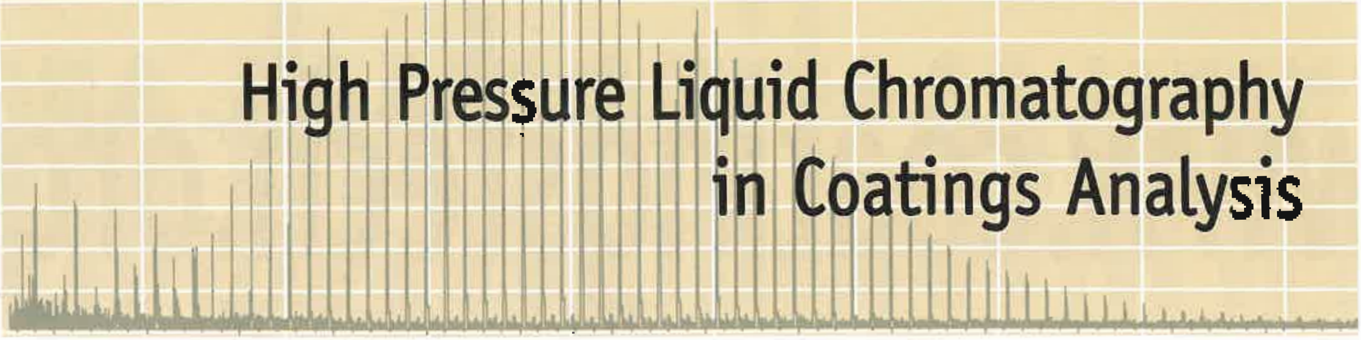

High Pressure Liquid Chromatography in Coatings Analysis

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High pressure liquid chromatography (HPLC) is an established standard analytical tool for the analysis of coatings and related materials. An extensive body of literature has been published in various analytical and related fields' journals on HPLC methods. These methods have been developed and used in the determination of small to very large molecules ranging from small organic impurities to polymer resins. In addition, fundamentals of HPLC and related methods have also been extensively covered in the literature and the reader is encouraged to review them as needed. The objective of this article focuses mainly on the applications of HPLC and gel permeation chromatography (GPC) methods in the analysis of coatings.

INTRODUCTION

Liquid chromatography (LC) is probably the most commonly used method of separation and analysis of chemical compounds and ions in solution. Increased understanding of liquid chromatography since its invention in 1906 has led to fascinating and dramatic development and usage of the technique in a variety of applications.[1-7] For example, instrumental advances, automation, and miniaturization of the technique has brought about the development of significant methods utilizing complex separation mechanisms, such as electrophoresis, supercritical fluid chromatography, microscale separations, and numerous powerful hyphenated techniques such as online and off-line liquid chromatography/nuclear magnetic resonance (LC-NMR), and very efficient multi-detector analysis systems for extremely complex analyses.

High pressure liquid chromatography (HPLC) is an analytical technique used for separation of low-to-moderate molecular weight compounds of resins. The instrumentation for HPLC and size exclusion (SEC) or gel-permeation chromatography (GPC) is similar, but the columns differ. A schematic diagram of HPLC components is shown in *Figure* 1.

HPLC components consist of the following: (a) solvent and/or solvent mixture, (b) solvent delivery system (pumps and controller), (c) sample delivery system (manual or automatic injection), (d) a column suitable for the separation of interest, (e) a detector system, and (f) a data system.

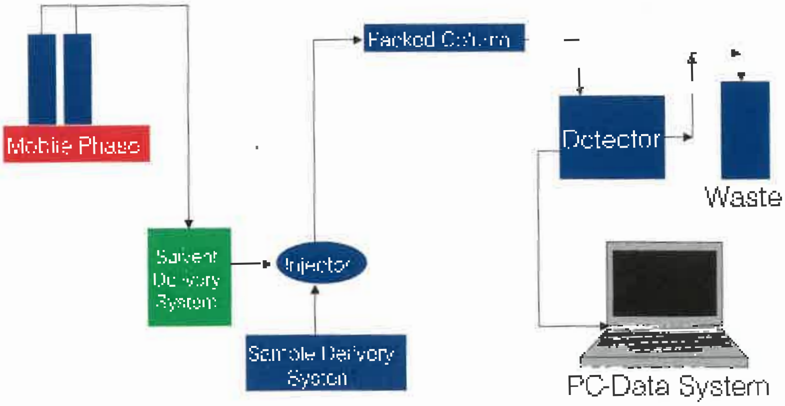
TYPES OF SEPARATION MECHANISMS IN LIQUID CHROMATOGRAPHY

There are numerous types of separation mechanisms in liquid chromatography. The most important ones include: affinity chromatography, ion chromatography, capillary electrophoresis, normal phase chromatography, reverse phase chromatography, supercritical chromatography, and microscale chromatography.

Affinity Chromatography

Affinity chromatography is a technique that uses like-like interactions for

Figure 1—Schematic diagram of HPLC components.



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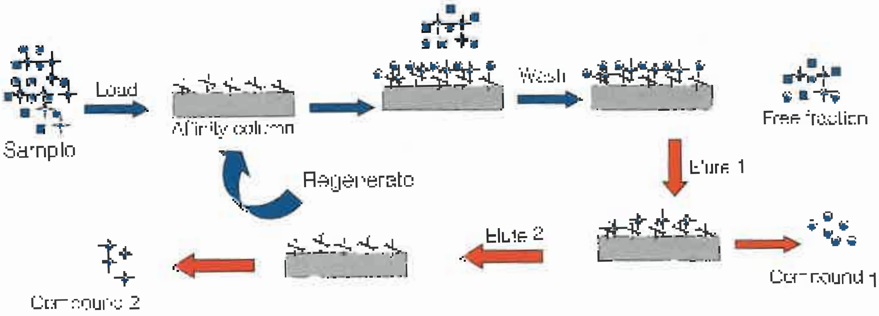
effective separation and analysis of sample components in solution. The column is designed to retain specific or similar analytes while allowing everything else through the column. The retained species can then be selectively eluted from the column by appropriate solvent. A schematic example of affinity chromatography is shown in *Figure* 2.

Figure 2—Schematic separation scheme in affinity liquid chromatography.



Ion Chromatography

Ion chromatography is a liquid chromatography method that can be used for the separation and quantification of anions and cations. For example, anions and cations that be separated and quantified are given in *Table* 1. A schematic anion separation and identification is shown in *Figure* 3.

In the context of this article, ionic chromatography is used in the determination of acid species in the acid/thermal decomposition of polymeric materials and ionic contamination in polymers and paints.

Capillary Electrophoresis

The capillary electrophoresis technique is based on the migration of charged molecules in an electrical field. The units are composed of a power source with a voltmeter and voltage regulator, an electrophoresis tank that holds the electrophoresis buffer, an anode and a cathode connected to the power source, a glass plate that holds the gel which is submerged into the electrophoresis buffer, and a comb sampler. These units are based on the simple relationship between the applied electric field (V), applied current (I), and resistance (R)- the Ohm's law:

$$V = I\ R$$

The applied electric field is measured in volts (V) and is proportional to the current (I) measured in milliamps. For a given voltage, a constant amount of current flows through the circuit and the voltage decreases across any element as its resistance increases. Molecules which have electrical charge due to groups capable of dissociating electrolytically (for example proteins), will migrate in an electrical field with a certain velocity and direction, which will depend on their electrical mobility. It has been shown that electrical mobility of a molecule is dependent on a variety of factors, such as electrical charge, coefficient of friction, shape, and molecular weight.

While capillary electrophoresis is a very important tool in the separation and identification of bio-molecules, it also finds important application in polymer analysis.[3]

Normal Phase Liquid Chromatography

Normal phase liquid chromatography (NPLC) a powerful separation technique, relies on the usage of polar stationary phase and nonpolar liquid mobile phases for the separation of polar species. See the Type of Column Phases section below.

Reverse Phase Liquid Chromatography

Reverse phase liquid chromatography (RPLC) is the most popular method of liquid chromatography. The name is derived from the reverse elution order of most solutes when compared to NPLC. It relies on the usage of nonpolar stationary phases with polar mobile phases. Typical mobile phases may include water with added polar organic solvent, such as acetonitrile. See the Type of Column Phases section.

Supercritical Fluid Chromatography

Supercritical fluid chromatography (SFC) is a technique that uses mobile phases as either gases or liquids taken above their critical point. The advantages of this approach include the solvating power of liquid mobile phases and diffusion coefficients closer to gases. The lower viscosity of SFC allows for higher flow rates compared to LC, and the solvating power can be adjusted by changing the pressure. A supercritical fluid chromatograph consists of a gas supply (CO_2), a pump, a column in a temperature controlled oven, a restrictor to maintain high pressure in the col-

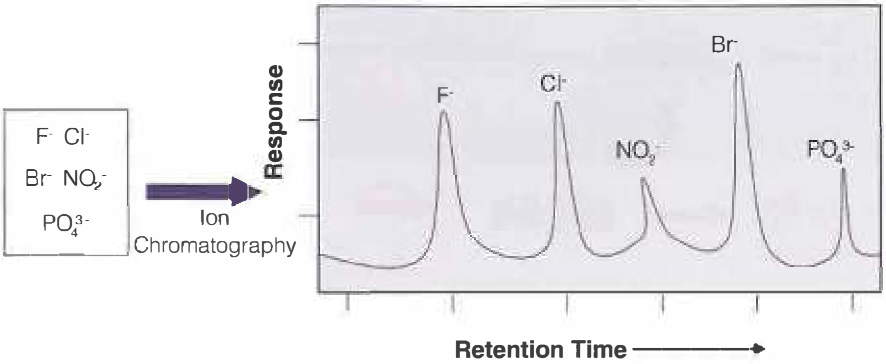
Abbreviations and Acronyms

FTIR - - - - - - - - -Fourier Transform Infrared
GPC - - - - - - - -Gel Permeation Chromatography
HPLC - - - - - - -High Performance Liquid Chromatography
LC - - - - - - - - - -Liquid Chromatography
MS - - - - - - - - - Mass Spectrometry
MWT - - - - - - - -Molecular Weight
NMR - - - - - - - - -Nuclear Magnetic Resonance
RPLC - - - - - - - -Reverse-Phase Liquid Chromatography
Pyro-GC/MS - - -Pyrolysis Gas Chromatography Mass Spectrometry
SFC - - - - - - - - -Size Exclusion Chromatography
THF - - - - - - - - Tetrahydrofuran
UV - - - - - - - - - -Ultraviolet

Table 1—Anions and Cations that can be Separated and Quantified

Anions		Cations	
Bromide	Br	Ammonium	NH_4^+
Chloride	Cl^-	Calcium	Ca^{2+}
Fluoride	F^-	Lithium	Li^+
Nitrate	NO_{3-}	Magnesium	Mg^{2+}
Nitrite	NO_{2-}	Sodium	Na^+
Phosphate	PO_4^{3-}	Zinc	Zn^{2+}
Sulfate	SO_4^{2}		

Figure 3—Schematic representation of anion separation and identification by ion chromatography. The identification of the species is made against known references. Detection limits can be as low as parts per billion (ppb) levels.



umn, and a detector. The flame ionization detector (FID) is most common, but other GC or LC detectors can also be used. SFC finds many applications in polymer additives analysis.[9]

Microscale Liquid Chromatography

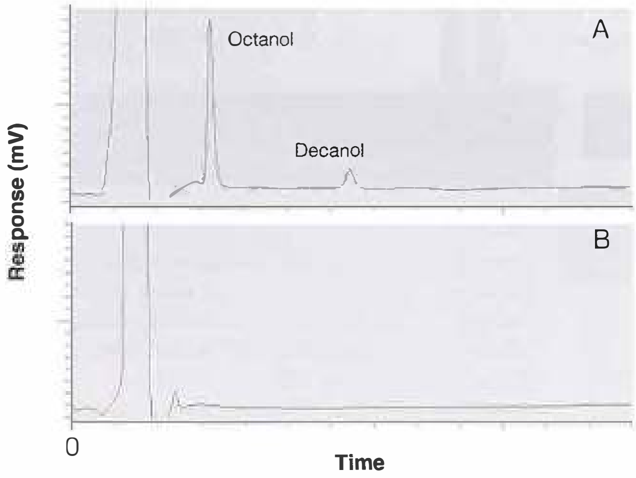
Microscale liquid chromatography is simply the miniaturization of liquid chromatography technique. The main advantages are the significant reduction of solvents, shorter analysis times, and overall improved sensitivities.

TYPE OF COLUMN PHASES

There are two main types of phase separation: (1) the normal phase HPLC which consists of a polar column material and relatively nonpolar solvents, and (2) reversed phase HPLC which consists of a nonpolar column material and relatively polar solvents.

Reversed phase HPLC is the preferred type of HPLC as it has proven to be the best for analysis of many types of resins. The most common column packing materials are nonpolar hydrocarbons, C_8, C_{18} and phenyl bonded phases columns. The most common polar solvents for resins include acetonitrile (ACN)/water, methanol/water, and tetrahydrofuran (THF)/water. They are normally used in the gradient elution mode because they allow one to start with low content of organic component in the eluent (ACN or THF) then the strongly retained components will move faster for improved resolution. Performance of gradient elution is strongly dependent on the instrumentation. Solubility of the material to be separated is a very important consideration in HPLC. For example, ACN/water is good for low molecular weight resins and is limited by solubility in higher molecular weight resins. THF/water is better and sometimes a mixture of ACN/THF/water may be the best for analyzing low to high molecular weight resins.

Figure 4—HPLC analysis of two batches of surfactants for residual alcohol impurities. Surfactant B is clearly purer than surfactant A (printed with permission from Dan Dohnmier, unpublished).



INJECTORS FOR HPLC

Samples are injected into the HPLC via an injection port. The injection port of an HPLC commonly consists of an injection valve and the sample loop. The sample is typically dissolved in the mobile phase before injection into the sample loop. The sample is then drawn into a syringe and injected into the loop via the injection valve. A rotation of the valve rotor closes the valve and opens the loop in order to inject the sample into the stream of the mobile phase. Loop volumes can range between 10 μl to over 500 μl. In modern HPLC systems, the sample injection is typically automated.

DETECTORS

Detection methods are critical to the successful application of HPLC methods in separation. Some of the conventional and newer detection methods are: UV/Vis, fluorescence, conductivity, and luminescence, Fourier transform infrared spectroscopy (FTIR), mass spectrometry (MS), and nuclear magnetic resonance (NMR). Exhaustive discussion of these newer detection methods has been reviewed in the literature.[10]

An example of HPLC Run conditions for polymer emulsion and/or paints can be as follows:

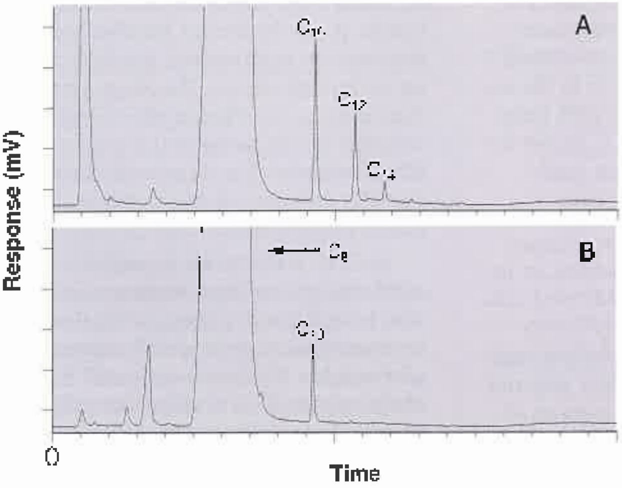
SAMPLE PREPARATION: The sample can be dissolved in THF at roughly 1% (wt/wt) and centrifuged at 40,000 rpm for 15 minutes. The supernatant is then filtered through 0.2 μm filters prior to injection on the HPLC system.

CHROMATOGRAPHIC CONDITIONS:

Column: PLRP-S 4000Å 8μ analytical column (Polymer Labs), 4.6 mm × 15 cm, 8 μm d_p.

Mobile Phase: 25:75 THF/methanol initially. Linear gradient to 75:25

Figure 5—HPLC of two batches of a sulfated surfactant that are supposed to be chemically identical. Surfactant A appears to have significantly higher levels of C_{10}-C_{14} and <C_8 hydrocarbons when compared to Surfactant B (printed with permission from Dan Dohnmier, unpublished).



THF/methanol over 35 min. Back to initial conditions in 5 min. Equilibrate for 10 min.

Flow Rate: 1.0 ml/min
Injection Volume: 10 µl
Column Temperature: Ambient
Detector 1: UV @270 nm
Detector 2: Evaporative Light Scatter-ing Detector (ELSD)

APPLICATIONS

Raw materials that go into the manufacture of paints are sometimes more complex than the supplier or formulators realize. Components such as surfactants may be sold as "pure" or within certain specifications but may often contain several by-products that may play an important role in the chemistry of the formulated paint. The following examples illustrate how HPLC can be used for raw materials and fully formulated paint analyses.

Analysis of Residual Alcohols and Alkanes in Surfactants: *Figure* 4 shows HPLC analysis of two batches of surfactants for residual alcohol impurities. In *Figure* 5, the HPLC of two batches of a sulfated surfactant that are supposed to be chemically identical are presented.

Analysis of Binder Type in Fully Formulated Paint Systems: Compositional analysis of paints can be a daunting task for analysts. The paint components can be dissolved in appropriate solvent (THF) and separated by either normal phase HPLC (polar column and nonpolar solvents) or reverse phase HPLC (nonpolar column and polar solvents). For example, a failed coating can be extracted by THF; however, depending on the composition of the formulated paint, analysts may encounter very challenging situations where answers to specific questions may depend very much on many variables. For example, the use of organic opacifiers has many benefits including increased opacity, low binder demand, and partial TiO_2 replacement, which signifi-

Figure 6—HPLC chromatogram of polybutylacrylate binder (top) and opaque polymer (paint additives to complement TiO_2 pigment) (bottom). Polybutylacrylate (pBA) has one main peak labeled B, at a retention time of about 9-15 minutes, while the opaque polymer has a main peak labeled D, at a retention time of about 22-31 minutes. Peaks labeled A and C are probably due to impurities or some low MWT components in the system (printed with permission from Haojie Yuan, unpublished).

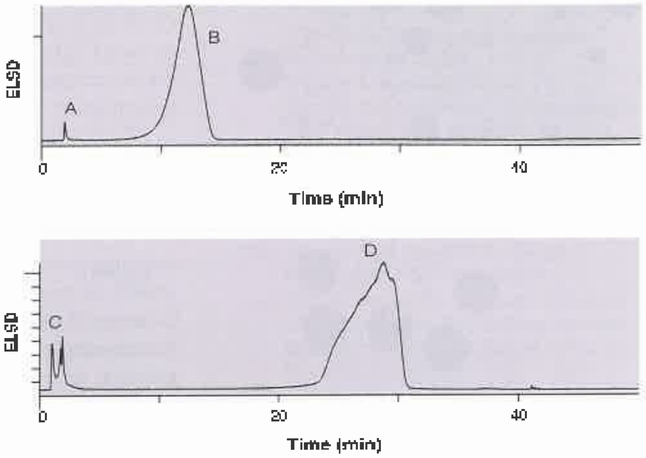


Figure 7—HPLC chromatogram of two paints: A styrenic primer (top) and an all-acrylic copolymer/opaque polymer (bottom). The primer (top) shows four peaks labeled: A—an impurity or low mwt component; B—polymer component #1; C—polymer component #2; and D—opaque polymer. The all-acrylic paint (bottom), on the other hand, shows three peaks labeled: E—an impurity or low MWT component; F—the main polymer component (all acrylic copolymer); and G—opaque polymer. Thus, HPLC can be used to determine the composition of fully formulated paint (printed with permission, Haojie Yuan, unpublished).

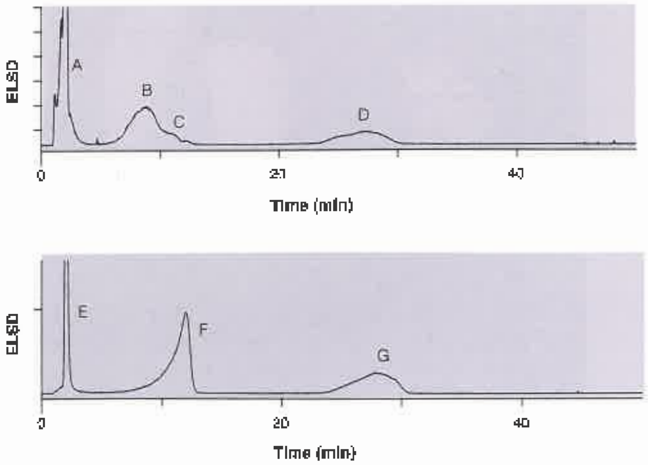
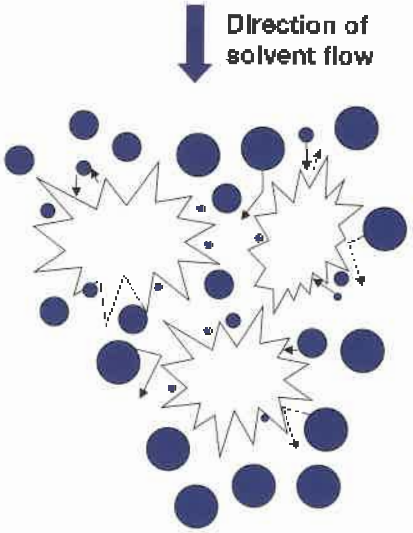


Figure 8—Schematic representation of the separation mechanism in a GPC column.



cantly reduces cost. The challenge of determining binder types and composition in fully formulated paints which may or may not contain organic opacifiers (mainly styrene, such as Ropaques from Rohm and Haas Company), can be very difficult. We have demonstrated in our labs that such systems can be analyzed by HPLC and/or HPLC/FTIR and/or off-line HPLC/Pyrolysis-GC/MS methods (see *Figures* 6 and 7).

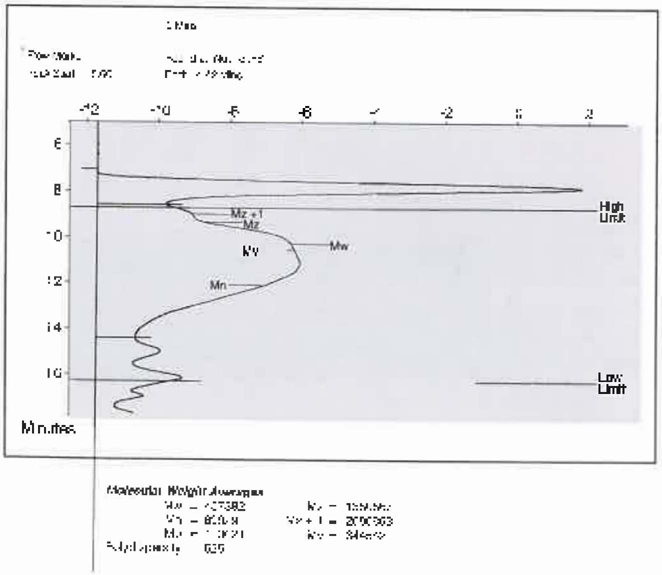
Analysis of Antifouling Additives in Paints: Antifouling biocides are important in paints and coatings. Some of these preservatives include chlorothanolin, dichlorofluanid, diuron, Irgarol 1051, and SeaNine 211. These are relatively small molecules and the most common method for analysis of their purity, efficacy, level, and fate in the environment when associated with paint particles is by HPLC.[11] HPLC allows for the separation, identification, and quantitative analysis.

Analysis of Epoxy Coatings Resins: Sheih and Benton have provided an in depth overview of how HPLC methods can be used in the analysis of epoxy coatings resins.[12] Epoxy resins are used widely in coatings due to their superior balance of properties such as good adhesion, impact resistance, chemical resistance, and flexibility.

GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (GPC), or size exclusion chromatography (SEC), is a branch of HPLC whose primary role is to provide molecular weight data on polymers and resins. GPC allows polymer synthesis chemists and paint formulation and application scientists to isolate and characterize low molecular weight additives and medium-to-high molecular weight polymers and resins in polymeric systems.

Figure 9—GPC profile of THF extract of an unknown paint. Using polystyrene standard, the molecular weight of the polymer was determined to be about 437,000 with a polydispersity of 6.25.



The two most common detectors are ultraviolet (UV) and refractive index (RI). Only samples that absorb in the UV region (with UV chromophore) can be detected by UV detection; for example, aromatic rings, or conjugated double bonds. If a polymer has no UV chromophore or is unknown, the RI detector is the best choice. The RI detector functions by monitoring the change in refractive index between the pure mobile phase and that containing the sample. The difference is the signal of the peak(s) of interest.

In GPC, the column is packed with a semi-rigid gel or small organic particles, which function as a physical barrier for separating molecules of different molecular weights. The key function of the stationary phase is to allow the polymer molecules to interact with the solvent molecules in such a way that those molecules that have more physical interaction with the pores of the column packing will take longer to elute than those that have no physical interaction with the pores. For example, high molecular weight polymers will elute faster. The separation mechanism in a GPC column is represented in *Figure* 8.

It can be simplistically shown that the smaller molecules can fit into the small pores and therefore take longer to elute through the column. The larger molecules, on the other hand, due to their big size, are unable to enter the pores and simply travel around the gel particles on their way out. Thus, the large polymer molecules are the first to elute out, followed by the medium size, and finally by the smaller molecules. It is important to point out that GPC also separates molecules according to their hydrodynamic volume.[13]

In order for the GPC data to be useful, it must be calibrated with polymers of known molecular weight. Polystyrene standards are often used because they are readily available over a wide range of molecular weights.

APPLICATIONS IN FAILURE ANALYSIS

Coatings scientists are always interested in determining the composition of polymers as they largely determine the chemical resistance properties of coatings. GPC is one of the best methods that can be used to measure the molecular weight of polymers in coatings. In order to accomplish this, the polymer must be isolated from the paint by using an appropriate solvent. In the example shown in *Figure 9*, the polymer was isolated from a paint by extraction in THF followed by centrifugation to remove the pigment and other THF insolubles.

In coatings failure analysis, GPC can provide data to show whether the failing paints conform to specification by comparing and finger-printing failed paint to a control paint. Sometimes, failures due to polymer decomposition can easily be detected. For example, GPC performed on a failing and on control paints showed a dramatic difference in molecular weight, with the failing samples being lower than the control.[14] There are numerous examples in the literature of how GPC can be used to investigate coating failures.[15] It is important to point out that GPC has two major limitations in coating analysis: it cannot be used on insoluble coating samples and it cannot provide chemical information. However, the chemical information limitation can be overcome by interfacing GPC to a variety of chemically sensitive tools, such as FTIR, NMR, and MS.[5-17]

SUMMARY

A general overview of the application of HPLC techniques for analysis of paints and related materials has been presented. We have discussed how HPLC can be used for raw materials and for fully formulated paint analyses. GPC has been demonstrated as one of the best methods that can be used to measure the molecular weight of polymers in coatings and coatings failure analyses. However, these methods require that the polymer or isolated components must be soluble in appropriate solvent(s). CT

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