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This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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PREFACE

The Chemistry Division of the Office of Naval Research is charged with the responsibility for research addressing the needs of the Navy and Marine Corps for lightweight, high-performance materials, including structural, conducting, and electronic materials; chemical detection and analysis; electrochemistry; synthesis of new materials; and surface chemistry.

As a result of discussions between the co-chairman of the Board on Chemical Sciences and Technology and the head of Office of Naval Research--Chemistry Division, the Board was encouraged to establish and oversee the work of a committee to advise on long-range research opportunities in chemical sciences and chemical technology that would be appropriate to the mission of the ONR. The committee would provide an important source of input from the scientific community as ONR formulates long-range plans for the chemical sciences, both in its core program and in special-focus initiatives. The committee may also explore the broad role of chemistry in the Navy's missions, including its role at in-house laboratories and educational centers such as the U.S. Naval Academy and the Naval Postgraduate School.

The committee, which expects to meet on a continuing basis, was extensively briefed by ONR-Chemistry Division staff at its initial meeting on September 30, 1985, regarding the division's current research programs and plans. In executive session following that briefing, the committee decided to prepare an interim report to assist ONR in a timely way rather than to wait until a more detailed study could be completed. The interim report presents the committee's consensus concerning research areas that merit significant support by the ONR because of the opportunities they present for major scientific advance and because of their substantial relevance to Navy missions. It is our hope that the report will enable the ONR-Chemistry Division to consider the committee's suggestions now in making plans for the coming fiscal years.

George W. Parshall
Chairman, Committee on ONR Chemical
Science Research Planning

INTRODUCTION

The Office of Naval Research has had a distinguished history of supporting basic research, largely at universities, on behalf of its general mission of buttressing national security in the decades ahead, not least in chemistry, which has long looked to ONR for leadership in funding important and exciting research.

A quick survey of a number of essential Navy programs that need attention might include, among others, the following:

- Fleet Air Defense
- Integrity of C^3 (command, control, and communications)
- Quiet submarines
- Submarine atmosphere quality
- Antisubmarine warfare
- Reduced drag for attack submarines
- C^3 resistance to damage from high-intensity radiation
- Long-term storage of weapons
- Safe disposal of nuclear wastes
- Explosives of greater effectiveness and reliability
- Chemical and biological warfare agent detection and protection
- Inhibition of ship corrosion and barnacle formation

Even a superficial examination of each of these topics immediately reveals the essential importance that basic chemical processes, phenomena, and materials play in developing solutions and improvements to each of these.

We cite several examples:

- Fleet Air Defense depends critically on the development of new lightweight high-strength materials. New composites are essential in the development of such materials, and the basic chemistry of solid-solid chemical interfaces is crucial to the understanding of how to make significant improvements in the strength of such new materials.
- C^3 in a ship depends critically upon miles and miles of wire or optical fiber communications. Wire coatings may be flammable, and in fact may actually conduct fire around a vessel. New chemical understanding of flammability and fire retardation of such materials is extremely important. In the case of optical fibers, the conducting

material itself is amenable to great improvement through study of the optical properties of newly synthesized materials.

- The need for quiet submarines leads to careful consideration of plastic-for-metal substitutes, chemical materials for acoustic insulation, and rubbery materials to dampen vibrations. Chemistry has much to offer in each of these areas.
- Removal of carbon dioxide and noxious fumes and odors from closed spaces is vital in submarines and elsewhere. Chemical processes and analyses are crucial to the adequate solution of these problems.

By examining a number of problems like these, one can identify particular areas of chemistry, the development of which is critical to the Navy. These areas deserve significant support to develop new principles and methods that may find applications, not necessarily this year or next year, but almost certainly in the decades ahead. These same areas need to be analyzed also as to their readiness for current development, the extent of current support, the quality of the individuals involved and the research already being done, and the likelihood that further funding would significantly accelerate the needed progress in obtaining new knowledge.

This is the ongoing task the NRC Committee on ONR Chemical Science Research Planning has undertaken; this report represents a preliminary and tentative set of suggestions in this direction. In making our recommendations, however, we are mindful that basic research leads to many surprises, and it is frequently impossible to predict just where new advances will occur that will have a significant influence on the Navy of the future. The committee therefore strongly urges that a paramount factor in considering research support be the selection of the highest quality of research, in whatever field of chemistry, as opposed to the funding of only the safer and more recognizably applicable research.

The early success of the ONR depended heavily upon this approach to quality. We urge that this long tradition be continued. It is the keystone to recognition by the chemical research community that the ONR is playing a vital role in chemistry research, and that recognition is crucial to attracting the best scientists of the nation to become interested in the needs of the U.S. Navy.

SUMMARY AND RECOMMENDATIONS

Based on discussions with Chemistry Division staff and in executive session on September 30, 1985, the committee arrived at consensus on six research areas that have significant merit for support by the division. In each area, the committee perceived both opportunity for major scientific advancement and substantial relevance to Navy missions. The first two areas listed clearly merit highest priority, but all six appear to be strong candidates for research initiatives.

- Chemistry of surfaces and interfaces. This topic is so exceptionally important in materials and in processes that the committee felt that it should be incorporated as part of the division's core program, although action might be initiated as an accelerated research initiative.
- Chemical design of materials for information storage. The potential for major advances in new magnetic, magneto-optic, and optical recording media is extraordinary and the technological impact on Navy operations could be substantial owing to major advances in synthesis chemistry.
- Chemistry of the reliability and integrity of materials.
- Chemistry of materials under intense laser radiation.
- Chemistry of combustion in enclosed spaces.
- New methods of process control and nondestructive evaluation.

The scientific bases and operational relevance for each area are outlined in the following chapters. The bases for the highest priority areas are presented in more detail than for the others. The general approach has been to keep this report brief in the interest of timeliness.

A second major subject of discussion was the balance between core programs and accelerated research initiatives in the funding of the Chemistry Division. The committee is concerned that the growing role of research initiatives as a source of funds could lead to emphasis on fashionable research areas to the detriment of stable support for areas of long-term importance to the Navy. This topic and the general role of chemistry in ONR will be considered in greater depth at a future meeting of the committee.

1. CHEMISTRY OF SURFACES AND INTERFACES

Although the surface of most objects is only a tiny fraction of the mass of the object, the properties of the surface often dominate the properties of the object. The chemistry of surfaces (or, technically, interfaces or interphases) plays an especially important role in materials science and engineering by determining the properties of critical interfaces. New techniques for investigating interfaces and rational techniques for the control of the composition and structure of these interfaces offer a major and timely opportunity to construct new technologies. These technologies can yield systems having improved performance and new capabilities for Navy missions.

NAVY PROBLEMS DEPENDING UPON INTERFACE CONTROL

A wide range of technologies relevant to the Navy depend upon control of the characteristics of interfaces.

Generic Fields	Technologies
Adhesion	Aircraft composite structures; multilayer substrate for microelectronics
Tribology	Design and construction of efficient, durable, and reliable equipment
Corrosion	
Interface rheology	Submarine security; drag reduction
Aerosols	Chemical and biological defense
Colloids	Ceramic production
Electrochemistry	Batteries, fuel cells

The properties of many composite structures, from high-strength engineering composites used in aircraft to multilayer substrates for microelectronics and communications, depend upon interfacial control to achieve their properties. In any circumstance in which moving parts are involved, durability and efficiency depend upon control of tribology. Corrosion is a generic problem in all Navy equipment. The properties of fluids moving next to solids are strongly influenced by the character of the solid-liquid interface: control of this interface is critical to drag reduction and noise reduction. The properties of fuel cells, batteries, capacitors, and many other energy storage devices depend critically on electrochemistry occurring at electrode-solution interfaces. The technologies currently used to control critical interfaces in these applications are often highly developed, but are often empirical in character and not under firm control.

INTERFACE CHEMISTRY, AN AREA OF SCIENTIFIC AND TECHNOLOGICAL OPPORTUNITY

The technological importance of interface science to the Navy is unarguable. The scientific base necessary to understand and control the chemistry and physics of interfaces is now developing rapidly. One major area of progress has been the development of analytical techniques for characterizing the chemical composition of solid-vacuum interfaces. A number of new types of spectroscopy (X-ray photoelectron spectroscopy, Auger, secondary ion mass spectroscopy, low-angle X-ray scattering, electron tunneling spectroscopy) probe this interface in great detail. Electron microscopy provides information about surface morphology. Less heralded but also important are the developing techniques for studying solid-liquid and liquid-liquid interphases: electrochemistry, Rutherford back-scattering, wetting, and surface enhanced Raman spectroscopy. Techniques for examining and characterizing solid-solid interfaces are still poorly developed, especially when high spatial resolution is required.

A second contribution to modern interface chemistry is the development of sophisticated but empirical technologies for modifying interfacial characteristics critical in the civilian sectors--such as surfactants for slurry and emulsion fuel transport and enhanced oil recovery; barrier film generators for corrosion inhibition; silane coupling agents for composites; stabilizers for colloids used in polymer-containing systems; and techniques for synthesis of heterogeneous catalysts.

Part of the science base required to study and control interfaces is available, but clear opportunities exist to develop additional, critically needed information. Chemistry can contribute at several critical stages of this science and technology: synthesis of new materials; development of new analytical and diagnostic techniques; theoretical rationalization of molecular and atomic-level surface properties; and new process technologies for surface modification.

CRITICAL SCIENTIFIC AND TECHNOLOGICAL PROBLEMS

The generic problems in materials science are two:

- understanding the relations between atomic/molecular level structures and macroscopic properties.
- controlling atomic/molecular level structure.

Broad areas of scientific opportunity include the following:

- The development of new analytical techniques applicable to solid-liquid and solid-solid interfaces. Characterization of interfaces at the 1- to 100-nm scale is particularly important. Characterization of amorphous, irregular, and unstable surfaces and interfaces is especially difficult; almost no techniques are now applicable to detailed characterization of interphases between solids.
- The testing of new theoretical techniques useful in surface chemistry. The spectroscopies used in surface/interface characterization rely heavily on theoretical interpretation. Perhaps more importantly, surfaces are intrinsically heterogeneous, and theoretical methods provide important techniques for understanding the properties of various sites present on surfaces.
- The contribution of analytical, theoretical and synthetic techniques to rationalize the relation between microscopic structure and macroscopic properties of interfaces, in order to relate these macroscopic properties to the performance of materials systems, and, ultimately, to design and engineer the chemistry of interphases to yield systems having desired properties.

EXAMPLES OF PROBLEMS

1. High-performance composites. The structural integrity of multiply fiber-reinforced composite structures increasingly used in high-performance aircraft is usually limited by interfacial properties. Failure on impact typically occurs at either the fiber-matrix or ply-ply interface. The ability to modify and strengthen these interfaces provides the most promising route to improvement in the performance of composite-containing structures.
2. Multilayer electronic substrates. The substrates used in modern computing and communications devices are usually composed of many active and passive layers: insulators, conductors, thin film dielectrics, interconnects, and others. The technology of manufacture of these systems is often dominated by severe problems in ensuring compability and adhesive bonding between layers having different physical properties. The ability to control these interfaces would dramatically lower the cost of manufacture and increase the reliability of such

devices. It should also make possible the production of devices with improved characteristics.

For example, a crucial problem in construction of multilayer microcircuitry is the adherence of a metal conductor film to a polyimide film or ceramic glaze that has been applied to produce a planar surface. The interaction of metals such as copper and titanium with polyimide and with alumina is complex and is critical to the function of the device. Studies of the detailed chemistry of this metal-insulator interface can have major impact on circuit fabrication and performance.

3. Magnetic information storage devices. A major method of storage is the magnetic disk. The lifetime of disks is now determined, in major part, by friction and wear occurring between the surface of the rotating disk and the read head. Control of the tribology at this interface is critical to the reliability of this class of devices.

4. Drag and noise reduction. These problems are central to submarine security. Reduction in noise from moving parts depends in part upon acoustic damping, and in part upon tribology control in the moving device itself. It may be possible to reduce drag by controlling rheology in the fluid layer immediately adjacent to the submarine hull.

5. High-temperature adhesives. Adhesives are increasingly favored for joining parts in naval aircraft and missiles. By eliminating welds and rivets, they make it possible to produce lighter, stronger structures. Adhesive-bonded structures are not, however, readily used in high-temperature devices such as rocket throat nozzles and aircraft leading edges. Adhesion failure in these circumstances can occur by several modes, but adhesion failure at the interface is prevalent (often promoted by water and by permeation of oxygen). Better control of the adhesive interface would lead to improved systems performance.

MANAGERIAL PROBLEMS

- Interface chemistry is broadly interdisciplinary. Chemistry provides critical components to the field of interface science, but major contributions from other fields are required. To achieve maximum value from a program in interface chemistry, it is important to identify well-defined focal problems at the outset, and to work actively at transferring science and technology rapidly to the materials science and engineering community.
- The instrumental facilities required in interface science can be expensive (a typical analytical laboratory, containing XPS, electron microscope, SIMS, and associated preparative facilities may cost $1 to $2 million and require up to $0.2 million a year to operate and maintain). Placing, managing, and maintaining these facilities constitute an important managerial problem in surface chemistry.
- Major objectives in this area frequently require 8 to 10 years of research to bring all the necessary science of a system to a level appropriate for development.

Because of this last characteristic and because of the pervasive nature of surface-interface chemistry in naval technology, the committee recommends that this area become part of the core program of the Chemistry Division. However, it is important to begin an active program promptly, and an accelerated research initiative should be considered as a start-up vehicle for a core program. Such a research initiative should be structured from the outset with the appropriate balance of short-term and long-range projects for transition to a core program.

2. CHEMICAL DESIGN OF MATERIALS FOR INFORMATION STORAGE

Progress in archival storage and in rapid retrieval of large amounts of stored information has to date been achieved by incremental improvement in magnetic storage systems. Future requirements of the military for advanced applications in both aerospace and hydrospace will require far more reliable data storage systems that can store orders of magnitude more information per unit space and also permit rapid retrieval. An additional concern to the military is the potential loss of stored information associated with major electromagnetic disturbances.

During the past 30 years, the primary storage systems have consisted of tape and rigid disks coated with a thin film of acicular magnetic particles embedded in a suitable resin matrix. There has been little or no change in the materials; the advances in recording density have been derived largely from thinner and smoother coatings and from reduced "flying height" of the magnetic transducer. Improvements in recording density require continued progress in these areas as well as new auxiliary technologies and materials innovation.

With the recent progress in optical data storage systems, it would appear that the potential for a major breakthrough in information storage exists. The high data capacity and large separation of the read-write transducer make this technology attractive in a current storage configuration. Beyond present two-dimensional systems, there exists the real potential of optically based three-dimensional systems. However, a number of critical material problems must be solved prior to successful implementation of an optical storage disk. Similarly, major materials innovation in magnetic storage could provide performance enhancements to meet most of the goals cited earlier.

A number of needs for advanced storage systems that depend almost completely on innovation in chemical materials and processes are enumerated below.

Magnetic recording. Key to development of greatly improved magnetic recording systems is the ability to fly the head closer to the disk, e.g., at distances ~1000 Å (heads now typically fly at 2500 Å), for improved signal to noise and resolution. Some key materials innovations required to achieve these goals are listed below:

1. Use of magnetic particulate technology still dominates the field, and significant opportunities for further performance enhancements exist with development of higher coercivity and higher moment particles. Such particles will require greatly improved stability and uniformity as well as new classes of polymeric dispersants to permit achievement of uniform coatings in the range of 1000 to 2400 Å. Enhancement of stability may require a detailed knowledge of the surface chemistry of the magnetic particles.
2. Resin binders that can flow to achieve surface planarization of the magnetic media and also provide a much tougher surface to minimize damage associated with head strikes. Appropriate binders can enhance stability of the magnetic media.
3. Smoother, lightweight, planar substrates with higher specific modulus, which would permit higher spinning speed with minimal flutter to improve data access and data transmittal rates.
4. Success in items 2 and 3 could open the way for vertical or perpendicular magnetic recording, which would yield a tenfold increase in data storage density compared to the best media today. Application of an oriented cobalt-chromium alloy film atop the planar surface would permit recording in magnetic domains oriented perpendicular to the disk surface rather than spread out in the plane of the disk.

Optical storage. Optical storage provides the potential for almost two orders of magnitude improvement in bit density as well as intrinsic stability against major electromagnetic disturbances. In addition, extremely rugged, fast access drive designs seem feasible, based on the fact that the head/disk spacing is orders of magnitude larger than for magnetic systems (typically 1 mm versus 0.1 μm). Furthermore, there is great potential for removability of the media from the drive with the operational advantages that this allows. At present, optical storage systems have not been fully perfected with respect to the number of write-erase cycles that magnetic storage permits. Opportunities for innovation in chemical materials for optical storage are indicated below.

1. Nonerasable optical media are very attractive as highly survivable data bases. Only a physical destruction of the storage device would erase the stored information. These media are predominately non-polymer-based, but there are systems under development, such as dye-polymer systems, that may be strong candidates for cheap compact disk, read-only-memories compatible with low-cost, low-energy solid-state lasers.
2. Reversible media. Industry today is focusing on magneto-optic systems, but there are a number of rapid chemical processes that involve reversible phase changes. These concepts have been explored only superficially.

3. Optically transparent substrates are required in most optical storage configurations. Design of rapid forming processes for optically transparent plastics that do not result in orientation and corresponding birefringence is necessary. In addition, it is desirable that such materials display very low permeability to water and corrosive gases.

4. Because of the sensitivity to moisture of most of the inorganic materials currently being considered for the magneto-optic change, it is essential that polymeric encapsulants be designed that begin to approach the hermetic character of ceramics.

In summary, there are a number of major needs for chemical design of advanced materials for storage of information. These needs are critical both to the competitive posture of the U.S. computer industry and to the future needs for DOD.

3. CHEMISTRY OF THE RELIABILITY AND INTEGRITY OF MATERIALS

The integrity of structural, power, and communications systems employed in naval operations is directly influenced by the chemistry of the materials involved. Failure mechanisms are usually the result of long-term chemical degradation, and the understanding and control of these reactions are a matter of critical importance. With metals, corrosion reactions mediated by water are dominant. For organic substances, a variety of chemical mechanisms are involved.

Organic polymers are part of our everyday life as materials used in coatings, structural applications, electrical insulation, and packaging. These substances are composed typically of many thousands of atoms, principally carbon and hydrogen, but often including nitrogen, oxygen, and sulfur. The structures contain long linear chains of atoms that may be branched or cross-linked. Cyclic structures may also be present as branches or in the main chain. The mechanism of degradation depends critically on the chemical structures employed. For example, hydrocarbon polymers decompose by a free radical chain reaction involving the formation of transient hydroperoxide species. When the oxygen content exceeds a few percent, the material becomes brittle and mechanically unsound, e.g., as wire insulation or sheathing. This form of degradation can be substantially eliminated for extended periods by incorporation of small concentrations of antioxidants, i.e., chemicals that interrupt the free radical chain reaction. Other polymers deteriorate by entirely different mechanisms, e.g., hydrolysis of polycarbonates or loss of plasticizer by polyvinyl chloride, requiring different approaches to stabilization. Ozone is uniquely important in rubber degradation chemistry. In addition, the chemistry of deterioration may be catalyzed by substances present in the environment, which further complicates evasive strategies. Photochemical processes also play a key role in many polymer degradation processes.

Composite materials composed of high-strength fibers (carbon or polymer) in epoxy or other polymer matrices are promising in naval applications as lightweight, corrosion-resistant structural materials. In composites, integrity of the material depends upon the specific chemistry of the interface regions as well as the bulk chemistry of the fibers and matrix material. This is an area of critical importance that must be investigated at the fundamental chemistry level. Fortunately, a number of newer instrumental methods offer attractive capabilities for this research.

THE CHEMISTRY OF DEGRADATION

In a reducing environment, degradation is often the result of selective C-C bond scission leading to hydrogenolysis or of C-N, C-O, or C-S bond breaking. This initial step is then followed by rearrangement of the organic microstructure in the proximity of the broken bond through isomerization, cyclization, or other restructuring processes. In an oxidizing environment, initial attack by oxygen atoms produces phenol, carboxyl, and aldehyde functional groups, which then undergo chemical reactions leading to depolymerization. Change of temperature or irradiation by light or by energetic particles (ions, electrons) will significantly modify the chemistry of the process.

CONTROLLED DEPOLYMERIZATION

While, for structural applications, degradation of a polymer is to be avoided, controlled depolymerization can be a desirable process. In etching or stripping of a photoresist with high-intensity radiation or a chemical treatment, precisely controlled conversion of a polymer to a volatile or soluble species is desired. Similarly, in removal of a polymeric binder from a ceramic object by chemical or thermal extraction, complete but controlled removal of the polymer is necessary to obtain a blister- and void-free object. In some circumstances, oxygen can be tolerated as a coreactant in the extraction process. These situations represent an accelerated version of the degradation processes that one seeks to avoid in structural polymers. The net effect is that fundamental understanding of the degradative processes applicable to structural polymers can be very useful in improvement of polymer processing technology for microcircuitry, ceramics, and other vital electronic components.

Development of a polymer that would depolymerize smoothly and quantitatively in the range 200 to 400°C would greatly simplify binder removal from ceramic "green parts." Evolution of a volatile, nontoxic product would be desired. Success in achieving this goal would open the way to new ceramic processing techniques such as injection molding. Many of the same properties would also be useful in a photoresist for construction of microcircuitry.

PHYSICAL VIS A VIS CHEMICAL EFFECTS

In order to design polymers with superior long-term properties, it is necessary to separate chemical and physical aging effects. Traditionally, most workers have not separated these two phenomena; hence most data on chemical aging (light, air, water effects) are complicated by physical effects. This problem is particularly true for glassy and semicrystalline polymers (even polyethylene terephthalate film), which can crystallize and embrittle over a long time. To provide a basis for rational design of stable polymers, we propose studies in which chemical and physical effects are determined independently.

SUMMARY

It is proposed that a combination of talents from all branches of chemistry be used to investigate the elementary and subsequent reaction steps of polymer degradation and depolymerization on the molecular level. Organic polymers play ever-increasing roles in building the instruments of a modern Navy. Understanding their degradation will provide us with the knowledge to prevent their failure and to increase their useful life.

4. CHEMISTRY OF MATERIALS UNDER INTENSE LASER RADIATION

The advent of widely available high-intensity laser beams has introduced the potential for a new chemistry: "nonlinear photochemistry." When a short pulse of intense laser radiation interacts with any material, new photochemical channels may be opened. As a result of such interactions, the following may occur:

1. The exposed material may be destroyed.
2. New photochemical products may be formed on the surface of the material being exposed.
3. Part of the material may be sublimed with the potential for forming new chemical species such as clusters.

MATERIAL DESTRUCTION

Studies of the first type of phenomena could take two directions: In one direction, research can be aimed at understanding the mechanism and the laser intensity requirement for the destruction of various structural, optical, and electrical materials. This approach can have important applications in the Strategic Defense Initiative. Questions can be asked such as: What are the minimum energy per pulse and the maximum pulse width required? What is the chemical mechanism of the destruction? At what laser power does the rate of bond breaking exceed energy equilibration? Answering these questions opens the door both for new chemical understanding and for possible defense applications.

In a second research direction, those structural factors that make a material resist laser destruction could be identified. For example, how does a mechanically strong polymeric material, which might be used for the construction of external components of airplanes, missiles, or satellites, resist high-power-laser radiation? Can a material be made that is light, has high mechanical strength, and is also resistant to high-power-laser damage? This area of research presents a new opportunity for ONR.

As a specific example, one may wish to tailor a polymer for low absorbance of visible and near-UV light (excluding many aromatic polymers) while retaining high-strength bonds in the polymer backbone. Fluoropolymers have some of the desired properties, but ingenuity will be required to develop postfabrication cross-linking techniques to give stiff, strong coatings and structural members for satellites.

PHOTOCHEMISTRY OF MATERIALS EXPOSED TO HIGH-POWER-LASER RADIATION

The wide availability of relatively high power continuous and pulsed lasers provides new opportunities and challenges for the understanding of chemical reactivity in the condensed phase. A qualitatively new kind of photochemistry may result from the interaction of a chemical material and an intense radiation field in the same way that nonlinear optical effects may result from the interaction of a dielectric material and an intense radiation field. In analogy to the latter phenomenon, this new type of photochemistry may be termed nonlinear photochemistry. Results employing high-power lasers in the gas phase have already led to many examples of nonlinear photochemical processes, in particular multiphoton absorption. The latter may involve a sequential absorption of photons, each absorption occurring from a well-defined state, or from the directly coupled interaction of molecules with an intense radiation field. In the latter case, as in the case of nonlinear optical effects, second and higher order terms in the mathematical expressions that describe the molecular-electromagnetic interactions are "turned on" when the field strength is sufficiently high.

Since one is dealing with qualitatively new phenomena, predictions based on past experience may not be reliable. Indeed, exploratory programs that are not bound to conventional paradigms that view absorption as a single photon event should be encouraged. Because many laboratories now possess high-power lasers that are ideal for such exploratory investigations and because such exploratory work may involve relatively simple exposures and analyses of selected systems, interdisciplinary efforts involving research groups with laser expertise and those with photochemical expertise should be encouraged.

With the above caveat in mind, it seems likely that new photochemistry and new photochemical mechanisms will be discovered as a result of investigations of chemical materials exposed to high-intensity radiation. Breakdown in optical selection rules may lead to the direct population of electronically excited states that are inaccessible by one photon processes. As a result, novel photochemistry may ensue. Materials that are viewed as "transparent" to conventional lamps may take on significant absorption behavior when exposed to an intense radiation field. Novel methods of imaging could be an important application of the expected novel photochemistry. Technology currently being developed for direct "writing" of microcircuitry with high-intensity lasers would benefit immensely from a knowledge of the chemical mechanisms for destruction of a polymeric resist material or deposition of a metal from an organometallic compound. Reduction of the needed laser exposure would greatly broaden the use of this approach for circuit production.

The new photochemical principles and mechanisms that could be developed from such research should assist in understanding and, therefore, in controlling the breakdown and degradation of materials subject to intense radiation. If so, device failure, repair, and protection could be dealt with rationally.

Knowledge of the novel photochemistry is of critical importance to the understanding and the control of many irreversible processes resulting from intense radiation on materials. Which bonds are broken or made? What products are produced? What are the time scales associated with the photochemical events? The accumulation of information related to these questions will provide scientists with the intellectual tools needed to solve a broad array of problems associated with the interaction of matter with intense radiation. It will help bridge the current knowledge gap in our understanding of the chemical nature and dynamics of such processes.

LASERS IN PHOTOCHEMICAL SUBLIMATION AND CLUSTER FORMATION

Lasers and supersonic nozzle beams have been used for cluster formation from metals and more recently from carbon. Methods are available for making clusters from different kinds of material: organics, organometallic, semiconductors, and so on. These clusters can be deposited on surfaces to produce interfaces with potentially important electronic, magnetic, or optical properties. The possibility of varying the property measured by varying the size of the product clusters has immense potential for making useful materials.

The understanding of the mechanisms of the different reactions taking place between clusters of different sizes (each size is a different chemical even if it is made from the same material!) with different surfaces opens a whole new field of chemistry. This approach offers an opportunity for making new surfaces with desirable properties as well as for understanding of the chemistry of surfaces in general.

5. CHEMISTRY OF COMBUSTION IN ENCLOSED SPACES

Fire is one of the most devastating forces encountered in normal experience. The adverse effects are multidimensional, involving extreme dangers to personnel, structures and equipment. Smoke and combustion products suffocate and poison, and heat inflicts unparalleled pain. Materials of construction are consumed or weakened, leading to physical failure and additional danger to personnel. When the fire occurs at sea or in the air, the problems are multiplied. Accessible space is limited, and living and working quarters are in close proximity with abundant supplies of combustible fuels (and possibly munitions). Strategies for avoidance and control of fire effects are highly complex and, at present, are based on an inadequate understanding of the underlying chemical and physical processes. It is thus important for the Navy to enhance the scientific and engineering basis for understanding the behavior of materials during destructive combustion.

Flammable materials are ubiquitous. Clothing, bedding, furnishings, sound and heat insulation, wire insulation and cable sheathing, and other components in the manufactured environment can fuel and spread fire as well as generate noxious combustion products. Further, it is likely that for reasons including light weight, high strength, and corrosion resistance, composite structural materials based on combustible matrices (and possibly fibers) will increasingly be used in Navy ships. This trend is already evident in aircraft, land vehicles, and pleasure boats, and the advantages will prove irresistible for application to naval vessels. Thus, research should be directed toward the understanding of the burning process, and efforts enhanced to discover and develop new materials and composites that will minimize the disastrous effects of fire.

The burning of solids is presently understood only at a primitive level. Radiation from the gas-phase flame must react upon the solid surface to generate more volatile fuel if the flame is to be sustained. This principle suggests that materials that form nonvolatile surfaces (char) when subjected to high levels of thermal radiation will be advantageous. Alternatively, materials that release compounds that when heated interfere with the flame chemistry may also be less flammable.* Both strategies have been employed with some success in materials development, but the major efforts have been essentially empirical, and the knowledge base for rational progress has been inadequately developed. The time is ripe for significant advances in the understanding of flame chemistry through a concerted application of experiment and theoretical modeling. Similarly, the complex chemical and transport process involved in combustion of solids can be attacked through the power of chemical theory, spectroscopic diagnosis, and computer modeling.

Although a truly nonflammable polymer does not exist, a number resist combustion, e.g., polyvinyl chloride, fluorocarbons, silicones, and polyphenylene sulfide. It is important to understand the chemical basis of this behavior in order to extend the list. Some progress has been made. For example, heated polyvinyl chloride releases hydrogen chloride, which helps maintain a cool surface and thereby reduces the flow of fuel to the flame. On the other hand, the hydrogen chloride is extremely disagreeable for people, equipment, and structures. There are many considerations, and much research remains to be done. Less is known about the other polymers.

Synthesis, fabrication, characterization and testing of new materials will be fruitful. Systematic study of chemical structure and flammability (under diverse conditions) will lead to advances that can provide better fire-resistant materials. This research is clearly of value to the Navy.

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*For example, it is well known that bromine compounds and antimony compounds are synergistic as flame retardants. The two materials are supposed to exert their effect in the gas phase by quenching radical chain processes that sustain a flame. This supposition is unproven, but study of the hot gas reactions of Br and Sb species could be very productive in design of new and better flame retardant compositions.

6. NEW METHODS OF PROCESS CONTROL AND NONDESTRUCTIVE EVALUATION

The fault-free manufacture and service of high-performance naval systems components is critically dependent upon the availability of effective physical/physicochemical techniques for nondestructive materials evaluation. Undetected flaws in systems as diverse as microelectronics and platform structural/propulsion components introduced either in the manufacturing process or brought about by heavy service can have disastrous consequences for the efficiency and reliability of systems. Importantly, many of these flaws are chemical in nature. Examples of components and flaws are enumerated below.

1. Integrated circuit devices--impurities, dopant inhomogeneity, microcracking, corrosion.

   For example, it is common practice to build multilayer circuitry by assembling alternating layers of insulating alumina and conducting metal circuits. Interconnections between circuit layers are made by metal-filled holes ("vias") in the ceramic layers. Electrical probe methods establish conductive integrity of the circuits, but do not detect structural defects that may lead to circuit rupture in use. A method to "see" inside the matrix to detect such structural irregularities would assist in establishing reliability of the circuits in Navy service.
2. Composite and polymeric components--coupling agent or corrosion-related matrix-filler failure, oxidation, deplasticization, stress cracking, impurities.
3. Metal components--corrosion-induced cracking, strain, precipitation phenomena, impurities.

The development of powerful, economical, and, in some cases, portable instrumentation to recognize and locate such flaws, as well as to provide a better understanding of their origin, represents a unique chemical research opportunity.

Several classes of instrumentation are now particularly attractive for the development of chemically related process control and nondestructive evaluation technologies. These technologies offer the opportunity to spatially "image" the location of flaws in three dimensions, to perform chemical analyses of the nature of the flaws at the molecular level, or both. Techniques, potential applications, and suggested components are enumerated in Table 6.1.

Research is envisioned to encompass the application of existing instrumentation to naval systems-related problems, the development of instrumentation with greater spatial and chemical resolution, and the development of instrumentation suited for use aboard ship or in remote locations.

TABLE 6.1 Instrumentation for Nondestructive Evaluation

Technique	Application	Component
NMR (3-D imaging, high resolution, solid state)	Detect and define the nature of chemical imperfections	Polymers, ceramics, composites
Electron spin resonance	Detect unpaired electrons resulting from flaws, fracture, deterioration	Polymers, ceramics, composites
Surface vibrational spectroscopy and microspectroscopy (Raman, infrared)	Detect corrosion, contamination, degradation, inhomogeneities	IC components, polymers, composites, metals
X-Ray photoelectron spectroscopy, scanning electron microscopy	Detect corrosion, contamination, degradation, cracking	IC components, composites, metals, ceramics
Thermal wave imaging	Detect inhomogeneities in thermal conductivity due to flaws, cracks, strain	IC components, metals, composites
EBIC (electron-beam-induced current)	Detect inhomogeneities in electrical conductivity due to flaws, cracks	IC components, metals, composites
Ultrasonic tomography	Detect cracks, inhomogeneities	Metals, polymers, ceramics, composites
X-Ray tomography and topography	Detect image strain, defects, cracks	Metals, polymers, ceramics, composites
Nonlinear laser harmonic generation	Detect surface defects, inhomogeneities	Metals, polymers, semiconductors