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Non-Electrical Measurement Techniques for Assessing the State of Coating Systems Deterioration

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ABSTRACT

Nonelectrical methods used to characterize early degradation in coating systems
were critically reviewed with respect to their ability to provide predictive
in-service performance data. The methods reviewed were classified into those
that measure chemical changes, coating/substrate interfacial changes, and
adhesion and mechanical properties. Although many methods are used to characterize
coating systems, only limited research has been done to relate early property
changes to in-service performance. Because of the complexity of the degradation
of coating systems, it was concluded that a combination of methods will be
needed to characterize early degradation in order that service-life prediction
of coating systems can be based on these measurements.

ACKNOWLEDGEMENT

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1. INTRODUCTION

All organic coatings subjected to service environments degrade over time; however, some coatings provide better protection and remain aesthetically pleasing for a longer period of time than others. To select and specify these coating systems, performance data are necessary. In the past, selection and specification have often been based on in-service performance data, since these data were available and were considered more reliable than that obtained from short-term tests. As a result of environmental and health regulations and improving coating technology, new coating systems have been introduced for which in-service performance data are limited. Thus, there is an urgent need for short-term testing procedures that will aid in the selection, specification, and quality assurance of these coating systems.

To meet this need, the Naval Civil Engineering Laboratory (NCEL) [1] has proposed three tasks that involve the development of improved 1) experimental procedures for aging coating systems, 2) improved characterization of deterioration of coating systems, and 3) improved statistically-based methods for experimental design and analysis of data. As part of the first phase of this work, non-electrical methods of detecting and characterizing early deterioration of coating systems were reviewed and are discussed in this report.

2. CHARACTERIZATION PROCEDURES

The deterioration of a coating system can be characterized at several levels including bulk and surface degradation, integrity at the coating/substrate interface, and adhesion and mechanical properties. Procedures for characterizing coating systems at these different levels are discussed below.

2.1 DEGRADATION

Exposure of coating systems to degradation factors, such as UV radiation, elevated temperature, temperature changes, moisture, and salts can change both the exposed surface and the bulk properties of a coating. Such property changes often stem from chemical changes in the polymeric components of a coating. Thus, characterizing degradation of the polymeric portion of the coating should provide useful data for predicting coating performance. In this section, methods which are capable of characterizing early changes in the bulk and surface properties of a coating are discussed.

2.1.1 Infrared Spectroscopy

The powerful combination of specific compound identification and functional group characterization has made infrared spectroscopy (IRS) the dominant tool for studying chemical changes in coatings and related materials [2]. The recent improvements in dispersive infrared spectrometers and the development of Fourier transform infrared spectroscopy have increased the capability of IRS to study deterioration of coating materials [3,4]. For polymers in solution and transparent free films, transmission IRS is the method of choice. However, for other samples, IRS combined with reflection/absorption (RA), total attenuated reflection (ATR), diffuse reflection (DR), photoacoustic (PA), or emission (EM)

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spectroscopy are more suitable methods. All of these techniques are nondestructive and require little material. The principle of each is shown schematically in figure 1 and discussed below.

2.1.1.1 Reflection/Absorption Spectroscopy

Infrared reflection/absorption (IR-RA), also referred to as external reflection, is a nondestructive technique for studying chemical species on reflective surfaces and the chemical constituents at the interface between a thin film and a reflective metal surface. IR-RA is not suitable for studies of thick opaque coatings or of transparent coatings on non-reflective substrates. In IR-RA spectroscopy, the spectrum of a surface film is determined by comparing the reflectivity of uncoated and coated specimens (figure 1-a and 1-b) [5]. The maximum interaction between the sample and the incident radiation occurs when the radiation is parallel polarized and strikes the surface at near glancing angles (80-89 degrees). Under optimum conditions, an IR-RA spectrum of a thin film ($<$ 50 nm) is 20-50 times stronger than that obtained by the conventional IR transmission technique. For thicker films ($>$ 50 nm), a single reflection and an angle of incidence of 45 degrees are sufficient to obtain good spectra.

RA spectra are complex functions of numerous factors [6], such as the refractive indices of the films and metals, the absorption constant and the thickness of the film, and the angle of incidence. Thus, the shape, position and intensity of strongly absorbed bands obtained by IR-RA are quite different from those obtained by IR transmission.

IR-RA has been used to study the structure and orientation of monolayers adsorbed on the surface of polished metals [7] and for studying chemical changes in films resulting from degradation. For example, it was used 1) to aid in identifying the role of the metal substrate on the mechanisms of photolytic, thermal, and environmental degradation of a polycarbonate coating [8]; 2) to study thermal, oxidative, and photo-degradation of various epoxy resins [9,10]; 3) to study the degradation of epoxy, polybutadiene, and polyurethane coatings on steel exposed to a corrosive environment [11,12]; and 4) to identify chemical reactions occurring during the zinc-phosphate coating of iron [13]. It has also been used extensively for studying the oxidation of polyethylene, polybutadiene, and poly(1-butene) [14,15,16,17].

2.1.1.2 Attenuated Total Reflection Spectroscopy

A widely used technique for studying the chemical changes on the surface of coatings is infrared attenuated total reflection spectroscopy (ATR). ATR is also known as internal reflection spectroscopy, multiple internal reflection spectroscopy, or sometimes as frustrated multiple internal reflection spectroscopy. ATR is a versatile technique that can be used to study the chemistry of thin and thick films on a wide range of substrate materials. Harrick [18] developed the technique, and discussed its theory and application.

In ATR spectroscopy, radiation is introduced into a prism (internal reflection element) that is in intimate contact with the sample (figure 1-c). The radiation is introduced into the prism at an angle above the critical angle to achieve total internal reflection. As the incident wave is absorbed by the

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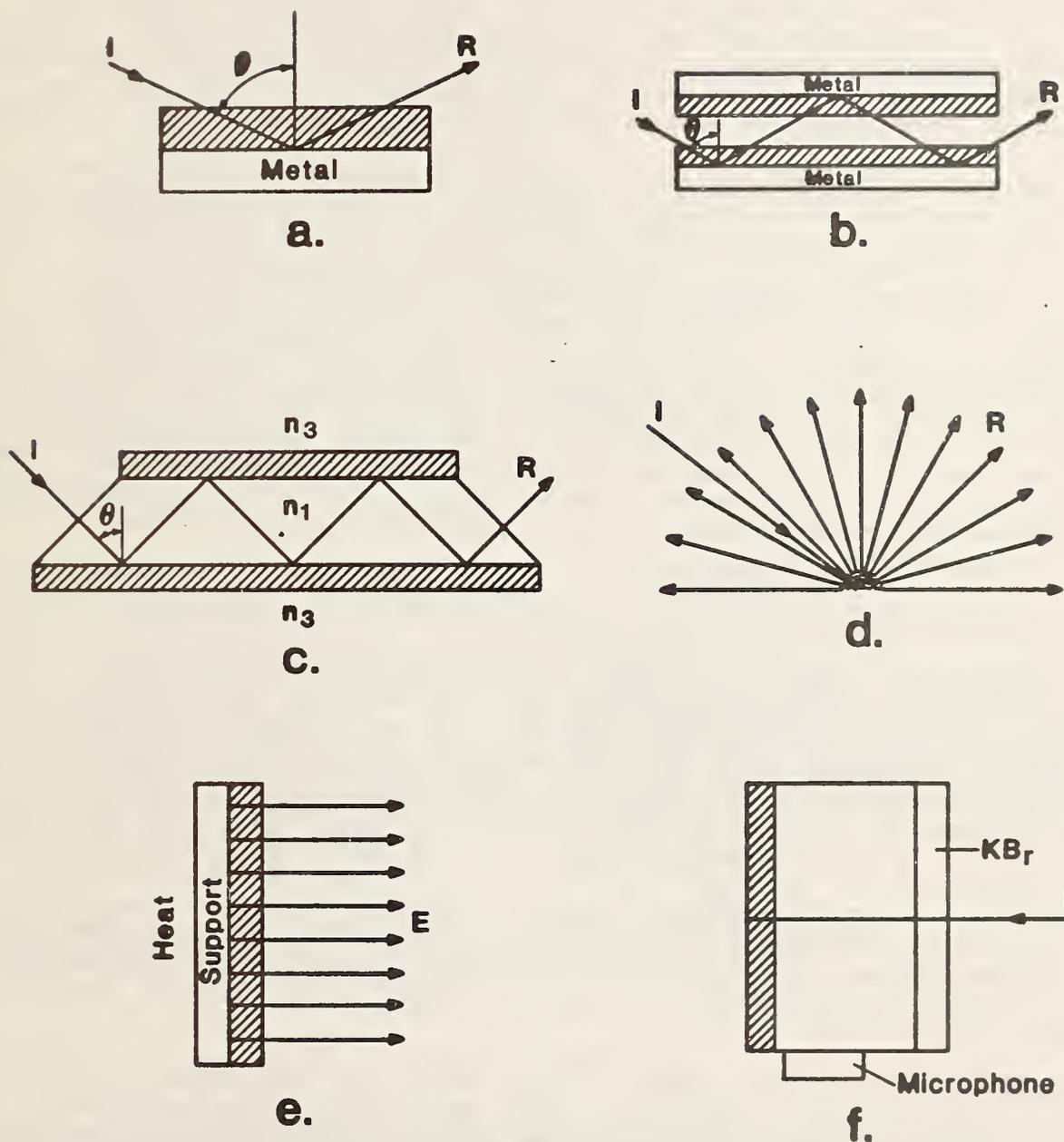Figure 1. Schematic representation of infrared spectroscopy techniques: a. and b. reflectance/absorption, c. attenuated total reflectance, d. diffuse reflectance, e. emission, f. photoacoustic, where I is the incident beam, R is the reflected beam, θ is the angle of incidence, ni is the refractive index of the coating, E is the emission, and KBr is the material of the transparent window.

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sample, the reflected radiation loses energy, giving rise to an ATR spectrum. The depth to which the radiation penetrates into the sample is usually a few micrometers but depends on the refractive indices of the prism and sample, the angle of incidence, and the wavelength of the incoming radiation. For ATR to be successful, good surface contact between the sample and the internal reflection element is essential. Soft, flexible coatings, which make continuous contact with the prism, produce excellent spectra, but hard or rough coatings give poor and nonreproducible spectra since achieving intimate contact is difficult.

IR-ATR has been widely used for various analytical problems in coatings and related materials [19,20]. Reports of its use as a sensitive surface analytical method for investigating the degradation of coatings are abundant. For example, it has been used for studying the oxidation, decomposition, and plasticizer leaching of a number of thermoplastic coatings, and for studying the rupture of crosslinks in thermosets exposed to accelerated and outdoor environments [21]. ATR has also been used to study accelerated and natural weathering degradation of poly(vinyl chloride), polyurethane, epoxy, and alkyd coatings [22,23,24], and the UV degradation of ethyl cellulose [25]. Other applications of ATR include determining the relationships between changes in spectra and service life of coatings [26], changes in the spectra and the adhesion properties of coatings as a function of exposure [27,28], and detecting the formation of corrosion products derived from chelating agents at the metal/coating interface [29].

2.1.1.3 Diffuse Reflectance, Photoacoustic, and Emission Spectroscopy

Diffuse reflectance (DR), emission (EM), and photoacoustic (PA) Fourier transform infrared (FTIR) spectroscopies have also been used for detecting chemical changes on coating surfaces [30,31]. The use of these techniques in the mid-IR (2.5 to 50μm) is now possible because of the improved sensitivity of FTIR spectrometers. In DR spectroscopy, light incident upon a solid or powdered surface is diffusely scattered and the scattered light is collected and directed to the detector (figure 1-d) [32]. The DR technique requires little sample preparation and has good sensitivity. In addition, DR spectra can be obtained from very small amounts of material. However the depth of penetration is wavelength dependent and the particle size of the powder must be uniform for quantitative studies. Diffuse spectroscopy has been used to study organosilane coupling agents on glass fibers [33], curing of epoxy resins [34], and coatings on paper substrates [35].

Emission spectroscopy (EM) is based on the principle that the radiation emitted is equal to that absorbed (figure 1-e) [36]. EM is particularly useful for obtaining spectra of remote samples and samples at high temperatures. Emission spectra can be obtained at room temperature, but the quality of spectra is better for samples having temperatures in the range of 50-150°C. The interference of background radiation is an inherent disadvantage of EM. In coatings related applications, EM has been used to determine the oxide formed during high temperature oxidation of metals [37].

Photoacoustic infrared spectroscopy (PA) is based on the generation of acoutsic waves when a sample is exposed to modulated radiation (figure 1-f) [38]. In dispersive infrared instruments, choppers are used to modulate the incident

infrared radiation. But in Fourier transform infrared spectrometers, no special choppers are needed since the interferometer acts as a modulator. In this technique, the sample is placed in a closed cell containing a sensitive microphone which is contructed with a window that is transparent to infrared radiation. When radiation is absorbed by the sample, the temperature of the sample surface increases, thereby heating the gas causing an increases in gas pressure. Thus, modulated radiation absorbed by the sample produces a pressure modulation in the gas and a sound is generated at the frequency of the radiation modulation and is detected with the microphone. By scanning over the wavelength range of interest, a PA spectrum is produced. The advantages of PA are that little sample preparation is required, it is relative insensitive to sample surface morphology, and it is suitable for studying surface phenomena. Disadvantages of PA include a low signal-to-noise ratio making long scan times necessary and difficulty in obtaining quantitative data. Information obtained from PA spectra has been compared with that obtained from diffuse reflectance or attenuated total reflectance [39]. In addition to obtaining spectra of powdered inorganic and organic material, foamed polymers and polymer films [40], PAS has been used for depth profiling within a film and for obtaining spectra of materials beneath thin films [41].

2.1.2 X-ray Photoelectron Spectroscopy

In X-ray photoelectron spectroscopy (XPS), also commonly known as electron spectroscopy for chemical analysis (ESCA), binding energies of electrons ejected from molecules close to the surface as a result of X-ray bombardment are measured [42]. This method provides information on the structure, chemical bonding, and elemental composition of the surface of a sample. The typical sampling depth of XPS is 2 nm. Thus, the technique complements other traditional techniques, e.g., infrared spectroscopy (penetration depth up to 5μm), microscopy, and surface free energy determinations, for surface characterization of organic solids. The disadvantages of XPS include the need for an ultra-high vacuum, sensitivity to surface contamination, and inability to provide the detailed chemical information that can be obtained with IR spectroscopy.

Applications of XPS for investigating chemical changes on polymer surfaces due to surface modifications or weathering are extensive [43,44]. It has also been used for studying the degradation of coatings [45], corrosion of base metals [46], and the deterioration of metals protected by coatings [24,47,48].

2.1.3 Electron Spin Resonance and Other Techniques

Electron spin resonance spectroscopy (ESR), also known as electron paramagnetic resonance spectroscopy (EPR), provides information on the structure and concentration of free radicals formed in polymers as a result of degradation [49]. It is based on the splitting of otherwise degenerate electron energy states by an external magnetic field. Although ESR is capable of detecting small concentrations of radicals, ESR measurements often must be made at low temperatures and the spectra are usually difficult to interpret. ESR has been used to follow the radical processes in the UV radiation of polymers [50,51] and the photodegradation of coatings [24,25].

Other less common methods used for studying the degradation of coatings include luminescence, nuclear magnetic resonance (NMR) and UV-visible spectroscopies, gas chromatography (GC), GC-FTIR, mass spectroscopy (MS), thermal analysis, and surface free energy determinations.

2.1.4 Measurements of Crosslinking

Chemically reactive species, such as free radicals, are capable of reacting with one another or with themselves to form a crosslinked (3-dimensional) polymer. Although crosslinking is a useful reaction for increasing the thermal and chemical stabilities of thermoplastics, it may be undesirable when the reaction occurs in-service. Examples of undesirable property changes caused by crosslinking reactions include increased modulus, increased glass transition temperature [52,53] (making the material more brittle), decreased compatibility of polymers and plasticizers (causing plasticizers to exude), film shrinkage, cracking, and film delamination. For thermoset coatings, where the degree of crosslinking is already high, further crosslinking will result in undesirable property changes similar to those in thermoplastics. Insufficient crosslinking also may result in poor coating performance [54]. Thus, information on the structure of crosslinked polymers, such as crosslink density or the molecular weight of chains between crosslinks, is important for predicting the performance of a coating.

Characterization of cross-linked polymers is more difficult than that of linear polymers. Typically, only lightly-crosslinked polymer structures above their glass transition temperature have been characterized. Research to characterize highly-crosslinked polymers or lightly-crosslinked polymers at temperatures below their glass transition temperature has been limited [55]. Techniques for characterizing crosslink density include solvent-induced swelling, elastic modulus and chemical analysis. These techniques provide a measure of the average crosslink density and are briefly described below.

2.1.4.1 Swelling

If an uncrosslinked polymer is soluble in a liquid, then the same polymer when crosslinked will swell in this liquid. The theory of swelling behavior of lightly-crosslinked polymers in solvents is fairly complete [56]. The swelling ratio is generally expressed as

$$\text{Swelling ratio} = q = \frac{\text{volume of swollen gel}}{\text{volume of unswollen gel}} \quad (2)$$

The number average molecular weight between crosslinks, M_c, is directly related to the swelling ratio. For $M_c \gg 5000$, the relationship is quite good. But for any polymer-solvent system, the generalization that as M_c decreases the swelling decreases appears to hold. Hence, swelling measurements may be useful in characterizing the network structure of highly-crosslinked polymers such as epoxy or polyurethane coatings.

2.1.4.2 Elastic Modulus

Based on kinetic theory, the equilibrium shear modulus of elasticity, G, at temperatures well above Tg is related to the crosslink density by [56]

$$G = dRT/M_c \{1-2M_c/M_n\}, \qquad (3)$$

where d is the density, T is the absolute temperature, R is the gas constant, and M_n is the molecular weight of the uncrosslinked polymer. Although this equation is valid only for lightly-crossed linked polymers, the elastic moduli of highly-crosslinked polymers appear to be nearly independent of the chemical structure of the network and to depend primarily upon the tightness of the newwork structure [56]. Thus, the elastic moduli of highly-crosslinked polymers may provide a good empirical assessment of the degree of crosslinking.

2.1.4.3 Chemical Analysis and Other Methods

Chemical methods used to characterize crosslink density are based on the principle that if one knows the concentration of a crosslinking agent, and if it reacts completely according to one's hypotheses of the chemical reaction, then it is possible to estimate the average M_c. Among chemical methods that have been employed with limited success are UV, IR, X-ray, Raman and NMR spectroscopies [57].

Other methods of determining degree of crosslinking involve measurements of glass transition temperature, creep [58], and mechanical damping [59]. These techniques are largely empirical. In spite of the lack of good theoretical justification, these methods are useful because of their sensitivity and ease of measurement, especially if they are calibrated by other techniques such as swelling or shear modulus.

2.1.5 Microscopy

In addition to overall surface deterioration of coatings, localized surface defects such as craters, pinholes, and vortex cells mar the appearance of coatings and may become sites for coating failures. Microscopy, both light and scanning electron microscopy (SEM), has been used extensively to follow changes in surface appearance and to detect and analyze surface defects [60]. For example, light microscopy has been used to monitor changes in time of the surface topology of epoxy coatings exposed in laboratory salt spray and sulfuric acid immersion tests [51]. Other studies have reported on the effects of chalking on the microscopic surface appearance of coatings [61,62,63], the detection of craters in coating films [64], and the spread of corrosion beneath an acrylic film [65].

2.2 COATING/SUBSTRATE INTERFACE

Deterioration of many coating systems begins at the interface between the coating and the substrate. Thus, methods that can be used to detect changes at the interface may provide information on early deterioration of a coating system. Many techniques have been used to study the metal/coating interface

[66,67]. In addition, research is being done to expand the use of established surface analytical techniques, such as secondary ion mass spectroscopy (SIMS) and variable angle ultrasoft X-ray fluorescence spectrometry, to interfacial studies [68,69]. Nondestructive and destructive techniques that have been used to assess changes at the coating/substrate interface are discussed below.

2.2.1 Infrared Thermography

Corrosion products on steel substrates and air- or water-filled blisters beneath intact coatings can be detected nondestructively using infrared thermography [70]. In this procedure, coated specimens are heated to a temperature 20-50°C above ambient temperatures and evaluated using a thermographic camera. Due to differences in emissivity and thermal conductivity, corrosion spots and blisters can be distinguished from nondeteriorated areas of the coating system.

The capability of this technique to distinguish corroded from non-corroded areas increases as the temperature of the substrate increases, but decreases as the coating thickness increases [71]. For example, corrosion spots on steel are easily detected under a 0.15 mm (0.006 in.) thick layer of pigmented epoxy coating, when the steel panel is heated to 60°C, but barely detectable when the panel temperature is 40°C. Similar results were obtained for pigmented alkyd coatings on steel substrates. Corrosion spots could not be detected under zinc-rich inorganic coatings that were on the order of 10 micrometers thick.

Air-filled blisters, that may or may not be detected visually, beneath organic coatings on wood and metals are easily detected thermographically. Water-filled blisters under coatings on metals can be detected but are difficult to distinguish in thermographic images from corrosion spots.

The spatial resolution of the method depends on the area of the field of view of the camera. Up to a point, the smaller the imaging area, the smaller the defect that can be detected. For example, when the imaging area is about 20 mm by 20 mm, rust spots or blisters having a 0.5 mm diameter can be detected.

Advantages to the use of infrared thermography include its ease of operation, interpretation, and analysis of images [72]. The major disadvantage of infrared thermography is that a coating must be transparent to radiation in the wavelength range of the thermographic detector in order for corrosion products to be detected beneath the coating; blisters are detected under opaque coatings.

2.2.2 Thermal Wave Microscopy

Thermal wave microscopy (TWM) can be used to detect minor variations in thermal properties of materials. The basic processes involved in a TWM experiment are schematically illustrated in figure 2 [73]. The sample is exposed to a focused, modulated beam such as a laser or an electron beam such as one in a scanning electron microscope. As the surface is scanned by the beam, energy is absorbed by the sample causing local periodic heating and thermal expansion of the surface. The periodic heating results in the formation of diffuse highly-damped thermal waves, whose wavelength is a function of the thermal conductivity,
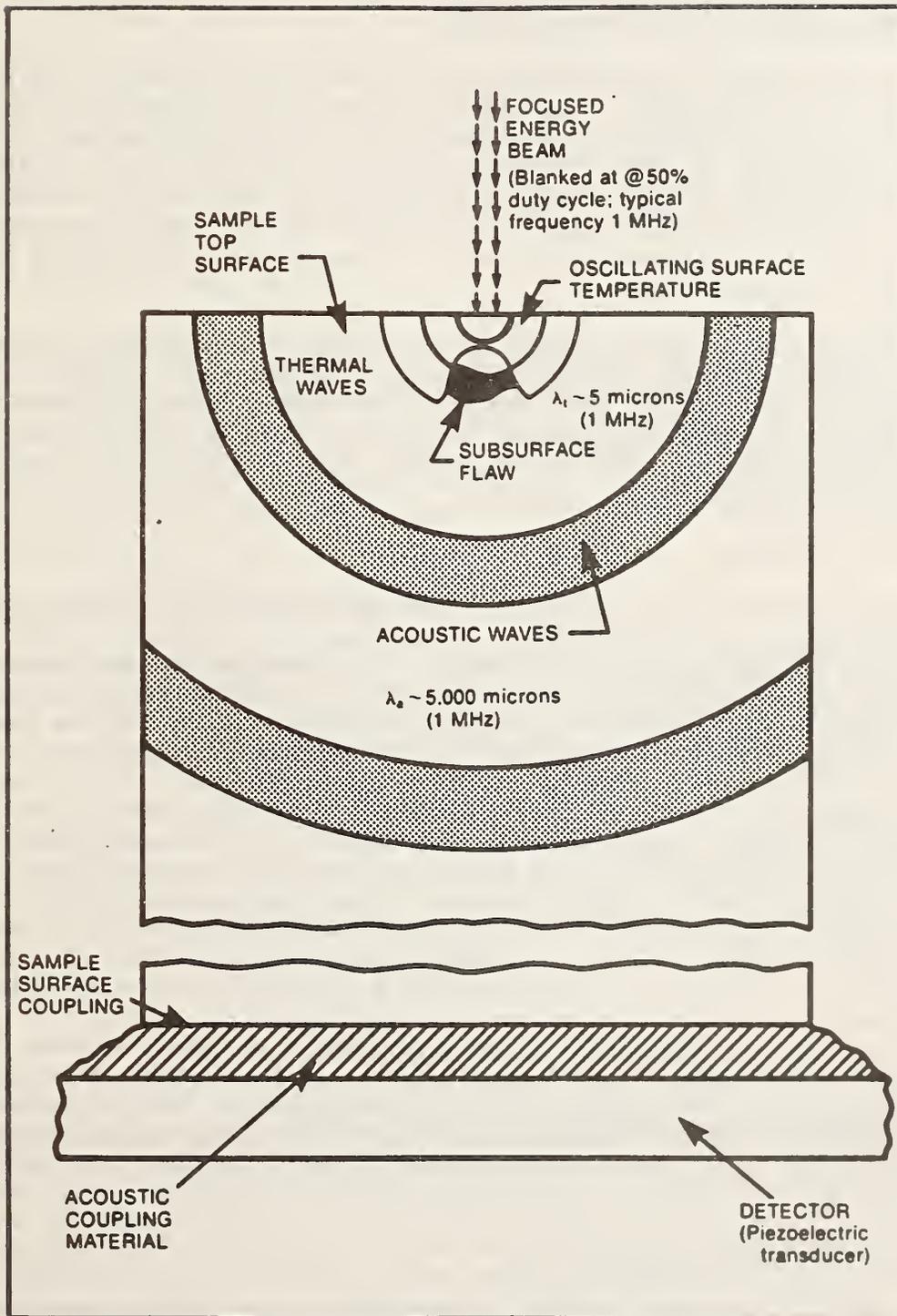
Figure 2. Schematic representation of thermal wave microscopy

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density, and specific heat of the material and the modulation frequency of the beam. Thermal waves behave similarly to other propagating waves in that features of materials different from the bulk will reflect and scatter them. Images of these features are obtained by detecting the thermoacoustic waves produced in the sample by the thermal waves.

The resolution of thermal wave microscopy is controlled by the spot size of the beam and the thermal wavelength. The resolution obtained for thermal conductors ranges from 0.2 mm for a modulation frequency of 100 HZ to 200 nm for a modulation frequency of 100 MHz. For poor thermal conductors, e.g., organic coatings, the resolution ranges from 0.02 mm at 100 HZ to 20 nm at 100 MHz. The depth of penetration of thermal waves is controlled by the signal-to-noise ratio and the thermal wavelength. The depth of penetration is typically about 4 times the spatial resolution.

In early investigative work [74], small corrosion spots (5μm diameter) under thin (2.5μm) pigmented alkyd coatings and thicker (10μm) clear coatings were observed. This method provides good resolution of defects, but may have limitations imposed by scanning electron microscopy, that is, sample size, high vacuum, and heating effects. The use of a laser beam, instead of an electron beam, may solve these problems.

2.2.3 Acoustic Emission

Acoustic emission (AE) is a technique that has been used for detecting crack formation and propagation in materials. It has been used extensively for evaluating crack growth in metals. Recently, the technique has also been applied to characterizing coating deterioration [75]. The principle of the technique is that any sudden movement within a material results in the release of acoustic energy which may be detected by a piezoelectric device.

The signals produced are complex, although in principle they can be characterized by their shape, frequency, amplitude, and the decay rate. Frequency and amplitude distributions were measured in the reported work on coatings. In these experiments, acoustic signals generated by pulling paint/substrate samples in tension were detected. Differences in acoustic emissions of an alkyd coating on aluminum foil were detected between unexposed samples and samples exposed for 300 hours and 600 hours in a xenon-arc weathering machine [75]. Differences in acoustic emissions were also observed between dry coatings and wet coatings (coatings tested immediately upon removal from a 100% relative humidity environment) and between epoxy coatings applied to phosphated and nonphosphated steel after weathering [75]. Research to detect acoustic emissions associated with the formation of interfacial corrosion and the subsequent microcracking of the paint above the corrosion products have not, as yet, been successful [76,77].

2.2.4 X-Ray Photoelectron Spectroscopy

X-Ray photoelectron spectroscopy (XPS), a sensitive surface analytical technique discussed in section 2.1.2, has also been used for interfacial studies [47]. In most of these studies, the coating was removed from the substrate and the interfacial areas of both the substrate and coating film were examined.

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Although a destructive method, it has provided useful information in the analysis of corrosion-induced adhesion loss of coatings and adhesives. For example, Dickie and coworkers [16] used XPS to show that, for some coatings, corrosion-induced delamination occurs within the coating close to the interface. They also found that the rate of delamination could be decreased by increasing the polymer crosslink density or by phosphating the steel surface. Other applications of XPS include studying 1) the interaction between iron oxide surfaces and polybutadiene coatings [78], 2) the degradation of coatings on galvanized steel [47], 3) the adhesion mechanism of chromated and nonchromated tin protected by organic coatings [79], and 4) adhesion improvement and corrosion reduction of coated metals associated with pretreatments [80].

2.2.5 Infrared Spectroscopy

Both reflection/absorption (RA) and attenuated total reflection (ATR) have been shown to be sensitive characterization techniques for interfacial studies. The literature on the applications of infrared spectroscopy to the study of polymer/metal interfaces has been reviewed recently [4,81]. In addition to the studies of polymer degradation discussed in section 2.1.1.1, RA spectroscopy has been used in studies of the orientation of polymer molecules on metal surfaces [82,83] and the interactions between polymer molecules and metal surfaces [84,85].

2.2.6 Auger Electron Spectroscopy

Auger electron spectroscopy (AES) measures the Auger electrons emitted from a surface, induced by electron bombardment of the surface [86]. It is another surface analytical technique that has often been used as a destructive method for studying the coating/metal interfacial region. Changes in the type and concentration of elements present on the surfaces examined have been determined. The sampling depth of AES is about 2 nm and the spatial resolution is on the order of 100 nm. AES is sensitive to elements with atomic number greater than 2. A disadvantage of AES is that it may cause decomposition of metal oxides and organic materials due to the high energy of the electron beam. Nevertheless, van Ooij [47] has used this technique, in combination with x-ray diffraction and XPS, to study the mechanisms of failure of zinc-rich primers on steel and the adhesion of paint to galvanized steel.

2.2.7 Ellipsometry

Ellipsometry is an optical technique that can be used to measure the thickness of a metal-oxide film beneath a coating by determining the change in the state of polarization that light undergoes when it is reflected by the metallic surface [87]. Although chemical information is not obtained using ellipsometry, Ritter [88] has shown that ellipsometry combined with electrochemical measurements can be used to follow changes in the metal-oxide film thickness and detect the development of remote cathodic areas under a transparent film, thereby aiding in the understanding of the mechanisms of delamination of coatings on steel.

2.3 ADHESION

For a coating to perform any of its functions, it is necessary that the coating remain bonded to the substrate. To characterize changes in bonding strength, it is helpful to understand the mechanisms by which debonding occurs. Several mechanisms have been proposed to explain the reduction or loss of bonding of coatings to substrates. For coatings on metals, these mechanisms are related to displacement of the coating by water at the interface [89], commonly referred to as adhesive failure, and to debonding associated with the high concentration of alkali at the interface due to corrosion reactions, commonly referred to as cathodic delamination. The reported mechanisms of cathodic delamination include displacement of the coating by aqueous solutions [90,91], degradation of the coating resin adjacent to the interface [92,93], and degradation of the protective metal-oxide film [94,95]. The mechanism has also been reported to depend on the resin type [96,97], the corrosion environment [98,99] and the pretreatment [100]. Although factors controlling cathodic delamination have not been completely determined [101,102], it appears that the chemical properties of the resin and the corrosion environment are the primary factors controlling the mechanisms of cathodic delamination.

Much less work has been done in studying the mechanism of adhesion loss of coatings on non-metallic substrates. Water displacement, degradation of the resin by alkali, and deterioration of the substrate surface, such as UV oxidation of wood, are the primary proposed mechanisms of debonding of coatings on wood and concrete [103,104,105].

2.3.1 Techniques for Measuring Bond Strength

In this section, methods to measure a so-called "practical" adhesion of coating systems are discussed [106]. Practical adhesion combines factors associated with adhesive and cohesive failure and other properties of the coating system. These methods have been reviewed recently by Bullet and Prosser [107]. Often these methods do not provide results that can be used to distinguish between adhesive or cohesive failure of the coating system but they do provide a technique for assessing change in practical bonding strength of a coating system as it ages and may be useful in the selection and specification of coatings.

2.3.1.1 Destructive Techniques

Several standard testing procedures are available for destructive adhesion testing. These include the "x" and cross-cut tape tests, the knife stripping tests, and direct pull-off tests, such as ASTM D3359, ASTM D2197 and ISO 4632, respectively. Results of tape tests tend to be highly subjective. However, they are widely used in the paint industry due to their simplicity and their ease of sample preparation. Pull-off tests, in which either laboratory universal testing machines or portable devices are used, are commonly used methods to measure tensile adhesion [108,109]. Although these techniques yield quantitative results, the results are seldom reproducible [110]. Several factors influence the results including substrate stiffness, loading fixture design, rate at which the assembly is pulled apart, secondary adhesive, and assembly alignment [111,112]. Because a loading fixture is cemented to the coating surface with

an adhesive, this method is suitable to in situ measurements in which the adhesive will cure.

Another destructive adhesion test is the "blister test" [113]. In this test, gas pressure is applied to the underside of a coating through a small hole in the substrate. The pressure required to lift a coating from the substrate is measured and the interfacial energy is calculated. Based on a limited amount of research, the reproducibility of this method appears to be good [114]. However, rather elaborate sample preparation is required.

2.3.1.2 Nondestructive Techniques

One nondestructive technique used to follow the deterioration of a coating/substrate bond is the ultrasonic-impedance technique [115]. In this test, a shear wave pulse of 5 to 30 MHz is transmitted obliquely to the coated surface of a substrate with nearly homogeneous reflectance properties. It is reflected off the surface opposite the prism surface from which it was transmitted and returned to the piezo-electric crystal, via the surface of oblique incidence. Changes in the intensity of the reflected pulse appear to correlate with changes in coating properties including adhesion. This technique has been used to follow the cure, setting [116], and adhesion failure [117] of various types of coatings in controlled environments on a quartz substrate. Although the results of early work were encouraging, its use appears to be limited, since the technique requires that the substrate have nearly uniform reflectance properties.

In another nondestructive method, reflected acoustic pulse, delaminations were observed in an epoxy/steel coating system [118]. By scanning the transducer over the specimen, coating delaminations were detected and the thickness of the coating (0.2 mm to 0.6 mm) and the depth of each delamination were determined.

Funke [119] proposed another nondestructive adhesion test, the cross-over time test. In this test, water up-take of fixed and free films placed in a high humidity environment is measured as a function of time. The time at which the up-take of water by the fixed film equals that of the free film is called the cross-over time. Loss of adhesion is assumed to be associated with the greater up-take of water of the fixed film. Thus, the cross-over time may indicate when the coated metal begins to lose adhesion if the primary mechanism of adhesion failure is water displacement of the coating.

2.4 MECHANICAL PROPERTIES

Mechanical properties of coatings are known to be related to the chemical composition of a coating [120]. Thus, changes in mechanical properties that accompany aging may be useful indicators of early coating deterioration and predictors of service life. Researchers have measured changes in mechanical properties, such as internal stress, internal strain, tensile stress-strain, and dynamic moduli, in efforts to relate these changes to durability. Results of their works are discussed below.

2.4.1 Internal Stress

As a coating cures, via solvent-loss, crosslinking, or oxidation, stresses are developed in the coating system. These stresses have been measured to range from 3.0 to 14.0 MPa (500 to 2000 psi) [121,122,123]. As the coating system ages, the strength of the film usually decreases and, in some cases, the stresses in the film increase. Failure of the film occurs when the internal stress exceeds the adhesive or cohesive strength of the film. Typical failure modes include cracking, peeling, and blistering.

Internal stress can be measured in several ways. The most common techniques use a freely supported cantilever beam [124,125,126], a clamped cantilever beam [122,124,127,128], or photoelastic material in which either the substrate [129,130] or the polymer [131,132] is the photoelastic material. Internal stress equations for the freely supported and clamped cantilever beams have been derived by Corcoran [124] using plate theory. For a freely supported or clamped cantilever beam, the coating is applied to one side of a metallic gauge stock and allowed to cure. As the coating cures, stresses develop in the film causing the metallic substrate to deflect. Deflection is usually measured with a microscope.

Knowing the moduli of elasticity, Poisson's ratios, and the thicknesses of the metal and coating, and the deflection of the gauge stock, one can compute internal stress. Results of internal stress measurements from clamped and freely supported cantilever beam experiments compare well [127,128].

Photoelastic methods have been used mainly by Russian researchers. In these methods, a glass or transparent amorphous polymer is used as a photoelastic substrate for the coating. As the coating cures, stresses develop in the photoelastic material changing its birefringent pattern. The principal stresses in the photoelastic material are computed from this birefringent pattern [133].

Many material variables affect internal stress including the resin type, molecular weight, modulus of elasticity, Poisson's ratio, filler concentration, plasticizer concentration, and coating thickness. Of these variables, the effects of plasticizers, including the solvent, fillers, and coating thickness on internal stress have been studied most. In general, as plasticizers are lost, the magnitude of the internal stress in the film increases [121,134]. In contrast, up to a critical concentration level, as the concentration of filler increases, the magnitude of the stress in the coating tends to increase [127,128,135]. At concentrations above this critical level, internal stress decreases. Coating thickness also influences internal stress. As the thickness of the coating increases, the magnitude of the stress at the interface between the substrate and the coating increases [130, 136]. Environmental variables, such as temperature, humidity, and ultraviolet radiation, also affect the internal stress in the coating. In general, the higher the temperature or relative humidity, the lower the stress in the film [122]. Ultraviolet radiation tends to cause scissions on the surface of the polymer which effectively reduce the coating thickness. The longer the exposure to ultraviolet radiation, therefore, the greater the decrease in the internal stress in the coating [122].

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In related procedures, strength and elongations are typically measured using free films, although coatings are often exposed on tin substrates. In this case, free films are obtained by amalgamating the tin prior to testing. Both strength and elongation typically decrease with weathering, with a greater decrease in elongation than strength. Thus, elongation is often the preferred indicator of deterioration [137,138].

2.4.2 Residual Strain

Residual strain is relatively easier to measure than internal stress and is used as an alternate method to determine internal stress in coatings [135,139,140,141,142]. The rationale behind measuring residual strain is that the coating will not fail as long as the residual strain remains below or does not exceed the interfacial work of adhesion [142].

Residual strain has been determined in two ways: 1) theoretically using plate theory [143], and 2) experimentally by applying a coating to a tin substrate, amalgamating the tin, and then observing dimensional changes in the film [139]. Limited available data shows that residual strain increases as solvent is lost and decreases as filler concentration increases [135,139].

2.4.3 Dynamic Tests

Dynamic mechanical tests, such as torsional braid analysis (TBA) and those in which a sample is flexed or stressed at a constant rate are being used to study the curing processes of coatings and follow changes in mechanical properties during aging [137,144]. In torsional braid analysis (TBA) tests, torsional oscillations are induced in the specimen and the natural frequency and decay of these oscillations are measured. From these measurements, storage and loss modulus properties are calculated. TBA measurements have been used for determining the time for thermo-oxidative embrittlement of poly(phenylene oxide) [144]. Other dynamic flexing tests, such as cyclic bending [136], have been used with limited success in predicting cracking in exterior exposures on wood.

3. SUMMARY AND RECOMMENDATIONS

Techniques for detecting early changes in chemical properties of coating systems are summarized in figure 3. Of these techniques, electron spin resonance (ESR) and fluorescence appear to be most sensitive. The information obtained from these techniques, however, is often complex, hard to interpret, and qualitative. X-ray photoelectron spectroscopy (XPS) provides early detection of surface deterioration, but sample preparation and measurement technique are difficult. Infrared spectroscopy provides more detailed chemical information than ESR, fluorescence, or XPS, but it is less sensitive to chemical changes. Very little chemical information can be deduced from SEM, surface free energy, and gravimetric techniques.

Adhesion and mechanical properties are known to be related to service life. However, present methods to measure practical adhesion are subjective and the observations are often hard to reproduce. Analytical techniques that can
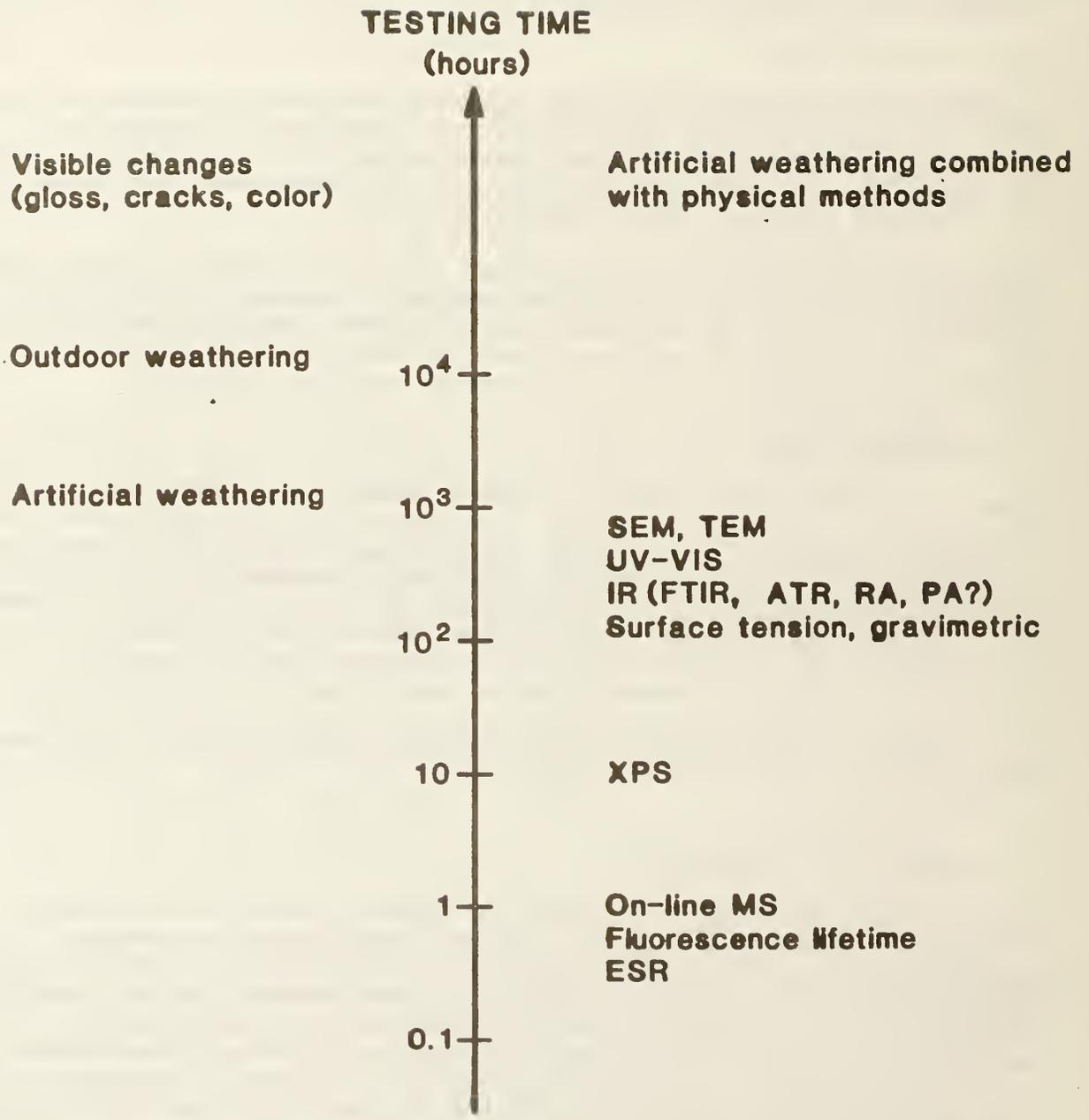
15

Figure 3. Summary of characterization procedures with respect to their ability to detect early degradation of coatings.

detect changes in interfacial bonds may be more suitable for assessing changes in adhesion than practical adhesion measurements. In situ mechanical property measurements are possible and limited research indicates that changes in some mechanical properties may be useful in predicting the service life of coating systems.

Among the techniques used to assess deterioration of the interface, infrared thermography and thermal wave imaging combined with image analysis appear to be the most promising. These techniques complement each other in that infrared thermography can assess corrosion and blistering under thick coatings, as well as visible engineering properties, such as corrosion, blistering and cracking, while thermal wave imaging can detect micrometer sized defects under thin coatings. Reflectance infrared spectroscopy can be used to obtain detailed chemical information of thin coating/reflective metal substrate systems while destructive techniqes such as X-ray photoelectron and Auger spectroscopies provide complementary chemical information.

Many of the analytical techniques described in this report have been used successfully to characterize the degradation and predict the durability of relatively pure polymeric materials [145]. Unfortunately, applications of these techniques to the study of coating systems is limited. Since coating systems are usually more complex than polymers, it is difficult to assess the relative merits of each of the techniques for characterizing coating system degradation.

In order to develop charaterization procedures that can be used to improve selection, specification, and quality assurance of coating systems, it is necessary to develop 1) procedures that can be used to quantitatively evaluate the engineering properties of a coating system, 2) procedures that are capable of quantitatively detecting early changes in a coating system which can be related to engineering properties, and 3) mathematical relationships between the changes in the chemical properties and the engineering properties. It is unlikely that a single characterization technique will satisfy all three requirements; instead the success of this endeavor will be greatly increased if a systematic investigation of degradation of coatings is used in which the factors causing degradation are unraveled one at a time.

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11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant
bibliography or literature survey, mention it here)

Nonelectrical methods used to characterize early degradation in coating systems were
reviewed and critiqued with respect to their ability to provide predictive in-service
performance data. The methods reviewed were classified into those that measure
chemical changes, coating/substrate interfacial changes, and adhesion and mechanical
properties. Although many methods are used to characterize coating system degradation,
very limited research has been done to relate early property changes to in-service
performance. It was concluded that because of the complexity of the degradation of
coating systems, a combination of methods will be needed to characterize early
degradation to the extent that service-life prediction of coating systems can be
based on these measurements.