10

Automotive paints

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10.1 Introduction

The demands and performance required for automotive coatings are considerable. There is a need for 'body' protection, such as anti-corrosion and stone-chip resistance, and for a durable and appealing finish. Products also have to be appropriate to mass-production conditions, and in this respect, must be robust, flexible, and economic to use.

Vehicle construction has gone through significant changes since its inception at the turn of the century. At the present time the substrate is generally of mild steel but may also contain other alloys and include plastic components; the shape is inevitably complex and certain parts of the vehicle are almost inaccessible and difficult to paint. Production rates are high, e.g. 45 units/hour, and this requires process and material technology to meet the limitations this imposes.

Vehicle production (passenger cars and commercial vehicles) throughout the world in 1995 was 47.6 million utilizing of the order of 900 million litres of paint. In relation to these figures, vehicle production in Western Europe was 12.6 million, requiring 254 million litres of paint.

These figures are broken down and represented in Table 10.1 and diagrammatically (refer Figs. 10.1 and 10.2).

The paint products used are principally primers and surfacers (fillers), designated the undercoating system, and the finish or topcoat. In a modern painting system the relative use is broadly in percentage terms, primer:surfacer:topcoat, 30:20:50. In different parts of the world there is often variation in product technology, particularly in topcoats, and this can have a significant influence on paint performance, specifications and details of the process.

The basic objectives of the painting process are to protect and decorate. In order to achieve this the process is broken down into a number of different component parts. These parts, or 'layers', are applied in a specific order and although the function of each 'layer' is specific it relates very closely to the others to provide the desired balance of properties.
The component parts of the painting system are:

- **Metal pretreatment**
- **Primer**
- **Surfacer (filler)**
- **Finish**

This fundamental process may be divided into three basic systems which may be classified as follows:

- spray priming system;
- dip priming system;
- electropriming system (currently most widely used).

The reason for this classification is that the method of priming is the major difference between them; the subsequent process is virtually identical. All these three systems are used over suitable pretreatments.

Spray application is used for surfacers and topcoats. There are a variety of different types of spraying systems, e.g. air atomized (hand and/or automatic) and electrostatic methods. These are described in more detail later.

### 10.1.1 Spray priming system

This comprises:

- Zinc-rich primer: internal sections only.
- Primer surfacer: 40–50 μm.
- Finish: 45–55 μm.

The zinc-rich primer is applied to the internal surfaces of body components before welding of the body is undertaken. This is to give corrosion protection to such surfaces which are otherwise inaccessible for painting in following operations.

The primer surfacer provides a measure of corrosion protection to the outer skins of the phosphated body.

This system was used before the advent of dipping primers but is now only found where low volume production does not justify the cost or plant to dip or electro-prime bodies.
10.1.2 Dip priming system

- Anti-corrosive dipping primer: 12–18μm.
- Primer surfacer: 40–50μm.
- Finish: 45–55μm.

This system was widely used on mass-production lines before the introduction of electropriming in the early 1960s. In addition to its normal function the primer
surfer needed to provide a measure of corrosion protection since the underbody dip primer only covers the lower sections of the unpainted car body.

Now more or less obsolete, this process still finds limited use where low volume production or other factors such as cost prevail.

10.1.3 Electropriming system

- Electrocoat (anodic or cathodic): 18–25 μm.
- Surfercer: 35–40 μm.
- Anti-chip coating: 50–100 μm.
- Finish: 45–55 μm.

Electropriming, predominantly cathodic, is currently the accepted standard in mass-production plants. It is an efficient, relatively simple operation with a high degree
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of automation. Introduced in the early 1960s with anodic technology, subsequently replaced by cathodic technology, it has set new standards in processing and corrosion protection.

Inclusion of an anti-chip coating to protect vulnerable areas has grown considerably over the past ten years. It simply reinforces the surfacer's resistance to stone-chipping and forms a highly important part of the overall painting system.

In the processes outlined above all coatings need stoving; this is required to achieve very high levels of performance and to facilitate processing in a conveyorized production line. Stovings vary from as high as 180°C for cathodic primers to as low as 80°C for repair finishes.

A typical modern paint process/plant is shown in Fig. 10.3 in schematic form.

10.1.4 Performance
Individual manufacturers have their own performance specifications and, for example, while they may vary on the type of finish and local plant/processing conditions, there are basic aspects which are common to all:

- Appearance: gloss and distinction of image.
- Durability: film integrity, colour and gloss retention, and free from blistering and corrosion.
- Mechanical properties and stone-chip resistance.
- Substrate: acceptable performance over a variety of substrates including plastics.
- Adhesion.
- Workability: amenable to modern methods of application.
- Ability to meet environmental requirements/regulations: product and process.
- Corrosion and humidity performance.
- Petrol and solvent resistance.
- Etch resistance.
- General chemical resistance, e.g. acid and alkali resistance.
- Hardness and mar resistance.
- Repair properties.

The products required to achieve these properties are described later. They require extremely sophisticated technology and a lengthy process involving various methods of application and stoving. Costs in energy, labour, space, and capital are considerable and future processes will have to take other factors into account, such as anti-pollution, while still continuing to improve performance standards. For example, new developments have to back up improved warranties from car producers such as a six year anti-corrosion guarantee and, with certain manufacturers, up to three year's overall coating performance.

10.2 Pretreatment
The pretreatment process has three purposes:

- To remove the mill and pressing oils ingrained in the steel and any other temporary protective coatings.
Fig. 10.3 — Paint plant process.
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- To improve paint adhesion by providing an inert surface of metal phosphate which will give a better key for the subsequent primer layer.
- To provide a resistance barrier to the spread of corrosion under the paint film.

A normal process for pretreatment may be summarized as follows:

1. rust removal;
2. alkali degrease;
3. water rinse;
4. metal phosphating;
5. demineralized water rinse.

Depending on individual requirements and throughputs, processes may be spray, spray-dip, or dip; the latter two are preferred for modern high volume installations.

10.2.1 Rust removal

The best method is by the use of mineral acid particularly where rust deposits are heavy or mill scale is present; phosphoric acid-based materials are normally preferred.

Although phosphoric acid is slower acting than hydrochloric or sulphuric, any salt contamination is less due to the low solubility of most metal phosphates.

10.2.2 Alkali degrease

Alkali cleaners are widely utilized in dip and spray installations where the oil and grease are partly saponified and emulsified into the alkali solution. The physical force generated by the jetting of the cleaner significantly assists in the removal of any solid matter present on the surface of the unit.

Formulations vary and are dependent on a number of factors such as the type of oil or grease to be removed, metals to be processed, etc. However, there is a need to restrict the strength of the alkali to prevent deactivation of the metal surface. Typical alkali chemicals are caustic soda, trisodium phosphate, and sodium carbonate: these are used in conjunction with various types of detergents for emulsification of oils and lubricants.

10.2.3 Metal phosphate (conversion coating)

There are two basic types of phosphates:

- Iron phosphate — coating weight 0.2–0.8 g m⁻².
- Zinc phosphate — coating weight 0.5–4.5 g m⁻².

As a generalization, increasing the phosphate coating weight increases the corrosion resistance and decreases the mechanical strength or adhesion of the subsequent paint coating. Clearly coating weight is an important parameter, the value being a compromise designed to achieve an acceptable balance of properties.

Iron phosphate produces an amorphous, non-crystalline coating of low weight used mainly on components such as refrigerators, washing machines, and metal furniture which do not have to stand up to rigorous corrosion conditions. The prime requirement for such components is mechanical strength/adhesion which makes the low coating weight or iron phosphate ideal for such purposes.
Zinc phosphate is used almost universally in automotive paint processes and is an integral part of the total paint system. Zinc phosphate coatings are unique in that they can be made to crystallize from solution onto the metal surface because of the existence of metal phosphates of different chemical form and the equilibrium that exists in aqueous acid solution.

A chemical equilibrium is set up as follows:

$$3\text{Zn(H}_2\text{PO}_4\text{)}_2 \rightleftharpoons \text{Zn}_3\text{(PO}_4\text{)}_2 + 4\text{H}_3\text{PO}_4$$

Zinc dihydrogen phosphate Tertiary zinc phosphate Phosphoric acid

(soluble) (insoluble) (free acid)

This equilibrium will remain unchanged until an influence is brought to bear which will affect the concentration of the chemicals present. The initial reaction, therefore, in the phosphating process is the attack on the metal by the free phosphoric acid.

$$\text{Fe} + 2\text{H}_3\text{PO}_4 \rightarrow \text{Fe(H}_2\text{PO}_4\text{)}_2 + \text{H}_2$$

Substrate Free acid Soluble iron phosphate Hydrogen

The equilibrium in the first equation is disturbed and the reaction moves to the right, the soluble zinc phosphate disproportionates to form insoluble zinc phosphate and free acid. Phosphate crystals start to grow and continue until the surface of the substrate is completely covered, at which time there is no more iron left with which the free acid can react, and the process stops. A build-up of soluble iron phosphate, which would ultimately slow down the reaction and poison the phosphate solution, is controlled by the addition of an oxidizing agent (toner) which precipitates the soluble iron phosphate as ferric phosphate (sludge).

10.2.4 Pretreatment as a corrosion inhibitor: mechanism

The steel surface, or substrate, is made up of a lattice of iron, carbon dissolved in iron, iron carbides, and undissolved carbon particles.

Rusting, or corrosion, is essentially an oxidation process aided by electrolytic action. On a moist steel surface electrolytic cells can be set up by the impurities in the metal (carbides, carbon, etc.) which give rise to cathodic (negative) and anodic (positive) areas. In the presence of water and salts (an electrolyte), these areas become the electrodes in a corrosion cell. Ferric ions form at the 'cathode', where the metal becomes pitted, combine with oxygen in the air and hydroxyl ions from the electrolyte to form iron oxide and hydroxide. Corrosion consequently starts to take place and to prevent it the corrosion currents must be prevented from flowing by insulating the metal surface.

Paint alone is a poor insulator since it is not impervious to an aqueous environment. Consequently, any damage to bare metal, by for example stone-chipping, results in corrosion taking place which spreads under the film owing to the inherent lack of adhesion of virtually all paint films to untreated metal surfaces.

Phosphate, however, acts as the perfect insulator. The phosphate crystals grow from active sites on the surface of the metal until the coating is completely impregnated and covers the whole surface. This crystalline structure acts as a type of 'ceramic' insulator unaffected by water, particularly when sealed with the paint
coating. Even damage due to stone-chipping, or other forms of mechanical abuse, is restricted.

10.3 Priming

The function of the primer is to provide corrosion protection. This is achieved by formulating a product which incorporates anti-corrosive pigments carried in a resin system providing unnecessary mechanical, as well as anti-corrosive, properties.

Vehicle construction has changed considerably over the past 50 years to the extent that different techniques in applying the primer layer are necessary in order to ensure all parts of the vehicle are coated. Table 10.2 identifies the evolution of the vehicle priming up to the present day.

Historically there have been two major advances in the priming of motor vehicles. The first was a direct result of the automated techniques developed during the Second World War, i.e. the advent of the spot welder produced the welded unit or monocoque body shell. In this type of construction many areas of the unit are virtually inaccessible, for example the various strengthening cross-members and the front end near door posts. This meant that spray application of primer was no longer feasible. As a consequence dipping procedures were introduced to make it possible to prime all parts of the vehicle, particularly the underbody.

Initially, dipping primers were solvent-borne, but in the 1960s water-borne primers were introduced to minimize fire and health hazards. However, although the water-borne systems failed to improve efficiency or economics they did lead on to the second major advance in autobody priming, i.e. applying the primer by electrodeposition.

10.3.1 Spray priming

This system utilizes a zinc-rich primer, and sometimes other anti-corrosive coatings, which is applied to the internal surfaces of body components before 'welding-up' of the body. As a result, corrosion protection is given to such surfaces that are otherwise inaccessible for painting in subsequent operations.

Before the advent of dipping primers this system was quite widely used. It is now used only where low-volume production does not justify the cost of plant to dip or electrocoat bodies, or where capital is not available to install such plant.

10.3.2 Dip priming

10.3.2.1 Products

These materials are used to provide protection to internal parts of the vehicle body. Since no further coats of paint are applied in such areas, dipping primers are formulated to have good corrosion resistance and good adhesion to various types of phosphating pretreatment, as well as untreated metal.

Because of the size and complexity in shape of autobodies, dip primers must have good flow characteristics. Also since the size of dip tanks is large, to accommodate car bodies, there is also a need for good stability.
<table>
<thead>
<tr>
<th>Period</th>
<th>Substrate</th>
<th>Body type</th>
<th>Primer type</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960-1966</td>
<td>Steel with iron/zinc conversion coatings.</td>
<td>Welded unit construction (monocoque).</td>
<td>Water-based dip primer.</td>
<td>Reduced fire hazard/pollution. Otherwise similar to solvent/dip process.</td>
</tr>
<tr>
<td>1992–</td>
<td>As above.</td>
<td>Welded unit construction (monocoque).</td>
<td>Cathodic electropaints.</td>
<td>Improved edge protection. Reduced lead content. Improved throwing power. Improved corrosion protection. Reduced 'combined oxygen' demand. Improved mechanical properties.</td>
</tr>
</tbody>
</table>
There are four basic types of dip primers still in use:

- alkyd;
- alkyd/epoxy;
- epoxy ester;
- full epoxy.

The majority of dip primers are solvent-based but water-borne variants are available. The most widely used in the industry were alkyd-based since they gave an acceptable balance between performance and cost. Epoxy types were introduced later to give improved corrosion resistance but are more costly and less easy to control in tip tanks.

10.3.2.2 Pigmentation

Traditionally, these were red oxide type products but the more common colour now is either black or grey.

Prime pigments:

- Red oxide and carbon black.
- Zinc chromate is often included for anticorrosive properties.

Extenders:

- Barytes (barium sulphate): hard with good blister resistance.
- Blanc fixe (precipitated barium sulphate): helps maintain dip tank paint stability.

Pigment volume concentration (PVC) is normally 20–30%.

10.3.2.3 Process

This process is now only used on a very limited scale where low volume production or other factors such as economic considerations are prevalent.

Dipping of the car body can be shallow ('slipper' dipping) up to windows or full immersion. In the 'slipper-dip' process the short dipping distance involved gives comparative freedom from runs and sags and the next coating of surfacer can be applied 'wet-on-wet' after appropriate draining and air drying. The two materials are then stoved as a 'composite'.

In the case of deeper dips the complex shape of the car body gives more runs and sags which have to be removed by solvent wiping, etc., before surfacer application. Sometimes the primer is stoved and rectification carried out prior to surfacer application.

An interesting form of dip priming used in the mid-1960s was roto dipping. In this process the body was mounted transversely on a spit and, by means of a suitable conveyor, carried through the pretreatment (dip zinc phosphate), primer, and then stoving operation.

The advantages of this method were the thorough pretreatment and even distribution of primer to all surfaces. However, the plant required was expensive and high in maintenance costs and could only be operated at relatively low line speeds. These and other factors led to it being superseded by electropriming in common with most other dipping processes.

In summary, dipping methods are dirty, laborious, and wasteful. The advent of electropriming showed great advantages (refer to Section 10.3.3), giving greater internal protection and eliminated solvent 'reflux' in box sections, a feature inherent in both solvent- and water-based dip primers.
10.3.3 Electropainting
Electropainting of motor vehicles began in 1963, some time after the principle had been established in other areas, although the technology was conceived in the 1930s. The electrocoat system consists of the deposition of a water-borne resin electrolytically, the resins employed being polyelectrolytes.

At the present time virtually all mass-produced vehicles are primed in this manner; the body shell is immersed in a suitable water-borne paint which is formulated as an anodic or cathodic resin system at very low viscosity and solids.

10.3.3.1 Anodic electrocoat
Until 1977 all electropaints used in the automotive industry were of the anodic type, primarily because the resin chemistry was relatively simple, readily available, and adaptable to the needs of the motor industry.

Resin systems
There are four main resin systems:

- maleinized oil;
- phenolic alkyd;
- esters of polyhydric alcohols (epoxy esters);
- maleinized polybutadiene.

Early anodic electropaints were based on maleinized oils and phenolic alkyds but these were superseded by epoxy esters and maleinized polybutadiene because of their superior corrosion performance.

Pigmentation
The pigmentation used in anodic electrocoat (and cathodic) should be:

- simple;
- non-reactive, i.e. stable (e.g. to stoving) and pure, containing no water-soluble contaminants (e.g. chloride and sulphate);
- in one form, or another, reinforce or improve corrosion performance.

Pigment volume concentration is normally in the region of 6%.
Prime pigments are high grade rutile titanium dioxide, together with a minimal amount of carbon black, in greys, and a very good quality red (iron) oxide for reds.
Extender pigments are high grade, free from soluble ionic species, such as chloride and sulphate.
A number of anti-corrosive pigments are available; a typical example is lead silico chromate.

Mechanism of deposition
During electrodeposition three basic reactions occur: electrolysis, electrophoresis, and electroendosmosis.
Note: solubilization of the resin:

\[ \text{RCOOH} + \text{KOH} \rightarrow \text{RCOOK} + \text{H}_2\text{O} \]

(insoluble) (soluble)

e.g. \( R = \text{epoxy/ester} \).
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(The base used here is potassium hydroxide, but others such as amines are also utilized).

1 Electrolysis

\[
\text{RCOOK} \rightarrow \text{RCOO}^+ \text{K}^+
\]

\[
4\text{H}_2\text{O} \rightarrow 3\text{H}^+ + 3\text{OH}^- + \text{H}_2\text{O}
\]

Reduction at cathode:

\[
\text{H}_2\text{O} + 3\text{H}^+ + 4e \rightarrow 2\text{H}_2 + \text{OH}^-
\]

Alkaline reaction from \( \text{OH}^- \) present; can be removed by electrodialysis.

Oxidation at anode:

\[
3\text{OH}^- - 4e \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{H}^+
\]

acidic reaction from \( \text{H}^+ \) present, i.e.

\[
\text{RCOO}^- + \text{H}^+ \rightarrow \text{RCOOH}
\]

\text{insoluble (electrocoagulation)}

\text{deposited coating}

Metal dissolution (minor reaction)

\[
\text{M} - ne \rightarrow \text{M}^{n+1}
\]

(favoured by presence of contaminating ions)

2 Electrophoresis. When a voltage is applied between two electrodes immersed in an aqueous dispersion the charged particles tend to move towards their respective electrodes. This effect is called electrophoresis.

In the electrocoat process, when a current is applied, negatively charged paint ions move towards the anode (positive). Electrophoresis is the mechanism of movement, and does not contribute to the actual deposition of the paint on to the anode.

3 Electroendosmosis. The layer of electrodeposited paint on the anode will contain occluded water. This is driven out through the porous membrane formed by the paint by the process called electroendosmosis.

Practical considerations

In practice the process simply involves the passing of a direct current between the workpiece (anode) and the counter-electrode (cathode). The resultant coating deposited on the workpiece is insoluble in water and will not redissolve.

The film is compact, almost dry, and has very high solids which adhere strongly to the pretreated (zinc phosphate) metal substrate. It is covered by a very thin dip layer which is easily removed by rinsing. After stoving (165°C) the resin cures to form a tough, durable polymeric film.

The amount of paint deposited is largely dependent on the quantity of electricity passed. As the film is deposited its electrical resistance increases and the film becomes polarized when the resistance is so great that it stops the flow of current and halts the deposition. Thus once an area has been coated the local increase in resistance forces the electrical current to pass to more remote areas. This effect ensures progressive deposition, or ‘throw’, into box sections and internal or recessed areas.
The result is exceptional uniformity of film thickness, free from runs, sags, and other conventional film defects. The process is very suitable for mass-production conditions, facilitating a primer coating over the whole surface of a welded monocoque carbody. It can be fully automated and is highly efficient in terms of paint utilization.

Basic plant requirements

- A powerful paint circulating system to preclude pigment sedimentation at the low solids (~12%) of operation and maximizing paint mixing.
- Sophisticated refrigeration and filtration to maintain stability and remove contamination.
- A smooth and stable direct current supply with suitable ‘pick-up’ gear to the car body.
- A paint rinsing system to remove the adhering dip layer. Incorporation of ultra-filtration (see Section 10.3.3.2) maximizes water and paint utilization as well as serving as a method of decontamination.

Control methods

The alkali bases generated at the cathode (see Mechanism of deposition above) by electrolysis during electrodeposition will increase the pH of the paint and must be removed to maintain optimum properties. This can be done in two ways:

1. Electrodialysis. This uses a selective membrane (ion exchange) around the cathode. Base ions are allowed to pass through the membrane, but the anions (colloidal paint particles) are prevented from doing so.
2. Acid feed/base-deficient feed. This is self-explanatory. The feed, or top-up, material is partly neutralized to compensate for the base generated during the process of deposition.

The difference in method of pH control gives rise to differences in other aspects such as resin system, means of neutralizing, and type of plant. Electrodialysis has the advantage of being fully automated with a consistent feed material to the tank; the ion exchange membrane having a considerable life unless subjected to physical damage.

Deficiencies of anodic electrocoat primers

The two main deficiencies are phosphate disruption and poor saponification resistance.

During anodic electrodeposition very high electrical field forces occur which rupture many of the metal–phosphate bonds (phosphate disruption). This leads to a weakening of the adhesion of the phosphate coating to the steel substrate.

When subsequent paint coats are applied, stresses are set up in the total paint film which when damaged to bare metal, tend to cause the total paint film to curl away from the damage point. In early anodic systems, as soon as corrosion started at any point of damage, the weakened phosphate layer allowed the paint to peel back, exposing more metal already chemically clean and very prone to corrosion. This failure was designated ‘scab corrosion’.

This property was improved by reducing the incidence of rupture of bonds by
simply increasing their number, i.e. phosphate coatings of densely packed fine crystals.

Such phosphate coatings are of low coating weight (1.8 g m\(^{-2}\)), and their introduction led to a marked reduction in the incidence of 'scab corrosion'.

Poor saponification resistance is due to the fact that the chemistry of anodic electropaints is such that they are formulated on acid resin systems. As a consequence the deposited stoved film, when exposed to an alkaline environment, will tend to form metal soaps soluble in water.

When damage occurs to bare metal, salt (as caustic) will simultaneously attack the steel substrate and the electrocoat film, producing rust and the sodium salt (soap) of the anodic resin. This dissolves the primer coating, leading to a loss of adhesion of the remaining paint film and general corrosion problems.

10.3.3.2 Cathodic electrocoat

Cathodic electroprimers had always been acknowledged to be theoretically desirable because of:

- their anticipated freedom from substrate disruption;
- the fact that cationic resins being 'alkaline' in nature would tend to be inherent corrosion inhibitors free from saponification.

However, the complexity of the required resin systems precluded their early introduction.

In the early 1970s successive outbreaks of serious motor vehicle corrosion in North America, combined with legislation for minimum corrosion standards, prompted the US motor industry to develop a process of guaranteed corrosion protection. The situation gave the impetus for the development of cathodic electrocoat in the USA, and it was introduced into the North American motor industry in 1978.

Resin system

All current cathodic products are based on epoxy/amine resin systems which are stabilized in water by neutralization with various acids. These products require a crosslinking agent to be present with optimum film properties being developed at high stoving temperatures (165–180°C).

Pigmentation

The basic properties are similar to those required for anodic electrocoat — simplicity, high purity, and the ability, in some form, to supplement corrosion performance and catalyse the curing process.

Pigment volume concentration is normally in the region of 10%.

Colour

The most popular colours vary from medium grey through to black, and the prime pigments and extenders align very closely to those used in anodic technology.

Mechanism of deposition

The same principles of electrochemistry apply as in anodic deposition. Key differences are as follows.
Solubilization of the resin:

\[
\begin{align*}
R & \quad R \\
R-N: + R'COOH & \rightarrow R-N-H' + R'COO^- \\
R & \quad R
\end{align*}
\]

\[(R = \text{epoxy}) \quad (R' = \text{solubilising acid})\]

Electrolysis of water:

\[
4H_2O \rightarrow 3H^+ + 3OH^- + H_2O
\]

Reduction at the cathode:

\[
\begin{align*}
H_2O & + 3H^+ + 4e \rightarrow 2H_2 + OH^- \\
R & \quad R \\
R-N-H' + OH^- & \rightarrow R-N: + H_2O \\
R & \quad R
\end{align*}
\]

Insoluble deposited coating

Oxidation at the anode:

\[
3OH^- - 4e \rightarrow H_2O + O_2 + H^+ \\
\text{acidic reaction}
\]

\[
H^+ \text{ removed by electrodialysis}
\]

\[
R'COO^- + H^+ \rightarrow R'COOH
\]

Performance characteristics

Cathodic technology rapidly replaced anodic products in North America since results from test track evaluations, and the field, confirmed the superior corrosion protection of cathodic systems. Where the cathodic system is particularly good is in its throwing power, being better than most anodics, and in its thin film (~12µm) performance particularly on unpretreated steel. This is found to be extremely important in box sections, etc., where the durability of the product is most vulnerable.

The Japanese automotive industry was also quick to change, with Western Europe following, even though European anodic technology was adjudged as being quite satisfactory at the time. Cathodic plants are now to be found in all parts of the world, e.g. Taiwan, Malaysia, Indonesia, Brazil, and the Philippines, with the overall objective to maximize standards.

Figure 10.4 clearly demonstrates the improvements made in corrosion protection, as measured by the ASTM salt spray test.

Plant requirements (refer Fig. 10.5)

Cathodic installations are basically similar to anodic plants in terms of paint circulation, refrigeration, filtration and the requirement for a smooth and stable direct current power supply.

However, there is a fundamental need to introduce either materials which are fully acid resistant or to use suitable acid-resistant coatings on mild steel. Stainless steel is the most common material, and pumps, valves, and piping are often made
of this. The high cost of stainless steel can often preclude its use and it is replaced with PVC and other plastics where feasible.

The electrocoat tank and rinse tunnels also need to be lined with acid-resistant materials although there are instances where stainless steel is used for rinse tunnel construction.

Dip rinsing
Cathodic electropaints operate at relatively high solids (20–22%) and the most effective method of rinsing has been found to be dipping. In this way ‘drag-out’ materials can be removed more effectively than the normal spray rinse procedure. Clearly, the more effective the rinsing, the better the economics.

The principal feature in design is to ensure turbulence in the dip rinse tank to effectively remove the dip layer (or ‘cream coat’).

Ultrafiltration
Ultrafiltration is pressure-induced filtration through a membrane material of very fine porosity. In the case of electropaints it can be regarded as a process which separates the continuous phase (water, solvent, and water-soluble salts) from the dispersed phase (resin and pigments). The velocity of the paint required to drive the process is about 4–4.5 m s⁻¹ (12–15 ft/s) or 150 litres min⁻¹. To avoid pigment precipitation in the tubes, and subsequent flux decay, this flow must be maintained.

The purposes of ultrafiltration are as follows:

- **Saving of paint.** This is the most important consideration. By utilizing the ultrafiltrate to rinse or wash the ‘drag-out’ paint (dip layer or cream coat) back into the tank, the efficiency of the paint usage can be improved by 15–20%.
Fig. 10.5 — Cathodic electrocoat plant.
• **Decontamination.** Soluble salts, which are derived from carry-over materials and which can significantly degrade performance and processing, can be purged or removed from the dip tank by simply discarding ultrafiltrate.

• **Control of paint performance.** In general terms, with cathodic electrocoat, purging is essential to maintain the paint within certain specified limits (normally 800–1200µS). This is needed to avoid any reduction in performance and for ease of processing.

• **De-watering.** When the tank solids are too low and tank value is high, solids may simply be increased by discarding ultrafiltrate and replacing with fresh paint.

**Control method**

The pH is controlled by the system of electrodialysis. A selective, ion exchange membrane is used around the anode and acid ions, generated during the electrolytic process, are allowed to pass through the membrane and are simply flushed away. Control is automated, using a recycling anolyte system, and the conductivity of the recycling liquid is maintained by integrating a conductivity meter with a de-ionized water supply.

**Pretreatment**

In relation to cathodic electropaints there have been quite significant advances in pretreatment development.

Spray phosphate systems suitable for anodic systems were found to give loss of adhesion under ‘wet’ conditions with cathodic products. The cause of this adhesion loss has been identified as cleavage of a secondary phosphate layer (chemically known as hopeite, \( \text{Zn}_3(\text{PO}_4)_2\cdot 4\text{H}_2\text{O} \)). This secondary phosphate has been termed ‘grass’ because of its appearance and because it ‘grows’ on top of the primary phosphate layer (chemically known as phosphophyllite, \( \text{Zn}_3\text{Fe}(\text{PO}_4)_4\cdot 4\text{H}_2\text{O} \)). In the anodic electrodeposition process this ‘grass’ is largely detached because of substrate disruption, but remains basically intact during cathodic deposition.

The high cohesive strength of the cathodic epoxy film exerts a pull on the weak secondary layer when swollen with the absorption of water. The net result is that cleavage takes place at this interface, which manifests itself in loss of adhesion.

As a result of this problem, with its associated mechanism, iron-rich homogenous zinc phosphate coatings of fine tight crystal structure were developed which had a minimal secondary phosphate layer. In fact, it is generally accepted that the greater the phosphophyllite content (i.e. the higher the iron content of the coating) and the lower the hopeite content, the better the likelihood of performance.

The phosphophyllite content of the coating can be derived by measuring the iron content of the coating, or better still by crystal structure analysis using X-ray diffraction. The result can be expressed as the so-called \( \text{P/P} + \text{H} \) ratio where \( \text{P} = \) phosphophyllite and \( \text{H} = \) hopeite contents of the coating.

Added insurance for optimum performance is often provided by a post-phosphate rinse with a weak chrome solution. This acts as a ‘knitting process’ which simply ‘knits’ the crystals together, aiding homogeneity.

European and North American manufacturers saw this post-phosphate route as an essential feature to maintain consistency of quality and performance. However, because of environmental restrictions, it was unacceptable in Japan. This led to dip phosphating being adopted in Japan since it had already been established that, by
utilizing the more controlled diffusion conditions afforded by dip processes, a higher degree of homogeneity in the phosphate coating could be achieved, i.e. the process favours the formation of the primary phase.

More recently there have been further developments in pretreatment technology. It has been clearly established that the achievement of optimum crystal structure is more important for good performance than simply obtaining a coating of low hopeite content.

Objectives have included developing products having a capability of being amenable to a truly multi-metal process (car-bodies now being constructed with a variety of metals apart from mild steel, e.g. aluminium, galvanized steel, etc.). Also there is a need for a reduction in energy demand (operating at <45°C).

Significant improvements have been achieved by incorporating other heavy metals rather than zinc, i.e. tricationic philosophy — zinc, manganese, and nickel in combination with crystal-modifying agents.

Benefits from this newer pretreatment technology are numerous:

- excellent performance under cathodic electrocoat;
- ease of operation of high zinc processes with none of the disadvantages;
- coating weight less critical;
- good crystal morphology;
- lower energy usage;
- multi-metal processing;
- optimum chemical efficiency;
- requirement of chrome rinse minimized and in most circumstances eliminated.

General appraisal and current developments
Cathodic electroprimers have led to major advances in corrosion protection. The levels of improvement have been significant and, in association with wax injection which is often applied in box sections, six years of anti-corrosion and freedom from perforation can be confidently expected. The product/process has shown itself to be stable and consistent in performance, a most important feature in mass-production terms.

However, the international motor industry continues to demand improvements to produce and process performance. The numerous influences on material formulation and the electrocoat process in association with market needs, and resultant development activities, may be briefly summarized as follows:

1. **Engineering.** Compatibility/paintability of a variety of substrates, i.e.:
   (a) plastics in body components,
   (b) bake hardened metals,
   (c) alloy coated steels,
   (d) pre-primed coil including ‘Bonazine’, ‘Durasteel’, etc.,
   (e) smooth steels, e.g. ‘Laser Etch’, etc.,
   (f) body shape and styling.

2. **Environmental:**
   (a) lower VOC and oven losses,
   (b) reduced effluent disposal/treatment (combined oxygen demand),
   (c) eliminate heavy metals and lower lead content.

3. **Performance:**
   (a) improved mechanical properties,
   (b) improved film smoothness and crater resistance,
4 Process:
(a) ease of usage, e.g. tank and ultrafiltration control,
(b) accommodation of line speed changes, e.g. effects on deposition time, stoving schedule, etc.

5 Economics:
(a) lower stoving temperatures (target 150°C),
(b) improved material utilization — uniformity of film thickness,
(c) reduction in ‘bake off’ losses.

Significant progress has already been made with many of the above properties but there is no doubt that developments will be on-going as performance standards continue to rise. In addition other pressures/needs such as environmental regulations and economic considerations will undoubtedly become more demanding.

10.4 Surfacers

10.4.1 Background
In spite of the development of more sophisticated priming and topcoat technologies, surfacers, sometimes referred to as fillers or middle coats, continue to play an important role in automotive coating systems. Originally designated primer surfacers, because of the basic undercoating system, their role as a primer diminished with the introduction of anodic electrocoat systems in the 1960s.

The role as a primer declined even further in the late 1970s with the advent of cathodic electrocoat. As a result of these changes in priming systems so newer surfacer technologies were developed not only to satisfy these changes but also to cope with more novel topcoats, new application techniques, higher performance standards, environmental requirements, and consumers’ expectations.

10.4.2 Introduction
When the assembled untreated metal car-body (often a mixture of steel and galvanized steel) arrives for painting the process, apart from protection and decoration, is expected to provide a degree of ‘filling’. This is necessary to hide any minor imperfections arising from the pressing and assembly operation. However, improvements in metal quality have been very significant and this has consequently affected the way surfacers are formulated.

The phosphating process has no filling potential and conventional dip and electroprimers have, because of their extremely low solids, minimal filling properties. Also, in the case of electroprimers, the inherent nature of the deposition process tends to emphasize any metal defects. As a result of this one of the primary functions of the surforcer was simply to ‘fill’ but with better standards of metal preparation this requirement is now much less important.

Furthermore, there are other highly important properties to be embraced, namely:
• mechanical properties such as impact and flexibility;
• stone chip resistance;
resistance to water/moisture;
- UV resistance — particularly significant when used in the basecoat clear process;
- good sandability/rectification properties;
- easy, efficient, and economical to use;
- amenable to a range of methods of application (i.e. good workability);
- tolerant to a variety of topcoats;
- provide a good even surface (with minimal or no sanding) to maximize the appearance and performance of the appropriate finish;
- good adhesion to both the primer (most probably cathodic electrocoat), anti-chip coatings, seam sealants, and the subsequent topcoat;
- adequate performance over phosphated or galvanized steel;
- tolerance to under- and over-baking at a recommended stoving schedule.

In addition to the highly important role of embracing the above properties, surfacers offer additional benefits such as flexibility and safeguards to the production process.

10.4.3 Product types and formulation
The development of suitable surfacers for mass production conditions has been strongly influenced by the following factors:

- new priming techniques/methods;
- improved quality of metal pressings;
- new topcoat technologies;
- overall improvement in performance standards;
- newer methods of application leading to more efficient and economical painting processes;
- requirements for lower levels of pollution.

Early primer surfacers were often formulated to give high build (40–50μm), were highly porous in nature with very high pigment volume concentrations (PVC) of 35–50% requiring heavy sanding, often ‘wet’ and by hand, to obtain an acceptable surface for finish application. Furthermore, because of the porous nature of the primer surfacer, a lowly pigmented sealer was sometimes applied to improve the appearance of the final topcoat. With the advent of electrocoat in the late 1960s surfacer film thicknesses were reduced (~35μm) with lower pigment volumes (PVC ~ 30%) and no need for different colour coats. Improvements in metal quality also had a significant role in reducing the level of ‘filling’ and current surfacers have PVCs down to ~15% giving the product topcoat-like properties.

These early products were also required to perform over pretreated steel and provide a level of corrosion protection. Applied in two coats, in a wet on wet procedure, the first coat was generally formulated with red oxide, supported by extenders and anti-corrosive pigments. This was then followed by a second coat of a grey or off-white primer surfacer. The difference in colour also minimized ‘rub throughs’ to the substrate, the ‘red oxide’ coat acting as a guide coat during the sanding operation. With the advent of electrocoat in the late 1960s surfacer film thicknesses were reduced (~35μm) with lower pigment volumes (PVC ~ 30%) and no need for different colour coats. Improvements in metal quality also had a significant role in reducing the level of ‘filling’ and current surfacers have PVCs down to ~15% giving the product topcoat-like properties.

In addition, there is now considerable use of ‘colour keyed’ surfacers formulated to align to specific coloured topcoats. There are two reasons for this. One is the drive for cleaner and brighter colours where opacity levels are often borderline and
the second is to economize in the use of highly expensive and sophisticated finishes.

In terms of gloss and appearance these types of surfacer have certain similarities to topcoats and are used quite satisfactorily inside engine and boot compartments. Also, because they are ‘colour keyed’ to individual topcoats they help bolster the opacity of the finish and minimize the use of expensive pigments.

In some Japanese plants ‘inner’ and ‘outer’ surfacers are often used. The ‘inner’ type of product has a high gloss (often using organic pigments in the formulation) and is very akin to a topcoat. They are applied directly to the electrocoat primer on all interior surfaces with no topcoat application. The exterior surfercer is of a more conventional nature and topcoat is applied in the normal way.

As far as resin systems are concerned a variety of alkyds were used in earlier products. These were superseded by epoxy-modified alkyds, epoxy esters, and more recently by polyester and polyester/polyurethane resins. Although solvent-based surfacers still tend to predominate, water-borne materials, because of their pollution advantages and good levelling, are attracting more and more attention and are now widely used in Europe. Water-borne surfacers are described in more detail later (see Section 10.13).

Epoxy-based products were commonly utilized over anodic electrocoat paints because of their excellent adhesion and water resistance. They were also used in the early days of cathodic electroprimers and minimal or non-sanding versions were developed to reduce the costly and labour-intensive sanding operation. However, during the late 1970s the advent of basecoat/clear metallic topcoats had a marked effect on the use of epoxy-based surfacers. Their poor resistance to erosion from UV radiation (chalking at the interface between topcoat and surfacer) led to delamination. As a result of this, polyester surfacers were developed which had far superior UV resistance.

Polyester surfacers, suitably modified with polyurethane resins, are now universally recognized as the best for all-round properties in modern undercoating systems. These products, with obviously accepted standards for chemical and physical properties, are designed for minimal or non-sanding to maximize their suitability for production purposes.

10.4.3.1 Resins systems

There are three distinct resin systems (Table 10.3) used in the formulation of surfacers:

### Table 10.3 — Main resin systems: comparison of properties

<table>
<thead>
<tr>
<th></th>
<th>Alkyd</th>
<th>Epoxy ester</th>
<th>Polyester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanicals</td>
<td>1</td>
<td>3</td>
<td>2 (3)*</td>
</tr>
<tr>
<td>Holdout</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Durability</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Chalking</td>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Levelling</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Sandability</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Filling</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

1 = poor, 2 = good, 3 = very good.
* PU modification.
alkyds;
epoxy esters;
synthetic polyesters.

All are reacted (crosslinked) with a suitable nitrogen resin and, in more modern systems, blocked isocyanates are incorporated. The crosslinking reaction is completed by stoving at a suitable stoving temperature, normally 20 min at 165°C (effective). Modification with epoxy resins was, and still is, included to improve certain properties and this will be described separately.

Alkyds
Alkyds surfacers, although now being replaced by other products, are based on a type of resin produced by the reaction of an alcohol (glycerol, glycol, etc.) and a dibasic acid (phthalic anhydride) and modified with a natural oil or fatty acid to give the desired balance of properties within an appropriate stoving schedule. For cost and other reasons typical oils are linseed, tall or dehydrated castor oil. Oil lengths are normally short, i.e. ~35%.

The crosslinking reaction needed to form a suitable film takes place between the alkyd and usually a melamine formaldehyde condensate involving N-methylol groups or their ethers.

Epoxy esters
As epoxy esters were developed they tended to replace alkyds in surfacer products because of their better all-round performance.

The terminal epoxide groups and the secondary hydroxyl groups of epoxy resins can be reacted with fatty acids to produce epoxy esters. Oil lengths of 30-50% (i.e. short) are normally utilized in surfacers and esters are usually based on linseed or tall oil. After stoving, in combination with a nitrogen resin, a harder film of superior adhesion, flexibility, and chemical resistance to similar alkyd/melamine formulation is formed.

The major weakness of epoxy esters is their instability to UV and this has led to problems of delamination of metallic finishes, particularly basecoat/clear materials.

Polyesters
Polyesters form the principal resin system of modern surfacers used currently in the motor industry. They are usually hydroxy functional saturated polyesters and are made from a range of synthetic fatty acids suitably balanced to generate an acceptable balance of properties. Polyesters have particularly good UV resistance and this was one of the reasons for their introduction. A typical example is a blend of the following monomers: isophthalic acid/teraphthalic acid/adipic acid/tri-methylol propane/neo-pentyl glycol.

Now 'modified' with polyurethane additions to improve mechanical properties they represent an excellently balanced product.

Epoxies: film modifiers
Epoxy resins have been used in surfacers, in one form or another, for a number of years because of their inherent strengths of adhesion, toughness, and corrosion resistance. They are still present in current polyester products to improve adhesion to
bare steel and to provide a degree of corrosion protection. In some cases stone chip performance is upgraded.

When formulating, epoxies should be considered as part replacement for the main resin at levels of about 10%. This amount is not normally exceeded because of UV instability. The low molecular weight epoxies give good adhesion but not particularly good flow. Increasing the molecular weight leads to slightly poorer adhesion but better flow.

The current trend is to move towards higher molecular weight due to carcinogenic concerns associated with lower molecular weight species. In fact some users are now specifying epoxy-free systems because of this concern. Often a blend of high and low molecular weight epoxies are used to achieve an optimum balance of properties.

Crosslinking resins
Traditionally melamine formaldehyde resin and, to a lesser extent, urea formaldehyde were used as the main crosslinking agents in surfacer formulations. Although cheaper, urea formaldehyde was dropped in favour of melamine formaldehyde over the years because of inferior performance, particularly over electrocoat primers.

More recently, isocyanates and benzoguanamine resins have been included (to improve certain properties).

Blocked isocyanates, normally hexamethylene diisocyanates, unblock at around 120°C to form a strong urethane linkage. These resins have been introduced to improve stone-chip resistance, film toughness, and impact resistance without leading to a loss in hardness. Surfacers formulated in this way are designated PU-modified.

Benzoguanamine resins are added to improve adhesion, flexibility, and overbake tolerance, i.e. there is no degradation in mechanical properties at elevated temperatures (up to 200°C) and/or extended stoving time. Conventional melamine formaldehyde resins would begin to break down and become brittle at such temperatures.

10.4.3.2 Pigmentation
Surfacers are highly pigmented products although more recent developments, in line with improved metal quality, have quite low levels of pigment and an appearance which almost lends itself to a topcoat. Traditionally, pigment volume concentrations (PVC) vary from 30 to 55% depending on physical and chemical requirements and the topcoat to be applied. The very high levels (55%) are limited to use with acrylic lacquers which have very poor adhesion properties. Modern surfacers, because of

<table>
<thead>
<tr>
<th>Description</th>
<th>Comments</th>
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<tbody>
<tr>
<td>Carbon black</td>
<td>Standard carbon black pigment</td>
</tr>
<tr>
<td>Inorganic yellow — iron oxide</td>
<td>Two types — both ‘dirty yellow’ but bluer alternative available</td>
</tr>
<tr>
<td>Organic blue — phthalocyanine blue</td>
<td>Standard prime pigment</td>
</tr>
<tr>
<td>Inorganic red — iron oxide</td>
<td>Two types — standard and ‘bluer’ alternative</td>
</tr>
<tr>
<td>Organic reds (range)</td>
<td>Normally restricted to ‘inner surfacers’ for use in interiors only</td>
</tr>
<tr>
<td>Organic yellows (range)</td>
<td></td>
</tr>
</tbody>
</table>
the reasons above, have PVCs as low as 15–20% with gloss levels of 80% measured on a 60° head.

The basic pigmentation is normally a blend of prime pigment (for opacity and colour) and extender pigment(s) (for economic reasons and where performance considerations allow).

In the past surfacers were spray applied in two coats wet-on-wet over dip primers or phosphated metal (film thicknesses were ~45 μm). The first coat was a red (iron) oxide followed by a second, normally grey. As mentioned earlier the first (red oxide) coat acted as a ‘guide coat’ to control sanding and to provide a measure of corrosion protection.

The advent of electrocoat has meant that the ‘red oxide’ coating has been dropped and now grey, off-white, and sometimes specific coloured surfacers are used, at a film thickness of 30–40 μm.

For example, a typical off-white surfacer would have a volume ratio of high grade rutile titanium dioxide (prime pigment) to barytes (extender) of 3:2 to 2:3 depending on required properties. The barytes contributes to reducing cost and resistivity, and to improving filling capacity: titanium dioxide to gloss and opacity.

Prime pigments
A good grade of rutile TiO₂, designed for high performance coatings, provides gloss and opacity. In the past, for reasons of economy, its content was kept to a minimum provided overall performance could be maintained. Nowadays, where high gloss levels are generally specified, TiO₂ predominates in the formulation with minimal and, sometimes, no extender present.

Anatase has poor UV resistance which is the reason it is not used.

Synthetic iron oxide used in past formulations provided colour and opacity. Although difficult to disperse it does have the important feature of good chemical resistance. This is important in surfacers.

Extenders
Extender pigments are much cheaper than prime pigments and, apart from reducing cost, can by careful selection improve certain properties of the finished product or dry coating. Proper choice can upgrade properties such as consistency, levelling, and pigment settling of the paint. They can also reinforce the dry coating’s mechanical properties and improve sanding and resistance to moisture and blistering.

The principal extenders are as follows:

- **Barytes** (barium sulphate). Originally the ‘natural’ form of barytes was used. It is extremely insoluble in water which gives good blister resistance but is hard with poor sanding properties and is difficult to disperse.

  It has now been replaced by blanc fixe, a precipitated form of barium sulphate. Precipitated forms of barytes are softer and easier to disperse than natural ones and are available in a range of particle sizes. All have very good blister resistance but they can lead to a level of thixotropy in the liquid paint. Fine grades may be used to give relatively high gloss levels in the final product.

- **China clay** (aluminium silicate). China clay, being inert and non-reactive, can play a useful role in the formulation of surfacers. It has a good colour and rubbing/sanding properties but its high oil absorption tends to reduce gloss.
In a typical surfacer pigmentation, to improve sanding properties and resistivity, 5–10% of barium sulphate may be replaced by china clay without significantly affecting overall properties.

- **Winnofil** (stearate-coated calcium carbonate). Provides ‘structure’ and anti-settling properties.
- **Talc** (magnesium silicate). The inert and hydrophobic nature of modern treated talcs, together with their availability in plate-like forms, can improve such properties as: water and humidity resistance; sanding properties (better than china clay); and film toughness.
- **Calcium carbonate** (chalk/Paris white). A widely used extender in the past, having properties of stability and cheapness. However, because of its reactivity with acids it has been removed from surfacer compositions. Evidence has suggested it contributed, in part, to the delamination of basecoat/clear finishes.

10.4.4 Polyurethane-modified polyester surfacer (including ‘colour keyed’ products)

10.4.4.1 Summary of basic parameters

**Solids content**

Unthinned material (45"/DIN 4/25°C)

- Normal solids: <63%
- High solids: <68%
- Colour keyed: dependent on colour (see below)

Thinned material (at spray viscosity)

- Normal solids: (~25"/DIN 4/25°C) ≤60%
- High solids: (~36"/DIN 4/25°C) ≤64%
- Colour keyed: (~36"/DIN 4/25°C)
  - Light Mid Grey Std: ≤64–66%
  - Inorganic pigments, e.g. off whites, pastels: ≤62–64%
  - Dark colours, e.g. blues, black grey, reds: ≤56–58%
  - Bright/transparent colours, e.g. light reds, yellows: ≤56–58%

**Specific gravity** (ASTM D1475)

1.2–1.4 (could be higher at high solids).

**Flash point**

≥21 °C.

10.4.4.2 Film properties (stoved film)

**Appearance**

After stoving the film must have a good appearance with no surface defects such as craters or ‘solvent popping’. Also it should have good flow (or levelling) and be free of mottle (orange peel) without tendency to ‘sag’ at high film thicknesses.
Film Thickness (dry): $-35 \pm 5 \mu m$.

Colour: off white/light grey: carried out visually. Needs to be within acceptable limits to original ‘approved’ sample.

Colour keyed: A match to original accepted standard.

Gloss (60° head): 75–85%.

Opacity (dry hiding): 25μm (black and white chart).

Sandability: the stoved surfacer must be amenable to wet sanding (P400 paper) or be dry sandable (P800 paper) by hand. Clogging of the paper, excessive sanding marks, and dusting are considered unacceptable.

10.5 Anti-chip coatings

10.5.1 Background and resin types

Introduced over the past decade the prime function of anti-chip coatings is to upgrade stone chip resistance on vulnerable areas. Particular areas are the door sills, front and rear ends below the bumpers, the underbody, and leading edges such as the front end of the bonnet. Sometimes, depending on the design of the car, these coatings are used up to ‘waistline level’ and, in some instances, as a complete coat but this is rather exceptional and uneconomic.

They are applied as high build products (50–100μm), wet-on-wet with the surfacer. Compatibility between the two coatings is essential to avoid problems such as cratering or poor ‘wetting’. The anti-chip coating is subsequently stoved (normally 20' @ 165°C) as a composite with the prior coat of surfacer.

There are three resin types:

- Polyester/PU. These are formulated with similar resin compositions to current polyester surfacers. Generally softer, they are crosslinked with melamine formaldehyde resins, applied at high film thickness of 50μm and have the advantage of superior appearance to the blocked isocyanate products described below.

- Isocyanate/cycloaliphatic diamine blends. One-pack products composed of a blocked aromatic isocyanate blended with a cycloaliphatic diamine. The final stoved film has a rubber-like character giving it exceptional mechanical properties but poor appearance.

- Powder coatings. Powder coating stone chip primers have found some limited use in the USA. These are described in more detail later.

10.5.2 Pigmentation

All types are pigmented in a conventional way with prime and extender pigments being included, although the level of extender has to be carefully controlled to avoid degradation of the mechanical properties in any way. Thixotropic aids such as Aerosil or Bentone are often used since they are extremely beneficial in reducing sagging tendencies at the very high film thicknesses of 50–100μm.

10.6 Inverted or reverse process

The established undercoating system, following the introduction of anodic electropainting was pretreatment/electroprimer/surfacer or sealer. Later the concept of
inverting, or reversing part of this process, was developed; the objective being to overcome some of the fundamental weaknesses of anodic electrocoat and maximize the performance of the paint components of the system.

A typical inverted process may be designated as follows:

- **Pretreatment (spray zinc phosphate)**
  - **↓**
  - **Spray surfacer to outer skin panels**
    - **(stove or partially stove)**
      - **↓**
  - **Electroprime (normal procedure)**
    - **↓**
  - **Final stove**

The main advantages are seen as:

- Higher film build and thus better corrosion protection on internal surfaces (due to insulating effect of coating on external and carbody interior).
- Improved filiform, scab corrosion, and blister resistance (no phosphate disruption on external surfaces).
- Better adhesion and stone-chip resistance of full finishing system — inverted surfacer can be formulated with suitable properties and greater tolerance to phosphate variations than electroprimers.
- Easier painting of composite metal bodies, e.g. steel, zinc, and aluminium: the different electrical properties of metals can give rise to problems during electrodeposition.

A number of manufacturers did experiment with this process utilizing solvent-based surfacers or powder coatings. Its adoption was inhibited by a number of factors:

- Poor appearance/performance at the surfacer/electroprimer interface. Although this problem may be resolved by the use of a water-borne surfacer having suitable electrical and compatibility properties.
- Capital cost required to modify existing plants.
- The advent of cathodic electrocoat and the simultaneous development of improved pretreatments and process control.

**Electro powder coating (EPC)**

This is another example of a reverse process but incorporating cathodic electroprimer. Originating in Japan, EPC is essentially a process in which a powder surfacer carried as a slurry in water is electrodeposited in a matter of seconds on to the phosphated carbody. Since the EPC has little or no throwing power it is confined to the outer skin panels. After rinsing and a set-up bake the car body is then cathodic electrocoated.

The cathodic electrocoat does not deposit on the electrically insulated EPC surfacer but rather is used to maximum effect in protecting the floor area, box sections, etc., and formulated accordingly.

The process has much to commend it from the standpoints of automation, quality consistency, elimination of a spraybooth, and the virtual absence of organic solvents. On the debit side, however, the present generation of EPC surfacers deposit films
of variable thickness and exhibit pronounced mottle or surface texture which requires considerable sanding before topcoat application.

10.7 Automotive topcoats

The differing and stringent demands made by the user, and the ultimate customer, have led to a number of different topcoat technologies. All have a different balance of properties closely aligned to particular test specifications and process requirements.

Automotive topcoats, being the final coat in the painting process, have need to both decorate and protect and this has to be reconciled with use in mass production. These requirements may be summarized as follows.

For decoration
- appearance/high gloss and smoothness;
- aesthetic/customer appeal.

For protection
- UV protection/colour stability/durability;
- humidity resistance;
- water resistance;
- chemical resistance;
- resistance to insect/bird effects;
- physical properties, e.g. mar resistance;
- mechanical properties;
- distortion resistance.

Materials to satisfy these needs are extremely sophisticated with can be subdivided into two basic forms — solid (or straight) colours and metallics:

- Alkyd or polyester finishes: solid colours.
- Thermosetting acrylic finishes (including NAD technology): solid colours and metallics.
- Thermoplastic acrylic finishes: solid colours and metallics.
- Basecoat/clear (solvent- and water-borne metallic systems): now include solid colours mainly in water-borne basecoat technology.

Alkyd/polyester finishes remain the most widely used throughout the world for solid colours, principally because of their low cost and ease of processing.

Thermosetting acrylic systems (or NAD) were originally introduced because of their good durability in metallic finishes, alkyds having poor performance. This type of finish was also adopted by many producers in solid colour form. However, at the present time, the use of this technology has greatly decreased. It can still be found in some truck plants (mainly in the USA), and in isolated plants in Japan where it is preferred to alkyds because of better acid resistance. Otherwise, its use is confined to various plants in the ‘rest of the world’.

Thermoplastic acrylic lacquers were widely used by General Motors for both solid colours and metallics. However, because of their very low solids content, which led to high levels of organic solvent emission, their use has diminished in recent
Automotive paints

years. They have been replaced by alternative solvent- or water-borne technologies to satisfy economic and environmental considerations.

Basecoat/clear metallics, both solvent-borne and water-borne, are now considered the ‘norm’ in the automotive sector for both appearance and performance. They have enhanced gloss, stylistic appeal, and outstanding durability — the clearcoat being based on a thermosetting acrylic resin ‘reinforced’ by a suitable UV absorber. This technology is also showing significant growth in solid colour technology, mainly because of performance and for reasons of technology rationalization where water-borne systems are used.

Water-borne basecoats, in metallic form, were originally introduced in the early 1980s to reduce the excessive solvent emissions from conventional basecoats. In addition, the proportion of metallic finishes versus solid colours was rising sharply, representing about 60% of production in the major manufacturing areas (Europe, USA, and Japan) further aggravating the emission problem. This technology now embraces solid colour basecoats as environmental demands have become more stringent and, as already mentioned, to rationalize the production process.

Their level of usage continues to grow rapidly throughout the world as stricter controls on solvent emissions have been introduced. Nevertheless growth did slow in the early nineties, principally because of the shortage of available capital for investment in new plant. Virtually all new plants which are being built have the capability of using water, e.g., stainless steel circulating systems, even if they are not doing so. This includes areas such as Eastern Europe.

Water-borne basecoats are now very widely used in North America, Japan, Germany, Scandinavia, the United Kingdom and other European countries mainly in line with environmental legislation. Current estimates suggest somewhere between 55% and 65% of European production is water-borne and that the worldwide figure is broadly very similar.

As far as solid colour basecoats are concerned a number of European manufacturers, e.g. Volkswagen, Volvo, BMW, and Mercedes, have all gone this way and are totally water-borne. Others are considering options and are likely to continue this way but they will be under increasing pressure to follow the water-borne route as environmental pressure increases.

10.7.1 Alkyd or polyester finishes

10.7.1.1 Basic chemistry

Alkyd finishes are based on a class of resins produced by the reaction of alcohols (glycerol, glycol, etc.) and dibasic acids (phthalic anhydride), and modifying with a natural or synthetic oil to give the designed balance of durability, flexibility, hardness, etc. The ‘oil’ or fatty acid is selected for its good colour and non-yellowing (non-oxidizing) characteristics, e.g. coconut oil fatty acid or 3,5,5-trimethyl hexanoic acid and simply acts as a reactive plasticizer. Typical alkyls are short/medium oil length (~35%).

Polyesters are typically isophthalic or adipic acid with pentaerythritol, neopentyl glycol, 1,6-hexanediol, or similar polyfunctional alcohols.

However, because of the ever-increasing demands of performance specifications and emphasis on higher solids there is much more use of alkyls produced from syn-
thetic fatty acids rather than oils (e.g. iso-nonanoic) which can give lower viscosity alkyds. Similarly, both alkyds and polyesters are frequently modified with Cardura E (see Section 2.5.1) to improve durability, chemical resistance, colour retention, and higher solids.

The crosslinking reaction, need to form an insoluble film, takes place between the alkyd (or polyester) and a melamine formaldehyde condensate involving \(N\)-methylol groups or their ethers. The melamine formaldehyde is normally alkylated but, as performance requirements and demands for higher solids have increased, isobutylated or ‘mixed’ are used rather than the traditional \(n\)-butylated type.

A stoving temperature of 20 minutes at 130°C is suitable for effecting suitable cure.

### 10.7.1.2 General properties

These may be summarized as follows. Widely used for solid colours in Europe, Asia, Pacific Rim, and the rest of the world. In North America acrylics predominate.

- Relatively high solids (~50% w/w).
- Low cost.
- Ease of processing.
- Good durability.
- Tolerant to a wide range of undercoats.
- Proneness to dirt pick-up (film wetness).
- Relatively poor polishing properties.

Their high solids, low cost, and ease of processing (40–50\(\mu\)m in two coats wet-on-wet application) has helped to maintain their popularity. These properties enable good build (and filling) properties and very good appearance after stoving. Also they have good durability, being equivalent to thermosetting acrylics after two year tests in Florida (5° south).

However, on the debit side they do have relatively poor solvent release, compared with acrylics, and the wet film is prone to pick up dirt. Clean operating conditions are particularly important as a consequence. Also their somewhat limited polishability makes minor rectification on a production line difficult.
More recently there has been a move in some plants to use basecoat/ clear
technology (refer Section 10.7.4) for dark colours to improve appearance, mar, and etch resistance. Also for 'lead-free' red topcoats when used in combination with a red 'coloured surfacer', to overcome appearance, durability, and coverage problems.

10.7.2 Thermosetting acrylic/NAD finishes
The use of thermosetting acrylic finishes has decreased significantly in recent years although the technology forms the basis of clearcoat formulations. In addition, NAD technology, i.e. the stabilization of discrete polymer particles in organic solvent, originated in the automotive sector and has since been extended into water-borne systems.

10.7.2.1 Basic chemistry
Thermosetting acrylics are based on complex acrylic copolymer resins produced by the reaction of a number of acrylic monomers selected to give the desired balance of properties. The required crosslinking reaction, with a suitable melamine formaldehyde resin, is facilitated by the presence of hydroxyl groups in the polymer backbone. The hydroxy-containing polymers are readily prepared by the use of hydroxy-acrylic monomers.

A stoving of 20 minutes at 130°C produces an insoluble crosslinked film:

\[
\text{Melamine} \quad \text{Formaldehyde} \quad \text{NHCH} - \text{OR} + \text{HO} \quad \text{Acrylic} \\
\downarrow \\
\text{Melamine} \quad \text{NHCH} - \text{O} \quad \text{Acrylic} \\
+ \text{ROH}
\]

Early thermosetting acrylic finishes were made from these resin systems, and they allowed the formulation of solid colours and metallic finishes. Durable metallic paints were made by incorporating non-leafing aluminium flake (via an aluminium paste) into the film. The non-leafing flake (15–45 μm in length) distributes randomly through the coating and produces specular reflection from almost any angle of view. Suitably pigmented with coloured pigments, extremely attractive colour ranges were produced.

These types of finish, introduced in the late 1950s and early 1960s, found wide usage through the world and in modified form still find use today. Their deficiencies are the requirement for three coats, because of solids content, and the difficulty in metallic application. The introduction of NAD versions of these finishes in the late 1960s enabled problems to be overcome.

Whereas with conventional thermosetting acrylics the resin is carried in solution, NAD finishes are based on the dispersion of similar polymers in a solvent mixture such that a significant proportion of the polymer is insoluble, even at application viscosity.

These dispersion are stabilized by the presence of aliphatic soluble chains (i.e. by the use of an amphipathic graft copolymer) which are chemically linked to the polymer particles during the polymerisation process. Such dispersions are referred
to as ‘super-stabilized’ to distinguish them from systems where stabilizer is held on the surface of the particle by physical or polar forces.

As long as a substantial proportion of aliphatic hydrocarbon is present in the continuous phase of the dispersion these chains are extended and provide a stabilizing barrier around each particle. In order to promote eventual coalescence of these particles into a continuous film the volatile portion of an NAD finish also contains some solvents for the polymer itself. The amount of such solvents is controlled so that the stabilizing chains are not collapsed while the finish is in the package or the circulating system at the automotive plant. These solvents can be shown to partition themselves between the polymer (leading to softening and swelling of the particles) and the continuous phase.

On application of the finish, evaporation of the aliphatic non-solvents leads to fusion and coalescence of the solvent-swollen polymer particles to give a continuous film; the process being completed by the stoving process. The structure of the final film is almost identical to that laid down from a conventional solution polymer.

Although the basic technology allows the preparation of dispersions where practically all the polymer is in the disperse phase, the rheology of ‘all disperse’ systems is not necessarily the optimum for achieving latitude necessary under production line conditions. However, definite benefits can be gained by having some polymer in solution and an important part of the technology consists of establishing the optimum ratio of disperse to solution resin for each polymer system. The rheological characteristics of such thermosetting acrylic formulations are unique and lead to greatly improved control of metallic finishes, better utilization of paint solids, and greater resistance to sagging and running.

10.7.2.2 General properties
These may be summarized as follows:

- Durable in solid colours and metallics (single coat).
- Solids lower than alkyds (~30%).
- Applied in two or three coats.
- Good polishing properties.
- Good solvent release.
- High performance undercoat required, e.g. polyester/PU.

Thermosetting/NAD acrylic finishes can be formulated in both solid colours and metallic and it is possible to produce a wide and attractive colour range. Their rapid solvent release minimizes dirt pick-up and their good polishing properties make them more amenable to local rectification in production lines. They require high grade undercoats, such as a polyester/PU type, to maximize their performance. One other important feature is that thermosetting acrylics can be used directly over electroprimers because of their inherent adhesion properties. Alkyd finishes cannot, and poor adhesion can result. It is for this reason that acrylic finishes are always used in the two-coat electroprimer/finish system adopted for commercial vehicle production.

10.7.2.3 Metallic appearance
A good metallic finish is designed to achieve a pronounced ‘flip’ tone, i.e. the polychromatic effect seen when viewed from different angles. It is simply an optical effect and depends on the orientation of the metallic flake parallel to the surface so
that the amount of light reflected varies with the angle of viewing. Thus at glancing angles the surface appears deep in colour. In fact, the aluminium flake can be regarded as a small plane mirror.

In order to achieve this optimum orientation it is necessary to ensure:

- spray application is uniform;
- maximum shrinkage of the film after application so that the aluminium flake is physically ‘pulled down’ parallel to the surface;
- minimum tendency for the flake to reorientate randomly after application.

Typical solution thermosetting acrylic finishes go some way to meeting these requirements by changes in solvent composition, resin flow and design and differing types of aluminium. High levels of operator skill during application are also necessary since uneven application leads to areas of different colour and overwetness allows the aluminium flake to move around producing lighter and darker patches (sheariness or mottle). Dark lines (black edging) can also form around the edges of holes in the body shell or along styling lines. To overcome these problems solution enamels are sprayed as dry as possible consistent with gloss and flow with low film thicknesses often resulting.

Introduction of dispersion systems, often in combination with solution technology, eased the situation considerably by introducing improved rheology to the paint film. As previously stated a dispersion does not exert such a strong viscosity influence in a film as a solution version of the same polymer. However, in passing from the dispersed state to the solution state as the non-solvent part of the liquid evaporates, a sharp increase in viscosity is introduced. As this change occurs in the wet paint film after spraying there is a faster increase in viscosity at this stage than would be produced purely by evaporation of the liquids. This effectively reduces the amount of movement available to aluminium flakes, restricts any tendency to reorientation and allows an even appearance to be produced more easily.

10.7.2.4 ‘Sagging’
The same rheological control described above, exerted by the change from disperse to solution phase, has resulted in a marked reduction in ‘sags’ and ‘runs’ with dispersion coatings. A higher build can also be applied to fill minor defects. These improvements are particularly marked in highly pigmented colours such as whites and oranges.

10.7.2.5 ‘Solvent-popping’ resistance
‘Solvent-popping’ (sometimes designated as ‘boil’) is caused by the retention of excessive solvent/occluded air in the film which, on stoving, escapes by erupting through the surface. It invariably occurs on areas where there is above-normal wet paint thickness. Solution acrylic thermosetting finishes are very prone to this because of their fast ‘set-up’ rate immediately after application.

It would be imagined that dispersion systems would suffer the same problem since the polymer compositions are similar. However, dispersion systems do show advantages. The reasons are probably two-fold:

- Better atomization during spraying leading to a finer droplet size.
- The utilization of non-solvents, not associated with the polymer; this leads to a faster and more effective ‘solvent’ release.
10.7.3 Thermoplastic acrylic lacquers

Acrylic lacquers were widely used throughout the world for many years by General Motors and prestige car producers such as Jaguar. Their enhanced appearance, particularly metallics, proven durability, and in-process flexibility (self-repair and polishability), made for an attractive technology.

Nevertheless, their high level of solvent emission during processing and high cost of application have led to a significant decline in their use. Recently, they have been replaced by other technologies more environmentally acceptable, particularly water-borne basecoats which are described in more detail later.

Although this technology is considered outdated it is still worth including in this chapter. One reason is for completeness, since the author would like to cover the whole range of topcoat technologies, particularly one that found such considerable use over the years. The other reason is that this technology forms the basis of repair lacquers because of its air dry and low bake capability.

10.7.3.1 Basic chemistry

Acrylic lacquers, in common with all lacquers, dry simply by the evaporation of solvent, and are based on a hard poly (methyl methacrylate) polymer that is suitably plasticized. Plasticizers are normally external and include butyl benzyl phthalate and linear polymeric phthalates derived from coconut oil fatty acid. The external plasticizer ensures a good balance of properties, i.e. improved crack resistance, adhesion to undercoats, solvent release properties, and flexibility.

Most common acrylic polymers for this type of finish have average molecular weights of approximately 90 000: these give outstanding gloss retention on external exposure. Polymers with average molecular weights greater than 105 000 tend to cobweb or form long filaments when applied by spray at commercially acceptable solids contents. Low molecular weight polymers result in poor film properties and poor durability. Furthermore, the improvement in gloss retention when the molecular weight is increased above 105 000 is proportionally small, and is more than offset by the reduced solids at application viscosity.

Solvent blends used for lacquers are balanced compositions, albeit expensive, chosen to given acceptable viscosity, evaporation, and flow characteristics. To avoid excessive solvent retention in the film it is necessary to use solvents free from high boiling 'tail' fractions, and to balance carefully the evaporation rates of the remainder. The external plasticizer assists in solvent release by maintaining a fluid film for as long as possible; this allows shrinkage stresses (considerable in acrylic lacquers) caused by the drying/stoving process, to be relieved.

Although acrylic lacquers will ultimately air-dry, in practice drying is accelerated either by a short stoving, 30 minutes at 90 °C, where polishing is required to achieve acceptable gloss, or by the bake-sand-bake process. In this latter process surface imperfections of the film are removed by sanding after a short set-up bake (15 minutes at 82 °C), and the film is reflowed (20 minutes at 154 °C) to give a glossy flaw-free film.

10.7.3.2 General properties

These may be summarized as follows:

- Very good durability in solid colours and metallics.
- Robustness and adaptability in production.
• Good polishing and self-repair properties.
• Reflow (bake–sand–bake) process
  set-up 15 minutes at 82°C
  reflow 20 minutes at 154°C (effective metal temperature).
• Excellent metallic appearance.
• Low application solids (15–20%)/multi-coat process.
• Requirement for large quantities of expensive thinners.
• High raw material costs.
• Special undercoats needed.

It is worth noting that the outstanding appearance of acrylic lacquer metallics is due to its inherent properties:

• Low solids products.
• Multi-coat process.
• Carried in high viscosity/high molecular weight acrylic polymer.

These properties meet the necessary criteria for optimum ‘flip’ tone, i.e. high shrinkage, rapid solvent release, and thin coats restricting by shear geometry reorientation and movement of aluminium flake.

The disadvantages of acrylic lacquers also stem from their fundamental characteristics:

• Low application solids means up to four coats are required to achieve the film thickness (55–60μm) necessary for reflow. Multi-coats also mean long spray booths with the inherent cost.
• Appearance on force drying at low temperature (80–90°C) is poor, requiring excessive polishing to achieve acceptable gloss.
• High raw material costs, especially for solvents.
• Poor intrinsic adhesion entailing the use of special undercoats (high PVC, 55% epoxy-ester). In fact the choice of undercoat has a greater influence on general performance than other types of finish. Special adhesion-promoting sealers are also used, which add even more to the cost of the process.

These weaknesses, particularly the high level of solvent emissions and processing costs, have been the main cause of the demise of this technology and it has been replaced by more economic and less polluting products, i.e. alkyds, basecoat/clear and water-borne topcoats.

10.7.4 Basecoat/clear technology

10.7.4.1 Solvent-borne
As has been described earlier, metallic car finishes have been used by the majority of large car producers for a considerable time. Metallics, because of their stylistic appeal, have been considered a very desirable feature of finishing by both colour stylists and designers alike. In the form of what are designated ‘single coat’ metallics they have been supplied either in thermosetting or thermoplastic acrylic technologies.

However, they do have a number of inherent disadvantages compared with solid colours:
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- Lower gloss levels — particularly in light metallics.
- Limitation in certain pigment areas such as organic pigments.
- Poorer resistance to acidic environments.
- Application difficulties: eased by the introduction of NAD thermosetting acrylics.

The concept of putting the aluminium flake in a separate foundation or basecoat and then overcoating with a clear resin was first thought of and applied several decades ago. ‘Flamboyant’ enamel technology used on bicycle frames is a case in point.

Certain European car manufacturers saw this type of technology as overcoming the weaknesses described above and introduced basecoat/clear technology into production in the late 1960s. The basecoat provided the opacity and metallic appearance while the clear imparted gloss, clarity, and overall durability. The use of this technology has subsequently grown considerably and is now considered the ‘norm’ for metallic finishes in Europe, Japan and North America.

In some plants there has been a move to solid colour basecoats for use in dark colours to improve appearance, mar, and etch resistance and also in red topcoats when used in combination with a coloured red surfacer.

Basic chemistry
The function of the two components has been described above, and this is achieved in the following manner.

The properties of the basecoat are:

- high opacity (~10μm) to facilitate application in thin films;
- rapid solvent release — short drying time (2–3 min) before application of clearcoat;
- low solids (<20%) to achieve maximum metallic effect;
- ‘compatibility’ with the clearcoat, i.e. good adhesion with no sinkage of clear.

Basecoats are thermosetting products modified with resins such as cellulose acetate butyrate to promote ‘lacquer dry’ and to accelerate solvent release. The basic resin component is either an oil-free polyester or a thermosetting acrylic polymer suitably reacted with nitrogen (melamine) resin. The features of these two types may be summarized as follows:

- Polyester type: initially a low solids product (10–12% w/w) recognized for outstanding metallic appearance and ease of application. In recent years there has been a tendency to move to ‘medium solids’ polyester basecoats (15–18% w/w) to minimize solvent emissions. This change has had a minimal effect on metallic appearance. (Main basecoat used in Western Europe.)
- Acrylic type: higher solids than polyester type (15–20%), less pronounced metallic effect, but better filling properties and shorter processing time. (Main basecoat used in Japan and USA.)

The properties of clearcoats are:

- good clarity of image and ‘compatibility’ with basecoat;
- offers a high level of protection to ultraviolet, i.e. >3 years’ Florida exposure.
There are two types of technology in use at the moment: thermosetting acrylic (solution and NAD), formulated on crosslinking thermosetting acrylics reacted with a melamine resin and modified with UV absorbers and light stabilizers. These materials are applied at a film thickness of 35–50μm to achieve maximum gloss and UV protection.

The features are:

- Solution acrylic type: a high gloss product giving outstanding clarity. Applied in one or two coats.
- NAD acrylic type: A single coat product with lower clarity than the equivalent solution type. (Has a low usage in the motor industry.)

Two-pack 2K clearcoats are two component acrylic compositions using an isocyanate crosslinking mechanism. Their features are:

- High solids (60–70%), applied in one coat.
- Low stoving temperature (80°C).
- Very good etch and mar resistance.
- Health risk/toxicity due to free isocyanate. Precautions needed.
- Expensive.

Application/process
The basecoat is applied as a two-coat wet-on-wet process with a short air drying time between coats. This is necessary to give acceptable opacity and evenness of appearance. After application of the second coat of basecoat has been completed, a short air drying time (2–3 min) is allowed, sometimes supplemented by a warm air blow, before the clear is applied in one or two coats.

Typical film thicknesses for the system are:

- Basecoat: 15μm.
- Clearcoat: 35–50μm.

Stove for 30 min at 130–150°C to effect crosslinking.

Colour/pigmentation
The pigments used in metallics in general are chosen for their potential transparency, realized when they are correctly dispersed and stabilized. Full transparent coloured pigments leave the metallic flakes free to contribute the maximum of brightness, sparkle, and flip tone.

Provided that satisfactory transparency exists, metallic appearance will depend upon the orientation of the flakes. As described earlier, if each flake is parallel to the substrate then this will give the optimum metallic effect or 'flip tone'. The light-reflecting quality of metallic coatings can be measured by a goniophotometer. This instrument is particularly useful for measuring the reflectance of unpigmented silvers, since the performance of different silver paints can be compared without any additional reflection and absorption by coloured pigments.

In Fig. 10.6, instrumental comparisons are made of various metallic technologies demonstrating the excellence of low solids polyester basecoats. At a standard angle of incidence (45°) reflectance is measured at various viewing angles, and a curve is plotted; the higher the peak the better the reflectance, indicating the extent of parallel metallic orientation.
Aluminium flake orientation
It has already been stated that the principal factor regulating aluminium flake orientation is film shrinkage during the drying process. Loss of solvent from the applied film during the flash-off and baking periods presents the flakes (typically of length from 10 to 25 μm) with an ever-decreasing freedom of movement. Surface tension, together with the large size of flakes, ensures that the flakes will align more or less parallel to the substrate.
However, the state of ‘almost parallel’ alignment can still cover great differences in visual appearance and metallic systems where all the flakes are aligned nearly perfectly parallel to the substrate will exhibit a far brighter appearance than systems containing many flakes at angles of, say, up to 20° to the surface. This is particularly true of very bright low solids basecoats. In addition dry film thickness is of the same order as, or even frequently less than, the flake length. This constrains flake mobility very effectively, particularly as the dry film thickness in the final stage of the drying process involves a very high degree of shrinkage.

All these factors combine to give low solids basecoats such an attractive, stylistic appeal.

Undercoats
In general terms basecoat/clear technology requires polyester/PU surfacers to maximize performance, particularly in the resistance to delamination. As described in Section 10.4 epoxy products tend to ‘chalk’ at the interface between undercoat and basecoat due to UV radiation. In the past this has led to breakdown in the field of early basecoat/clear systems.

Nowadays the use of polyester surfacers, combined with UV absorbers and light stabilizers in the clearcoat, has resolved this problem. In fact the performance of basecoat systems both on test at Florida and in service is exceptional (see below).

Performance/durability
Durability testing at Florida (5° south) is a universally accepted measure of exterior durability in the automotive industry. Florida is very suitable for such testing because it is high in ultraviolet and humidity.

Early clearcoats were based on alkyds but failed due to cracking (UV degradation) within 12 months. Modern thermosetting acrylic clearcoats have quite outstanding durability — a minimum of three to five years can be confidently expected. Such high levels of durability are unique to basecoat/clear technology, since the normal accepted standard is two years at Florida free from defects.

It is also possible to use a wider range of pigments in basecoat technology than thermosetting or thermoplastic acrylics; not only because of the pronounced face/flip contract but also because it is feasible to use a much wider range of organic pigments than hitherto without sacrificing colour stability on exposure.

Organic pigments have high transparency but poor coverage and often poor durability. However, since there are no gloss constraints with basecoats, high levels of such pigments can be used at low film thicknesses (15μm). The clearcoat provides gloss and offers the necessary ultraviolet protection.

10.7.4.2 Water-borne
During the past 20 years car manufacturers have been under increasing pressure to reduce, and possibly eliminate, volatile organic solvents present in such coatings.

This pressure has come in two forms:

- From environmental and health and safety agencies, anxious to preserve the environment.
- As an economic pressure to maximize the efficiency of production processes to meet competitive market conditions.
The environmental and ecological pressures were, and still are, particularly strong in North America. Europe likewise has introduced stricter controls on solvent emissions over the past 20 years.

In terms of the stoving operation the use of mechanical, thermal, and chemical techniques, including after-burners, scrubbers, and carbon absorption units, has improved the situation. However, there still remains the vast amount of solvent-laden air from spraybooths to cope with. Figure 10.7 shows the level of solvent emission for a typical low solids solvent-borne basecoat system. Clearly, the basecoat contributes the highest level of solvent emission and if you consider the introduction of more and more stricter controls over such emissions then a technology needed to be developed to resolve this problem.

Water-borne systems were considered to be the best solution to the problem particularly when compared with the alternatives (see Section 10.13). Development began in the late 1970s with the following objectives:

- To achieve the highest standards of appearance.
- Current ease of application.
- Use of existing spraybooth/processing conditions.
- Greatly reduced solvent emission levels.
- Use of current and future clearcoat technologies.

Once the objectives were clearly defined the following formulating principles were used in the development programme:

![Fig. 10.7 — The basecoat clear process (total emissions).]
• Use of aqueous polymeric dispersions.
• Water release aided by low basecoat film thickness (12 μm) and a high pigment content.
• Novel rheological control introduced via the polymer system.

The development and introduction of this technology has been quite rapid and its use continues to grow throughout the world (detailed in the introduction to this section).

The main features of water-borne basecoats are summarized below and its effect on reducing emissions is shown in Fig. 10.8:

• Film properties at least comparable to existing standards.
• Maintains the highest appearance standards (Fig. 10.6).
• Excellent durability under a wide range of clearcoats.
• Similar processing requirements to existing products.
• Adaptable to automatic (robotic) and electrostatic application.
• Low solvent emission.
• Improved usability and user environment.

Processing
The general application and processing of water-borne basecoats has been less of a problem than would have been anticipated from the experience with early water-borne technologies. It is also being broadened into solid colour basecoat technology because of the need for process rationalization and the technology's outstanding performance.

Characteristics
Detailed plant and processing requirements may be summarized as follows:

<table>
<thead>
<tr>
<th>85%</th>
<th>75%</th>
<th>60%</th>
<th>13%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>Medium solids</td>
<td>High solids</td>
<td>Water-borne basecoat</td>
</tr>
</tbody>
</table>

Fig. 10.8 — Emissions of metallic basecoats. --- % organic solvents (100% = wet paint).
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- Force dry (blow off, 2 min at 40–70°C) required before clearcoat application.
- Operating humidity needs to be controlled: 40–80%.
- Stainless steel paint circulation equipment.
- Isolated material feed needed for electrostatic application.

In summary, water-borne basecoat technology is not only highly innovative but it is unique. This uniqueness is twofold in that it has maintained and improved topcoat appearance and performance and also, with the aid of rotory atomizers, made a significant impact on reducing solvent emissions.

Its future is soundly based. It is expanding into solid colour basecoats and, with newer clearcoat technologies in the pipeline, it is likely to become a permanent feature of the car painting process for many years to come.

\section{10.7.5 Pigmentation of automotive topcoats}

The choice of pigmentation for any particular colour must be considered in the context of the requirements of the market in which the product is to be used. In this respect the motor assembly market is probably the most demanding of all, requiring class ‘A’ matches at all times, excellent durability under severe conditions, and good opacity at minimum cost. Thus, for most types of topcoat many of the lower-cost pigments with inferior lightfastness cannot be considered, and the range of colours which can be used is limited in comparison to other markets, e.g. decorative paints.

\subsection{10.7.5.1 Solid colours}

Pigmentation practice for all types of automotive technology is very similar. As a general rule (apart from some relatively minor differences in performance) alkyds/polyesters and thermosetting acrylics can be treated as identical. However, in acrylic lacquers whites are more prone to chalking, reds and violets tend to fade more in pale shades, and colour retention of some phthalocyanine blues is not as good as in the other technologies. The following general constraints apply.

\textbf{Durability}

Many organic pigments are completely excluded or can be used only at certain concentrations or when combined with other pigments of excellent durability.

\textbf{Opacity/gloss}

Very clean, bright, pure colours are often non-feasible because the pigment loading required to achieve opacity reduces gloss to an unacceptably low figure. Inorganic pigments should always be used where possible because of their opaque nature but stronger organics such as blues, greens, and violet are also helpful.

\textbf{Cost}

Most organic pigments are very expensive and in many cases of relatively poor tinting strength. The most notable exceptions are phthalocyanine blues and greens which are less costly than most and, because of good tinting strength, can be used in lower concentrations.

\textbf{Bleed}

Many organic reds and yellows are excluded because of a tendency to bleed.
Metamerism
This describes the phenomenon observed when two samples are similar in colour under one set of lighting conditions but different under another (commonly daylight and a tungsten filament lamp). This usually occurs where pigments of a different type to those in the original ‘master pattern’ have been used. Pigments especially prone to this are iron oxides and phthalocyanines.

Use of lead chromate pigments
Automotive topcoats are heavy users of lead chromate/sulphate/molybdate pigments because of their brightness of colour, good tinting strength, and low cost. Their limitations are, however, considerable:

- On exposure to sunlight lead chromate pigments darken. This is particularly obvious in the bright yellow shade and varies with seasonal changes at the exposure site and the degree of pollution in industrial atmospheres.
- Lead chromates are also susceptible to attack by dilute acids, the colour being bleached out. This can show as white spots or as an overall effect.
- Acid-catalysed repair films will also darken more readily because of the influence of the acid on the surface coating of the pigment.

Environmental pollution problems are leading to more and more demands for automotive paints to be lead/chromate-free. Unfortunately, many of the alternatives available for production of clean, bright colours are very costly, difficult to achieve opacity/gloss to meet specifications and, particularly with yellows, of poor durability. However, a reasonable range of lead-free reds can now be produced although there are still many problems to be overcome before the totally lead-free situation is reached to the satisfaction of all concerned, i.e. colour stylist, paint manufacturer, end user and environmentalist.

10.7.5.2 ‘Single coat’ metalics
General pigmentation practice is the same for both thermoplastic and thermosetting acrylics, although some organic pigments, particularly certain yellows and phthalocyanines, perform slightly better in the former technology. The following constraints apply:

Durability
There are even more constraints on organic pigments than in solid colours, particularly with pale shades. These are often borderline for feasibility unless performance is boosted by the use of a UV absorber or the inclusion of transparent iron oxide pigment. This is normally the only inorganic pigment used in metalics. Both red and yellow shades are available, can be prepared in highly transparent form, are of excellent durability (apparently having some UV-absorbing property), and are cheap. Their only disadvantage is weakness/dullness of colour.

Opacity/gloss
In any metallic finish aluminium flake contributes most of the opacity, since transparency of the tinter is essential for tone metallic appearance (flip tone). Deep, clean metallic colours (low aluminium level) are therefore usually more difficult to formulate than pale shades unless some black can be included. The most difficult areas of all are the clean, bright red shades where the majority of durable pigments avail-
able have poor tinting strength and the aluminium level must be kept low to avoid producing a greyish pink tone.

**Cost**
The cheapest durable pigments available for metallics are the transparent iron oxides which account for the popularity of metallic gold, beige, brown, and bronze colours. Phthalocyanine blues/greens also feature prominently because of their high tinting strength and relatively low cost.

**Colour matching**
Metals must match the master pattern at all angles of viewing. Colour achieved from a metallic is very considerably influenced by conditions during film formation. The paint must be formulated and applied such that during drying the aluminium flakes align parallel to the substrate surface to ensure maximum brightness and degree of flip. Obviously any variation from one sprayout to another will result in a different colour and for this reason automatic application is used wherever possible, particularly when colour matching. Spraybooth conditions, i.e. temperature, humidity, and air-movement, also need to be closely controlled.

**Choice of aluminium flake**
Various grades are available differing principally in particle size. As a general rule, as size increases sparkle increases, colour becomes brighter (less grey), and flip tone increases. On the debit side, gloss, image clarity, opacity, and tinting strength diminish. Therefore the usual compromise is between adequate opacity/gloss and degree of brightness. The medium/fine grades are most popular and least likely to give problems. Very coarse flakes should be avoided whenever possible.

**10.7.5.3 Basecoat/clear metallics**

General pigmentation practice is the same for both types. Constraints are as follows:

**Opacity**
This is normally expected to be in the range of 10–20μm. As with 'single coat', most of the opacity is obtained from aluminium, therefore the same basic constraints apply, particularly with the low solids polyester type where a very high degree of flip is expected. Again, bright reds are the most difficult. The big advantage over 'single coat' is that no consideration need be given to gloss, therefore much lighter colours can be achieved because of the higher aluminium levels permitted.

**Cost**
The same constraints as for single coat apply.

**Colour matching/durability**
A much wider range of pigments is available for use in basecoat systems because of the protection afforded by the use of UV absorbers and light stabilizers in the clearcoat (which serve a dual purpose in preventing breakdown of clearcoat due to UV and also protect pigments in the basecoat). Many of the organic pigments prone to fade on exposure can therefore be used in base/clear systems, and the range of colours available is much greater. This is particularly true of the bright pastel shades where a combination of wider pigment range and better aluminium laydown produces some very attractive colours.
The same constraints on application parameters apply to basecoats as to single coat.

Choice of aluminium flake
As with 'single coat', medium-fine flake is preferred. Coarse flakes cannot be used. In addition to poor opacity, with the very low (10–20μm) film thickness of basecoat films applied, the flakes size (up to 30μm) is such that if application is not perfect, flakes may protrude through the surface of the basecoat, giving a seedy appearance and the danger of film breakdown.

In addition to this, coarse flakes can cause safety problems on electrostatic application (discharge to earth through the pipework of the circulating system). Table 10.5 provides a comparison of the basic processing properties associated with automotive topcoats.

10.8 In-factory repairs

After the initial paint process the car body is trimmed and final assembly completed. During this latter part of the process minor paint damage can often occur which will require repairing; the quality of such repairs must of need align to the quality of the original paint finish.

Final repairs can be effected in two ways:

- Panel repairs, e.g. doors, bonnets, etc.
- Spot repairs.

The type of repair possible is directly related to the type of technology used for the original finish.

10.8.1 Thermosetting finishes (panel repairs)
Technologies include alkyds, thermosetting acrylics and basecoat/clear (solvent-borne) systems. The original enamel, or the clearcoat in the case of basecoat/clear, is catalysed by a small addition of an acid catalyst and stoved 30 minutes at 90°C/10 minutes at 100°C. Higher temperatures are not feasible because of possible damage to trim, plastics, etc.

The use of two-pack '2K' (polyurethane and acrylic) materials for in-factory repairs has grown rapidly. Such products have good durability and appearance needing only minimal temperatures, 15 minutes at 80°C, to cure. However, toxicity problems due to isocyanate catalysts require particular respiratory precautions. '2K' clearcoats are mandatory for use with water-borne basecoats since performance (humidity resistance) is unacceptable with acid-catalysed thermosetting acrylic clears.

Another recent trend in basecoat technology is that there is much more use of spot repair utilizing techniques developed in the refinish market, i.e. ‘fade out’ thinners, etc., even for in-line repairs.

10.8.2 Thermoplastic acrylic lacquers (spot repair)
The very nature of these products facilitates self-repair. The technique of spot repair is mainly employed, although if the damage is extensive a panel repair can be done
<table>
<thead>
<tr>
<th>Type property</th>
<th>Alkyd/melamine or polyester/melamine</th>
<th>Thermosetting acrylic/NAD</th>
<th>Thermoplastic acrylic</th>
<th>Basecoat/clear (solvent-borne)</th>
<th>Basecoat/clear (water-borne)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Appearance</strong></td>
<td>Solid colours</td>
<td>Solid colours and metallics</td>
<td>Solid colours and metallics</td>
<td>Solid colours and metallics</td>
<td>Solid colours and metallics</td>
</tr>
<tr>
<td></td>
<td>High gloss</td>
<td>High gloss</td>
<td>High gloss</td>
<td>High gloss</td>
<td>High gloss</td>
</tr>
<tr>
<td></td>
<td>85% at 20°</td>
<td>55% at 20°</td>
<td>90% at 20°</td>
<td>90% at 20°</td>
<td></td>
</tr>
<tr>
<td><strong>Solids at</strong></td>
<td>Alkyd: 50–60%</td>
<td>30–35%</td>
<td>12–18%</td>
<td>Basecoats (polyester) Metals</td>
<td>Basecoats (polyester) Metals</td>
</tr>
<tr>
<td>Spray (weight)</td>
<td>Polyester: 50–60%</td>
<td></td>
<td></td>
<td>12–18%</td>
<td>15–20%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Solid colours 25–40%</td>
<td>Solid colours 25–40%</td>
</tr>
<tr>
<td><strong>No. of coats</strong></td>
<td>Two</td>
<td>Two/three</td>
<td>Three/four</td>
<td>Two basecoat</td>
<td>Two basecoat</td>
</tr>
<tr>
<td><strong>Sensitivity</strong></td>
<td>Tolerant (poor adhesion to electrocoat)</td>
<td>Reasonably tolerant (good adhesion to electrocoat)</td>
<td>Specific-high PVC (~55%) surfacer required.</td>
<td>Polyester/PU Surfacers recommended</td>
<td>Polyester/PU Surfacers recommended</td>
</tr>
<tr>
<td><strong>to undercoat</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Stoving temperature</strong></td>
<td>20 min at 130°C</td>
<td>20 min at 130°C</td>
<td>30 min at 155°C (reflow)</td>
<td>20 min at 130–150°C</td>
<td>20 min at 130–150°C</td>
</tr>
<tr>
<td><strong>Polishability</strong></td>
<td>Poor</td>
<td>Good</td>
<td>Excellent</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td><strong>Repair</strong></td>
<td>Panel repair (acid-catalysed)</td>
<td>Panel repair (acid-catalysed)</td>
<td>Spot (self) repair</td>
<td>Limited spot repair TSA clearcoat — acid-catalysed or 2K clearcoat</td>
<td>Limited spot repair 2K clearcoat</td>
</tr>
</tbody>
</table>
just as easily. Their excellent polishability also allows minor imperfections, such as
dirt or dry spray, to be conveniently removed by polishing.

This use of the same product, unmodified, makes for considerable process flexi-
bility and minimizes any colour matching problems. A minimum stoving of only 15
minutes at 80°C is required, followed by polishing to maximize gloss.

10.9 Painting of plastic body components

Since the 1970s there has been considerable growth in the utilization of plastic mate-
rials in motor vehicle construction. These products are now finding more and more
use as exterior components such as bumpers, ‘spoilers’, ‘wrap-arounds’, and venti-
lation grills. Apart from advantage in weight-saving there are benefits in styling,
resistance to minor damage, and corrosion resistance. The use of plastics for major
body parts, such as door panels or bonnets, is seen as the next logical step forward.

The use of plastic does, however, bring particular painting problems such as adhe-
sion, stoving limitations, solvent sensitivity, and matching for appearance. Currently,
the autobody painting process is designed to coat a mild steel monocoque con-
struction, and such processes involve high temperatures such as 165°C for primers
and 130°C for finishes. As more plastics are used, either they will have to align with
current practice or new systems will have to be developed.

There are many different types of plastics with a variety of different properties
which affect their painting. The principal ones are as follows.

10.9.1 Sheet moulded compound (SMC) and dough moulded compound (DMC)
The main advantages over other plastics are its high flexural modulus (stiff enough
for horizontals), its high distortion temperature which will withstand the 180°C elec-
trocoating schedule, and its high solvent resistance.

Disadvantages are a surface profile prone to waviness and ‘outgassing’ on stoving,
causing topcoats to bubble. Normally, it is usual to seal the surface either by an in-
mould coating or with a spray-applied polyurethane.

10.9.2 Polyurethane: PU RIM and PU RRIM
Reaction injection moulded (RIM) polyurethane and reinforced reaction injection
moulded (RRIM) polyurethane have the following main advantages: a very wide
range of moduli (from rigid to rubber-like) and toughness. Disadvantages are vari-
able porosity which is sometimes at, or very near, the surface, dimensional instabil-
ity (the material ‘grows’ when overstoved particularly when glass reinforced), and
solvent sensitivity, which is aggravated by the presence of glass fibre.

10.9.3 Injection moulded plastics
These materials include polycarbonate, ABS (acrylonitrile–butadiene–styrene),
polyamide (mainly glass reinforced), and polypropylene (modified with EPDM, eth-
ylene propylene diene methylene). Their general advantages are toughness and
strength, good surface quality, and a wide range of flexibility from rigid to ductile.
Their general disadvantages are that some are excessively brittle at lower temper-
atures, heat distortion temperature (HDT) is fairly low in many cases, and the amorphous types are notch-sensitive.

10.9.4 Painting problems

10.9.4.1 Adhesion
It is difficult to get consistently adequate adhesion to some modified polypropylenes and special adhesion promoting primers are required. With some other plastics adhesion is no problem.

10.9.4.2 Heat distortion
Plastic parts will warp or sag at elevated temperatures. The temperature to which a part can be taken without distorting depends not only on the polymer but also on fillers, reinforcement, shape, size, and degree of mechanical support.

Thus for a given polymer there is an absolute upper limit at which it begins to melt or decompose, but well below this temperature there will be a practical heat distortion temperature for a particular moulding and mounting.

Depending on the heat distortion temperature the plastic may have to be painted entirely off-line (e.g. most PU RIM) or fitted after the electropainting oven (e.g. some PBT, glass reinforced polypropylene, most polyamides) or can be fitted in the ‘body in white’ (e.g. some polyamides, SMC, and related materials).

Where painting is off-line, colour matching to the body is difficult.

10.9.4.3 Surface texture
For true appearance matching of different materials meeting in the same plane, it is virtually essential to use a common undercoat.

10.9.4.4 Solvent sensitivity
Some plastics are affected excessively by common paint solvents, causing the surface to craze and degrading the mechanical properties of the component. On the credit side a mild degree of solvent attack can be beneficial to adhesion.

10.9.4.5 Degradation of mechanical properties
If the paint film fails by cracking when the painted part is impacted or flexed the effect in some cases is to induce failure by cracking of the plastic substrate. Thus an unsuitable paint system will weaken the part.

10.9.5 Paint processes and products

10.9.5.1 On-line
The conventional painting process, using a monocoque construction, has already been well described. Of the possible plastics only SMC-related materials and some grades of polyamide can withstand electropaint stoving schedules (165–180°C) without distorting, and also accept standard body finishing systems.

A typical process for an SMC component is to use either an in-mould coating or a sprayed polyurethane coating to ‘bridge’ or seal the surface. Subsequently the component is fitted to the ‘body in white’, passed through cleaning, phosphating,
and electropainting (where it remains relatively unaffected) before receiving the standard spray surferacer and topcoats.

10.9.5.2 Off-line
In this process the plastic part is painted off-line, maybe at a moulders or painting subcontractor and fixed to the car-body after the final paint oven. This practice enables the paint system and process to be designed to suit the plastic, but if the part is to be in body colour it makes colour matching, particularly in metallics, difficult.

PU RIM is always painted off-line. If the parts are fully jigged they can be painted with a one-pack flexible polyurethane/melamine formaldehyde finish and stoved at 120°C. This is standard practice in the USA but in Europe two-pack flexible clears and non-metallics are used for RIM and ductile thermoplastics. The two-pack method gives lower stoving temperatures (100°C), more formulation scope, and a shorter painting process: problems of toxicity are diminishing as automatic processes are introduced.

Colour matching in off-line painting may be more or less critical according to the shape and position of the component. A styling break or a change of plane where the off-line and on-line painted parts meet will conceal minor differences. With basecoat/clear metallics use of the same basecoat on plastics and metal is a major help, alternative clears (normal and two-component) complete the finishing process. In the longer term a common clear such as 2K is a good objective.

10.9.6 Part-way down paint line
A final method is to fit the particular plastic component between the electropaint oven and the colour spraying station, provided the paint system is suitable for the part. This procedure is commonly used for small parts such as ventilation grills in polyamide. Some other reinforced plastics will withstand normal topcoat schedules and also retain satisfactory impact performance when painted in a standard system.

10.10 Spray application
The introduction of the automobile mass production line, in combination with the development of new synthetic paint technology, was the major factor in the adoption of spray application. The basic principle of spray painting is to atomize the liquid paint into a fine spray and subsequently direct this spray on to the car body. Originally, compressed air was the atomizing medium but other techniques such as electrostatic spray are being more and more employed because of improved transfer efficiency.

This method of application, however, generates overspray and provision must be made to carry off this overspray and exhaust it to the atmosphere or, in some instances, retain it through a recovery system. Nowadays water washed spraybooths are used, being efficient and free from fire hazard. In this type of booth the exhaust is drawn through water which ‘carries’ the overspray into a tank for effluent disposal.

The main basic properties required for spray application are as follows:
To offer a fast, flexible, reliable and robust method of application which will achieve the necessary film thickness in the limited time available.

To provide a smooth film with good flow free from defects such as mottle (orange peel), 'popping' (air entrapment), sags, and craters. Surface-active agents are often used to good effect to ease problems such as cratering.

In the spraying process to produce a wet film capable of absorbing its own overspray.

With metallics, to produce shear-free films.

To maximize material utilization/transfer efficiency without impairing film appearance and processing.

For many years conventional air spray was the most favoured application. Nevertheless, although offering an acceptable level of film appearance and meeting most of the criteria above, it is inefficient and wasteful in terms of paint usage.

To improve transfer efficiency newer methods such as air-assisted electrostatic and full electrostatic have been developed. These systems, particularly the latter, are now mostly fully automated and constitute the main methods of application in modern high volume car plants.

Sometimes a mixture of air assisted (for interiors) and automatic airspray (for exteriors) is used as a compromise. Alternatively, a mixture of air assisted and full electrostatic is incorporated. Such compromises are often necessary because of facility limitations and cost implications.

10.10.1 Air spray

The principal method used in mass-production is the 'pressure feed' system although suction feed techniques are used for small-scale operations such as minor repairs and laboratory work.

In pressure feed, thinned paint (suitably stored and circulated) is fed by pressure through paint lines to the spray gun and leaves the gun through a needle valve — the amount of paint being controlled by a trigger and the pressure applied. The fine stream of paint leaving the gun is atomized by jets of compressed air flowing out of openings in a removable air cap at the head of the gun. The jets can be directed to produce an even spray pattern. This is diagrammatically represented in Fig. 10.9.

Fig. 10.9 — Spray air-cap.
Because of its versatility and speed the spray gun has dominated since its inception. In spite of significant paint losses caused by the fact that not all the atomized paint is deposited it remains widely used for surfacer, sealer, and topcoat, including metallic application.

10.10.1.1 Spray losses
As already stated the spray gun is essentially a device for atomizing liquid with compressed air and projecting this cloud of fine droplets so formed onto the surface of the car body. When the fan of paint droplets sprays from the gun, a part of the fan passes to the side of the unit as it hits the surface being coated. This loss is acceptable as edges need to be well covered, but a portion of the atomized paint is pulled away by the compressed air current deflected by the surface, and the paint appears to rebound or ‘bounce-back’.

At that particular moment the paint droplets are subjected to two actions. One is caused by their forward velocity which tends to push them along their course towards the object; the other is the air current which will deflect them from their trajectory and drag them in a different direction. Obviously this latter action will be stronger if the droplets are very fine and the air current very fast. A coarse spray needs less air pressure and the rebound can be reduced, but the quality of the finish will be poor as a result.

A compromise has to be reached between the air pressure necessary to produce the desired quality of the coating and an acceptable degree of ‘bounce-back’ and overspray. Other factors that affect the air pressure used are the surface tension and the viscosity of the paint. The higher these are, the greater the energy required to ensure atomization and the more powerful the air jet.

The actual efficiency of an air spray gun under normal production conditions is low. Only 40% of the paint reaches, and remains, on the car body. Of the 60% lost, 20% is due to ‘bounce-back’ and 40% to overspray.

The need to improve efficiency is obvious. Automatic machines are beneficial but there have been other developments in recent years which have offered very significant paint savings. The means of reducing losses and associated developments are:

- Air spray gun
  - lower pressure (already described)
  - automatic spray
  - low pressure hot spray
  - air-assisted electrostatic
  - air-assisted

- Electrostatic spray
  - bells
  - discs

The newer techniques, which are described later, are often fully automated and offer a range of benefits such as personnel savings and consistency of performance apart from marked improvements in transfer efficiency.

10.10.2 Automatic spray
A common method to improve spray efficiency is to use automatic machines with some ‘hand reinforcing’ in difficult recessed areas and interiors. It has the added advantage of reducing labour.
Automatic machines are either attached to a fixed base or to a moveable carriage and controlled by electronics to prevent the equipment spraying when the car body is not in the correct proximity. The gun carriage normally reciprocates transversely for painting vertical and horizontal surfaces of the carbody. A typical installation is shown in (Plate 10.1).

This method is ideal for the exterior painting of vehicles with interiors being sprayed by hand. In the past systems did exist for spraying interiors automatically. This was achieved by means of extension nozzles which were actuated by pistons and thereby inserted into interiors and then withdrawn. It is suitable for, say, the interior of vans but it is not ideal and problematical compared to modern procedures.

### 10.10.3 Low-pressure hot spray

This technique has found some use in the application of primer surfacers, but it is rarely used in modern installations and is probably now more or less obsolete in the automotive sector.

Plate 10.1 — Automatic spray application (Courtesy De Vilbiss Ransberg).
Heating of the paint to 60–80°C reduces viscosity and surface tension, making atomization easier. Consequently, lower pressures can be used and higher solids at application reduces ‘bounce’ or rebound losses. However, overspray losses can increase because of the wastage of high solids and can limit solvent selection. Evaporation losses can also be a problem.

10.10.4 Airless spray
This procedure is often used for applying anti-chip coatings to sills, lower sections, etc. Atomization is produced by a combination of pressure and heat. The high pressure forces the paint through the gun nozzle at a greater velocity than the critical velocity of the liquid coating breaking it into small droplets (i.e. atomizes the stone-chip primer).

The anti-chip coating can be heated to reduce viscosity to improve atomization, care being taken to control temperature thermostatically. It is most likely applied automatically with the guns located in fixed positions.

10.10.5 Electrostatic spray
The principle of electrostatic spray is simple. If paint particles are atomized in an electric field they will become charged and drawn towards the article to be painted, which is usually at earth potential. There are many different types of electrostatic spray systems but the most widely used in the motor industry are rotating bells or discs, covering the whole range of undercoats and topcoats.

Figure 10.10 represents a typical system. The paint is pumped to the atomizers from pressure feed containers via a hollow drive shaft. The rotation of the atomizers spins the paint to the periphery where it is partially atomized by centrifugal force but mainly by the electrostatic field.

As the paint particles leave the atomizer, under the attraction of the electrostatic field, they are drawn to the unit being painted. Any particles which pass are attracted to all sides giving electrostatic its very high efficiency of paint utilization. Generally adopted parameters are rotation speeds of 30,000–40,000 rpm and high voltages in the region of 90–110 KV for maximum efficiency. The reduced overspray also means less efficient and expensive spraybooths with reduced effluent. This system also lends itself to full automation with the attendant benefits.

![Electrostatic spray: basic system.](image-url)
There are basically three main bell sizes currently in use, 75, 68, and a 50 mm mini-bell. Rotation speeds vary between 25,000 rpm for the larger 75 mm bell to 48,000 rpm for the small 50 mm type.

The small bell (designated mini-bell) does have other benefits:

- More easily mountable for robotic use.
- Capable of reciprocating at different speeds.
- Amplitude is programmable.

A modern electrostatic application system is shown in Figs. 10.11 and 10.12. However, in some instances certain recessed and other areas are difficult to paint with this method since paint is attracted to the nearest part of the complex shaped car body and does not have sufficient velocity to penetrate further. Air-assisted electrostatic guns can overcome this weakness. These use compressed air and electrostatic techniques for atomization.

Air-assisted equipment has an insulating barrel having an earthed handle with a high voltage electrode in the air cap which is usually charged from 30 to 60 KV. The discharge current flowing from the high voltage electrode creates a region, adjacent to the atomization zone, rich in unipolar ions that attach themselves to, and charge, the paint spray particles.

Fig. 10.11 — Electrostatic spray installation (automatic turbo bells) (Courtesy of De Vilbiss Ransberg).
In the vicinity of the spray gun the inertia of the aerodynamic forces usually dominate, but as the paint particles get nearer to the earthed car body the forces on the charged particles (owing to the electrostatic field between the charging electrode of the spray gun and the unit) become more significant. These forces drive the spray particles towards the workpiece.

Maximum paint savings are generally obtained by maintaining the charging voltage as high as possible, giving a high depositing field strength between the gun and the workpiece and by keeping the spray velocity in the vicinity of the article being sprayed as low as possible to give good atomization and flow of the ‘deposited’ film.

Air-assisted guns can be used either manually or automatically. They offer a measurable compromise between the less efficient air spray and the highly efficient electrostatic system, and compared to the latter process give better film uniformity and smoothness.

In general terms the advantages of electrostatic spray may be summarized as follows:

- Speed of production.
- Uniformity of production — free from the ‘human element’.
- Economizes on labour — highly automated.
- Versatile and flexible.
- High transfer efficiency — leading to large paint savings/less effluent.

Electrostatic spray — metallic appearance
The controlling factors in metallic appearance have been clearly stated in previous sections. In practice, electrostatic spray diminishes the high flip (tonal contrast) of
metallic finishes quite significantly. There has been much investigation into the cause of this phenomenon and the considered view of the mechanism is as follows.

In comparing the velocities at which paint is applied, and the degrees of atomization, there is a considerable difference in the various application systems employed. For example, typical flow rates for a low solids basecoat are:

- Atomization: Full electrostatic (high speed bells): 200–300 cm³ min⁻¹
- Fair
- Air-assisted: 450–500 cm³ min⁻¹
- Good
- Air spray: 800 cm³ min⁻¹
- Very good

In an air (pneumatic) spray system the basecoat is applied at very high velocity and is extremely well atomized. There is evidence to suggest that at the moment of impact of a spray droplet with the substrate, the aluminium flakes are thrown flat against the surface by a considerable shearing force. Subsequently a certain amount of reorientation takes place as the wet film builds but shrinkage and surface tension effects quickly take over and 'pull' the flake into ideal alignment (parallel to the substrate) for optimum effect.

The lower velocities and relatively poorer atomization of electrostatic systems means that, on impact, shearing forces are lower and the flakes are not forced totally into parallel alignment and tend to be more randomly orientated. The shrinkage and surface tension effects improve the orientation but, because of the initial starting point, the final film does not align in the perfect manner of hand spray. It is for this reason that metallic basecoats are applied by a 'mix' of application methods to optimize appearance and efficiency and to minimize repair colour matching, i.e. two coats — first coat by electrostatic spray followed by a second coat using air spray (either hand or automatic).

There is, however, a new development in electrostatic systems to improve aluminium orientation. This uses a hybrid bell with very high 'shroud air'. This gives a compromise between the alignment of the aluminium flake and transfer efficiency.

Resistivity
An extremely important feature in the spraying of a product electrostatically is its electrical resistance. This is easily measured by one of the various commercially available meters. If the resistance is too high, the paint will not accept the charge and is not sufficiently attracted to the car body, i.e. 'wrap around' is poor. On the other hand, if the resistance is too low, as is the case with water-borne systems, the high voltage at the head of the gun is likely to be conducted back to earth via the paint-feed pipeline and the main paint mixer which is more frequently earthed.

The correct resistance (i.e. specification) for a solvent-borne coating is regularly established by a system of trial and error for an individual plant making addition of polar solvents or special additives, e.g. Ethoquad C25® to lower resistance and increase conductivity.

(Refer to Tables 10.6, 10.7, and 10.9 for typical resistivity ranges.)
and to maintain and are 'out of date' very quickly. They also require meticulous maintenance to overcome the inherent dirty application caused by overspray from the use of high fluid rates and air pressures.

10.10.7 Electrostatic application of water-borne automotive coatings
At the present time, the most favoured method of application is automatic electrostatic spray using high speed rotary atomizers. This combines the low polluting nature of the water-borne products with a high transfer efficiency, thereby maximizing emission reduction.

However, by their very nature water-borne coatings are highly conductive. So as to ensure that high tension does not leak through the paint circulating lines special systems have been developed to isolate the 'charge':

- Circulating systems designed specifically to insulate the paint from the internally charged bell or atomizer.
- Externally charged or 'crown of thorns' bells.

10.10.7.1 General plant design features
All metal in contact with water-borne technology must be stainless steel, including spraybooth panelling. Nevertheless, certain plastics such as polyamide ‘11’ and ‘12’ are suitable for low diameter pipework.

10.10.7.2 Paint circulating system for electrical insulation
A typical system designed to isolate the main paint circulation equipment from the electrostatic atomizers is shown in Fig. 10.13. It is principally used for water-

Fig. 10.13 — System for electrical insulation.
borne surfacers where internally charged guns are adopted. In the case of other water-borne products, e.g. basecoats, its use is restricted to only a few individual producers.

The main paint circulating system is isolated by using separate header and feed tanks ‘H’ and ‘F’. The feed tank ‘F’, the circulation pipework and atomizers are insulated from earth and connected to the high tension equipment. Tank ‘H’ is switchable by a high tension potential or to earth. It is filled with paint from the main mixer through earthed circulating pipework. During this filling procedure the header tank is at earth potential.

The lower tank is replenished automatically from the header tank during gaps between car bodies at designated intervals or, sometimes, at the end of a shift.

10.10.7.3 Externally charged atomizers
In the application of water-borne (and conventional) basecoats the externally charged or ‘crown of thorns’ electrostatic bell is preferred by most car manufacturers. Although this system has marginally lower transfer efficiency (approximately 3–5%) there is no need to isolate the paint.

The original so-called ‘crown of thorns’ bell had an array of 32 electrodes at the gun head, recently modified to 6 electrodes.

Most production lines are now equipped with externally charged bells (first coat of basecoat) followed by a pneumatically applied second coat, most often by automatic reciprocator. Solid colour basecoats are applied in one coat. Hand reinforcing after bell application is very seldom necessary.

10.10.8 Application efficiency — practical considerations and processes
In terms of absolute efficiency for any particular type of equipment it is difficult to be specific. There is considerable variation from plant to plant (whether the system is manual or automatic, available spraybooth space, and the differing shapes of the unit being sprayed) and practical figures can differ significantly from the ideal.

However, some mean figures are quoted below based on data available from various installations. They are intended only to give the reader a realistic indication of the transfer efficiencies of systems currently in use.

<table>
<thead>
<tr>
<th>Method</th>
<th>Variance ± 5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>High voltage electrostatic</td>
<td>75%</td>
</tr>
<tr>
<td>(high speed bell)</td>
<td></td>
</tr>
<tr>
<td>Air-assisted electrostatic</td>
<td>60%</td>
</tr>
<tr>
<td>Air spray</td>
<td>40%</td>
</tr>
</tbody>
</table>

In practice the principle of ‘mixing’ or ‘blending’ the various methods is often used in mass production. Such systems balance the various strengths and weaknesses of the individual spray methods and can realize the following benefits:

- Maximizes appearance standards at required film thicknesses.
- Maintains optimum level of transfer efficiency.
- Copes with the complex nature of a monocoque unit which comprises internal and external surfaces.
- Provides an optimum application procedure within the time and space available.
- Minimizes labour.
10.10.9  Modern spraybooth design — ventilation modes

The air flow through spraybooths is extremely high and ‘once through’ ventilation means high energy consumption for heating and humidification. In fact, spraybooths consume approximately 50% of the energy consumption in the painting process. A feasible method of reducing energy demand is to recirculate the air, with or without intermediate solvent separation.

Recirculation of 70–90% of the booth air, and treatment of the bled-off air, can be used in booth zones where increased solvent concentration up to 2–3 g/m^2 can be expected, i.e. zones with automatic operation, electrostatic bells, etc.

For zones with manual operation the air has to be cleaned from solvents before it is reintroduced into the booth. The cleaning is preferably done by rotor concentrators.

There are, however, limiting factors with direct recirculation:

- Solvent concentration must not exceed 25% of the lower explosion limit (LEL).
- Finishing quality can be influenced by solvent concentration, e.g. evaporation, flow, sagging, and ‘solvent popping’.
- Extreme accuracy is required in booth construction, particularly the ducting since ‘outwards’ leaking must be avoided and ‘inwards’ leaking must be controlled.

10.10.9.1  Preconditioning the air

When recirculating air, or when taking it through a concentrator with absorbent, it is necessary to recondition the air necessitating the following:

- To clean the air further of paint overspray.
- To dehumidify and reheat the air to be recirculated to the booth.
- To adjust the relative humidity of the air — generally by heating it 6–8°C before it enters an activated carbon or zeolite absorbent filter.
- To ‘smooth’ solvent concentration variations in the air.

10.10.9.2  Concentrators

Rotors with absorbents are used as concentrators for solvent-laden air. There are two types, disc or cylinder, with activated carbon or zeolite material on a carrying structure often with a honeycomb geometry. The rotor turns slowly, 0.5–4.0 revolutions per hour.

The air to be treated passes through typically 75% of the face area where the solvents in the air are absorbed. In the remaining part of the rotor a small amount of heated air passes in the opposite direction and the entrapped solvents are desorbed.

The dissolved air, with a high solvent concentration (often ten times the concentration of the process air), is then fed either to an incinerator for combustion, to a fixed bed absorber, or to a condenser for solvent recovery.

10.10.10  Process details: typical application parameters — turbo bells

Tables 10.6–10.9 summarize some general application conditions for a number of different products, solvent-borne and water-borne, using high speed rotary atomizers under mass-production conditions.
**Table 10.6** — Typical application parameters (turbo bells): solvent-borne polyester/PU surfacer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Application viscosity (at 25°C)</td>
<td>19–40s DIN4</td>
</tr>
<tr>
<td>Resistivity</td>
<td>650–1000kΩ</td>
</tr>
<tr>
<td>Bell rotation speed</td>
<td>20–25000revs/min</td>
</tr>
<tr>
<td>Shrouded air</td>
<td>0.6–2.0 bar</td>
</tr>
<tr>
<td>Voltage</td>
<td>70–80kV</td>
</tr>
<tr>
<td>Nozzle</td>
<td>1.2 mm</td>
</tr>
<tr>
<td>Typical track speed</td>
<td>7.5m/min⁻¹</td>
</tr>
<tr>
<td>Fluid delivery</td>
<td>Spraybooth temperature 23°C</td>
</tr>
<tr>
<td>Bell body distance</td>
<td>250–300mm</td>
</tr>
<tr>
<td>Number of coats</td>
<td>Two</td>
</tr>
<tr>
<td>Flash time (between interior and exterior)</td>
<td>5 min</td>
</tr>
<tr>
<td>Spraying sequence</td>
<td></td>
</tr>
<tr>
<td>1st Station</td>
<td>Interior</td>
</tr>
<tr>
<td>2nd Station</td>
<td>Exterior</td>
</tr>
<tr>
<td>(3rd Station</td>
<td>Back-up)</td>
</tr>
<tr>
<td>Flash time (before stoving)</td>
<td>5–7 min</td>
</tr>
<tr>
<td>Film thickness</td>
<td>~35–40μm</td>
</tr>
</tbody>
</table>

**Table 10.7** — Typical application parameters (turbo bells): polyester solid colour

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Application viscosity (at 25°C)</td>
<td>15–17s DIN4</td>
</tr>
<tr>
<td>Application solids</td>
<td>~50%</td>
</tr>
<tr>
<td>Resistivity</td>
<td>700–1000kΩ</td>
</tr>
<tr>
<td>Bell rotation speed</td>
<td>23000revs/min serrated edge bells</td>
</tr>
<tr>
<td>Shrouded air</td>
<td>0.6–2.0 bar</td>
</tr>
<tr>
<td>Voltage</td>
<td>70–90kV</td>
</tr>
<tr>
<td>Nozzle</td>
<td>1.2 mm</td>
</tr>
<tr>
<td>Fluid delivery</td>
<td>Spraybooth temperature 21–24°C</td>
</tr>
<tr>
<td>Bell body distance</td>
<td>220–250mm</td>
</tr>
<tr>
<td>Number of coats</td>
<td>One</td>
</tr>
<tr>
<td>Flash time (between interior and exterior)</td>
<td>1–5 min</td>
</tr>
<tr>
<td>Flash time (before stoving)</td>
<td>4–7 min</td>
</tr>
<tr>
<td>Film thickness</td>
<td>45–50μm</td>
</tr>
</tbody>
</table>

### 10.11 Stoving procedures

The various types of materials used in autobody painting have already been described. They vary from water-based epoxy technology for electropainting to sophisticated solvent-borne finishes such as alkyds/polyesters and acrylics. The organic solvents involved are complex blends of aliphatic and aromatic hydrocarbons, alcohols, esters, and ketones. These paint materials are either applied by some form of dipping process or spray-applied by one form or another. Subsequent to application all of these products require stoving, for the following reasons:

- To achieve the high level of performance demanded by the motor industry, i.e. to form durable and protective films.
Table 10.8 — Typical application parameters (turbo bells): water-borne basecoat

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Application viscosity (typical)</td>
<td>500-3000 mPas @ 0.2 s⁻¹ shear</td>
</tr>
<tr>
<td>Application solids (range)</td>
<td>Solid colours: 20-35%</td>
</tr>
<tr>
<td></td>
<td>Metallics: 14-20%</td>
</tr>
<tr>
<td>Resistivity</td>
<td>Not normally measured</td>
</tr>
<tr>
<td>Bell rotation speed</td>
<td>50 mm bell: 45 000 revs/min</td>
</tr>
<tr>
<td></td>
<td>68 mm bell: 28 000 revs/min (flat edged bell)</td>
</tr>
<tr>
<td>Shrouded air</td>
<td>1.2-2.5 bar</td>
</tr>
<tr>
<td>Voltage</td>
<td>70-90 kV</td>
</tr>
<tr>
<td>Nozzle</td>
<td>1.2 mm</td>
</tr>
<tr>
<td>Fluid delivery</td>
<td>70-300 cc min⁻¹ depending on zone track speed</td>
</tr>
<tr>
<td>Bell body distance</td>
<td>250-350 mm</td>
</tr>
<tr>
<td>Number of coats</td>
<td>Solid colours: one</td>
</tr>
<tr>
<td></td>
<td>Metallics: two</td>
</tr>
<tr>
<td>Flash time (between coats)</td>
<td>1-2 min typically</td>
</tr>
<tr>
<td>Flash time (between coats</td>
<td>Depending on line construction 1-6 min</td>
</tr>
<tr>
<td>(interior/exterior)</td>
<td></td>
</tr>
<tr>
<td>Flash time (before stoving)</td>
<td>2-5 min before infrared preheat zone</td>
</tr>
<tr>
<td>Film thickness</td>
<td>Solid colours: 15-25 μm</td>
</tr>
<tr>
<td></td>
<td>Metallics: 10-14 μm</td>
</tr>
<tr>
<td>Hand reinforcing</td>
<td>Only when ‘robots’ are used</td>
</tr>
</tbody>
</table>

Table 10.9 — Typical application parameters (turbo bells): clearcoat (thermosetting acrylic)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Application viscosity (@ 25°C)</td>
<td>26-30 s DIN4</td>
</tr>
<tr>
<td>Application solids (range)</td>
<td>40-45%</td>
</tr>
<tr>
<td>Resistivity</td>
<td>700-1000 kΩ</td>
</tr>
<tr>
<td>Bell rotation speed</td>
<td>23 000 revs/min</td>
</tr>
<tr>
<td>Shrouded air</td>
<td>0.5-2.0 bar</td>
</tr>
<tr>
<td>Voltage</td>
<td>60-80 kV</td>
</tr>
<tr>
<td>Nozzle</td>
<td>1.2 mm</td>
</tr>
<tr>
<td>Fluid delivery</td>
<td>80-200 cc min⁻¹ per bell</td>
</tr>
<tr>
<td>Bell body distance</td>
<td>250-300 mm</td>
</tr>
<tr>
<td>Number of coats</td>
<td>Normally two (gives better appearance and ‘hold-up’ on verticals)</td>
</tr>
<tr>
<td>Flash time (between coats)</td>
<td>1 min typically</td>
</tr>
<tr>
<td>Flash time (between coats</td>
<td>1-5 min</td>
</tr>
<tr>
<td>(interior/exterior)</td>
<td></td>
</tr>
<tr>
<td>Flash time (before stoving)</td>
<td>4-8 min</td>
</tr>
<tr>
<td>Film thickness</td>
<td>45-55 μm</td>
</tr>
</tbody>
</table>

- To facilitate processing in the limited time available on a conveyerized production line.
- To control or accelerate solvent release and minimize dirt pick-up.

The stoving operation simply cures the film by effecting certain chemical or crosslinking reactions which form a protective and durable coating. During such film formation solvent and by-products are released which can, and do, provide pollution problems.

Stoving temperatures vary. Modern cathodic electropaints require up to 20 minutes at 180°C to cure, while at the other end of the scale repair requirements can be as low as 15 minutes at 80°C. In the initial stages of stoving the temperature
must be increased at a controlled rate to prevent possible film defects such as 'solvent popping' or 'boil' (owing to entrapped solvent or occluded air). Once the required temperature is reached it is maintained for a period sufficient for effective cure to occur. These times are typically 8–10 min to heat up of the paint film, and 20 min held at a specified temperature.

10.11.1 Oven technology
There are two types of oven that can be used to stoke automotive coatings, although the former are by far most commonly used:

- Convection heating ovens.
- Radiant heating ovens, e.g. infrared.

Convection ovens rely upon air movement and its even distribution over the unit, ideal for the complex shape of a car body. Radiant heating is better suited to regular shaped items but it is often used in conjunction with convection ovens, e.g. to offer preheating in the initial zone to minimize dirt pick-up or to supplement the heating of heavier sill areas of the car body.

10.11.2 Design considerations of convection ovens
Optimum design requires that a number of parameters be considered to effect the best compromise between process requirements, plant layout, energy consumption, anti-pollution requirements, maintenance, and capital cost.

10.11.2.1 Oven configuration
There are two stages in the stowing of the painted body, i.e. the controlled heat-up followed by a ‘hold’ period during which the resin system either reacts or, in the instance of acrylic lacquer, reflows. This requires specific oven zones, each with their own heating and control systems. The convected air is introduced at high velocity into the oven enclosure, normally via distribution ducting mounted at roof level. Individual heat-up and ‘hold’ zones may be further divided into two or more zones.

10.11.2.2 Oven ventilation
The stoving of automotive paints releases into the oven atmosphere combustible compounds which can cause an explosion hazard. For this reason fresh air is introduced into the enclosure to ensure a safe installation. This requires that a ‘balancing’ volume of air be exhausted from the enclosure; obviously this contains the diluted combustible compounds released from the painted surface, which are also a source of fume and odour and generally undesirable.

10.11.2.3 Oven heating
Each zone of the oven is fitted with a recirculation/supply fan which extracts a volume of air from the oven, mixes this with any fresh air required for ventilation purposes, supplies heat to that mixture to satisfy the zone heat load, and then it returns it via either distribution nozzles or slots to the oven zone.

10.11.2.4 Fresh air requirements
The fresh air quantity supplied to an oven is calculated from the anticipated solvent quantity entering the body, and to ensure that a maximum of 25% of the LEL of
that solvent is not exceeded. This air quantity may be introduced into the oven as
filtered fresh air into the zone heating system, as air infiltrating at the oven airseal,
or as combustion air to direct heating zone burners.

10.11.2.5 Fuel available/heating method
In the United Kingdom, and most of Europe, it is normal to use natural gas as the
heating fuel. As this is a sulphur-free fuel it has resulted in the adoption of direct
fired heating systems on installations for all parts of the painting process since
testing, and experience, has shown this to have no detrimental effect on the quality
of the coating where natural gas is not available. Butane or propane are utilized,
both having negligible sulphur contents.

Other systems involve burning a distillate of oil; this results in the use of a less
efficient indirect fired system (an indirect fired heater being about 70% efficient).

In the past, ovens tended to be direct fired using oil or ‘synthetic’ gas as the
heating fuel. This often lead to problems, particularly with surfacers, of what was
designated ‘gas fouling’. It showed itself as a surface defect, i.e. low gloss and a ‘frost-
like’ appearance which, in the case of surfacers, lead to major intercoat adhesion
problems.

The cause was premature oxidation/cure at the surface of the coating owing to
impurities (sulphur) in the heating fuel. The main types of materials to suffer were
oil-modified products such as alkyd topcoats and alkyd or epoxy ester surfacers. It
often could be alleviated by the addition of small amounts of acid catalyst or increasing
the ‘acid value’ of the resin to effect a consistent ‘through cure’. Alternatively,
retard the crosslinking reaction by the addition of an amine, e.g. triethylamine.

10.11.3 Fume and odour emission
As has been mentioned earlier, the stoving of automotive coatings releases certain
materials during the curing process. These are either mixtures of organic solvents,
products of the chemical reaction and some decomposition products. This can lead
to visible fume and odour problems from the exhaust stack and to condensation in
the stack.

While the problem of visible fume, odour, and exhaust stack condensation are
not over-serious, the high level of solvent emission can be a major concern. Legislation
exists in the USA to control such emissions and there are significant safeguards in Europe.

The control of the exhaust emissions from industrial plant, and in this instance
stoving ovens, originated in the USA in the 1960s. Since the majority of coatings are
stoved and based on organic solvents, such solvents became recognized as potential
sources of pollution because of the toxic nature of the products formed by their
photochemical reaction in the atmosphere. In the late 1960s the Los Angeles County
and San Francisco Bay area in the USA introduced regulations which limited the
amount of certain organic solvents to be used in organic compositions. These regu-
lations were called Rule 66 or Regulation 3 by their respective bodies; and where
pollution control is required under this code it is stipulated that 90% or more of
the hydrocarbons from the process be oxidized to carbon dioxide before exhaust-
ing to the atmosphere.

More recently in the USA, federal regulations have provided guidelines on the
permitted hydrocarbon emission. The actual limits depend upon the location of the
These can vary from 1.4 to 2.3 kg per hour and 100-300 tonnes per annum. This level of emission can be achieved by adopting pollution control of the oven exhaust or by a process modification such as a change of paint formulation/technology, or by a combination of both.

In France and the UK the Rule 66 legislation is still widely adopted but in other parts of Europe the German TA-Luft is becoming more widely used. In this latter instance precise limits are set for permissible emissions for all solvent types and for various flow quantities.

The 1986 TA-Luft stated that for automotive paint shops these limits should be 60 g m⁻² for solid colour topcoats and 120 g m⁻² for metallic finishes. These figures are maximum levels — local authorities can stipulate even lower limits.

Proposed European Union Regulations are on a similar level, i.e. 45 g m⁻² for coated surface area (or 3 kg/unit); 50 mg C m⁻² carbon in the exhaust of the oven.

Besides new paint technology a number of methods of achieving pollution control are now available. These include thermal incineration, catalytic combustion, carbon absorption, liquid scrubbing, and odour masking. Of these, thermal incineration is the most widely accepted and reliable method of achieving control but, more recently, catalytic combustion has proved successful in a number of installations.

10.11.3.1 Thermal incineration

Thermal incineration consists simply of passing the fume-laden exhaust air through a highly efficient combustion system where a primary fuel is burned in order to raise the temperature of the effluent to a critical reaction point and holding this for a specific period. In this way the complex hydrocarbon compounds are oxidized to carbon dioxide and water vapour. The primary fuel may be gas or distillate oil.

10.11.3.2 Catalytic combustion

The application of catalytic combustion techniques has been gaining acceptance for the control of exhaust gases emitted from various processes and show a substantial reduction in fuel consumption when compared with thermal incineration systems, with limited or no heat recovery equipment included.

The exhaust gases supplied to the catalyst cell contain organic compounds which, when passed over the catalyst surface, react with the oxygen present in the airstream.

The application of catalyst combustion to stoving in the automotive industry is a fairly recent development and was, in fact, introduced in the mid-1970s. Catalyst cells do not have indefinite life but if contamination or poisoning can be avoided then a service life of five years can be expected.

10.11.4 Future stoving developments

The development of alternative curing systems will obviously be linked to developments in paint technology. The two overriding considerations from the point of view of the curing system will be the most economical use of energy and the elimination of the effluent problem.

Any changes in the curing process will involve the adopting of new radiant heating technology, as the present convection type oven is very close to its optimum efficiency. There are a number of radiant curing techniques at present used in the curing of flat stock such as boards, sheet metal, fabrics, paper, and plastics. Perhaps these technologies will be adopted for use in a more general way in the metal fin-
ishing industry. Among these are electron beam and ultraviolet curing and induction heating.

At this stage it is not certain which of these processes will be adopted. Electron beam and UV curing have the advantage of being suitable for plastic parts which are being used increasingly to reduce body weight. Infrared stoving has the advantage of rapid curing time, reduced length of line, minimal dirt, and flexibility (such as its use in conjunction with convection ovens).

Typical store schedules are given in Table 10.10.

### Table 10.10 — Typical stoving schedules

<table>
<thead>
<tr>
<th>Category</th>
<th>Stoving Schedule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipping primers</td>
<td>30 min at 150°C/20 min at 165°C</td>
</tr>
<tr>
<td>Electroprimers</td>
<td>Anodic type 20 min at 165°C/20 min at 175°C</td>
</tr>
<tr>
<td></td>
<td>Cathodic type 20 min at 165°C/20 min at 180°C</td>
</tr>
<tr>
<td>Primer surfacers</td>
<td>20 min at 140°C/20 min at 165°C</td>
</tr>
<tr>
<td>Topcoats</td>
<td></td>
</tr>
<tr>
<td>Alkyds, thermosetting acrylics/NAD</td>
<td>10–20 min at 130°C/140°C</td>
</tr>
<tr>
<td>Thermoplastic acrylic lacquers</td>
<td>Reflow 30 min at 155°C</td>
</tr>
<tr>
<td>Repair schedules</td>
<td></td>
</tr>
<tr>
<td>Thermostet products</td>
<td></td>
</tr>
<tr>
<td>Catalysed enamels/clearcoats</td>
<td>30 min at 90°C/10 min at 100°C</td>
</tr>
<tr>
<td>Two-pack enamels</td>
<td>15 min at 80°C</td>
</tr>
<tr>
<td>Thermoplastic products</td>
<td>Minimum stoving 15 min at 80°C</td>
</tr>
<tr>
<td>Self-repair</td>
<td></td>
</tr>
</tbody>
</table>

All temperatures are metal (effective) temperatures not air temperatures.

10.12 Performance/Testing

The performance of automotive coatings has been outlined. The testing of the paint system, and the component ‘layers’, is designed to simulate conditions likely to occur in practice so as to give some measure of performance in the field. Obviously the testing of undercoats has a different emphasis from that of topcoats but the interaction of these products in a total system is of equal, or more, importance.

Performance standards have improved dramatically in recent years as warranty periods have been extended. For example, the 240 hours Salt Spray test used as an acceptable standard for anodic electropaints has been extended to 1000 hours for current cathodic primers and further improvements are being aimed for. The acceptable standard of exterior durability was considered to be satisfactory after 12 months Florida testing; for modern basecoat/clear systems it is three to five years.

There is also now a greater emphasis on chemical (environmental) resistance properties such as resistance to acid and insect/bird effects. For example, rather than very dilute acids/alkalis being used in testing for long periods at room temperature, more modern procedures involve shorter times, stronger acids/alkalis at elevated temperatures. In fact a variety of tests exist and a number are described later in this section.

The subject of testing and durability is a complex and detailed subject and is dealt with in Chapter 19 of this book. However, key properties, performance, and testing of automotive paints/systems are summarized below and comparisons are made. Also included is a brief description of important and suitable test methods.
A comparison of various topcoat processing properties was made in Section 10.7. In terms of performance, apart from utilizing standard stoving schedules, underbake and overbake of both surfacer and topcoat are assessed, sometimes at variable thicknesses. This is to simulate every possibility that can occur in the production process.

Testing may be divided into two categories: appearance and performance. The qualities to be assessed are given in note form in the next two sections.

10.12.1 Appearance
Colour; opacity (coverage); smoothness, i.e. freedom from defects such as cratering, solvent ‘popping’, mottle, or orange peel; gloss and distinction of image (DOI) — important for consumer appeal.

Note: apart from the formulation and quality of the finish the quality of the undercoating system has a significant effect on the final appearance.

10.12.2 Performance

10.12.2.1 Physical properties
Hardness; flexibility; impact resistance; mar resistance; adhesion; stone-chip resistance; cold crack resistance, i.e. stability to extremes of temperature and humidity; curing efficiency.

10.12.2.2 Chemical resistance
To petrol, acid, insect/bird effects, alkali, water, humidity, corrosion, scab corrosion. External durability, i.e. resistance to ultraviolet irradiation and humidity.

10.12.3 Test procedures
Typical test procedures and performance properties are listed in Table 10.11. The following descriptions are mainly in summary form and are fairly typical. Different car manufacturers have their own variants and different emphasis. These procedures are used for full painting systems and for primer only, as appropriate.

10.12.3.1 Cure (test for crosslinking products)
Twenty double rubs with a clean white cotton cloth soaked in MIBK (methyl isobutyl ketone)
Pass: no removal or marking of paint film.

10.12.3.2 Sandability (surfacers)
The stoved surfacer must be amenable to wet sanding (400 paper) or be dry sandable (P800 paper) by hand. Clogging of the paper, excessive sanding marks and dusting are considered unacceptable.

10.12.3.3 Adhesion: crosshatch test (1.5mm or 2.0mm template)
Test panels are evaluated by crosshatch before and after water immersion, normally 120, 240, and 480 hours. (Refer below for details of water immersion test.)
Pass: <5% removal (after taping with Scotch tape).
Table 10.11 — Typical performance properties: various finishing systems

<table>
<thead>
<tr>
<th>Performance test</th>
<th>Gloss (20°)</th>
<th>Hardness (Tukon-Knoop)</th>
<th>Adhesion (cross-hatch)</th>
<th>Petrol resistance (some Super Shell — slow drip)</th>
<th>Acid resistance (non-staining 1N H₂SO₄ × 48 h)</th>
<th>Alkali resistance (non-staining 1N NAOH × 48 h)</th>
<th>Surface distortion</th>
<th>Impact resistance</th>
<th>Stone-chip Resistance</th>
<th>Water-soak (40°C)</th>
<th>Humidity resistance (100% RH at 40°C)</th>
<th>Corrosion (salt spray) resistance</th>
<th>Scab corrosion resistance</th>
<th>Florida exposure/20° gloss (washed) after 2 years</th>
<th>Primer</th>
<th>Surfacers</th>
<th>Pretreatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alkyd melamine</td>
<td>Thermosetting acrylic/NAD</td>
<td>Thermoplastic acrylic lacquer</td>
<td>Basecoat/clear (solid colours metallics)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Gloss (20°)</strong></td>
<td>85%</td>
<td>80%</td>
<td>85%</td>
<td>90%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Hardness</strong></td>
<td>5–7</td>
<td>8–14</td>
<td>14–18</td>
<td>8–12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Adhesion</strong></td>
<td>&lt;5% removal</td>
<td>&lt;5% removal</td>
<td>&lt;5% removal</td>
<td>&lt;5% removal</td>
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<tr>
<td><strong>Petrol resistance</strong></td>
<td>Excellent</td>
<td>Very good</td>
<td>Fair</td>
<td>Very good</td>
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<tr>
<td><strong>Acid resistance</strong></td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
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<tr>
<td><strong>Alkali resistance</strong></td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
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<tr>
<td><strong>Surface distortion</strong></td>
<td>—</td>
<td>—</td>
<td>55–65°C (depending on colour)</td>
<td>—</td>
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<tr>
<td><strong>Impact resistance</strong></td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
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<tr>
<td><strong>Stone-chip Resistance</strong></td>
<td>Excellent</td>
<td>Very good</td>
<td>Good</td>
<td>Excellent</td>
<td></td>
<td></td>
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<tr>
<td><strong>Water-soak (40°C)</strong></td>
<td>No blistering &gt;500 h</td>
<td>No blistering &gt;500 h</td>
<td>No blistering &gt;500 h</td>
<td>No blistering &gt;500 h</td>
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<tr>
<td><strong>Humidity resistance (100% RH at 40°C)</strong></td>
<td>No blistering &gt;240 h</td>
<td>No blistering &gt;240 h</td>
<td>No blistering &gt;240 h</td>
<td>No blistering &gt;240 h</td>
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<tr>
<td><strong>Corrosion (salt spray) resistance</strong></td>
<td>1000 h</td>
<td>1000 h</td>
<td>1000 h</td>
<td>1000 h</td>
<td></td>
<td></td>
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<tr>
<td><strong>Scab corrosion resistance</strong></td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
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<tr>
<td><strong>Florida exposure/20° gloss (washed) after 2 years</strong></td>
<td>70%</td>
<td>65%</td>
<td>75%</td>
<td>80%</td>
<td></td>
<td></td>
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<tr>
<td><strong>Primer</strong></td>
<td>Cathodic electrocoat</td>
<td>Cathodic electrocoat</td>
<td>Cathodic electrocoat</td>
<td>Cathodic electrocoat</td>
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<tr>
<td><strong>Surfacer</strong></td>
<td>Polyester or polyester/PU</td>
<td>Polyester or polyester/PU</td>
<td>High PVC (~55%) epoxy ester</td>
<td>Polyester or polyester/PU</td>
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<tr>
<td><strong>Pretreatment</strong></td>
<td>Zinc phosphate</td>
<td>Zinc phosphate</td>
<td>Zinc phosphate</td>
<td>Zinc phosphate</td>
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</table>
10.12.3.4 Hardness (‘Tukon indentation’—Knoop hardness)
The Tukon hardness is the generally accepted test in the automotive industry, particularly for topcoats. Other tests include Pencil Hardness, Sward Rocker, Pendulum Hardness (König, Perzoz, etc.).

10.12.3.5 Stone-chip resistance
This is a key test for the full paint system and, in particular, for surfacers and anti-chip coatings. Poor chip resistance can be a major source of paint warranty claims and, as a result, test procedures have become more and more rigorous as newer products have developed.

There are a variety of pieces of apparatus and procedures for checking this property. Originally the equipment and test were relatively simple but now they are much more sophisticated. Typical examples are as follows:

1 In the past, although the method was relatively basic it was actually quite efficient. Carried out on the full paint system as follows:
   (a) 100 × \(\frac{1}{4}\)" (6mm) Whitworth nuts are dropped down a 15 feet (457cm) pipe (2.5 inches or 6.0cm in diameter) onto a coated panel held at 45°.
   (b) Panels are graded by degree of removal of paint. The test was normally carried out at ambient, room, temperature.
   (c) Pass: <4% removal of paint.

2 A more up to date test is to 'shot blast' the test panel for a prescribed time using a constant pressure at constant temperature. The fully painted panel is 'shot blasted' for >10 seconds with 0.75kg of angular iron grit (4–5mm in size) at 0.1 MN m⁻² @ 20–26°C.

   After 'shot blasting' the panel is subjected to 72h salt spray (ASTM B117) then rinsed with deionized water, dried and retested as above.

   Performance is measured against a prescribed standard usually in the form of photographs.
   Pass: <5% paint removal to substrate. (Sometimes the performance required is even more stringent.) Note: all stone-chip failure to be noted, i.e. intercoat and down to metal substrate.

3 Stone-chip resistance — anti-chip coatings. Testing in this case is even more severe. In the procedure just described the weight of 'shot blasted' iron is increased to 2kg and the pressure to 2 bar at 20–26°C. As before performance is related to prescribed standards.

   Pass: <5% removal (all chipping — see ‘Note’ above).

10.12.3.6 Impact test
A 1kg weight dropped from 24cm and 50cm onto a painted test panel (impacted from reverse side).
Pass: no cracking of paint film.

10.12.3.7 Flexibility
This is quite common in topcoat specifications. Typical are the Erichsen Indentation and/or Bend Test. Erichsen figures of 5–6mm minimum are typical.

10.12.3.8 Acid resistance
Test panels are immersed for 96h at room temperature in 0.1 N sulphuric acid.
Pass: film is not affected.
10.12.3.9  Alkali resistance
Test panels are immersed for 240h at room temperature in 0.1 N sodium hydroxide.
Pass: film is not affected.

10.12.3.10  Acid and alkali resistance (alternative procedure)
A more modern, and demanding, test to the above is carried out by subjecting the test panel to consistent sized droplets of various test solutions which are covered by watch glasses (the surface of the panel having previously been ‘activated’ by exposure to UV light).
Duration of test: $24\, h \pm 1\, h \at 23^\circ C$.
(Test solutions removed by rinsing with deionized water and drying in a stream of air.)
Test solutions:

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium hydroxide</td>
<td>0.5% by weight</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>0.5% by weight</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>0.5% by weight</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>38% by weight</td>
</tr>
<tr>
<td>Citric acid</td>
<td>10.0% by weight</td>
</tr>
</tbody>
</table>

Pass: film is not affected.
Note: tests above are alternatives to those shown in Table 10.11.

10.12.3.11  Water immersion (continuous)
Panels are immersed in a stirred/agitated demineralized water bath at 40°C.
Pass: no loss of adhesion, blistering, colour change, loss of gloss, or ‘sinkage’ (of the topcoat) after a minimum of 240h. In excess of 500h is expected.
Note: before testing panels would, by necessity, be aged at least 16h after immersion.

10.12.3.12  Humidity resistance (continuous)
Panels are placed in a humidity cabinet — 100\% RH at 40°C; some auto-producers use 50\% C.
Pass: no loss of adhesion, blistering, colour change, loss of gloss, or sinkage (of the topcoat) after a minimum of 240h. (Also refer ‘Note’ above.)

10.12.3.13  ASTM B117 Salt Spray (5\% salt solution at 35°C)
Test panels in a cabinet at the conditions stated above. Panels are ‘X’ scribed before testing.
Results are evaluated at 240, 480, and 840h (often over 1000h and sometimes to ‘destruction’) by inspection and tape strip (over 240h is normally only applicable to cathodic electroprimers.
Pass: not more than 2mm corrosion at scribe (assessed by taping).
This is a key test for primers and is carried out in primer only and a full system situation.

10.12.3.14  Scab corrosion test
This procedure is designed to simulate scab corrosion of a car body after water contact and stone-chipping.
Initially, the painted panel (full system) is immersed in a stirred water bath at 40°C. It is then subjected to a stone-chip test and subsequently to ASTM B117 Salt Spray. In addition it can be further exposed.

Pass: no scab corrosion (interaction of the pretreatment and primer is critical in respect of this phenomena).

10.12.3.15 Florida exposure (5° south)
Florida is the site preferred by the majority of motor manufacturers for the exterior durability testing of automotive finishes. It has a high humidity combined with a high level of ultraviolet; this provides an extremely rigorous environment for topcoat technology. Ideal for testing colour stability of pigments, film (polymer) integrity, gloss retention, and erosion.

Although it can be considered a good absolute test of a coating, certain factors should always be taken into account. Performance can often be affected by the time of year when exposure begins and the particular weather conditions in that year. Another hazard, which can often be misconstrued as microblistering, is fungal growth — characterized by small ‘pits’ in the film and threads or filaments leading from this defect. Consequently testing is normally ‘relative’ with known standards included in any test programme, to avoid misinterpretation or results.

Pass: typical results are shown in Table 10.11. The accepted standard is good gloss and colour retention, free from defects after up to two years (e.g. alkyds, thermosetting/NAD acrylics and acrylic lacquer). Basecoat clear systems have expected Florida performance up to 5 years.

10.12.3.16 Peel resistance: Florida 5° south
This test procedure is designed to simulate the UV resistance of the surfacer under basecoat/clear topcoat systems.

The stoved surfacer is coated with an approved thermosetting acrylic clearcoat (+UV absorber) at a film thickness of 30–35μm (i.e. low and critical).

Exposure times are:

+ UV absorber (i.e. normal in practice): 12 months
– UV absorber: 3 months

After exposure the surface of the clearcoat is assessed mainly for blistering and whether there is any indication of peeling at the interface between the clearcoat and surfacer.

10.12.3.17 Accelerated weathering
The development of a new paint formulation requires an early appreciation of the exterior durability characteristics and it is not possible to wait for a two to three year exposure at Florida to obtain this information. Recourse is therefore made to an accelerated weathering device which can indicate probable durability performance.

A variety of machines are available which subject the paint film to UV light in combination with humidity and temperature. No machine can accurately predict the Florida performance because of the difficulty of producing a UV spectrum identical to natural sunlight by artificial means. Nevertheless, a composition which has
withstood 2000 h on one of the more severe accelerated cycles can confidently be
predicted to show acceptable Florida performance.

Typical machines are marketed by Atlas (carbon arc or xenon lamp UV source),
Q-Panel Company (QUV apparatus using xenon lamp), Xenotest (xenon lamp).
Natural sunlight concentrated by mirrors is the basis of an accelerated weathering
process devised by Desert Sunshine Exposure Tests of Arizona (EMMA and
EMMAQUA cycles).

10.13 Future developments

The future development of automotive coatings technology and/or processes will
depend on a number of factors, namely, economics, energy saving, environmental
considerations, and consumerism (the demand for improvements in durability and
appearance). There are a number of options open, each having their respective
advantages and disadvantages and a compromise, to satisfy the various conflicting
demands, will undoubtedly evolve.

As far as environmental controls are concerned, they have become more and
more stringent, for example, the European Union proposal for 1996 introduction
brings emission levels down from the current 60 g m\(^{-2}\) to 45 g m\(^{-2}\) for all new plants
producing more than five thousand cars per year. Existing plants will have to come
down to 90 g m\(^{-2}\) within five years and 60 g m\(^{-2}\) within ten years.

Nevertheless progress has been made in reducing the level of solvent and stoving
effluent released to the atmosphere. The introduction of water-borne basecoats and
surfacers, higher solids products, e.g. polyester topcoats, and the limited use of
powder coatings have all played a significant part in reducing emissions. Modern
application systems have also contributed by significantly improving transfer
efficiency.

In addition, mechanical, thermal, and chemical methods are already available and
in use for reducing stoving effluent. These include ‘after burners’, scrubbers, and
carbon absorption paints.

However, there still remains a vast amount of solvent-laden air to be dealt with
from spraybooths, and the high amounts of energy consumed during the painting
process (>50% energy is, in fact, consumed by the spraybooths simply moving and
heating the air and water). High curing temperatures are also an area requiring con-
sideration, particularly if the concept of plastic components is to be fully realized.

In economic terms the cost of organic solvents will continue to rise in line with
oil prices. This increases the pressure to move away from solvent-borne to water-
borne, not only from an environmental point of view but also from an economic
standpoint.

Three basic routes are being followed as a means of reducing or, ultimately,
eliminating organic solvents in spray coatings: high solids technology, powder coat-
ings, and water-borne products. These will now be discussed.

10.13.1 High solids technology

The benefits and problems associated with this type of technology may be summa-
rized as follows, in relation to existing products:
Benefits | Problems/Disadvantages
---|---
Use current manufacturing techniques | More difficult to achieve equivalent film properties
Use current application equipment | More difficult to achieve equivalent appearance in metallic finishes
Use similar process parameters | Rheological control difficult
 | Automatic spray equipment with high transfer efficiency essential for good economics

Solids range:
Pigmented products — up to 70%, metallic (basecoats) 20–40%, clearcoats up to 55%.

Resin types:
Alkyd, polyester, acrylic.

Types of product involved:
Primers, surfacers, sealers, anti-chip coatings, solid colour and metallic finishes.

The obvious advantages are that high solids products normally have similar manufacturing, application and process methods to present low(er) solids technology. Problems and disadvantages arise basically from the fact that lower molecular weight/viscosity resins must be used. These, however, tend to give excessive flow on application, leading to lower run/sag resistance and, therefore, some form of rheological control is essential to facilitate suitable application properties. Furthermore, lower molecular weight resins require higher degrees of reactivity to form coatings with acceptable chemical and physical properties.

10.13.1.1 Higher solids surfacer technology
At the present time higher, or ‘medium solids’ as they are sometimes designated, are used fairly extensively particularly in Europe. In comparison with normal solids products the solids difference is small but significant.

| Polyester/PU surfacer (normal solids): | $\leq 60\%$
| Polyester/PU surfacer (higher solids): | $\leq 64\%$

Rheological control is normally achieved by the addition of small amounts of aerosil or bentone which are thixotropic aids and help to provide the necessary balance between flow and sagging.

10.13.1.2 High solids polyester topcoats
Solids are already fairly high and not likely to go much above current levels (up to 60% at the gun for white). However, because of the lower molecular/low viscosity resins needed, application is difficult particularly now that most application is ‘one-coat’ by electrostatic high speed bells where 35–60μm dry film thickness is expected. Sag resistance and ‘solvent popping’ problems are major issues and rheological control is often effected by the use of microgels. Microgels are essentially organic extenders and are used in small amounts; they also have crosslinking potential and some form an integral part of the film after curing.
The requirement for improved appearance, mar, and acid etch resistance is pushing more plants towards basecoat/clear technology particularly for dark colours. However, this causes problems with higher levels of solvent emission and cost which is why it has not been more widely adopted.

10.13.1.3 *Higher solids basecoats*

There has been a trend with solvent-borne basecoats to move to what are designated 'medium' solids basecoats where a change to water-borne systems is difficult for one reason or another. The increase in solids is only marginal (~12% low solids/18% medium solids) but it is significant enough to reduce the level of solvent emissions. A slight decrease in 'flip tone' is not seen as a particular disadvantage.

10.13.2 *Ultra high solids coatings*

This relates to products with solids contents in excess of 70%. There are, however, severe constraints in their development. For example, metallic finishes cannot be considered in this context since the loss of cosmetic appearance would be so dramatic as to make them unacceptable.

Pigmented (solid colour) products would have to be formulated as two-pack products using a reactive monomer or high solids activator because of their limited pot life. In any mass-production plant such products would undoubtedly call for dual-feed application equipment with a complex metering system. While equipment manufacturers have made certain progress, the cost and complications involved have severely limited the exploitation of such products, and currently they are of purely local interest.

10.13.3 *Water-borne products*

<table>
<thead>
<tr>
<th>Benefits</th>
<th>Problems/disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environmentally acceptable; cheap and available diluent</td>
<td>Water release on stoving</td>
</tr>
<tr>
<td>Use normal manufacturing methods</td>
<td>Need for tighter control of temperature/humidity for application</td>
</tr>
<tr>
<td>Use normal application equipment</td>
<td>Excessive flow: need for rheological control</td>
</tr>
<tr>
<td>Use similar process parameters</td>
<td>Resin limitations (stability); prone to surface defects through contamination</td>
</tr>
</tbody>
</table>

Solids range:
No environmental restriction.

Resin types:
Alkyd, polyester, epoxy, acrylic.

Product types:
Primers, surfacers, sealers, anti-chip coatings, solid colour, and metallic basecoats and clearcoats.
10.13.3.1 Surfacers
In Europe, over the past few years, there has been a significant growth in the use of water-borne surfacers and, to a lesser extent, in Japan. This trend is likely to continue as environmental demands become more severe and car producers aim for a total water-based coating system.

Water-borne surfacers have actually been around for a number of years. Early products were based on water-soluble resins, mainly alkyds. However, their film performance was marginal and application properties led to difficulties.

The present range of resin systems are in emulsion form and polyesters with PU modification (where applicable) predominate. These developments have been in line with the improvements in the stability of polymer systems in water in general. As already mentioned, emulsion systems tend to release water more rapidly than solution types. Add to this the relative high levels of pigments (and extenders) then you have a system which is very usable under mass-production conditions minimizing the need for tight control of humidity.

The need for rheological control is important to assist in the balance between flow and sagging on application. This is normally provided by the use of a thixotropic aid mainly in the pigmentation, e.g. small amounts of either bentone or aerosil are the most common.

At the moment, the overall performance of water-borne surfacers is slightly inferior to the best solvent-borne products. Yet they are considered, for the reasons detailed previously, the most favoured future option.

10.13.3.2 Basecoats
While the aqueous dispersion route has greater scope for formulation it is not been possible to produce aqueous finishes which can be used in the 50μm range (e.g. automotive solid colour topcoats) without strict control of temperature/humidity. However, such polymer systems can be used to good effect in the formulation of aqueous basecoats where basecoat film thicknesses of 10-15μm need to be applied. In these, the bulk of the film thickness is contributed by the clearcoat.

The aqueous dispersion controlled rheology approach permits good atomization of the basecoat through a conventional spray gun, while providing suitable control of flow in the applied film. Aqueous metallic basecoats can be formulated to give similar brightness and varied hue to the best low solids (12%) solvent-borne but at an ‘equivalent’ solids when related to organic solvent level of 55-60%. Such basecoats are much less dependent on temperature/humidity levels than would be ordinarily expected and they can be used in similar facilities to the solvent-borne type, with the assistance of a warm airblow before application of the solvent-borne clear.

Water-borne basecoats can now be considered an established technology. Its use has been well described in Section 10.7 and formulating, processing, and performance details appear under a separate heading (Section 10.7.4.2).

As emission legislation becomes more widespread and tighter (1996 in the European Union) the future direction towards water-borne basecoat/clear for both metallics and solid colours seems more and more likely. This will require major capital investment which is possibly the main reason of its non-adoption by certain plants/manufacturers.
10.13.3.3 Water-borne clearcoats
This technology is described in more detail later but it should be noted its development is still at a very early stage in what is considered something that could complete the ‘total water’ painting process.

10.13.4 Powder coatings and aqueous slurries

<table>
<thead>
<tr>
<th>Benefits</th>
<th>Problems/Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% solids (solvent-free)</td>
<td>Need for specific manufacturing equipment</td>
</tr>
<tr>
<td>High application efficiency</td>
<td>Need for specific application equipment</td>
</tr>
<tr>
<td>Good film properties (at high film thicknesses)</td>
<td>Limited colour range for good economics; colour ranges difficult; metallics non-viable; difficult to repair; need for high film thickness to achieve acceptable appearance; surfacers require heavy sanding to achieve acceptable topcoat appearance; difficult to coat complex shapes economically; higher temperature needed for flow/cure; dust explosion risk</td>
</tr>
</tbody>
</table>

Resin types: epoxy, polyester, acrylic
Internationally the use of powder coatings in the automotive sector is patchy. There is no real activity in the European motor industry but in the USA some powder stone-chip primers are being run and there is some minimal use of powder surfacers in truck/commercial vehicle plants.

Their single major advantage is the absence of solvent pollution and its recycling capability. This ability to be recycled is now becoming a key issue in some companies.

However, there have been inherent problems concerned with appearance (flow), high stoving temperatures, and cost, although there has been progress in the problem of reducing the baking schedule (to 165°C) and general appearance.

Nevertheless, this technology is generating a lot of interest as a clearcoat with a number of manufacturers who see it as the only alternative to water. This is described in more detail later (Section 10.13.6).

10.13.4.1 Aqueous powder slurries
Such materials would overcome some of the inherent problems associated with powder coatings. However, there would still remain the question of high energy and cost, repair difficulty, and lower standard of appearance because of the coarse powder particles.

10.13.5 Solid colour basecoats
This type of basecoat can be formulated either in solvent-borne or water-borne technology. They have a high pigment content with excellent coverage in a thin film and are independent of gloss level. The main performance criteria are solvent release, smoothness, and film properties.
The principal benefits are the alignment with metallic analogues, more assured durability, and scope to use pigments which are difficult to employ in, say, polyester type solid colours (the performance being mainly dependent on the clearcoat). This latter property is particularly beneficial in the use of lead-free pigmentation.

The requirement for improved appearance, mar, and acid etch resistance is pushing more plants towards solid colour basecoat/clear technology, particularly for dark colours. However, in solvent-borne systems this causes problems with higher levels of emissions and cost which is why solvent-borne solid colour basecoats have not been widely adopted.

10.13.6 Clearcoats
At the present time normal thermosetting acrylic clears have an application solids of 45–48% by weight and are generally referred to in Europe as ‘medium solids’ clearcoats. A move to higher solids products is not presently considered to offer enough benefits compared to more novel types under development, i.e. water-borne and powder.

The main concerns at the present time are performance, i.e. (a) acid etch resistance and (b) scratch/mar resistance. In a typical hydroxyacrylic/MF system any steps to improve (a), would be to cause deterioration in (b). As a consequence of this significant developments in resin technology have been necessary.

Improvements in ‘acid etch’, which is a prime target in North America, have been achieved by a number of routes. These include blocked isocyanate resins, siloxane functional acrylics and epoxy/acid crosslinking chemistry. Scratch/mar improvement has a higher priority in Europe and this has been achieved by blending in more flexible polyester or acrylic resins, acrylourethanes or by changes in the MF resin.

Whereas these two areas are where most clearcoat activity is currently concentrated, i.e. Europe and North America, some Japanese producers have gone to the so called ‘low maintenance’ clearcoats incorporating fluoropolymer resins. However, due to cost implications, they are generally confined to the luxury car market.

‘2K’ clears, because of their greater ability to ‘reflow’ after scratch damage and inherently better acid resistance, would be a possible solution to these problems. However, they still suffer because of health and safety concerns and have not been very widely adopted. A few European plants use them but in all cases they are processed in combination with water-borne basecoats. In North America about 15% of plants use ‘2K’ and a number of these are truck installations.

The one area where usage of ‘2K’ is high is on plastic parts but in overall volume terms this is very small.

Water-borne clear is still in its infancy. There is only one plant in the world running this technology and this is in Europe in a total water-borne installation.

Most European manufacturers are involved in test programmes but it is generally accepted that the development of water-borne clearcoats has not proceeded at the pace many people expected. This is for a variety of reasons:

- Application is more difficult than for water-borne basecoats.
- Appearance standards are not so easily achieved.
- The advantages of water- over solvent-borne clears are much less than for basecoats.
Automotive paints

Powder clearcoats are still generating a lot of interest with a number of producers seeing it as the only real alternative to water. Recycling capability is one of its plus points and this property is considered highly important by some companies.

No one is yet running powder clears on a regular basis and use is presently limited to coating small parts in North America. Problems of inadequate appearance, compared with other technologies, and contamination during the recycling process have delayed introduction on a large scale.

10.13.7 Pigmentation

All the general principles described in Section 10.7.5 still apply but there is a major requirement for cleaner, brighter tones. This has led to a high usage of lead-free (organic) reds and yellows.

These types of pigment have become the norm because of the toxicity problems associated with lead chromates/molybdates which has led to their near demise.

It is now much easier to formulate with organic pigments. This is because of the high usage of basecoats, where opacity (and gloss) considerations become less difficult, and the increasing use of colour keyed surfacers.

The biggest change in pigmentation technology in recent years has been the use of ‘effect’ pigments. Micas, particularly coloured ones, are widely used either in combination with aluminium or alone with pigments. This has led to a better range of cleaner, brighter metallic/mica shades to be produced, particularly reds, greens, and blues.

Currently, mica containing colours probably constitute 60% or more of total non-solid colours. Opacity, in many cases, is not as good as its metallic counterparts but again this is less of a problem because of the use of coloured surfacers.

10.13.8 Painting of plastics

The problems of painting a composite car body built of different metals and plastic has been described in Section 10.9. The particular requirements of such an integrated unit will have to be taken into account in the design of new paint systems as the growth in the use of plastics continues.

A major factor is the temperature constraint, and the development of novel low-curing resin systems is the principal solution to the painting of the wide range of plastics available.

It is worth noting that there has not been the growth in plastic in body construction as previously envisaged. However, this has not minimized the problems associated with the numerous plastic parts that require painting, quality standards having to align closely to the overall coating system.

10.13.9 Electrodeposition and spray application

The process of electrodeposition (EDP), using cathodic technology, is established world-wide and will continue to be improved. The EDP process is an extremely elegant method of coating complex units, being virtually solvent-free, and is the most efficient and economic of all methods of application. Its virtues are such that its future is assured for some time to come.
In the field of spray application, which applies to surfacers and topcoats, the use of robotics and automatic high speed rotory atomizers (electrostatic) is now very much the norm and growing in use. Such equipment provides a high level of transfer efficiency, reducing solvent emissions, with additional benefits such as consistency of application/quality with a low labour content.

Finally, improvements in oven and spraybooth design have also played, and will continue to play, an important part in reducing emissions, effluent, and energy consumption. Their role cannot be underestimated as newer technologies have been introduced so designs have been continuously upgraded to maximize performance and satisfy environmental demands.

10.13.10 Summary
It is evident that the high solids approach to reduce solvent emissions has limited potential compared to the more novel water-borne and powder technology. As a consequence the likelihood is that less and less effort will be put into high solids coatings in the longer term.

The use of water-borne systems in surfacer and basecoat technology have been widely adopted world-wide and will no doubt increase as environmental regulations are more strongly enforced. Usage of solid colour (water-borne) basecoats will also undoubtedly broaden so as to rationalize production processes and upgrade overall performance.

A major issue still to be settled is the future of clearcoat technology. The contenders are water-borne, powder, and ‘2K’ products each having its particular strengths and weaknesses. At the present time there are major developments in each area, progress is being made and some use can be found in various locations. Europe appears to favour the water-borne option, North America powder technology and 2K is common to both continents. In the longer term much will depend on the resolution of certain basic problems and it is most likely that it will take until the end of the century before one of these clearcoat technologies predominates throughout the international motor industry.

The future of the EDP process looks assured, its benefits having been well documented. Developments leading to continued improvements in performance and process refinements should see this system being retained as a permanent feature of the car painting process for the foreseeable future.

In conclusion, a combination of low polluting coatings with new equipment, i.e. electrodeposition and automatic/robotic high speed electrostatic spray, is clearly the way ahead. Such a package should satisfy the growing demand for energy constraints, ecological considerations, high performance standards, and the need for economical and shorter processes.

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**Bibliography**


