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FMP 1918 coatings

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Urethane Coatings for Metal Substrates

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Polyurethane coatings have excellent gloss, hardness, flexibility, abrasion resistance, chemical resistance, and ultraviolet (UV) durability. In addition, higher-solids polyurethane coatings meet current regulations for volatile organic compound (VOC) emission without compromising performance. Because polyurethane coatings offer so many advantages, they are the market leader for coating metallic substrates in the following end-use markets: automotive refinish, aircraft, and chemical agent-resistant coatings (CARC). Moreover, polyurethane coatings have sustained especially rapid growth in automotive OEM, industrial maintenance (such as bridges), and appliances markets.

This article describes polyurethane chemistry, applications, and performance requirements for coating metallic substrates. Discussion is limited to 2-component solventborne, 1-component solventborne, and powder coatings based on polyurethanes as applied to the automotive refinish, automotive OEM, aircraft, and industrial maintenance end-use markets.

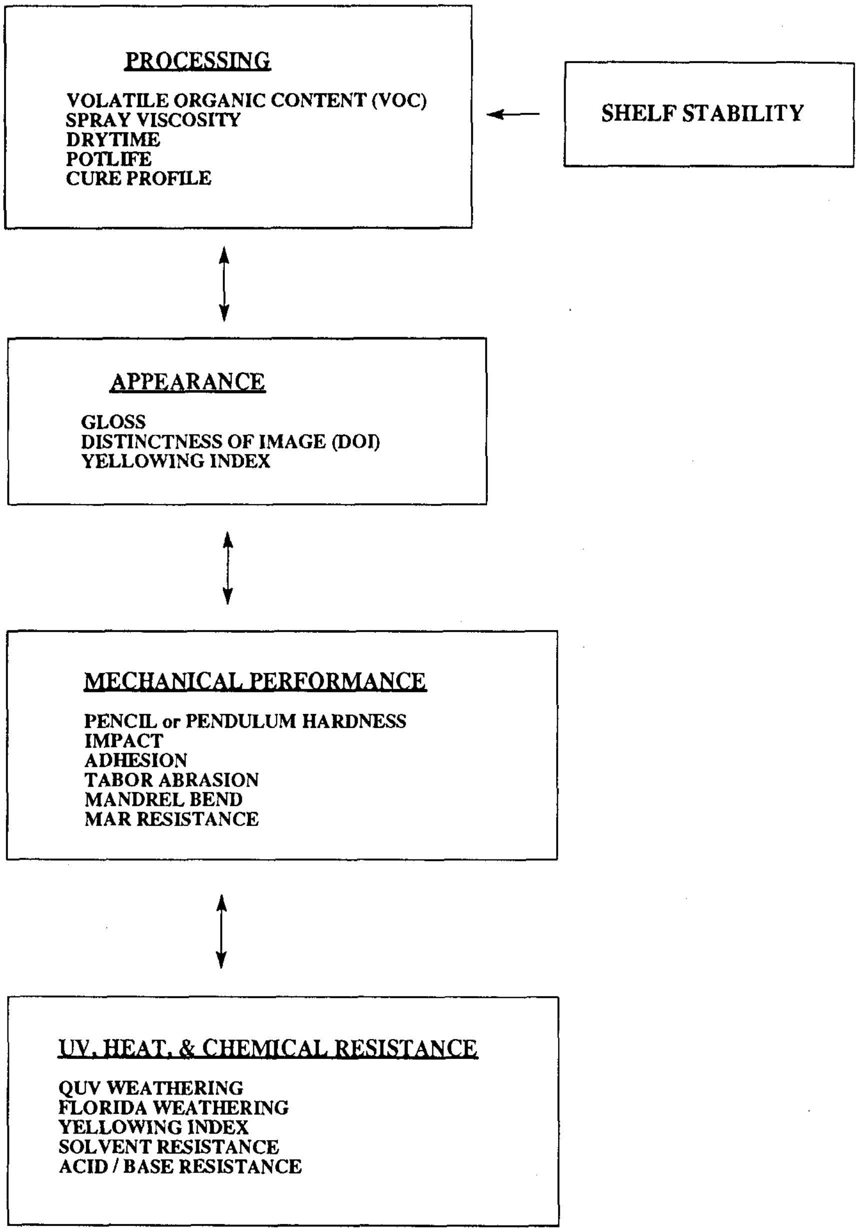

Figure 1. Schematic of coatings formulation process.

POLYURETHANE COATINGS FORMULATION

The performance of any coating can be divided into five elements: processing applications, appearance, mechanical performance, heat and UV resistance, and chemical resistance.

Figure 1 outlines the elements, including test methods, used to measure performance. Coating scientists use Figure 1 as a laboratory blueprint defining the important steps in the formulation process. A formulator will modify this blueprint, as required, to meet specific performance objectives. For example, in automotive refinish, formulators focus first on optimizing the application and appearance before maximizing the mechanical performance and resistance testing (UV and chemical). In industrial maintenance, formulators are most concerned with optimizing application and chemical resistance, whereas mechanical performance and appearance are less important. If a performance property fails the specification, the formulator adjusts the concentrations of the chemical reactants and restarts the design process.

Solventborne Coatings

Coating scientists begin the formulation process by selecting chemical reactants that form a good film. They then blend, adjust, and readjust concentrations following the formulation outline until the finished product has met all performance requirements. Polyurethane solventborne coatings used for metal substrates contain some or all of the following chemical reactants: aliphatic polyisocyanates, polyols (hydroxylated acrylic or polyester), solvents, catalyst, pigments, and additives

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TYPICAL APPLICATIONS:

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· Acid Chloride Zinc

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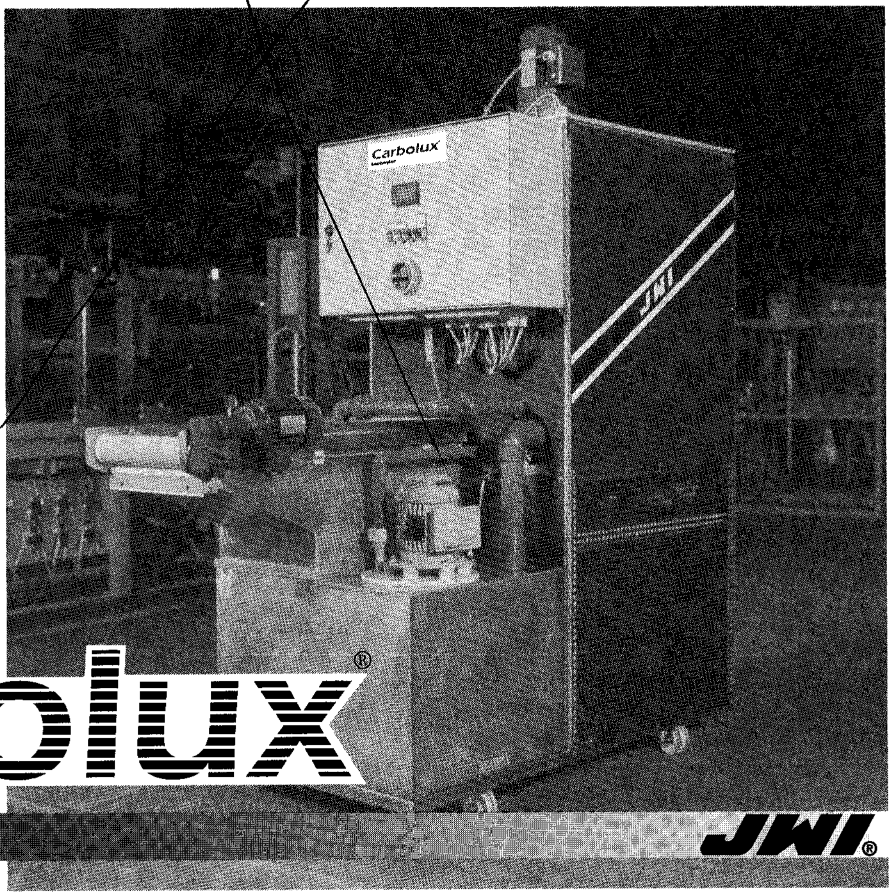

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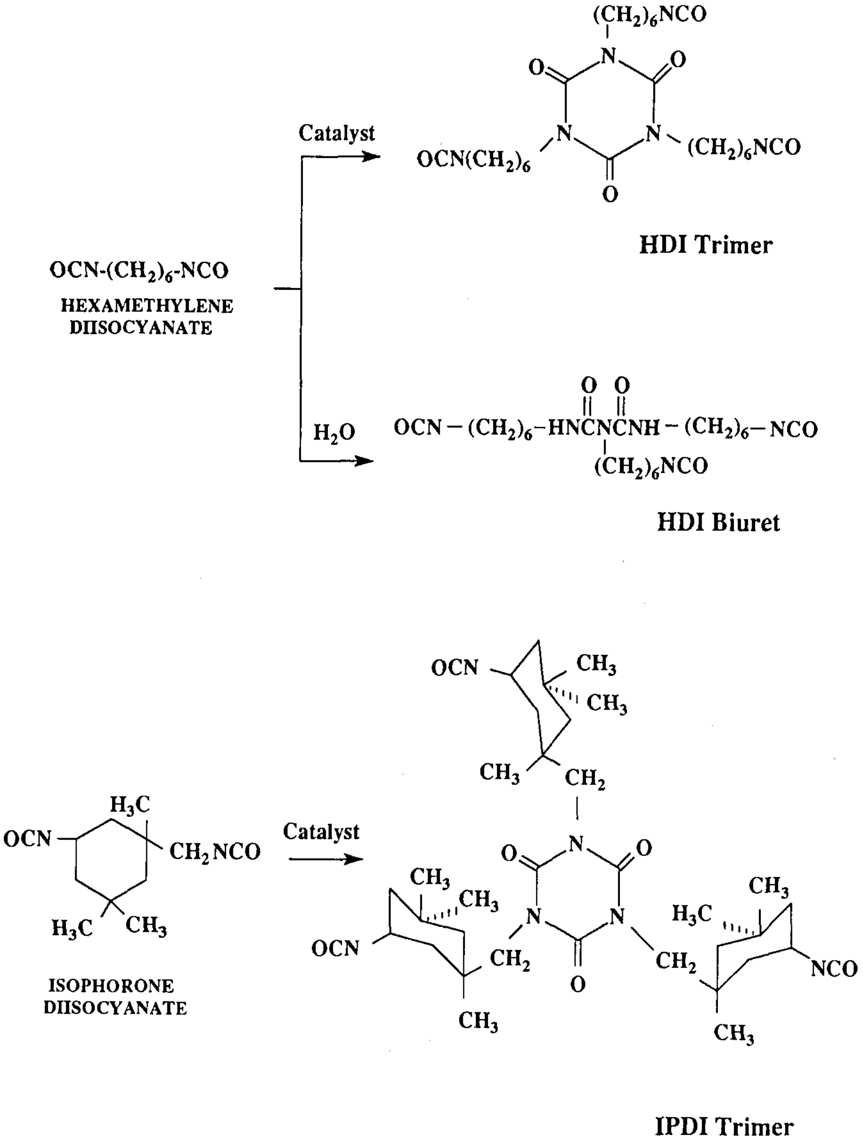

Figure 2. Polyisocyanate structures.

(e.g., UV stabilizers, reactive diluents, rheology control, etc.).

The first polyisocyanate commercialized for a solventborne coating was the reaction product of toluene diisocyanate (TDI) and trimethanolpropane (TMP). Commercialized in 1955, this product is still used for metallic industrial finishes as a co-binder for magnetic media (audio/video tapes) and for wood coatings. However, the TDI/TMP polyisocyanate yellows severely when exposed to direct sunlight, as do all aromatic polyisocyanates. This disadvantage led to the development of light-stable aliphatic polyisocyanates made from hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and their adducts (see Fig. 2).

Three commercial HDI-based polyisocyanates are used for coating metals. Finished coatings based on HDI trimer (polyisocyanurate) chemistry have significant advantages, including low viscosity (reduced VOC), excellent color, and low free-monomer content. Two commercial polyisocyanates based on biuret chemistry are also available for coating metals. Both HDI biurets are higher in color and in free-monomer content than the HDI trimer. The low-viscosity biuret is higher in isocyanate content and lower in equivalent weight than the HDI trimer. The high-viscosity HDI biuret is higher in viscosity and similar in isocyanate content and equivalent weight to the HDI trimer.

Adducts made with IPDI trimer were introduced in the late 1960s. Because of a different monomer structure, these trimers are higher in viscosity, color, and free-monomer content and lower in cross-linkability (cross-link sites per unit molecular weight) than the HDI trimer. Table I summarizes the important physical properties of polyisocyanate adducts used for metal coatings.

The performance of the finished coating depends on several factors: the adduct (HDI trimer or HDI biuret), polyol, solvents, and catalyst. Table II rates and ranks the coating performance of the various commercial polyisocyanates. Each polyisocyanate offers distinct advantages and disadvantages depending upon the performance requirements of the finished product. These characteristics must be considered by the formulator prior to the start of the formulation process.

Coatings made with IPDI trimer are harder and have higher tensile properties and better chemical resistance than coatings made with HDI-based polyisocyanates, as illustrated in Table II. To take advantage of both sets of performance characteristics, coating formulators typically blend IPDI trimers with HDI-based adducts to enhance the performance of the finished coating. HDI and IPDI trimer blends are used in automotive refinish

Table I. Polyisocyanate Used for Metal Coatings

	HDI Trimer	HDI Biuret (low v)	HDI Biuret (high v)	IPDI Trimer
Solids	Neat[a]	Neat[b]	Neat	70[a,c]
NCO Content (%)	21–23	22–24	21–23	12.2
NCO Eq. Wt.	190	182	191	344
Viscosity at 25°C (cp)	2,000–3,000	2,700–3,700	8,000–15,000	1,000–1,600
Color, APHA	60	200	200	200
Free monomer (%)	0.2	0.7	0.7	0.7

v = viscosity.

[a] Commercially available, blended with butyl acetate/Aromatic 100.

[b] Commercially available, blended with butyl acetate/xylene.

[c] Commercially available, blended with butyl acetate.

Table II. Coating Performance of Polyisocyanates

	HDI Trimer	HDI Biuret (low v)	HDI Biuret (high v)	IPDI Trimer
Polyisocyanate Shelf Stability	Best	Good	Good	Best
Processing				
Meets Current VOC Regulations for Key End-Use Markets	Yes	Yes	No	No
Dry-time Speed	Fast	Slow	Slow	Fast
Pot-life Open Time	Long	Short	Short	Long
Appearance				
Gloss, DOI, and Nonyellowing Specifications	Better	Better	Good	Best
Mechanical Performance				
Hardness and Abrasion Specification	Better	Good	Good	Best
Adhesion, Impact and Flexibility Specification	Good	Good	Better	Poor
UV Resistance				
Field (Test Fence) Specifications (Nonyellowing, Nonchalking, and Gloss Retention)	Better	Good	Good	Best
Chemical Resistance				
Field (Test Fence) Specifications	Better	Good	Good	Best

v = viscosity; DOI = distinctness of image.

and automotive OEM to speed up dry time and reduce damage to the clearcoats caused by acid rain.

Polyols

Numerous acrylic and polyester polyols are available to use as co-reactants with polyisocyanates. The hydroxyl (OH) functionality on the acrylic or polyester structure reacts with the isocyanate (NCO) functionality on the polyisocyanate. Polyol selection plays an important role in achieving performance goals. Leading polyols (and their physical properties) for automotive refinish and OEM, aircraft, and industrial maintenance markets are summarized in Table III.

Acrylic polyols are generally preferred in automotive and industrial maintenance applications. Urethane acrylic coatings have excellent appearance, very good UV stability, and meet the overall performance requirements for these end-use markets. Polyester polyols are preferred for use on aircraft and, to a lesser extent, in industrial maintenance. Urethane polyester coatings have excellent mechanical performance (flexibility and toughness) as compared with acrylic polyols but are lacking in UV resistance.

Catalysts and Solvents

Coatings are cured (hardened) by the reaction of the polyisocyanate (NCO functionality) with the polyol (OH functionality). Coatings can cure at room temperature or may be accelerated by heat. The addition of catalysts will speed up the final cure. The catalysts of choice among formulators are dibutyltin dilaurate (DBTDL), tertiary amines, alkali metal octoates, acetylacetonates, titanates, and blends of these catalysts. Newer catalysts, such as dimethyltin dilaurate and dibutyltin diacetate, are gaining popularity. In addition, formulators blend different combinations of catalysts to decrease the overall time required to complete the curing process. Most common organic solvents are suitable (esters, ketones, aromatic hydrocarbons, and so on) as thinners for polyurethanes, provided the solvents do not contain groups that react with isocyanates or contain impurities (alcohols, thiols, amines, carboxylic acids, or water).

Two-Component and One-Component Coatings

Two-component polyurethane coatings are formulated from the list of chemical co-reactants outlined in *Solventborne Coatings*. As the name implies, 2-component coatings are supplied to the end user in two separate containers and are mixed prior to application. One

Table III. Polyols Used in Automotive Refinish and OEM, Industrial Maintenance, and Aircraft Markets

End-Use Market	*Polyol*	*% Solids*	*Viscosity at 25°C* (cp)	Equivalent Weight (as supplied)	Color, APHA	T_g (°C)
Automotive Refinish and OEM	Acrylic	70[a]	12,000	815	30	30
Industrial Maintenance						
Heavy Duty	Acrylic	70[a]	8,500	655	80	61
Medium Duty	Acrylic	77[b]	5,100	650	50	18
Light Duty	Acrylic	80[c]	5,000	1,000	100	12
Medium Duty	Polyester	75[a]	10,000	519	300	—
Aircraft	Polyester	80[b]	2,600	500	200	—

[a] PM acetate.
[b] Butyl acetate.
[c] n-Methyl amyl ketone.

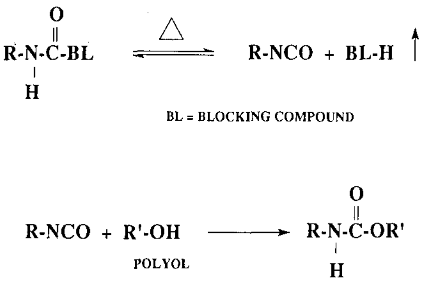

Figure 3. Unblocking–curing reaction of blocked polyisocyanates.

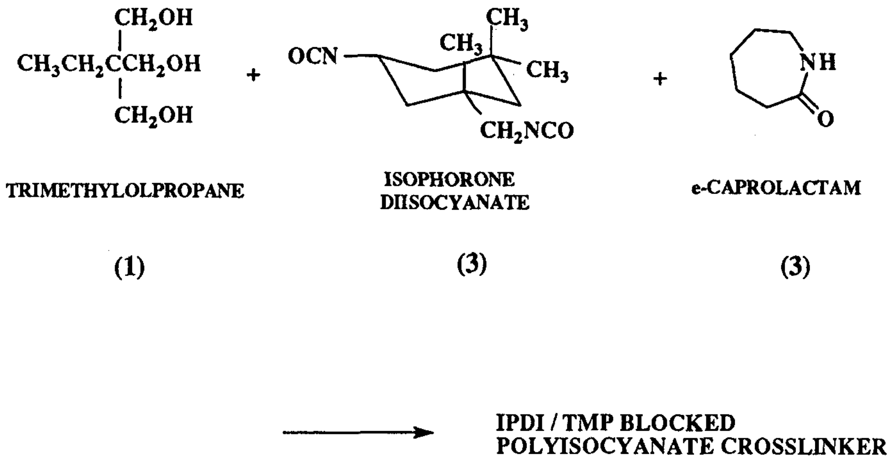

Figure 4. Powder coating-blocked polyisocyanate.

container (component A) holds the polyol, catalyst, solvent, and additives (rheology control agents, etc.). The second container (component B) holds the polyisocyanate, solvent, and additives (UV stabilizers). Each container is individually shelf stable.

The isocyanate/hydroxyl (NCO–OH) reaction begins as soon as the containers are combined. The mixing ratio of the components can be based either on volume or weight and is precisely calculated to achieve stoichiometry of the co-reactants (NCO–OH = 1). This ratio gives a finished coating optimum mechanical performance and optimum chemical resistance. If necessary, the NCO–OH ratio may be varied to change coating properties. If the NCO–OH ratio is <1, some OH functionality is unreacted and the coating has increased flexibility, better adhesion to substrates, and reduced solvent and chemical resistance. If the NCO–OH ratio is >1 some NCO is unreacted, and the coating needs a longer time to dry and surface harden. The final product is harder, solvent and chemical resistance is increased, flexibility is decreased, and adhesion to the substrate is reduced. A rule of thumb in coatings formulation is to maintain the NCO–OH ratio of 1.03–1.05.

In the formulation process, drytime and potlife are determined by the amount of catalyst in component A. The amount of solvent used in the formulation depends upon the applications requirements as well as on VOC regulations for the finished coating. Coating formulators will blend, adjust, and readjust the concentrations of the coating reactants until the finished product has met all the required performance goals.

One-component solventborne polyurethane coatings utilize the same chemical reactants used in 2-component coatings and are formulated by the same process except for three modifications: the polyisocyanate adduct is blocked, all chemical co-reactants are blended into one container, and the coating must be heat cured.

Blocked polyisocyanates utilize a chemical moiety to protect the isocyanate functionality from reaction during shelf storage at room temperature. The chemical moiety blocks, or caps, the isocyanate by reacting with the NCO functional groups. With the addition of heat, the blocked isocyanate breaks apart, regenerating the isocyanate functional groups (NCO) at the higher temperature. (See Fig. 3 for an illustration of this process.) After the NCO functional group is regenerated, the coating cures by the reaction of the NCO group with the OH group (acrylic or polyester) on the polyol. One-component coatings are used in end-use markets (such as automotive OEM) where no mixing or metering prior to application is required and where curing ovens are available.

Most blocked polyisocyanates require high (>300°F) unblocking temperatures. This disadvantage has slowed the growth rate of 1-component polyurethane coatings. Material suppliers are working on novel unblocking chemistry to lower the required temperatures.

Powder Coatings

Use of urethane powder coatings for metallic substrates is a rapidly growing coating technology that offers significant advantages over solventborne coatings. The co-reactants used in polyurethane powder coatings are: a solid blocked polyisocyanate (blocked with ε-caprolactam), a solid polyester resin, catalyst (dibutyltin dilaurate), and pigment and flow aids.

Isophorone diisocyanate is reacted with trimethylolpropane (IPDI/TMP) and then blocked with ε-caprolactam (see Fig. 4). This polyisocyanate, which is the leading choice for powder coatings, is co-reacted with polyesters. The cross-linker must be a solid with a T_g of 55°C. The polyester must also be a solid with a T_g of 50–60°C. The co-reactants are melt blended, extruded, cooled, and pulverized to produce the final powder coating (see Fig. 5). Powder coatings can be applied by fluidized bed or electrostatic spray. The coated metal substrate requires heat to melt and flow the powder and to unblock the isocyanate to complete the cure. Standard curing conditions are 10 min at 360°F for catalyzed coatings and 30 min at 360°F for uncatalyzed coatings. Table IV lists the physical properties of the IPDI-blocked polyisocyanate and polyester resin used in powder coatings.

Use of urethane powder coatings for metals is a rapidly growing segment of the coatings industry. Finished coatings have good chemical resistance, corrosion resistance, and mechanical performance as well as very good exterior color and gloss retention. Because finished products are available in all colors, clearcoats, and textured coatings, they are in demand for appliance, automotive wheel covers and trim, playground equipment, and garden tractors.

FUTURE PERSPECTIVES

In addition to the ongoing demand from end users for products that con-

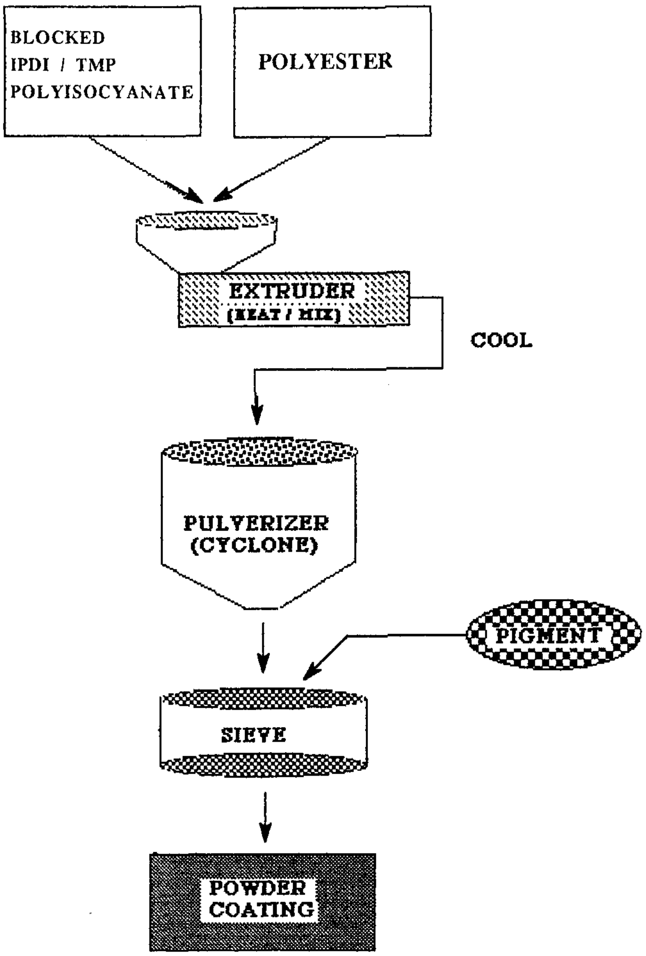

Figure 5. Urethane powder coating manufacturing process.

tinue to perform better, the enactment of the Clean Air Act Amendments in 1990 and other related environmental legislation highlighted the need for more environmentally friendly systems. To comply with these regulations, VOC reduction has become the most important goal for all coating manufacturers. Urethane-based coatings, because of the flexibility and versatility of urethane chemistry and the development of new generations of isocyanate adducts and derivatives, allow coating formulators greater freedom in designing new high-solid systems for 2-component or 1-component coatings and VOC-free waterborne or powder coatings. Urethane-based coatings also allow the coating formulators to tailor coating formulations to specific applications. Today, many of these emerging urethane coatings are either already in use or are under development for metal substrate applications.

In the automotive industry, the superior weathering and acid rain etching resistance of polyurethane-based topcoats and clearcoats have been widely recognized. As a result, despite their premium prices, polyurethane coatings have penetrated 70% of the European automotive topcoat market. In the United States, a polyurethane topcoat is currently used for approximately one quarter of new cars, primarily high-end models. With today's car-buying customers increasingly demanding better performance, such as excellent surface appearance and acid rain etching protection, urethane topcoats are certain to be used on more American models in the future.

One-component heat-curable OEM coatings have recently been developed for clearcoat applications using blocked polyisocyanates. These coating formulations not only perform as well as 2-component systems, but they also do not require on-site mixing, have long potlife, and have the benefit of reducing the paint-line cleaning and preparation time. Furthermore, these 1-component coatings also eliminate handling of the potentially hazardous isocyanate curing agents in the paint lines. With these benefits, the 1-component automotive OEM coatings systems based on blocked polyisocyanates are expected to grow rapidly, replacing conventional acrylic melamine systems. Newer blocked polyisocyanates are also becoming available that not only offer lower unblocking temperatures and faster heat cure time, but also additional performance benefits such as better yellowing resistance at overbake conditions and no VOC increase.

In addition to the emerging applications of urethane coatings for the automotive clear topcoats, anticorrosive electrodeposition primers for automobiles have relied on polyurethane systems for quite some time. With the need to reduce VOC, the development of waterborne polyurethane systems for this application has already made good inroads. In the past several years, use of heat-cured waterborne chip-resistant coatings has also been reported. Some of the newly developed waterborne polyurethane coatings are 2-component polyurethanes that improve performance by allowing further cross-linking to occur during the droplet coalescence stage. The development of these systems is made possible in many respects by the development of low-viscosity polyisocyanates.

For automotive refinish applications, 2-component polyurethane coatings have prevailed for many years as the best coatings in terms of performance and productivity. The trend to-

Table IV. Powder Coatings

	ICO Viscosity (200°C) (poise)	Gardner Viscosity	Equivalent Weight	Combining Weight
Blocked Polyisocyanate		S-W at 65% (MAK)		240
Polyester	30–45		1,020–1,250	

MAK = Methyl amyl ketone.

ward using more plastic automotive OEM body panels, which are easy to coat with polyurethanes, will only further enhance the domination of polyurethane-based coatings. As in other industries, automotive refinish coating formulators face the challenges of reducing hazardous emissions. To comply with increasingly stringent environmental regulations, automotive refinish formulators are moving toward higher-solid systems. Because the surface appearance will always be the most important requirement for automotive refinish applications, new high-solid polyurethanes must reduce VOC without significantly increasing the viscosity of the resulting coatings. Development of low-viscosity polyisocyanates will allow polyurethane coatings to continue to dominate the automotive refinish market.

Improvements in VOC recovery systems have enabled the coil coating industry to compete with powder coatings for many metal-finishing applications. The benefits of precoated metal have been recognized by many large users, including manufacturers of appliances, automotive under-the-hood parts, and prefinished building panels. Currently, polyurethanes have only a minor presence in these applications; however, for the coil coatings industry to be competitive in these important applications it must provide coatings with better flexibility in combination with better chemical and solvent resistance. To address these demanding challenges, formulators are developing new technologies that combine urethane with other traditional epoxy or polyester formulations. These emerging technologies provide coatings with desirable performance and a good performance–cost balance.

Because of the high performance requirements in durability, flexibility, and corrosion protection, aerospace and military camouflage coatings have traditionally used 2-component polyurethane systems. As in other coating applications, the need to reduce VOC emissions is leading to new developments. In addition to the 1- or 2-component waterborne polyurethane systems, high-solid solvent-based coatings were also developed for many applications. Some of these high-solid systems are also being developed as a 2-component self-priming topcoat that, due to the elimination of a separate primer, further reduces its VOC content.

In architectural and industrial maintenance applications, the labor cost has increased rapidly in recent years. For maintaining outdoor metal structures that are exposed to harsh environments, the cost of the paint represents a much smaller portion of the total cost than the time-consuming, labor intensive repainting process. Urethane coatings offer the best weathering and chemical resistance in these environments. The ability to extend repaint cycle times gives urethane protective coatings significant competitive benefits in these applications. Furthermore, longer repainting cycles have the additional benefit of reducing emissions to the environment.

To meet the challenge of air quality regulations, today's high-solid maintenance urethane coatings have already achieved 2.8–3.5 lb/gal VOC levels. The future development of low-viscosity polyisocyanates, lower molecular weight resins, and waterborne urethane coatings will enable these emissions to be further reduced without compromising the coating performance.

CONCLUSIONS

Polyurethane coatings offer many advantages for metal substrate applications. Polyurethanes have excellent appearance ("wet look"), mechanical performance, UV resistance, and chemical resistance compared with those of other coatings. Polyurethanes can be applied as higher solids or powder coatings without loss of performance. As a result, polyurethanes are the market leader for coating metallic substrates in numerous high-end and highly visible applications today. In the future, the performance of urethane coatings will enable their use in a broader spectrum of metal substrate applications. **MF**

Shop Problems

Plating and Anodizing

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Carbonate Build-Up

Q: We have experienced a huge build-up of carbonates in our silver cyanide plating tank. What is the latest technology for the removal of this build-up?

J.G.

A: If the bath contains sodium salts the best procedure is to freeze and decant leaving the carbonates as a precipitate. Should the bath be based on potassium salts then it will be necessary to add barium cyanide to precipitate the carbonates as barium carbonate. Start by placing the solution in a standby tank. Determine the level of carbonates and add enough barium cyanide to reduce the carbonates to 2–3 oz/gal. Allow to settle, then pump out from the top through a fine filter back to the plating tank.

Determining Coating Weight

Q: Is there a standard procedure that can be used to determine the weight of both chromate and zinc coatings on electrogalvanized steel?

D.B.

A: The basic procedure used is to weigh a measured area of coated sample, strip off the coating, and then reweigh to determine the coating weight by the difference in the two measurements. Chromate on zinc is determined by stripping cathodically in an alkaline cyanide solution. Zinc is then determined by stripping in inhibited hydrochloric acid.

Details are provided in ASTM B 767, Standard Guide for Determining Mass per Unit Area of Electrodeposited and Related Coatings by Gravimetric and Other Chemical Analysis Procedures. A copy can be obtained by contacting the American Society for Testing Materials (ASTM), 1916 Race St., Philadelphia, PA 19103; 215/299-5400.

Copper Immersion Deposits

Q: We recently converted a copper strip tank to a hydrochloric acid pickle. It seems some copper remained in the tank and the pickle now precipitates copper onto parts. Is there any way to make the copper plate onto some scrap parts and therefore remove it? The tank is approximately 450 gal.

W.M.

A: The copper will deposit onto scrap, such as steel wool, immersed in the tank. You could also use aluminum sheets to remove it. An alternative is to prevent deposition by filming the steel using a proprietary additive.

Acid versus Cyanide Copper Strike

Q: What are the merits/demerits of using an acid copper strike to replace a cyanide-based strike prior to silver plating?

A.G.J.

A: The acid copper strike doesn't throw as well as the copper cyanide. If it's essential to eliminate cyanide, try using a strike based on copper pyrophosphate. The disadvantage here is that the pyrophosphate tends to break down and must be replaced more often. **MF**