acidic polysaccharide mucilages that either encapsulate cells or form pads, stalks, or tubes.[6] Examples can be multiplied with ease, but formulators of antifouling coatings need to realize that nature does not rely on one mechanism for adhesion, but uses many, and all of them must be defeated, all at the same time.

During the past 17 years, our work has been directed to the formulation and testing of coatings that offer a minimum of adhesive interaction to other materials, es-

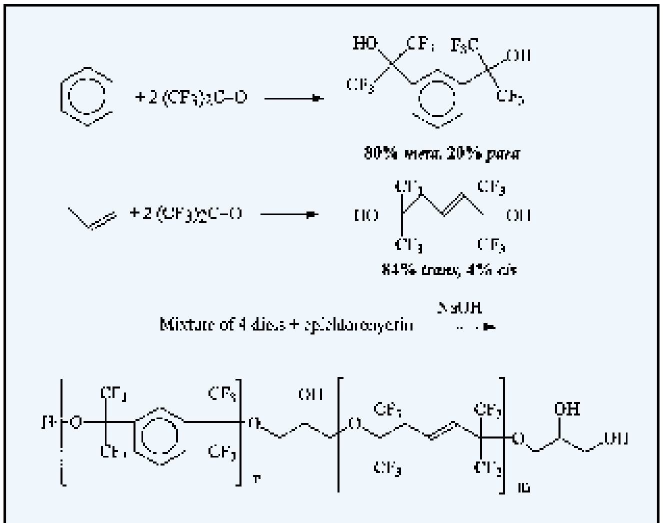


Figure 2—The fluorinated polyol used in early fluorinated polyurethane coatings.

pecially to the biological polymers used by marine organisms to bind themselves to objects in the sea.[11-14] We limit ourselves to organic coating technologies that conform to environmental and worker safety regulations and are drop-in replacements for current industrial applications.[15] In this paper I review our formulations and field studies of fluorinated, hydrocarbon, and silicone coatings. From lessons learned in this work, I will develop insights into the release mechanisms through which these coatings operate, and requirements for designing effective fouling-release coatings.

Fluorinated Coatings

In the 1950s and 1960s, Dr. William A. Zisman led research programs at the Naval Research Laboratory (NRL) that focused on the design and properties of advanced lubricants. An important discovery of his work was that a decrease in the surface energy of a lubricant significantly improved its lifetime and performance. Zisman demonstrated that a surface of closely packed trifluoromethyl groups exhibited a very low surface energy, 6 mJ m^{-2}. On October 29, 1971, Zisman presented his work in the 23rd Mattiello Memorial Lecture[16] which he entitled "Surface Energetics of Wetting, Spreading, and Adhesion."

Zisman's demonstration of the properties of surfaces of fluoropolymers inspired a generation of NRL chemists to develop polymers that contain numerous trifluoromethyl groups and to formulate fluorinated coatings from them. James R. Griffith designed polyol resins containing many bis(trifluoromethyl) moieties. Jacques G. O'Rear carried out the demanding syntheses of these resins and described them in a series of papers[17] and patents.[18] The synthesis of the fluorinated polyol resin is shown in *Figure* 2. Benzene and propene react separately with hexafluoroacetone to produce mixtures of diols. These mixtures are combined and reacted with epichlorohydrin to produce the polyol. This resin has a backbone consisting entirely of stable carbon-carbon and carbon-oxygen bonds, and aromatic rings in the backbone confer rigidity and thermal stability. The epoxy rings are too few for the production of robust resins through epoxy-amine chemistry, but the abundant hydroxyl groups promote adhesion to polar substrates and serve as sites for reaction with isocyanates.

Tough polyurethane coatings were formulated from these fluorinated polyols by Donald E. Field.[19] A distinct advantage of these fluorinated polyurethane coatings is their ability to wet polytetrafluoroethylene (PTFE), and PTFE is used essentially as an extender pigment in them. Until this coating was invented, depositing a film of PTFE presented many practical difficulties because PTFE does not melt and is not dissolved in, softened, or even wetted by conventional solvents. It is now possible to put as much as 38 vol% of PTFE into our fluorinated polyurethane, but this produces a soft coating. Our conventional coating contains 24 vol% PTFE, and a starting point formulation for it is given in *Table* 1. This coating was the first material that could deposit by conventional coatings technology a film with the low surface energy characteristic of PTFE.

Trials of this coating on the hulls of a harbor tug,[20] a 65-foot patrol boat, and a 132-foot patrol hydrofoil ship, the USS Hercules, have been documented.[15,21] The coating is a significant improvement over the vinyl copper antifoulants used at the time, even though shell fouling

Table 1—Formulation for a Gray PTFE-Pigmented Fluorinated Urethane Coating

Material	Pounds	Gallons	Brand Name	Manufacturer
Base				
Fluoropolyol resin	224.3	16.38		21st Century Coatings
Titanium dioxide	98.3	2.99	R-960	DuPont
Polytetrafluoroethylene	248.5	13.15	Halon	Allied Signal
Methyl isobutyl ketone	324.0	48.59		Shell
Dibutyltin dilaurate 1.7% w/w in methyl isobutyl ketone	5.3	0.79		Aldrich
Curing agent				
Biuret of hexamethylene diisocyanate solution, 75% w/w	160.0	18.10	Desmodur N-75	Bayer
TOTAL	1060.4	100.00		

adheres to the coating. If attended to early, the fouling is detached easily by hand scrubbing, but if allowed to remain for some months, fouling adheres as strongly as to other coatings. The chemistry of the fluorinated polyol resin has been patented and licensed[22] and is finding commercial applications as an interior lining for bulk fuel storage tanks.[23]

Much later, Salvatore Bonafede and I conducted a systematic study of the fouling release properties of a series of fluorinated polyurethane coatings.[24] We used three fluorinated polyols and four polyisocyanates (one fluorinated) to produce fluorinated polyurethane films containing 31-67% fluorine, and we measured the fouling resistance, surface energy, glass transition temperature, modulus, and indentation hardness of each. Films contained 31-67% of fluorine and had surface energies of 12-33 mJ m^{-2}, but all accumulated significant fouling and retained stain. The poor resistance to fouling was attributed to the polyurethane functional groups that provide polar carbonyl and amine groups that participate in dipolar and ionic interactions with marine adhesives.

We have also studied a fluorinated coating developed by Donald L. Schmidt and co-workers.[25] They obtained a coating with a surface composed of oriented, immobilized perfluoralkyl (R_F) groups by crosslinking a reactive perfluoroalkyl polymeric surfactant with poly[(2-isopropenyl-2-(oxazoline)], as illustrated in *Figure* 3. The fluorinated surfactant moieties self-assemble at the air-liquid interface from a water media. Upon loss of solvent and heating, the surfactants polymerize, form covalent crosslinks, and lose ionic charge. Because of the high crosslink density in the coating, the oriented R_F groups are strictly immobilized and tend to resist both the infiltration of adhesive molecules and adhesive-induced molecular rearrangement. By virtue of the low energy of the surface, its interface with the adhesive is not strong, and by virtue of the high resistance of the surface to molecular interdiffusion and rearrangement, its interface to the marine adhesive is sharp, well-defined, and easily cleaved. These coatings resist attachment of marine fouling more effectively than any fluoropolymer we have tested.[26] These coatings are effective because not only do they have closely packed, oriented CF_3-terminated perfluoroalkyl groups on their surface but they are also crosslinked to minimize surface molecular diffusion or rearrangement when exposed to an adhesive. It is important to remember that even surfaces of PTFE accumulate marine fouling rapidly, because marine adhesives invade cavities in the surface and cure inside them, creating a secure mechanical interlock where chemical compatibility does not exist.[27]

Hydrocarbon Films

Zisman's work also showed that films of hydrocarbons have the lowest surface energies but for fluorocarbons. This prompted us to investigate the fouling properties of hydrocarbon films of polyethylene and isotatic polypropylene.[28] These polymers are chemically uncomplicated; because they contain only carbon and hydrogen atoms, only dispersive interactions are possible; dipolar and ionic interactions are precluded. Systematic variations in extrusion conditions produced polypropylene films that contained between 34 and 47% crystallinity. We also produced a hydrocarbon surface by reacting a telechelic polymethylene diol with a urethane primer containing excess isocyanate groups,[29] and demonstrated by attenuated total reflectance infrared spectroscopy that the surface was composed only of methylene groups. All of the polypropylene and polyethylene films accumulated much slime and algae and some barnacles; all required scraping to remove shell fouling. The polymethylene diol surface gathered less fouling and held it less tightly; the surface could be cleaned with a brush or sponge. The crystallinity of these films did not correlate with their resistance to fouling.

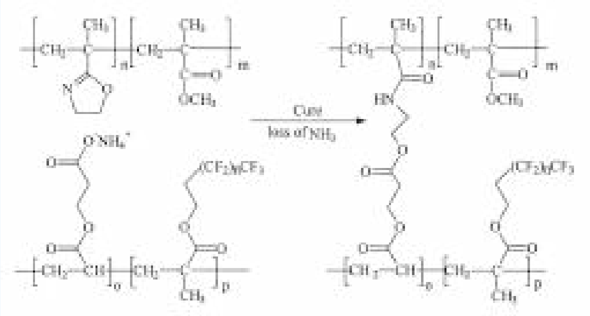


Figure 3—Water-based two-component fluorinated acrylic coating.

Silicone Coatings

Our earliest trials of silicone fouling release coatings were conducted on aluminum patrol boats in the Chesapeake Bay.[15] The hull was blasted to a near-white finish[30] and primed with 0.7-1.1 mils of a polyurethane-polysulfide primer. An adhesion promoter was applied to the primer before it was coated with a condensation-cured polydimethylsiloxane (PDMS) topcoat. Titanates were more successful than reactive silicones as adhesion promoters, and brush application was more easily controlled than spray application. During testing, which lasted for only one fouling season, the coating on the titanate adhesion promoter was sturdy and effective. Some grass and barnacles settled on the coating but were removed by bare hand or brush. The coating suffered some damage from abrasion, but disbonding did not spread from the abraded sites.

Wynne and co-workers have discovered that these condensation-cured silicone resins (formed by the elimination of water from silanols) lose mass during immersion in water.[31] Decrease in mass is attributed to hydrolytic instability of the siloxane resin and subsequent loss of unbound calcium carbonate filler. The surface of the resin becomes increasingly rough and predisposed to adhesion. Thus in our subsequent syntheses of silicone resins we avoided condensation-cured chemistry in favor of addition-cured chemistry.[32]

We prepared three silicone-modified polyurethanes. First, a polyurethane primer which had an excess of isocyanate groups was reacted with amino-terminated

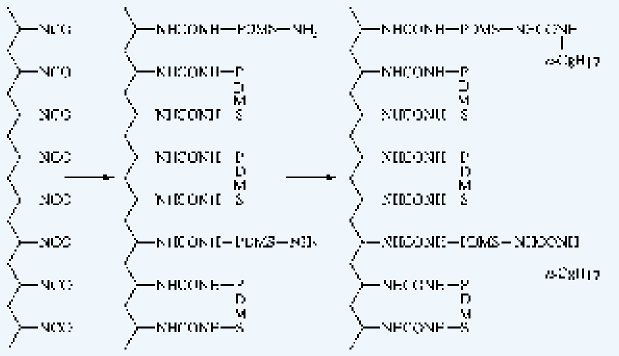
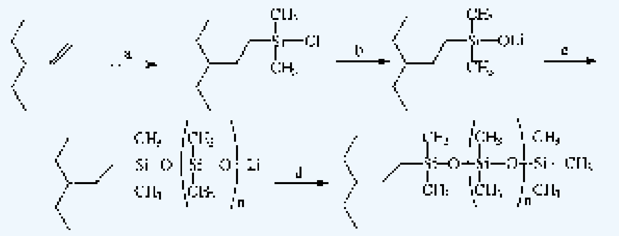


Figure 4—Reaction scheme for grafting polydimethylsiloxane chains onto an isocyanate-rich backbone and endcapping the chains with hydrocarbon units.

polydimethylsiloxane oligomers (molecular weight 2,400 or 10,000) to produce a coating with PDMS loops or chains on its surface (*Figure* 4). Then the amino-groups in this coating were end-capped with *n*-octyl isocyanate to bury the polar amino group beneath the surface (*Figure* 4). In a separate reaction, pendant PDMS chains were grafted to polybutadiene (in which nine percent of the monomer reacted *via*, 1,2-addition) by successive reaction with dimethyldichlorosilane, hydrolysis with lithium hydroxide, chain extension with hexamethylcyclotrisiloxane, and endcapping with trimethylchlorosilane (*Figure* 5). In field testing, these materials demonstrated increased toughness and resistance to impact, gouging, and abrasion, but their resistance to fouling was not improved in comparison to the patrol boat coatings.

We also prepared silicone-modified polyurethane coatings using a hydroxy-functional silicone resin as part of the polyol, using the formulation shown in *Table* 2.[33] This coating adhered well to neoprene rubber and to epoxy-primed steel and gave two years of fouling-free service. We subsequently discovered that its effectiveness was due to the presence of about 20% of unreactive cyclic siloxane oligomers contained in the "reactive" silicone additive. The oligomeric oil slowly migrates from the interior to the surface of the coating, and thence into the water, taking with it the early stages of fouling. Oil on the coating surface forms a weak boundary layer and discourages marine adhesives from wetting, spreading, and bonding to their surface. These unreactive oligomers also plasticize the coating. However, they leach from the coating and are exhausted in two years, and then the coating becomes brittle and forms strong bonds to fouling.



Reagents: a: dimethylchlorosilane, chloroplatinic acid; b: 5% lithium hydroxide; c: hexamethylcyclotrisiloxane; d: trimethylchlorosilane

Figure 5—Reaction scheme for grafting polydimethylsiloxane chains onto a polybutadiene backbone and endcapping the chains with trimethylsilyl groups.

Despite the encouraging performance of this formulation, we elected not to pursue it further because we see two drawbacks to this approach. First, the siloxane oligomers are eventually lost, with several consequences. The mechanical properties of the coating deteriorate significantly and sharply, as evidenced by the coating becoming brittle and cracking. The weak boundary layer is no longer formed, and fouling settles and adheres with tenacity. Second, silicone oligomers are released into the environment. Although there is no toxicity associated with these compounds in seawater, we believe that a policy of absolutely no release to the environment will prove best in the long run.

To date, nontoxic silicone fouling release coatings have been used on Taurus-class hydrofoil patrol boats of the United States Navy and on Collins-class submarines of the Australian Navy. We have collaborated with the Australian and Canadian navies in a program to test and evaluate both commercial silicone coatings and coatings formulated in our own laboratories.[34] Testing is carried out in three of the 12 fouling zones in the world: Port Philip Bay, Victoria, Australia; Esquimalt, British Columbia, Canada; and the Chesapeake Bay, Maryland, United States. Joanne Jones-Meehan at the Naval Research Laboratory has conducted extensive tests of silicone coatings on U.S. Coast Guard boats.[35] No discussion of these coatings would be complete without acknowledging Alex Milne, who pioneered fouling-release silicone coatings for hulls in a series of papers[36] and patents,[37] and other workers who have also made important contributions to these coatings.[38]

MECHANISMS OF FOULING RELEASE

As a result of the work described, we have a wealth of field data on a variety of different coatings, trialed on panels and vessels in many of the fouling zones of the world, during all seasons. We also have detailed knowledge of the composition and structure of the coatings, how they were manufactured and how they were applied. We must now look for the unifying principles that govern their behavior and apply these principles to the design and manufacture of improved fouling-release coatings.

Marine organisms instigate adhesion by producing an adhesive and causing that adhesive to wet the substrate and spread upon it. After the adhesive has spread onto the substrate, adhesion may take place by any of the following four principal mechanisms, either singly or in combination. All of these must simultaneously be defeated in a practical fouling-release coating.

Chemical Bonding: Dispersive, dipolar, ionic, covalent, and other forms of chemical bonding form strong interactions between adhesive and substrate. Although dispersive forces will always be present, they are weakest of these. Chemical bonding may be discouraged by creating a surface of nonpolar and non-reactive functional groups, and by creating conformationally mobile surfaces that present "moving targets" to the functional groups of marine adhesives.

Elastrostatic Interactions: Dipolar and ionic groups may interact electrostatically as well as chemically. Electrostatic interactions are prevented by ensuring that no heteratoms, or polar or ionic groups are on or near the surface of the coating.

Mechanical Interlocking: The adhesive may penetrate into cavities in the substrate and cure to form a lock-and-key bond, even on a material with low surface energy and even in the absence of chemical compatibility. It was mentioned earlier that barnacles form strong bonds to PTFE by exploiting its porosity.[27] Note that the adhesive does not need to wet the substrate in order to bond in this way. Mechanical interlocking may be defeated by creating surfaces as hard, smooth, and nonporous as possible.

Diffusion: Marine adhesive may induce movement in surface molecules, creating ephemeral voids that may be penetrated by the adhesive. Diffusion may be defeated by assembling on the surface oriented, closely packed functional groups, and crosslinking them to prevent rearrangement and intrusion of the adhesive.

Thus the preferred approach is to keep the marine adhesive from wetting the surface and spreading over it. But it is a practical fact that barnacles stick to essentially every coating yet made, because it is impossible to perfectly remove or defeat all attractive forces. So we must tolerate the formation of no more than a weak bond between fouling and surface, and so construct the coating system as to facilitate the breaking of that bond. In this context it is instructive to look at, for example, a barnacle that has successfully attached itself to a coating, and understand what would be required to cause a fracture at the joint between the coating and the barnacle.

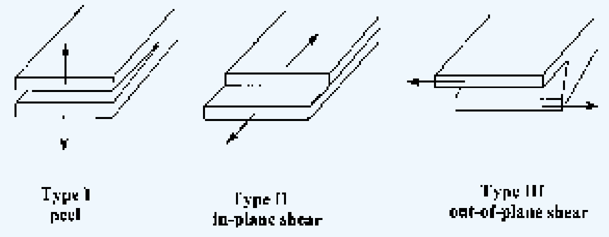


Figure 6—Fracture mechanisms for failure of a joint.

Fracture Mechanics

Fracture mechanics is the study of the process of breaking bonds. This discipline assumes that no joint is entirely free of defects, and that the cracks that exist on a microscopic scale are stress-raisers where the growth of a crack is initiated. Fracture mechanics considers three kinds of crack-opening modes (*Figure* 6): (1) peel (or tensile); (2) in-plane shear; and (3) out-of-plane shear. Failure in peel requires less energy than failure in shear, and most common failures of adhesive joints are in peel.

Materials fracture in many ways: from the application of external loads (impact), by repetitive loading (fatigue), and by time-dependent deformations under load (creep). Fracture mechanics is the scientific discipline that describes fracture processes by focusing on

Table 2—Formulation for a Silicone-Modified Aromatic Polyurethane Coating

Material	Pounds	Gallons	Brand Name	Manufacturer
Base				
Polyester polyol	230.60	23.86	Desmodur 1100	Bayer
Polyester polyol	96.25	9.96	Desmodur 1700	Bayer
Black iron oxide	44.11	1.07	BK-5000	Elementis
Organoclay thixotrope	0.50	0.03	Bentone SD-3	Rheox
Amorphous silica	40.10	1.82	Imsil A-15	Illinois Minerals
Diatomaceous silica	94.75	4.95	Celite White Mist	Johns Manville
Polytetrafluoroethylene	55.14	2.90	Halon	Allied Signal
Propylene glycol monomethyl acetate	29.08	3.62		
Butyl acetate	39.60	5.41		
Leveling/anticrater additive	2.01	0.30	Troysol S-366	Troy
Air release agent	3.01	0.44	Dow 7 additive	Dow Corning
Reactive silicone	20.05	2.15	Dow 1248	Dow Corning
Dibutyltin dilaurate 10% w/w in methyl amyl ketone	0.20	0.03		Aldrich
Methyl amyl ketone	146.68	21.64		
Curing agent				
Aromatic polyisocyanate	176.46	18.26	Mondur 744	Bayer
Methyl amyl ketone	24.06	3.55		
TOTAL	1002.61	100.00		

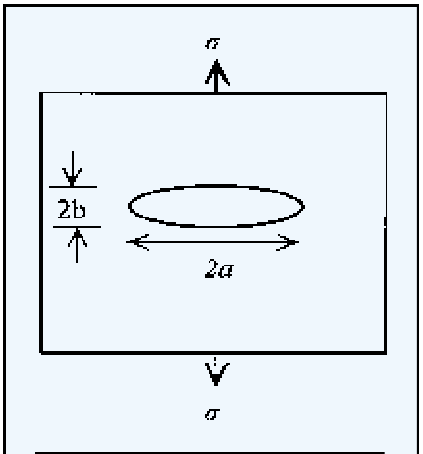


Figure 7—Model of an elliptical cavity in a plate under uniform stress.

the nucleation and propagation of cracks that lead to the complete separation of a joint. For example, when a crack propagates a distance *a* in an elliptical cavity in a plate under uniform stress as shown in *Figure* 7, the increase in energy required to form two new surfaces of area *2A* must come from the difference between the work *dW* done by external forces and the change in elastic energy dU_e, stored in the stressed object.[39] Stated in thermodynamic terms, a necessary condition for crack propagation is

$$-\frac{\partial(W-U_e)}{\partial A} \geq G \qquad (1)$$

or

$$-\frac{\partial U_T}{\partial A} \geq 0 \qquad (2)$$

where *G* is the Griffith fracture energy per unit area (also known as the critical strain energy release rate) and U_T is the total energy of the system. In its simplest form, *G* is 2γ, twice the surface free energy per unit area (also known as Dupré's work of adhesion) of the newly created surfaces.

Equation (1) can be applied to the problem of determining the change in energy needed to enlarge the elliptical cavity seen in *Figure* 7 under a uniform uniaxial stress σ. The crack will propagate at a critical stress

$$\sigma_C = \sqrt{EG/\pi a(1-v)^2} \qquad (3)$$

or, equivalently, at a critical pull-off force P_c (operating on area $A - \pi a^2$)

$$P_C = \sqrt{\pi EGa^3/(1-v^2)} \qquad (4)$$

where E is the elastic modulus and ν is Poisson's ratio.

In real materials, however, energy can also be expended around the crack tip by plastic flow, by viscoelastic processes, and by friction between the interfaces undergoing separation.[40] Polymers and adhesives are known to have fracture energies orders of magnitude greater than their surface energies due mainly to viscoelastic processes. Therefore, the stresses needed to separate polymer and polymeric adhesives are very dependent on parameters that control viscoelasticity, such as elastic modulus, temperature, and speed of removal.

Formulas for the force (stress) required to pull off rigid solids attached to thick and thin elastomers can be derived from equation (2) and used to model the adhesion behavior of elastomeric solids.[41] For example, consider the pull-off force P_c required to detach a rigid disk attached at its end to a thin (t<<a) elastomeric glue film on a rigid substrate, as illustrated in *Figure* 8. The total energy U_T of this strained system is equal to the sum of surface energy, strain energy in the elastomer (in the volume directly under the contact), and potential energy applied by the load:

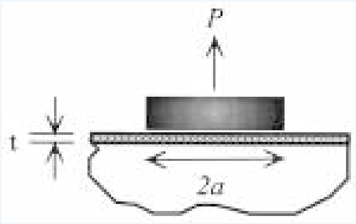


Figure 8—A film of elastic adhesive held between a rigid substrate and a rigid disk.

$$U_T = -\pi a^2 G - \frac{P^2 t}{2\pi K a^2} \qquad (5)$$

where P, t, a, K, and G are normal force, thickness of the film, contact radius, bulk modulus, and Griffith fracture energy per unit area between disk and film, respectively. Applying Griffith's failure criterion to equation (5) gives the following expressions for critical stress σ_c and critical force P_c to remove the disk:

$$\sigma_c = \left(\frac{2GK}{t}\right)^{1/2} \qquad (6)$$

$$P_c = \pi a^2 \left(\frac{2GK}{t}\right)^{1/2} \qquad (7)$$

For a thick (t>>a) elastomeric adhesive film, the equations become[43]:

$$\sigma_C = \sqrt{2EG/\pi a(1-v^2)} \qquad (8)$$

$$P_c = \sqrt{2\pi EGa^3/(1-v^2)} \qquad (9)$$

Equations (8) and (9) are nearly identical to equations (3) and (4) for crack propagation force and stress derived for the elliptical cavity shown in *Figure* 7, but in the latter case only one-half of the "cavity" is being stretched. Both sets of solutions make clear that fracture, or removal, processes involve not only surface energies, expressed either as γ or *G*, but also the elastic properties of the material and the geometry of the crack. Let us take a careful look at each of these factors and see what insight each may yield for the design of a fouling release coating.[42]

Surface Energy

The critical surface tension γ_c of a polymer, measured by the method of Zisman,[43] is the property of a polymer surface that is most frequently correlated with resistance to bioadhesion. A generalized relationship between γ_c of

Table 3—Physical Properties of Some Polymers

Polymer	Relative Adhesion	Critical Surface Tension (γ) mN m^{-1}	Elastic Modulus (E) GPa	$\sqrt{\gamma E}$
Poly(hexafluoropropylene)	21	16.2	0.5	2.85
Poly(tetrafluoroethylene)	16	18.6	0.5	3.05
Poly(dimethylsiloxane)	6	23.0	0.002	0.21
Poly (vinylidene fluoride)	18	25.0	1.2	5.48
Poly(ethylene)	30	33.7	2.1	8.41
Poly(styrene)	40	40.0	2.9	10.77
Poly(methyl methacrylate)	48	41.2	2.8	10.74
Nylon 66	52	45.9	3.1	11.93

the polymer surface and the relative amount of bioadhesion, known as the Baier Curve[44] and shown in *Figure* 9, has been reproduced in a variety of marine exposure studies, and also in *in vivo* biomedical applications such as vascular prostheses and dental implants. A remarkable feature of this curve is that the minimum in bioadhesion does not occur at the lowest critical surface tension.

It is revealing to note that, of the polymers used to construct *Figure* 9, all but one have rigid carbon-carbon backbones.[45] The sole exception, polydimethylsiloxane (PDMS), has a freely rotating silicon-oxygen backbone that imparts great freedom of motion to functional groups on the polymer.[46] This rapid motion of functional groups impedes their ability to remain close to, orient with, and form dipolar or hydrogen bonds with complementary functional groups on marine adhesives.

Chaudhury and co-workers performed peel tests to assess the adhesion strengths of viscoelastic adhesives attached to fluorocarbon, hydrocarbon, and PDMS surfaces.[47] Although conventional theories predict that adhesion is proportional to the surface free energy of the substrate, the observed peel forces follow the opposite trend: fluorocarbon (γ = 10 mN/m) >> hydrocarbon (γ = 20 mM/m) > PDMS (γ = 22 mN/m). Video microscopy of the peel events suggests that slippage of the adhesive at the peeling interface provides an early-release path that bypasses the more energy-consuming viscoelastic dissipation of better-adhered joints. Thus the minimum in *Figure* 9 is indeed real, but it results from the superposition of a mechanical effect over a surface energy effect.

Elastic Modulus

According to the fracture mechanics solutions derived in equation (9), the critical pull-off force P_c is proportional to $(E\gamma)^{1/2}$ or $(EG)^{1/2}$. *Table* 3 lists literature values for the critical surface tension[48] and elastic modulus[45] for some polymers, and the square root of their product. When the relative adhesion value obtained from *Figure* 9 is plotted against $(E\gamma_c)^{1/2}$, *Figure* 10 is obtained. Despite some scatter in the data, *Figure* 10 demonstrates that adhesion correlates far better with $(E\gamma)^{1/2}$ ($R^2 = 0.91$) than with either surface energy (R^2 = 0.75) or elastic modulus ($R^2 = 0.82$). The minimum in adhesion in *Figure* 10 in fact coincides with the lowest value of elastic modulus tested, although this does not correspond to the lowest surface energy tested, demonstrating that elastic modulus is at least as important as surface energy in determining the performance of fouling-release coatings.

Thickness

Kohl and Singer[49] have investigated the relationship between pull-off force and thickness of an easy-release

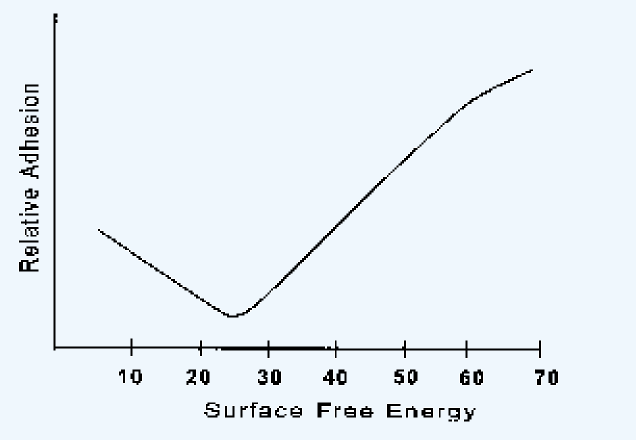


Figure 9—The empirical relationship between surface free energy and relative adhesion.

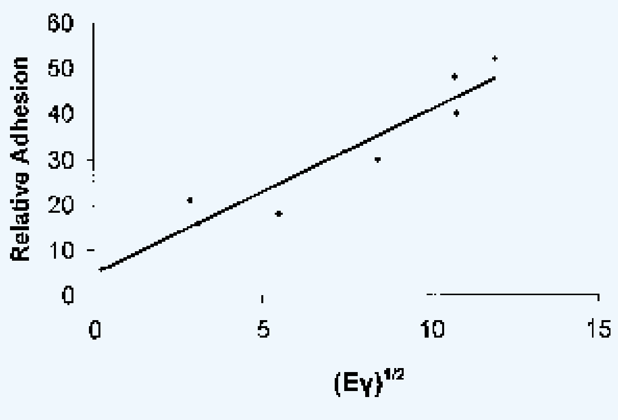


Figure 10—Relative adhesion as a function of the square root of the product of elastic modulus and surface energy.

elastomer using the geometry represented in *Figure* 8. An epoxy adhesive was used to mimic barnacle glue; the adhesion of epoxy adhesive to silicones[50] has been shown to correlate with the adhesion of barnacles to silicones.[51] The elastomeric coating is a two-layer system consisting of a bond layer of a stiffened silicone interpenetrating polymer network made from silicone and butyl acrylate-styrene polymers, and a top layer of a condensation-cured PDMS elastomer (RTV-11 silicone). Epoxy-coated studs, 7 mm in diameter, were adhered to duplex silicone layers 0.1 to 0.9 mm thick. The critical pull-off force P_c decreased as the thickness of the coated layers increased, in qualitative agreement with the model of release from a thin elastomeric adhesive layer. Equation (7) was then modified to account for two layers. The resulting critical pull-off force P_c is given by

$$P_c = \pi a^2 \left(\frac{2GK}{t^*} \right)^{1/2} \qquad (10)$$

where t* is an effective thickness that depends on the bulk moduli K_t and K_b and thicknesses t_t and t_b of the top- and bond-coats, respectively, according to

$$t^* = t_t \left(1 + \frac{a}{\beta} \right) \quad \alpha = \frac{t_b}{t_t} \text{ and } \beta = \frac{K_b}{K_t} \qquad (11)$$

DESIGN CRITERIA FOR LOW-ADHESIVE COATINGS

We are now able to formulate several essential criteria for the design of fouling-release coatings. All coatings tested have several properties in common that are essential to their performance. These are:

- A surface that is smooth at the molecular level, to avoid infiltration of biological adhesives leading to mechanical interlocking, and to provide a sharp, easily-cleaved interface;
- Absence of heteroatoms, ions and dipoles on the surface of the coating, to avoid ionic and dipolar interactions with marine adhesives; and
- Chemical and physical stability in the marine environment.

Beyond these common factors, it is decisive to note that fluoropolymer and silicone fouling-release coatings achieve their effectiveness through different mechanisms, and thus the criteria for a successful coating are distinct in important ways. Surface energy, which historically has received the emphasis in fluoropolymer coatings, is important but it is not the only factor, nor is it the dominant factor in silicone coatings that operate by encouraging the fracture of bonds on their surface. Because the release mechanisms for fluoropolymer and silicone fouling-release coatings differ, their design criteria must differ as well.

Design Criteria for Fouling-Release Fluoropolymer Coatings

The most productive route to fouling-free performance is to discourage the initial bonding of marine organisms. This is accomplished by constructing a well-organized surface that resists rearrangement and penetration of marine adhesives, driving its surface energy to the minimum achievable value (6–12 mJ m^{-2}), and crosslinking or otherwise stabilizing the surface in that arrangement. Minimization of fouling accumulation is facilitated by:

- A surface composed exclusively of fluorinated groups. Zisman has shown that the relative efficiency of deploying fluorine to reduce surface energy is in the order $CF_3 > CF_2 > CF$;
- Sufficient fluorine in the bulk of the coating to effectively control the organization of fluorine at the surface;
- Concealing dipoles such as $-CF_2-CH_2-$ well beneath the surface; and
- A stable, crosslinked surface that holds fluorine in place and resists rearrangement and infiltration of marine adhesives.

Design Criteria for Fouling-Release Silicone Coatings

The most effective route to fouling-free performance is to encourage the release of fouling organisms from the surface by predisposing the adhesive joint between the foulant and the coating to quick and easy failure. Coating systems should be designed so that failure of the foulant–coating joint occurs by peeling rather than failure by in-plane or out-of-plane shear. This is accomplished by judicious control of the thickness and elastic modulus of the silicone coating. Fouling release is best enabled by:

- A flexible linear silicon–oxygen backbone;
- A sufficient number of groups on the backbone to diminish surface energy while preserving backbone mobility;
- Low elastic modulus consistent with physical toughness;
- Hydrolytic stability, to avoid loss of mass and development of surface roughness; and
- A thickness that controls the fracture mechanics at the interface and favors failure by peel over failure by shear at the coating–foulant joint.

FUTURE

There will always be a need for coatings to protect a ship's hull from corrosion and fouling. Likewise, environmental pressures will grow in importance and urgency. As coatings formulators and as citizens we will strive to produce simultaneously the highest-performing coatings and the cleanest environment. Evaluation of real-world problems, formulation of possible solutions, and execution of scientific investigations and field tests will take time. Nevertheless I confidently predict that in far less than another 28 years a third person from the Naval Research Laboratory will deliver a Mattiello Memorial Lecture in which she or he details many years of success with nontoxic fouling-release coatings.

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It is a poorly kept secret that one is not invited to present a Mattiello Memorial Lecture based on his personal achievements alone. I acknowledge my great debt to my colleagues at the Naval Research Laboratory mentioned elsewhere in this paper and in the references. I hardly knew William A. Zisman or Jacques G. O'Rear, but I have benefited greatly from their accomplishments. My colleagues James D. Adkins, Salvatore J. Bonafede, Donald E. Field, Terry Foster, James R. Griffith, John A. Lewis, Kathryn S. Love, Ann E. Mera, Gregory T. Pawlikowski, Mary Ann Roe-Short, Donald L. Schmidt, and Irwin L. Singer performed the lion's share of the work described in this paper, introduced me to many new concepts, and involved me in distant areas of science, the relevance of which to nontoxic fouling-release coatings I would never have realized had it not been for their friendship, perseverance, and patience. I have been fortunate to work for people with intellectual curiosity, foresight to see the value of these coatings to the U.S. Navy, and the patience to wait for the work to mature. James S. Murday, William B. Fox, William B. Moniz, and Desmond Sheehan supported this work for many years, gave me their full confidence, and provided all the stability they had to offer, and for this I will always be in their debt.

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References

(1) Kienle, R.H., "Physical Chemical Research in the Protective Coatings Industry," *Official* Digest, *22,* No. 300, 11-51 (1950).

(2) Schulenberg, F., "Lest We Forget," *Am. Paint & Coat. J. Convention Daily*, November 8, 1989, p. 7.

(3) Greco, W. J., "The History of the NYSCT," an address to the New York Society for Coatings Technology on its 50th Anniversary, April 1, 1969; available at http://nysct.org/history2.htm.

(4) Schulenberg, F., "The Gallows Birds," *Am. Paint & Coat. J. Convention Daily*, November 8, 1989, p. 8, 41.

(5) Payne, H.F., "Philosophy of Coatings," *Official* Digest, *32,* No. 430, 1371- 1434 (1960).

(6) Callow, M., "Ship Fouling: Problems and Solutions," *Chem. & Ind.*, 123-27 (1990).

(7) Pain, S., "How to Rule the Waves," *New Scientist, 162*, No. 2191, 54-55 (June 19, 1999).

(8) *IMO News*, The Magazine of the International Maritime Organization, 43 Albert Embarkment, London SE1 7SR, United Kingdom, Number 4, pp. 8-10 (1998).

(9) Naldrett, M.J., "The Importance of Sulphur Crosslinks and Hydrophobic Interactions in the Polymerization of Barnacle Cement," *J. Mar. Biol. Assn. U.K., 73*, 689-702 (1993).

(10) (a) Waite, J.H., "Evidence for a Repeating 3,4-Dihydroxyphenylalanine- and Hydroxyproline-Containing Decapeptide in the Adhesive Protein of the Mussel, *Mytilus edulis* L.," *J. Biol. Chem., 258*, 2911-15 (1983); (b) Waite, J.H., "The Formation of Mussel Byssus," in Case, S.T. (Ed.), *Results and Problems in Cell Differentiation,* Springer-Verlag, Berlin, Vol 2, pp. 27-54, 1992; (c) Papov, V.V., Diamond, T.V., Biemann, K., and Waite, J. H., "Hydroxyarginine-Containing Polyphenolic Proteins in the Adhesive Plaques of the Marine Mussel *Mytilus edulis,*" *J. Biol. Chem., 270*, 20183-92 (1995).

(11) Brady, Jr., R.F., "In Search of Nonstick Coatings," *Chem. & Ind.*, 219-22 (1997).

(12) Brady, Jr., R.F., "Fluorinated Polyurethane Coatings for Unique Defense Applications," *Eur. Coat. J., 31*, 267-69 (1995).

(13) Brady, Jr., R.F., "Coming to an Unsticky End," *Nature, 368*, No. 6466, 16-17 (1994).

(14) Griffith, J.R. and Brady, Jr., R.F., "Ready for the Market: An Intriguing Class of Coatings," *Chemtech, 19*, 370-373 (1989).

(15) Brady, Jr., R.F., Griffith, J.R., Love, K.S., and Field, D.E., "Nontoxic Alternatives to Antifouling Paints," Journal of Coatings Technology, *59*, No. 755, 113-19 (1987).

(16) Zisman, W.A., "Surface Energetics of Wetting, Spreading, and Adhesion," Journal of Coatings Technology, *44*, No. 564, 41-57 (1972).

(17) (a) O'Rear, J.G., Griffith, J.R., and Reines, S.A., "Some New Fluorinated Epoxies and Polymeric Derivatives," Journal of Paint Technology, *43*, No. 552, 113 (1971); (b) Reines, S.A., Griffith, J.R., and O'Rear, J.G., "Substitutent Effects in the Reaction Rates of 2-Arylhexafluoroisopropyl Gylcidyl Ethers with Dibutylamine," *J. Org. Chem., 36*, 1209-13 (1971); (c) Griffith, J. R., O'Rear, J. G., and Reines, S. A., "Fluorinated Epoxy Resins," *Chemtech*, 311-16 (1972); (d) Reardon, J.P., O'Rear, J.G., and Griffith, J.R., "Preparation and Wetting Characteristics of Some Poly(Fluorinated Aromatic Glycidyl Ethers)," *Ind. Eng. Chem. Prod. Res. & Dev., 11*, 365 (1972); (e) Griffith, J.R. and O'Rear, J.G., "3,3-Bis(Trifluoromethyl)Oxiranes," *Ind. Eng. Chem. Prod. Res. & Dev., 13*, 148 (1974); (f) Griffith, J.R. and O'Rear, J.G., "Synthesis of 1,3-Bis[2-Hydroxyhexafluoro-2-Propyl]-5-Perfluoroalkyl Benzenes," *Synthesis, 7*, 493 (1974).

(18) (a) O'Rear, J.G. and Griffith, J.R. (to the Secretary of the Navy), "Bis(Trifluoromethyl) Epoxides," U.S. Patent 3,849,450 (November 19, 1974); (b) O'Rear, J.G. and Griffith, J.R. (to the Secretary of the Navy), "Highly Fluorinated Diglycidyl Ethers," U.S. Patent 3,993,631 (July 9, 1975); (c) O'Rear, J.G. and Griffith, J.R. (to the Secretary of the Navy), "Fluoroanhydride Curing Agents and Precursors Thereof for Fluorinated Epoxy Resins," U.S. Patent 4,045,408 (August 30, 1977); (d) Griffith. J.R. and O'Rear, J.G. (to the Secretary of the Navy), "Cis-Trans Fluoropolyol Polyacrylate," U.S. Patent 4, 284,747 (August 18, 1981).

(19) (a) Field, D.E. and Griffith, J.R., "Cross-Linked Fluoropolymer Coatings," *Ind. Eng. Chem. Prod. Res. & Dev, 14*, 52-54 (1975); (b) Field, D.E., "Fluorinated Polyepoxy and Polyurethane Coatings," Journal of Coatings Technology, *48*, No. 615, 43-7 (1976); (c) Field, D.E. and Griffith, J.R. (to the Secretary of the Navy), "Fluorinated Network Polymers," U.S. Patent 4,157,358, June 5, 1979.

(20) (a) Bultman, J.D. and Griffith, J.R., "Fluorinated Naval Coatings," *Ind. Eng. Chem. Prod. Res. & Dev., 17*, 8-9 (1978); (b) Griffith, J.R. and Bultman, J.D., "Fouling Release Coatings," *Naval Engineers J.*, 92, 129-132 (1980).

(21) Moniz, W.B., Griffith, J.R., Brady, Jr., R.F., and Thompson, C.M., "Fluorinated Organic Polymers for Diverse Applications," *NRL Memorandum Report 5517*, March 6, 1985.

(22) 21st Century Coatings, Inc., 1439 N. Great Neck Road, Virginia Beach, VA 23454; 757- 496-9008; fax 757-496-9050.

(23) Brady, Jr., R.F., "Formulations and Field Performance of Fluorinated Polyurethane Coatings," in *Organic Coatings for Corrosion Control*, Bierwagen, G. P. (Ed.), ACS Symposium Series *689*, American Chemical Society, Washington, D.C., Chap. 22, pp. 282-91, 1998.

(24) Bonafede, S.J. and Brady, Jr., R.F., "Compositional Effects on the Fouling Resistance of Fluorourethane Coatings," *Sur. Coat. Int., 81* (4), 181-185 (1998).

(25) (a) Moore, G., Zhu, D.-W., Clark, G., Pellerite, M., Burton, C., Schmidt, D.L., and Coburn, C.E., "Water-Borne Crosslinkable Fluorochemical Coatings, *Sur. Coat. Int., 79*, 377 (1995); (b) Schmidt, D.L., DeKoven, B.M., Coburn, C.E., Potter, G.E., Meyers, G.F., and Fisher, D.A., "Characterization of a New Family of Non-Wettable, Non-Stick Surfaces," *Langmuir, 12*, 518 (1996); (c) Lin, J., Zhu, J., Swanson, D.R., and Milco, L., "Cross-Linking and Physical Characteristics of a Water-Based Nonstick Hydrophobic Coating," *Langmuir, 12*, 6676-80 (1996).

(26) Brady, Jr., R.F., Bonafede, S.J., and Schmidt, D.L., "Self-Assembled Waterborne Fluoropolymer Coatings for Marine Fouling Resistance," *Sur. Coat. Int.*, in press (1999).

(27) Saroyan, J.R., Lindler, E., Dooley, C.A., and Bleile, H.R., "Barnacle Cement—Key to Second-Generation Antifouling Coatings," *Ind. Eng. Chem. Prod. Res. & Dev., 9*, 123-28 (1970).

(28) Bonafede, S.J., Pawlikowski, G.T., and Brady, Jr., R.F., "Macrofouling of Hydrocarbon Polymers which Contain Variable Proportions of Crystallinity," *Biofouling, 14*, 1-14 (1999).

(29) Brady, Jr., R.F. and Pawlikowski, G.T. (to the Secretary of the Navy), "Robust Nontoxic Antifouling Polymers," U.S. Patent 5,652,027 (July 29, 1997).

(30) Anon., "Surface Preparation Specification No. 10, Near-White Blast Cleaning," *Steel Structures Painting Manual,* Keane, J.D. (Ed.), Steel Structures Painting Council, Pittsburgh, Vol. 2, pp. 47-48, 1982.

(31) Bullock, S., Johnston, E.E., Wilson, T., Gatenholm, P., and Wynne, K.J., "Surface Science of a Filled Polydimethylsiloxane-Based Alkoxysilane-Cured Elastomer: RTV-11," *J. Colloid Interfac. Sci., 210*, 18-36 (1999).

(32) Adkins, J.D., Mera, A.E., Roe-Short, M.A., Pawlikowski, G.T., and Brady, Jr., R.F., "Novel Nontoxic Coatings Designed to Resist Marine Fouling," *Prog. Org. Coat., 29*, 1-5 (1996).

(33) Brady, Jr., R.F. and Adkins, J.D., "Antifouling and Nonfouling Coatings for Sonar Dome Rubber Windows (SDRWs) and Sonar Rubber Domes (SRDs); Progress Report," NRL Letter Report 6120-260, August 30, 1993.

(34) Lewis, J.A., Foster, T., and Brady, Jr., R.F., "Environmentally Acceptable Flexible Fouling Release or Prevention Coatings," *Final Report, TTCP MAT Group Assignment MAT-TP-6-O9,* June 1997.

(35) Jones-Meehan, J., Cella, J., Montemarano, J.A., Swain, G.W., Wiebe, D., Meyer, A. and Baier, R.E., "Advanced Nontoxic Fouling Release Coatings," Naval Research Laboratory Report NRL/PU/6110-99-388, July 27, 1999.

(36) Milne, A. and Callow, M.E., "Non-Biocidal Antifouling Processes," in Smith, R. (Ed.), "Polymers in a Marine Environment," London, *Trans. Inst. Marine Eng. (C), 97*, Conference 2, Paper 37, 229-33 (1985).

(37) (a) Milne, A. (to The International Paint Company, Ltd.), "Anti-Fouling Marine Compositions," U.S. Patent 4,025,693 (May 24, 1977); (b) McLearie, J., Finnie, A.A., Andrews, A.F., Millichamp, I.S., and Milne, A. (to The International Paint Company, Ltd.), "Anti-Fouling Coating Compositions," U.S. Patent 5,302,192 (April 12, 1994).

(38) Ghanem, N.A., El-Awady, N.I., El-Hamouly, W.S. and El-Awady, M.M., "New Approaches to Non-Toxic Antifouling Coatings for Ship-Hull Protection," JOURNAL OF COATINGS TECHNOLOGY, *54*, No. 684, 83-88 (1982).

(39) Griffith, A.A., "The Phenomena of Rupture and Flow in Solids," *Philosophical Transactions of the Royal Society (London), A221*, 163-198 (1921).

(40) Kinloch, A.J. and Young, R.J., *Fracture Behaviour of Polymers,* Applied Science Publishers, London, 1983.

(41) Kendall, K., "The Adhesion and Surface Energy of Elastic Solids," *J. Physics D: Appl. Phys., 4*, 1186-1195 (1971).

(42) Brady, Jr., R.F. and Singer, I.L., "Mechanical Factors Favoring Release from Fouling Release Coatings," *Biofouling,* in press (1999).

(43) Zisman, W.A., "Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution," in Gould, R.F. (Ed.), *Contact Angle: Wettability and Adhesion,* American Chemical Society, Washington, D.C., *Adv. Chem. Ser. 43*, pp. 1-51 (1964).

(44) Baier, R.E. and DePalma, V.A., "The Relation of the Internal Surface of Grafts to Thrombosis," in Dale, W.A. (Ed.), *Management of Occlusive Arterial Disease,* Yearbook Medical Publishers, Chicago, pp. 147-163, 1971.

(45) Brady, Jr., R.F., "Properties Which Influence Marine Fouling Resistance in Polymers Containing Silicon and Fluorine." *Prog. Org. Coat., 35*, 31-35 (1999).

(46) Roland, C.M. and Ngai, K.L., "Segmental Relaxation in Poly(dimethylsiloxane)," *Macromolecules, 29*, 5747-50 (1996).

(47) a) Zhang Newby, B.-M., Chaudhury, M.K., and Brown, H.R., "Macroscopic Evidence of the Effect of Interfacial Slippage on Adhesion," *Science, 269*, 1407-1409 (1995); (b) Zhang Newby, B.-M. and Chaudhury, M.K., "Effect of Interfacial Slippage on Viscoelastic Adhesion," *Langmuir, 13*, 1805-1809 (1997).

(48) Brady, Jr., R.F., "Fluoropolymers," *Chemistry in Britain, 26*, 427-430 (1990).

(49) Kohl, J.G. and Singer, I.L., "Pull-Off Behavior of Epoxy Bonded to Silicone Duplex Coatings," *Prog. Org. Coat., 36*, 15-20 (1999).

(50) Swain, G.W., Schultz, M.P., Griffith, J.R. and Snyder, S., "The Relationship Between Barnacle and Pseudo-Barnacle Adhesion Measurements: A Method to Predict the Foul Release Properties of Silicones," in Brady, Jr., R.F. and Park, Y. (Eds.), *Proceedings, Workshop on Emerging Nonmetallic Materials for the Marine Environment,* Office of Naval Research, Arlington, pp. 1-60 to 1-69 (1997).

(51) Swain, G.W., Griffith, J.R., Bultman, J.D., and Vincent, H.L., "The Use of Barnacle Adhesion Measurements for the Field Evaluation of Non-Toxic Foul Release Surfaces," *Biofouling, 6*, 105-114 (1992).