History of Coatings Science and Technology

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ABSTRACT

Dating from prehistory and Cro-Magnon man, coatings developed slowly from artistry to technology. Decorative values prevailed well past the Renaissance; the protective function of coatings emerged after the Industrial Revolution. Research in film-formers which converted coatings into a high-technology industry is summarized, and the stimulation provided by the need for coatings to comply with regulations is discussed.

PREHISTORY

Decorative Coatings

Cro-Magnon Man

Coatings history extends further into the past than does any other facet of polymer science. Although today's coatings serve both a protective and decorative function in most instances, prehistoric coatings were purely decorative. Long before the Renaissance they told of the culture of a society that used art as a means of communication.

Interestingly, no one knows the reason for stone age art. Why was the grand bison shown in Fig. 1 painted on the low ceiling of a centuries-forgotten cave known as Altamira? How did the artist illuminate the ceiling without depleting his own oxygen supply and without coating the ceiling with soot? Were these feats accomplished
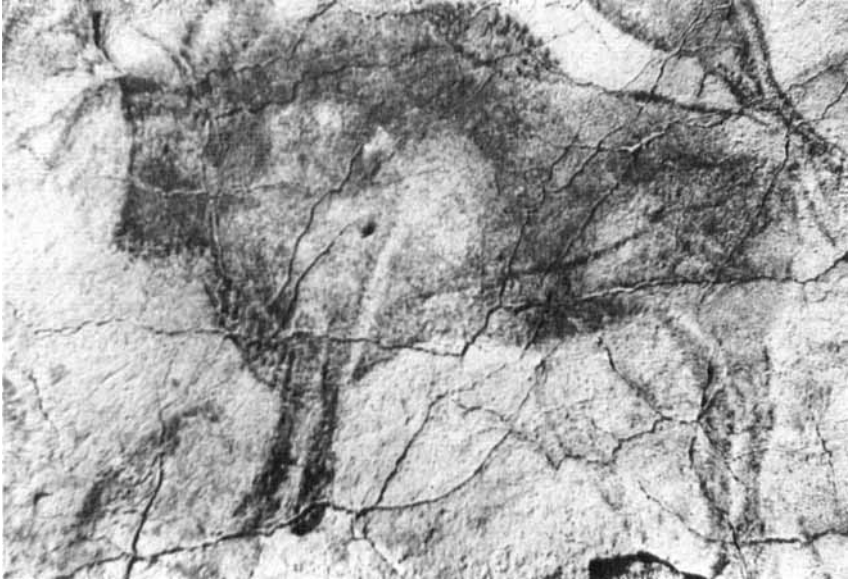
FIG. 1. Grand bison, Altamira. 15,000 years old.

in order to guarantee a successful hunt, or were they part of the fertility rites practiced at that time? Conjectures abound, but no hard facts.

Although the effect is not evident in a print, dimensionality was imparted to Altamira paintings by taking advantage of the natural embossing effect of the rock surface. This technique is best illustrated by the crouching bison of Fig. 2, found on a wall near the grand bison.

Of significant interest to the polymer scientist is the question of how the paintings lasted as long as they did. ^{14}C dating of wood found in some of the fire pits nearby indicate that the period in question dates back to 15,000 B.C. Seventeen millenia are not to be ignored in these days of five-year guarantees.

Before tackling the science of these early cotaings, one should examine an even more artistic and technical achievement on the other side of the Pyrenees. Here one finds a higher level of artistry, even though the cave paintings at both locations are practically contemporary. Lascaux ranks as the Sistine Chapel of Cro-Magnon art: the techniques deserve as much adulation as do those of the Renaissance masters, and the culture revealed by the techniques employed is that of a fairly sophisticated populace. For example, the Chinese horse (Fig. 3) which has figured in modern pigment advertisements required three different application methods to display a highly

FIG. 2. Crouching bison, Altamira. Exploiting natural embossing of the rock surface.

spirited animal about to be killed, captured, or impregnated. The wash-on effect deliberately avoids following the body outline and suggests a contour without relying on the natural embossing of the substrate. Lascaux techniques allowed the artist to portray action by choice rather than by following the dictates of the surface.

The three applications methods are shown in Fig. 4. A swab technique to be described later delineates the flank; a chalk technique outlines the body; and an innovative third technique, in which dry pigment is blown through a hollow bone onto a previously wetted surface, provides a vignette effect for the mane.

Vignetting reached its peak of perfection in the portrayal of nostrils. The large auroch detailed in Fig. 5 best demonstrates the velvetlike effect achieved by fine-tuning of the technique.

Europe was glaciated during the period of Altamira and Lascaux paintings. Animals roamed the southern fringes of the glacier and evidently served as food for Stone-Age humans. That the paintings depicted or encouraged a successful hunt is one hypothesis of their origin, in competition with the hypothesis that the paints had a religious or sexual meaning unrelated to the hunt.

Originally referred to as paint, coatings occupy a high-technology position today. One generally thinks of a fluid suspension of pigment in a binder when reference is made to paint, whereas a "coating"
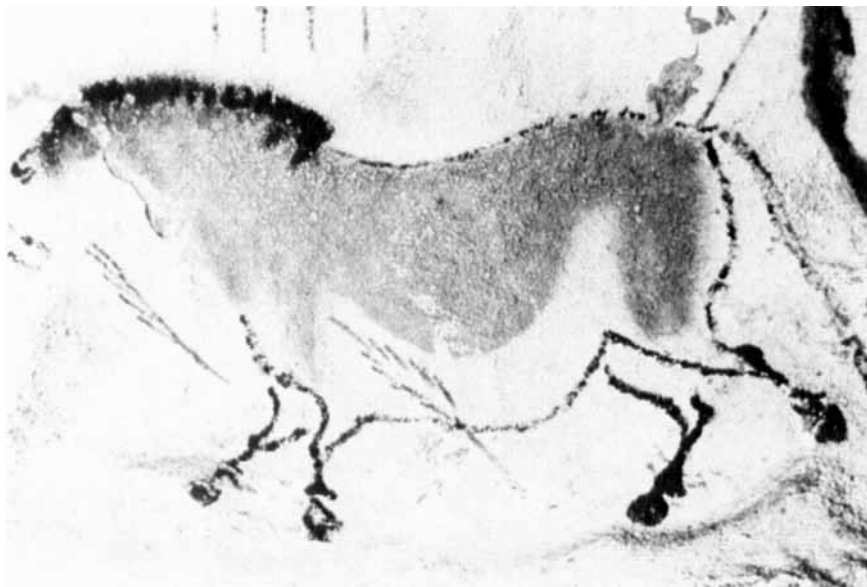
FIG. 3. Chinese horse, Lascaux. Three application methods in evidence.

refers to the system ranging from the wet material in the can to the coated article.

Coatings do not trace their origins to polymer seience. The earliest paintings found at Altamira and Lascaux owe their permanence to their composition: the pigments used and the substrates decorated were minerals. Binders were not necessarily used.

The days have passed when the casual visitor can view these works of art. The professional with an interest in their composition can learn from various sources that earth pigments on earth substrates do not guarantee resistance to man's depradations. Traces of binder do not exist and the paintings lack integrity. They wear; they support the growth of stalactites and fungus; they suffer spalling when an occasional piece of wall flakes away.

Natural colloids and polymers of the type found in blood and egg white were believed to be the Stone-Age artist's medium. Polymers from vegetable oils that possessed the capability of forming a solid continuum for the coating appear to have come later. In order to trace this development it is necessary to travel to the opposite side of the world.

FIG. 4. Chinese horse detail. Powdered mane, chalk outline, brushed body.

Later Cultures

Because the receding glacier determined the climate of southern Europe 17,000 years ago, it was responsible for the abundance of animals on its fringes. In an obverse situation, the passing of the last glacial age was responsible for the influx and subsequent isolation of the second wave of Aborigines to Australia.

The dominant second wave settled in Arnhem Land on the northern part of the continent and produced paintings which are clearly designed to ensure good hunting. Edible species abound in these paintings, ranging from fish to turtles to kangaroos, as shown in Fig. 6.

Earth pigments, including chalk, were used in these paintings; and evidence of binder persists in the form of considerably more gloss in some of the examples of Aboriginal art than in the European art. Unfortunately, the Aborigines had the habit of retouching the paintings of earlier cultures, and so the legendary 5000-year age for these paintings must be accepted with some skepticism. Dating by the museums and galleries of the Northern Territories of

FIG. 5. Large auroch, Lascaux. Nostril softened by vignetting.

Australia is based largely on the style of the paintings; carbon dat-
ing is hampered by the fact that living flora abound in the open re-
cesses of the aboriginal paintings. The sequence of photos compris-
ing Fig. 7 shows that, at least in the Obiri Rock paintings, the
gallery was protected only by overhanging rock.

The Aborigines had migrated to Australia from Asia, using the
land-sighting bridges created by the receding level of the ocean
during the glacial period, then becoming isolated on the island con-
tinent when the water returned to its postglacial level. It would be
expected that aboriginal art owes more to the Asian influence than
any other culture.

Although the early peoples of Oceania used paints to decorate
temples, a connection cannot be established between them and the
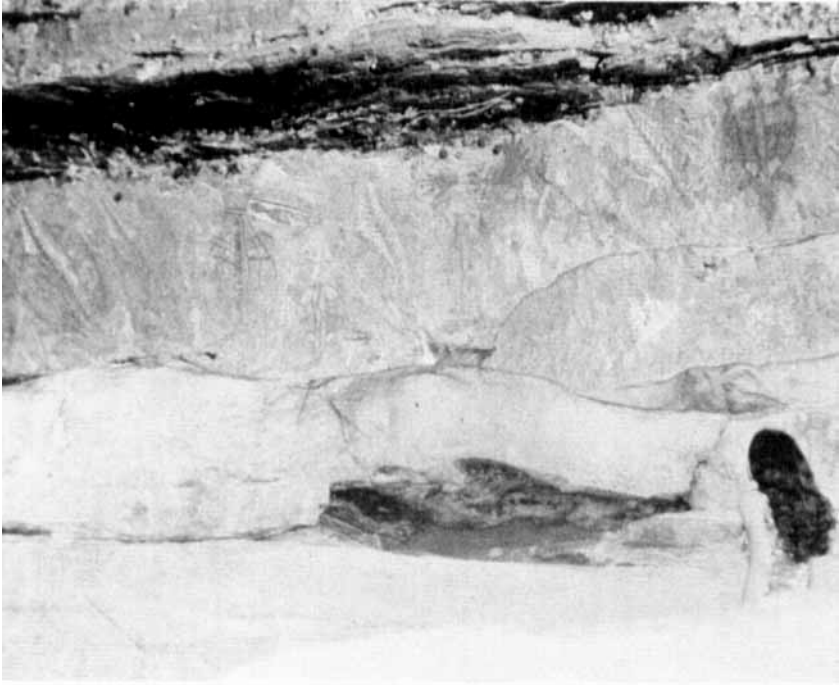
FIG. 6. Obiri rock paintings. Various fauna, considered edible by the Aborigines.

Aborigines on one side and mainland Asians on the other. Natural colors were used as pigments in all cases, with the Asians enjoying a wide variety of colors; and clay was used as a thickener. Some organic pigments were developed before 6000 B.C., and vehicles came from a variety of sources: gum arabic, egg white, gelatin, and beeswax. The introduction of polymers as a main component in coatings led to the development of lacquer, which was used in China at least as early as the Chou dynasty (1122-221 B.C.) for carriages and weapons.

Protective Coatings

Origin

The first use of protective coatings was by the Egyptians, who employed pitches and balsams to seal ships, a practice followed by

FIG. 7(a). Obiri rock main gallery sequence. See also Figs. 7(b) and 7(c). Exposure to the elements is apparent.

the rest of the world. In the Middle Ages the use of paint as a preservative for exposed wood surfaces was extensive, considering the fact that the coatings were handmade and used costly raw materials. By the 17th century, when lead paint became available, few domestic structures were covered by anything more than thatch and ivy. It was not until the Industrial Revolution when machinery required protection against corrosion that large-scale production of coatings began. Repainting was frequent, for the polymers in use at that time were made from oxidizable vegetable oils.

Resins, Natural and Synthetic

The history of protective coatings is, indeed, a history linked to polymers. Improvements in binders from the days of the Egyptians and the Chinese were responsible for paint emerging from the category of being a costly luxury, although the emergence was not evident until the Industrial Revolution, largely because of expensive pigments and manufacturing techniques.
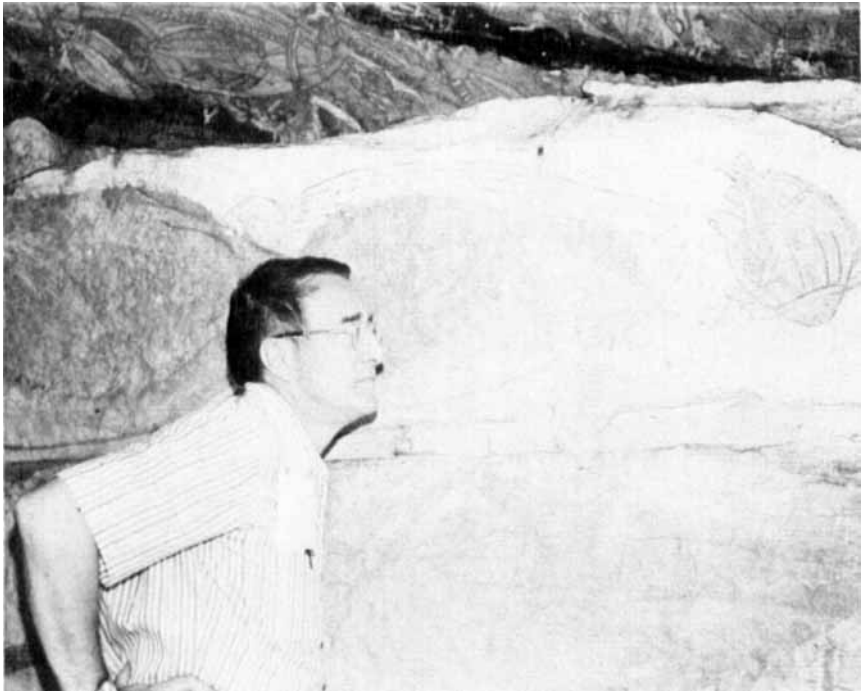
FIGURE 7(b).

Naturally-drying vegetable oils became the backbone of what has come to be known as the oleoresinous type of coating that has lasted since the 14th century. The most popular oil is extracted from flax seeds and is known as linseed oil. It is mainly a nonconjugated diolefin containing a 17-carbon tail and an ester group, most likely a glyceryl ester. Because of their natural occurrence, the vegetable oils contain varying amounts of unsaturation. Upon contact with oxygen, this diolefin reacts, first at a position adjacent to a double bond, and then by cross-linking through peroxy linkages to the double bond of a neighboring molecule.

Events since the Industrial Revolution have been responsible for the emergence of coatings as a high-technology industry. The variety of vehicles is as great and as important to meeting a variety of demands as is the selection of colors via control of the pigment content, which these days is done by computer. Drying oils have given large shares of the market to synthetic resins in solutions or emulsion, latexes, and waterborne polymers.

FIGURE 7(c).

COATINGS AND POLYMER SCIENCE

Requirements of a Coating

Scientific Requirements

Coatings technology is a prime example of applied polymer science. From the initial selection of the binder in which the pigment is to be dispersed to the final curing of the dried film, the coating must meet an array of requirements, as shown in Table 1.

Paint manufacture involves the intimate dispersion of pigment particles and the development of an extensive interface between the solid pigment and the vehicle. If the vehicle is a polymer solution, both the polymer and the solvent compete for sites. Gloss and penetrability of the film depend on these interactions. Protection and decoration are affected.

One of the first physicochemical principles which was discovered as an outgrowth of coatings research was the concept of a critical pigment volume concentration. As the pigment loading is increased to a point at which fluid can no longer fill the interstices, gloss and

TABLE 1. Requirements of a Coating

Wet the substrate
Flow evenly
Adhere on drying
Maintain film integrity
Develop optical properties
Develop hardness
Resist the elements
Serve as a barrier

blistering tendency decrease markedly, and penetration by water and gases increases.

The colloid chemical basis of coatings is perhaps the most interesting one of all, especially if all of the interfacial interactions are included in this category. A polymerizable or polymer-laden fluid contacts not only pigment surface but also the surface of what is invariably a solid substrate. Surfaces are rarely the simple composition attributed to the materials they represent; they contain oxidation products, contaminants, adsorbed moisture, and other species that generate a weak layer somewhere in the adhesive sandwich. Adhesion may not become the limiting factor in the evaluation of a coating until the rigors of drying have been encountered. Shrinkage invariably occurs; and if the coating suffers much volume reduction after it has developed a permanent set, the shrinkage will take place in the direction normal to the interface. Lateral stresses will develop and the ultimate response may be cohesive or adhesive failure.

The requirements of a coating do not stop here, however. The need for coatings science is made apparent by the twofold requirement that the coating protect as well as decorate. Recent developments have imposed a third requirement, namely, that it not pollute. This may be the hardest task of all.

Solvents and Their Effects

Resin technology leans heavily on solvents, for the practical side of polymer coatings requires that they be of high molecular weight and cross-linked, for many applications at least. One could start with an oligomer, as in the case with natural drying oils, and expect it to polymerize after the coating had been established. Ambient conditions using oxygen, water, or impurities to carry out the reaction are highly desired in these days of energy shortage; however, the resulting coating is liable to be soft and vulnerable. Baking helps, but requires energy.

Ambient species are not always used to increase the degree of polymerization of oligomers. Self-condensation can occur, or reaction can be initiated with a coreactant in the film. Or one can start with a high polymer in solution. The choice depends on the application and on the physical properties desired in the ultimate coating; in all choices the coating develops residual lateral stresses on drying, owing to the reduction in volume which occurs from the reaction or from the solvent loss.

Solvents need to be minimized because restrictions exist on the amount of volatile organic material which may be discharged when the coating is applied and allowed to dry. These restrictions have led to the development of low-solvent coatings, powder coatings made from 100% solids, and aqueous systems. Radiation curing is a specialty market type which requires no solvent but runs the risk of releasing highly reactive and toxic species.

Coatings Design

Synthetic Resins

The first resins were of natural origin. As long as they were transparent, hard, amorphous, and chemically stable, they held excellent potential for being made into what came to be called varnish (solutions of natural resins which yielded the hard resin on evaporating). These formulations often cracked and yellowed on aging, and one never set a drink on a coffee table coated with natural varnish.

Synthetic resins are now the heart of the coatings industry. Through endless variations in the polymer backbone and in the pendant groups, it is possible to duplicate and even surpass the range of physical properties of natural resins. Even in the face of a petroleum crisis the availability of resins from petroleum feedstocks is more reliable than that offered by Nature's living flora and fauna.

The two main types of synthetic resins are those formed by condensation polymerization and addition polymerization. In the former category are polyesters, phenolics, amino resins, polyurethanes, and epoxies. In the latter category are the acrylates and the vinyls.

Condensation Resins.   The most widely used condensation resins are the alkyds, formed from a dibasic acid and a polybasic alcohol. Brittle and insoluble in common solvents, they are most frequently made in the presence of a plasticizer. By altering the nature of the acid or the alcohol, one can make alkyds more or less viscous, more or less hard as a coating, and of various degrees of solubility and compatibility with other ingredients, including pigments.

Phenol reacts with aldehydes to form oil-soluble resins which dry rapidly to hard, resistant coatings. Although their chemical resistance is considered fairly good, phenolics tend to yellow on outdoor exposure.

Condensation resins made from urea or melamine and formalde-
hyde (amino resins) are nonyellowing and alkali-resistant.

Polyurethanes and epoxies both involve a high degree of competence
in synthetic organic chemistry. The properties of coatings made from
these resins are superlative: hardness, inertness, adhesive qualities,
and thermal resistance.

Addition Polymers. Two classes of synthetic resins can
be conceptualized as derivatives of polyethylene. Acrylic resins have
an ester group pendant to the ethylene fragment which serves as the
polymer backbone

$$\sim\sim CH_2 - CH \sim\sim$$
$$|$$
$$C = O$$
$$|$$
$$OR$$
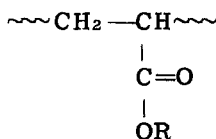
whereas in the case of vinyl resins the polymer backbone is formed
from the side chain

$$\sim\sim CH_2 - CH \sim\sim$$
$$|$$
$$O$$
$$|$$
$$C = O$$
$$|$$
$$R$$
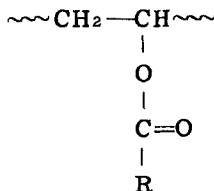
The main point of departure in the synthetic capabilities of these
resins is that vinyl resins can have any functionality ranging from
halogen to fatty acid fragments pendant to the vinyl. The acrylates,
in turn, offer versatility only in the choice of R and in the substitu-
tion of a methyl group at the branch carbon.

Ethylene, itself, can be made into a translucent, inert, waxy poly-
mer. Because of the lack of functional groups, this polymer is not a
readily adherent coating. This lack of functionality is responsible for
sustained interest in polyethylene as an ingredient in coatings, for
their inertness and resilience are valuable features.

Polyvinyl acetate, a useful resin that softens below the boiling
point of water, is water-sensitive. Vinyl resins are used either in
organic solvents or as dispersions in water. Sometimes they are co-
polymerized with acrylates which have excellent nonyellowing prop-
erties.

Latexes have been growing in popularity in the coatings industry
since 1948. In a latex, as distinguished from an emulsion, the binder
monomer is suspended in water and polymerization occurs around
micelles of surfactant situated across an intervening expanse of

water. Molecular weights in the millions are achieved, but the viscosity of suspension remains low because its value is independent of molecular weight. The desirable features of latex coatings responsible for their development were rapid drying, ease of application and clean-up, resistance to alkali and oxidants, nontoxicity, absence of fume hazards, low odor, and applicability to damp surfaces.

Ecological Considerations

Latex formulations have received a boost from another quarter. EPA restrictions on volatile emissions during coatings manufacture and application have mandated that solvents be kept to a minimum in the formulation of coatings, at least of the trade sales variety. There is a second class of coatings used in industrial installations where solvents could be captured in fume hoods, but even in that category the economics of coatings application calls for reduction of the solvent content.

The use of water as the vehicle affords a logical solution to this problem. Latexes are well-accepted in do-it-yourself quarters as a viable solution, but certain properties inherent in the use of latexes have caused the finishing industry to seek alternatives. Latexes are inclined to be porous, nonglossy, of limited composition, and loaded with surfactants and other debris that collects at the interstices among the coalesced latex spheres. The need for high polymer spheres to coalesce into close-packed polyhedra on drying (in order to form a continuum) necessitates that they be plasticized; this requirement leads to softened films and calls for organic coalescing aids. As a result, alternatives to latexes are being sought for industrial coatings.

One alternative is high-solid coatings. If these systems are formulated in solution, the resins must naturally be low molecular-weight oligomers rather than polymers. The problem then becomes one of selecting oligomers that will react either with themselves or with the solvent to produce a high polymer. These systems are referred to as thermosetting, regardless of whether baking is used in the drying process, as contrasted with the thermoplastic coatings that result from many solution polymers.

A second alternative to latexes is the 100% solids coatings system. Polymers selected for this category are applied as thermoplastic powders, either by means of electrostatic spray or in a fluidized bed in which the object to be coated is immersed. In either case, the coated article is baked in order to convert the deposit into a level coating.

A third alternative, under development, is to attach acid groups to a polymer such as an acrylate. Solubility, or at least dispersibility, in water is conferred by amine neutralization. Upon drying, the amine vaporizes and the acid groups serve as attachment points to the substrate. If cross-linking agents are used in the process, the resulting coating is hard, durable, and water resistant.

Problems associated with these waterborne coatings are found in their application. At low relative humidities they tend to release water explosively and cause the film to develop craters. At high relative humidities they sag. Stability also appears to be a problem.

With so many alternatives to synthetic resins in organic media, there are bound to be shifts in coatings technology to respond to the needs of various markets. Coatings manufacturers have already seen their industry move into a high technology category as the result of conventional systems containing organic solvents in abundance. These manufacturers and the finishers who use coatings are now being faced with the need to understand three or four technologies in order to select the one best suited for their requirements. The problem will get worse as each alternative technology develops and becomes even more sophisticated.

RHEOLOGICAL PROBLEMS

Colloid and Interface Chemistry

The first step in the formulation of a coating is to incorporate pigment in a vehicle. The result is a colloidal dispersion. Enormous surface area is involved, and selective absorption occurs involving competition between the resin and the solvent. Or the pigment competes and causes the system to flocculate. The rheological properties of the coating at this point and the optical properties of the dried coating are both affected by this competition.

Interfacial chemistry is involved, also, when the coating is applied to the substrate. The wet coating may spread evenly over the surface and yet the dry coating may fail adhesively. Or it may fracture. Simply solving the surface chemistry is not enough.

Surface preparation is important. The two main reasons for careful preparation of surfaces is to ensure good adhesion and to combat deterioration of the substrate. All coatings are porous to a significant extent, and their ability to protect substrates relies as much on their preferential attachment to the surface as to their barrier properties. For example, corrosion of a metal cannot be stopped simply by covering the surface with a thin film; corrosion is electrochemical in nature and can arise from irregularities in composition, aggravated by slow diffusion of water and oxidants through the film. For complete protection, one applies a primer with depolarizing ingredients, followed by a finishing coat.

Coatings Application

Rheology, the monitor of coatings formulation, becomes the controlling factor in its application. For decades coatings have been

applied by brushing, rolling, spraying, and doctoring. Recently there have evolved such techniques as curtain coating, electrodeposition, and fluidized beds, all conducted on a commercial scale. In all cases the wet films show distinctive marks or tracks which must be obliterated on drying.

Brushing and rolling are two common methods of application. The average shear rate encountered in these operations can be as high as 50,000 reciprocal seconds, a figure which may not be difficult to visualize in the case of brushing (where one divides the velocity of the brush by the coating thickness) but which is equally high in the case of roll application as the result of the pumping of coating through the roll nip.

A form of high-speed rolling called coil coating is used to finish panel stock. Printing also is a high-speed web-fed process.

High shear rates naturally generate high stresses. Some primers are formulated more for their chemical resistance than for their mechanical properties, and in some cases they may not accept a brush or roll topcoat. Spraying largely avoids stresses at the interface. Moreover, spraying imparts an even coating to irregular objects, expecially in conjunction with the use of electrostatics to attract the coating to the workpiece.

Small objects are coated by a slow-dip process wherein a lacquer is allowed to dry as the object is withdrawn, thereby avoiding sagging. Fast-dip processes are used in coating larger objects. Tumbling in the coating material is used to coat small irregular objects which have no sharp projections.

Drying and Film Formation

Trade Sales Coatings

Trade sales coatings generally are allowed to dry in the ambient environment. No control over the relative humidity, limited control over the temperature, and the need to cover imperfect substrates characterize the conditions under which these coatings dry to a useful, adherent, protective film.

The earliest natural drying oils took advantage of the oxygen present in the atmosphere to dry as thermosetting resins. In fact, these oleoresinous systems were man's first 100% solids coatings. But their residual unsaturation and to a lesser extent their prevalence of ester groups led to their large-scale replacement.

Most coatings available from retail outlets dry by evaporation. Some still contain volatile organic solvent as the main component and form coatings from the residue left behind by the evaporating solvent. Because gelation of the coating sets in before the last traces of solvent leave, the resulting film is porous.

Evaporation of water from latexes also leaves behind a porous film. The spherical particles crowd together as evaporation proceeds; at

the gelation point they adopt a close-packed array and make tangential contact with each other and with the substrate. As interstitial water begins to escape, the particles deform into the interstices.

Film formation is a more complicated phenomenon than simple hardening or freezing. It involves transient and irreversible conversions that are subject to many independent variables, including temperature, humidity, the interfaces, and the rate of drying.

Industrial Coatings

With a variety of controls over the ambience, the substrate, the application method, and the effluent, industrial installations enjoy a wider selection of film-formation methods.

There are two basic ways to produce a rigid film on a substrate: continual growth of an oligomer until it crosses the threshold between liquid and solid, and aggregation of finely dispersed polymer that has already terminated its growth as a molecule. The former method is chemical; the latter, physical. Combinations exist in which the initial stage is physical and curing is effected chemically.

Three strictly physical means of film formation are: 1) deposition of resin from solution, 2) coalescence of particulate matter from dispersion, and 3) solidification of a melt. Three strictly chemical means are: 1) reaction with a component of the atmosphere, such as oxygen or water; 2) interaction of components already present in the formulation, using heat or radiation; and 3) reaction with a reagent or in the presence of a catalyst added just before application.

The ultimate cure or final drying of many organic coatings is provided by baking. Track marks are leveled at this point, residual stresses resulting from volume shrinkage after the gelation point are minimized (but new residual stresses are introduced by shrinkage on cooling), and in general the rheological and optical properties are optimized by the use of elevated temperatures.

An alternative to baking is the use of high-energy radiation. Ultraviolet induces many photochemical reactions that are not triggered by light, and electron beams have been used in some flat line operations. Radiation is severely limited to thin coatings where the pigments do not shield the polymer from the radiation.

In conclusion: Coatings have been the pacemaker of society. As a consequence, the history of coatings science and technology abounds with examples of great achievement. Progress in applying coatings and in improving their performance has been traced to improved control of rheology and related disciplines.