where R is the reflectance of the sample, τ is the distance on the surface between two points, ω is the angular frequency, k is the wave number, f is the focal length of the incident radiation, and σ is the rms height of the surface. A 2D analysis of the optics has been carried out by Ogilvy (*35*). Whitehouse concluded (*34*) (for undulations with length scale greater than the wavelength of the incident radiation) that the surface appeared glossy if the probability density of the slopes on the surface was strictly confined to a narrow angle.

Biocompatibility. Finally, biological interactions with a surface have also been found to depend on its topography. A good review of the topological control of cell adhesion and activity on a surface has been made by Curtis and Wilkinson (*36*), and a more general review of the role of polymer biomaterials may also be found (*37*). Such considerations are relevant for a number of in vivo and in vitro applications, such as biological sensors, hip replacements (*38*), and more complex tissue implants such as replacement bone, where the growth of cells within the artificial structure is to be encouraged. For example, the size and morphology of crystals at the surface of octacalcium phosphate–coated collagen have been shown to affect the interaction of cells with the surface, as illustrated in Fig. 4. The larger scale topography was found to lead to less favorable spheroidal cells that formed fewer intercellular connections (*39*). In some cases, the topography of a surface may be carefully controlled to promote cell adhesion (*40*, *41*).

Conclusion

The topography of a surface is a direct result of the nature of the material that defines it. The analysis of the topography of a sample, made possible on the nanoscale by the development of AFM techniques, needs to be carefully considered in order to relate the complexity of a 2D surface to the material's properties. The result will be the better control of a number of properties, such as optical finish, and of the interaction of a surface with a secondary material, whether that be an adhesive, a secondary component of a composite, or a biological species.

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42. The authors acknowledge contributions to this work from A. Briggs, D. Bucknall, V. Burlakov, J. Czernuska, and S. Wilkinson from Oxford University; N. Marston and I. Robinson from Lucite International; and Y. Tsukahara from the Toppan Printing Company.

VIEWPOINT

20th- to 21st-Century Technological Challenges in Soft Coatings

Robert R. Matheson Jr.

Coatings are among the most ancient technologies of humankind. Relatively soft coatings comprising organic materials such as blood, eggs, and extracts from plants were in use more than 20,000 years ago, and coating activity has been continuously practiced since then with gradually improving materials and application techniques. The fundamental purposes of protecting and/or decorating substrates have remained ubiquitous across all the centuries and cultures of civilization. This article attempts to extrapolate the long tale of change in soft coating technology from its current state by identifying some key problems that attract research and development efforts as our 21st century begins.

Humans have been decorating and protecting various surfaces for many thousands of years. One very useful way of accomplishing either or both of those tasks is to apply a thin layer of some new material with appropriate characteristics (of appearance, durability, adhesion, and application requirements) directly onto the surface of interest. That new material is a coating. Understandably, the early history of coatings is a story of very specialized, often unique material combinations, as trial and error achieved goals with only the materials at hand in nature. This heritage of customization is still detectable in the modern coatings world, which demands a tremendous amount from the materials—often synthetic but some still containing or made of natural products—to be thinly applied on a surface. They need to be easily and uniformly applied; set up within a reasonable amount of time and process constraints; have a minimal environmental impact in their synthesis, combina-

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tion, and application; resist the effects of environmental assault; and provide good economic value. I examine five important forces that are driving how such coatings are made and improved today.

Nomenclature

The long, decentralized, and empirical evolution of coating materials and processes has left behind an arcane and frequently confusing vocabulary (*1*). It will be helpful to define three terms that are frequently used but also are indiscriminately interchanged. A lacquer (from the Arabic word *lakk*) is a coating that forms on a surface (frequently by evaporation of solvents) without the intervention of covalent bonds forming between the film-forming ingredients. In contrast, a varnish (from the Medieval Latin *vernice*) is a coating that essentially requires chemical reactions between film-forming ingredients during a curing process after its application to a substrate. Enamels (from the Germanic *esmail*) are a very common subset of varnishes, which use a heating (stoving) step to carry out the curing process. These classifications were sharp and distinct in the past, but current developments are beginning to weaken their clarity. However, they will be useful here in highlighting the particular challenges facing coating development.

Minimizing the Environmental Footprint

One of the most commonly recognized challenges is the reduction or elimination of volatile organic compounds (VOCs) from the formulations of modern coatings (*2*). In the quantities generated by today's population and particularly in the concentrations produced in industrialized urban environments, VOC emissions contribute to air pollution problems. Clearly, this problem is most acute for lacquers. The mutually unreactive components of a lacquer absolutely depend on some processing aid (commonly a solvent) to make them malleable enough for application, and those aids must then be removed to leave the coating robust enough to protect and decorate.

Solvent minimization finds its ultimate expression in lacquer versions of powder coatings, where solvents are replaced with heat, which is used to apply the coating. Upon cooling, the properties that develop can sometimes be adequate to the task at hand. However, these products are limited in that if the coating is heated to a temperature where its application is possible, then it will soften and deform once again. Moreover, because most coating films are either amorphous or semicrystalline, their ability to retain a minimum hardness and to resist sustained loads begins to fall off quite noticeably at temperatures well below those where rapid flow and leveling are achieved (*3*).

Acceptable solvent substitution basically amounts to using the liquid form of substances that are naturally present as gases in the atmosphere (such as water and carbon dioxide). Liquid or supercritical carbon dioxide is limited to industrial applications because of the requirements for high pressure. Water is easier to use widely as a coating solvent, but it is not a panacea. One example of a problem that comes with water is the inevitably wide variation in drying times that accompanies application in environments of different relative humidity. Because relative humidity can change almost hourly, this is a serious complication. In fact, virtually all waterborne coatings today contain quite substantial levels of organic "cosolvents." The VOC content of waterborne coatings is greatly reduced as compared to that of older, conventional solvent-borne coatings, but it is not fully eliminated. A major activity in modern coating development is the search for balanced chemistry that will push back these limits on environmentally more favorable lacquers while retaining the attractive simplicity, the synthetic control, and the low cost of the technology.

VOC release is not the only environmental impact factor that is important for driving change in coating technology. In the United States, regulations on so-called hazardous air pollutants (HAPs) are important (*4*). This is an explicit list of solvents, typically aromatic, that are used in large quantities and are either known to cause or suspected of causing human health problems with chronic exposure. A variety of other, similarly local constraints for particular ingredients exist around the globe. One very widely experienced restriction is that on heavy metals. There are many historical examples where fairly large amounts of particular metals have found use in soft coatings (*5*). Some examples are the use of lead for anticorrosion in cathodic electrocoat coatings, of hexavalent chromium in metal coatings, of both lead and cadmium in various pigments, of divalent tin in antifouling marine coatings, and even of mercury as an antifungal agent for some interior paints. In common with other areas of materials processing, coating technology now has to look for alternative ingredients without uncontrollable, long-term environmental consequences. No similarly general technical solutions have yet been found, although progress is being made, particularly with respect to anticorrosion coatings.

Beating Back the Environment

Chemical and mechanical resistance to environmental insult is a common feature of many coating systems and a key reason for their application. Biological attacks are classic problems encountered over the years, and their catalog defines the current frontier. Underwater coatings that can resist the attachment and degradation of aqueous organisms (such as worms and barnacles) are needed for shipping and for structures. Exterior coatings that can resist particular insect, bird, and plant excretions are frequently needed in local geographies. Interior coatings that can resist mildew, other fungal damage, molds, and bacteria are frequently desired. The general challenge is nearly always the same: specific resistance to a defined class of biological insult without nonspecific toxicity or irritation. It is natural to work toward this set of objectives with additives tailored to each task. Experience shows this natural path to be expensive and usually imperfect, but occasionally fruitful. Still, it is probably fair to say that no examples exist where the performance of the broadly toxic, heavy metal–based additives has been achieved with the more specific modern tools.

A new idea is to produce counteragents in situ by tapping the chemical reactions that must accompany biological attack or even simple weathering in the active environments near Earth's surface (*6*). For example, biological damage may be accompanied by hydrolytic scission of coating components. If those can be designed to hydrolyze into antiseptic, antifouling, or anti-whatever products tailored to the task, then perhaps an effective solution can be found.

Maximizing Control Through Molecular Architectures

It is important to look beyond environmental attack on the coating itself. The classical role of coatings is to protect something else from the environment. This protection can be mechanical or chemical in nature. Varnishes have been developed particularly for these purposes, because in situ or "on the work" cross-linking is a very effective technique for augmenting the coating's material properties while avoiding compromises in application.

An extremely active area of development in modern coatings is directed to improving the control of such reactions. Inevitably, these must be carried out in a variety of work environments. Near one extreme are coatings used in controlled chambers, as for the radiation or thermal curing of a coating used to seal a connection between electronic components. The variables of concern may be film thickness at various points, surface cleanliness, and small temperature gradients arising from materials of different thermal conductivity. Near the other extreme are the grossly fluctuating environments that can be found in a railroad locomotive shed, where humidity, temperature, air flow, application rate, surface preparation, and maybe even surface material are all variables.

One idea for meeting these challenges is to take great care in synthesizing the varnish ingredients so that no especially troublesome reactions can ever occur. Some side reactions are understandably more deleterious than others, and the goal is to leave no opportunity for the most troublesome, no matter what conditions might appear. This leads to the use of controlled polymerization techniques [exemplified but certainly not limited to group transfer polymerization (*7*) for acrylic materials], rigorous exclusion of nonfunctional (unable to participate in curing) matrix materials, and optimizing molar mass distributions to avoid untimely immiscibility during cure and similar strategies. The specific field of automotive coating has been in the forefront of this activity because of the extremely high performance standards and powerful economic incentives found in mass-producing automobiles. Some of the new synthetic and analytical techniques being introduced for controlling and monitoring automotive enamels have been described (*8*).

Decorative coatings in particular need to incorporate pigments, dyes, reflective metal, and mica flakes for many applications. One common technique for effectively distributing such particles is to cover their surfaces with dispersants that aid in their dispersion in the bulk of the coating and prevent reagglomeration under the variety of circumstances that might arise later. Exquisite control of the molecular structure is needed in order to achieve good distribution of the particles, minimal mobility once applied to a surface, the ability to resist forces that drive reagglomeration, and compatibility with the bulk coating and yet not induce problems with adhesion, application, or long-term performance. Because pigments are very frequently the most expensive ingredients in a decorative coating, it is important to use them efficiently. Additionally, as solvent concentration and variety are decreased because of the environmental pressures previously cited, opportunities for managing dispersion problems by modifying the coating medium (the coating vehicle) decrease. Small wonder that the chemistry used to make modern dispersants provides an exceptionally clear picture of the state of the art in molecular control in coatings. Techniques for making block copolymers (each block designed for affinity to either a surface or the solvent environment) have been developed and commercialized and are still being improved. The patent art is extensive and growing, but that from C. Hosotte-Filbert (*9*) is a representative example.

Functional Coatings

A fourth modern frontier in the world of soft coatings can be descriptively called "postcure reactivity" for varnishes, or perhaps "in-use reactivity" for lacquers. Such reactions have been recognized for a long time in examples such as the long-term oxidation of alkyd varnishes and many lacquers based on natural products. Historically, these have been viewed as troublesome instabilities. However, it has been learned that some instances of postcure chemistry have advantages, with one example being the slow condensation and interchange of siloxane bonds in organosilane enamels (*10*). These can act to relax stresses that otherwise grow uncompensated in light- and oxidation-stressed exterior coatings. Heterogeneous coatings that react to cracks or fractures by releasing postcure repair ingredients have been postulated (*11*).

Even more sophisticated uses in controlled release or other transport control problems can be sketched today. It should be noted that a great many instances exist in which coatings are used to manipulate (generally to retard, delay, or prevent) the transport and exchange of materials. Atmospheric oxygen contacting food, carbon dioxide exiting carbonated beverages, the release of pharmaceuticals into the body, electrical charge leaking into a device component, heat exiting an isothermal environment, or water and ionic materials contacting corrosion-susceptible metals are examples where the transport characteristics of coatings are important in determining performance. The long-term capability of a coating to improve or at the least react to compensate for a declining transport characteristic may be just as useful as the same ability to offset declining mechanical characteristics.

Industrial Scale Challenges

A final class of problems driving innovation in modern coatings can be found in the costs and limitations of the heating step in enamel processing. Not surprisingly, these problems include the capital and energy costs associated with heating objects with large thermal masses, damage to heat-sensitive substrates, and the inventory problems that accumulate with long cycle times in any process. The most direct approach is to reduce the required baking temperature and/or time. There is scope here for novel chemical reactions and catalyst innovations, both of which command attention today. Alternatively, if the curing reactions can be activated by a mechanism other than simple heating, then problems can be minimized without losing the cure-induced improvements in coating performance. Much current work is directed to radiation-curable (with ultraviolet light, electron beams, and even visible light) coatings and efforts to extend their current embodiments to complex articles and long-term use (*12*). Powder coatings and liquid coatings are both objects of study and innovation. The major challenge faced in such development arises from limitations on the uniformity of cure for incompletely transparent coatings (shadowed areas do not receive the same flux of radiation) or coatings on complex shapes.

Examples of specific new products arising in response to one or another of these five general development areas can be found in many places and from many development laboratories. Perhaps no example exists that illustrates all, but there is at least one that comes close. A need exists in the automotive world for a painting system with lower environmental emissions (particularly VOCs), improved resistance to environmental damage (particularly mechanical scratching), outdoor durability approaching a decade, corrosion resistance of the coated metal for the same period of time, and improved application robustness. This need has been recently met with what might be considered an exemplary modern coating system. Four layers of coating are used: First, an anticorrosion coating (now free of heavy metals) is applied by cathodic electrodeposition; second, a powder primer (now with zero VOCs); third, a waterborne layer containing pigments (now with minimal VOCs and minimal HAPs with modern polymeric dispersant molecules); and finally, a new clearcoat (now with more than 20% lower VOCs, greatly improved scratch resistance, and excellent resistance to acid rain, chemical attack, and photochemical exposure). All this is applied with the use of existing infrastructure, including both automatic and manual equipment when required, at commercial rates and with lower total energy input and improved visual quality. The automotive use environment is harsh for coatings, and this new system has only begun to be used. It is risky to foretell decade-long success so far in advance, but the step appears to be an important one in the evolution of soft coatings that can resist all the major pressures.

Looking Forward

The five general development frontiers appear to indicate two strong trends in today's soft coating development. The first is a trend toward ever-improving control of structure at all length scales. Whether in cure-site distributions for more robust varnishes, molar mass distributions in environmentally friendly lacquers, or optical path distributions for ultraviolet curables, the path of improvement and innovation goes along the line of improved structural uniformity and control. The second trend is the historically familiar one toward blurring the distinctions between and thereby removing some limitations from familiar coating classes. Whether by slow in-use reactions for nominal lacquers and ambient varnishes or by radiation-assisted cross-linking in nominal enamels, the technology trend is toward the boundaries laid down by the descriptors. One can phrase these trends in the form of two strategic questions for coating development: What kind of structural irregularity do you want to eliminate for an intended characteristic, and where do you want to carry out the chemistry required for that control (in intermediate production, during cure, or in use)?

A final observation might be made to complete this perspective on current technological challenges. In one important sense, the challenges are still within the long, long historical pattern of coatings. Coatings have been a derivative technology in which materials primarily intended for other purposes (coloring pigments alone excepted) are combined in complex mixtures for comparatively small-volume specialized use. Coatings are always at least partially custom-tailored to the problem at hand. Today's challenges are to decrease the environmental footprint and improve biological, mechanical, and transport longevity, while minimizing the application requirements for soft coatings. Challenges need to be met with only minimal need for brand-new materials, maximum use of component synergies, and maximum use of natural or by-product material streams. The custom tailoring is to be done with minimal resources and, therefore, maximum intelligence. The historical character of coatings innovation is well aligned with the modern curbs on new material registrations, capital investment, and waste management. Today, we are only at one intermediate stage in a long sweep of coatings development from the distant past into the future.

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