Study Guide
ADVANCED MODULE 513

Thermosetting Coating Powders – Media

By M. Griffiths

Summary

This Module investigates the various media used to manufacture thermosetting coating powders, the chemistry involved and some of the important factors that affect the formulation process.

Special attention is paid to the use of additives in optimising the manufacture, application and performance of the products. The final Section considers recent innovations, such as thin films powders and those systems cured by combined IR/UV radiation or other low temperature techniques.

Note: *It is assumed that the student already has a thorough grounding in powder technology and some understanding of basic chemistry. Module 204 gives an overview of powder coatings and Module 311 describes the more common resin systems used in their manufacture.*

It is expected that it will take approximately 8 to 10 hours to complete this module, including the practical work involved.

Structure of the Module

The module consists of 2 sections, 1 set of Self Assessed Questions (SAQ), 1 Computer Marked Assessment Questions (CMA), 1 Assignments (ASG) and an End Test (TMA).

The module is designed to take about 8 – 10 hours of study. This excludes the time taken to write up your report for the ASG.

Self-Assessment Questions (SAQ)

Are designed to enable you to check your own progress. Questions are asked as you progress through the module. You should write down your answers and then check them against the answers given in the Appendices. No marks are awarded for SAQs.

Computer Marked Assessment Questions (CMA)

Are a multi-choice question set that tests your understanding of the module. Please carry out this test before you submit any other work for marking by your tutor. These are completed online, you will need to log onto your study portal and then follow the CMA link/ instructions.

Assignment (ASG)

The ASG are an exercise in which the student research into and reports on certain objectives. You can discuss your proposed assignment with your tutor and mentor before commencing work. You will need to write a report on the assignment, which is then sent to your tutor for marking. Please see further instructions included in the Appendix on ASG Guidance Notes.

Tutor Marked Assessment (TMA)

Is a mandatory end test question paper taken under 'closed books', fully invigilated exam conditions. These are normally held on-site with an invigilator in attendance, which is normally your workplace mentor. The student or mentor will contact Lorraine Beard, and she will arrange for the TMA and instructions to be sent, by email to the chosen invigilator, and then this is then given to the student on the day and time that has been chosen.

Marks for the module

CMA	20%
ASG's	35%
TMA	45%
	100%

An overall mark of 50% or more is necessary for successful completion of the module, with students achieving at least 40% of the marks available in each element. In addition, an

overall mark of 50% - 64% must be achieved for a PASS to be awarded, an overall mark of 65% - 84% must be achieved for a Merit and over 85% for a Distinction.

Module Pre-requisites

The main prerequisite for persons taking Modules at Advanced level, is an interest in surface coatings. Preferably, they will be employed in the coatings or a related industry. They may also be employed by a user of paints, lacquers, inks or powder coatings.

These modules include references to scientific concepts relating to coatings technology. For example, those identified with an asterisk contain many references to chemical formulae and reactions. Therefore, it is a requirement that you have a scientific education, with Chemistry and Physics to at least UK Advanced Level or higher, of which you can provide evidence.

[Overview of qualification levels](#)

Successful completion of six modules, including at least four at level 5, entitles a student to a full, Level 5 International Certificate in Coatings Technology (ICCT), awarded by The Coatings Training Institute. However, individual certificates are also presented if the student chooses to take less than six modules.

Note: *The subject of powder coatings is dealt with in detail in:*
Polymer powder technology - *edited by M. Narkis & N.Rosenzweig* - Wiley

OBJECTIVES

At the end of this module, you should be able to do the following:

<u>Section 1 -   Resin systems</u>

1.1.	Differentiate between curing agents, catalysts and accelerators.
1.2.	Describe the types of epoxy systems available
1.3.	Describe the various polyester systems available
1.4.	Describe the types of acrylic systems available.

<u>Section 2 - Additives</u>

2.1.	Describe the effects of flow and wetting agents and discuss their importance
2.2.	Describe the various additives used for reducing gloss
2.3.	Discuss the techniques used to create special effects such as textured finishes and hammer finishes

<u>Section 3 - Formulation</u>

3.1.	Discuss the materials and techniques used in formulating epoxy-based powders, giving examples.
3.2.	Discuss the materials and techniques used in formulating polyester-based powders, giving examples.
3.3.	Discuss the materials and techniques used in formulating acrylic-based powders, giving examples
3.4.	Discuss the materials and techniques used in formulating structured finishes, giving examples.
3.5.	Discuss the materials and techniques used in formulating metallic effects, giving examples.
3.6.	Discuss the factors that affect the formulator's choice.

<u>Section 4 - Special developments</u>

4.1.	Discuss the pros and cons of thin film powders.
4.2.	Describe radiation curing systems

STUDY MATERIAL

Section 1. Resin Systems

As we have seen in Modules 310 and 311, earlier in the series, there are two distinct types of resin used in coating manufacture to achieve a solid, coherent film after their application as a dry powder:

•   Resins which already have the necessary performance characteristics and which have physical properties that allow them to melt and coalesce at reasonable temperatures. These are the *thermoplastic resins*.

•   Resins that need to be chemically reacted in some way, during the curing process. In reacting, a suitable resin would increase in molecular weight, thereby changing its physical properties (and hence its performance) to meet the specification. These are known as *thermosetting systems,* and here, the word 'system' identifies the fact that, apart from the resin, there are other important components involved, which usually need to be present in specific, chemical ratios. In Module 311, we learned the definitions of the terms '*equivalent weight'* and '*acid value'* for use in calculating those stoichiometric quantities.

In this Module, we will concentrate only on the thermosetting systems and the mechanisms involved in cross-linking.

1.1.   Curing Agents, Catalysts and Accelerators

There is a variety of active agents used to bring about cross-linking within the medium. These agents are as important as the resin in determining the properties of the cured coating, each one conferring its own 'signature' on the properties of the resulting film. This is important to the formulators, allowing them some latitude when developing powders for specific applications.

The term '*curing agent'* applies to those components in the medium that react in a stoichiometrical ratio with the resin during the cross-linking process. They are also commonly referred to as *hardeners*.

The type of curing agent selected determines both the type of chemical bonds formed and the degree of cross-linking between the polymer chains. Therefore, the curing agent not only influences the physical, chemical and electrical properties of the coating powder but also affects such factors as the degree of yellowing of the film and its gloss and flow.

For ease of processing and to ensure good storage stability, the curing agent should:

- be readily miscible with the resin,
- be a solid at room temperature, containing no volatile material,
- have low reactivity at temperatures up to those used in compounding and
- have a high reactivity at the curing temperature.

There are other additives used to trigger, accelerate or retard the curing process. *Catalysts* initiate the reaction and may speed it up but, although they may take part as an intermediate during the reaction, they end in their original form. *Accelerators* do just that - they speed up the reaction. Catalysts and accelerators do not have to be present in stoichiometrical quantities.

We shall discuss these in detail, as we consider the different resin systems.

1.2.   Epoxy systems

Epoxies were the first resins to become widely used in thermosetting powder coatings because of their basic characteristics:

- their chemistry was well documented, which meant that they could be manufactured to a controlled quality in a number of variations, giving the formulator scope when trying to meet a specification.

- they had melting characteristics suitable for the early compounding equipment and yet were brittle enough at ambient temperatures to allow them to be easily ground to a free-flowing powder.

- they provided a finished product which was stable under normal conditions but which was able to cross-link with a range of reactants to form acceptable films, under suitable conditions.

- they had good melt-flow and cure characteristics, forming films with acceptable appearance and performance characteristics.

Of course, these are the essential elements for any powder coating resins, but epoxies were the first. Developments since those early days have led to a range of alternative resin systems but, as we shall see, the epoxies remain an important option.

A large number of epoxy resins are possible, but those used for powder applications are generally based on *diphenylol propane* (also called *Bisphenol A*) and *epichlorhydrin*. Epoxy resins are characterised by presence of the reactive epoxy or *ethyloxylene* group at the end of the molecular chain (see Figure 1). You may find references to *'epoxide',*

which is a term, used interchangeably with *'epoxy'* to describe the active chemical groups in the molecule. Both terms are also used as generic names for the resin types.
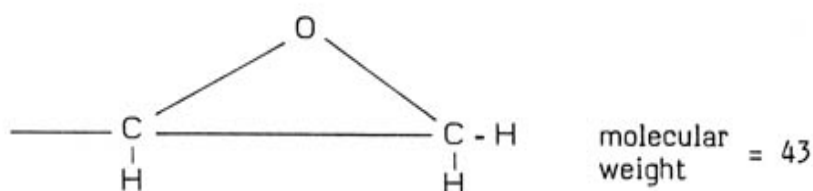

Figure 1

Like all other reactive chemical groups, the stability or reactivity of this ring is affected by the molecular structures in close proximity to it and by the nature of the reactive agent. It is possible to 'design' degrees of reactivity into resins by modifying the polymer during manufacture. The groups on the polymer can increase or reduce the small, positive or negative charges that naturally exist across bonds, due to the relative 'pull' of the atomic nuclei on the more mobile electrons. These small charges create the sites where chemical attack can take place.

In epoxies, the ring is the site where these charges are most mobile and where the bonds are most vulnerable to attack by suitable agents. The chemical attack begins in one of two ways:

- a negatively charged agent (a nucleophile) attacks the most positively charged point on the ring - usually at the carbon atom with the least substitution.

- a positively charged agent (an electrophile) attacks a negatively charged point on the ring - the oxygen atom.

In either case, the bond between the oxygen and one of the carbons is loosened, leading to ring scission (cutting). This produces two sites that are highly chemically active, which then cross-link with other components in the mixture to produce the higher polymers. In some cases, the curing agent makes the initial attack. In other cases, a catalyst or accelerator may combine with the hardener or the resin to produce a more reactive, intermediate molecule, which then cross-links.

Amine Cure of Epoxies

Dicyandiamide or *1-cyanoguanidine* was the first important curing agent for epoxy powder. The formula is shown in Figure 2. The molecule disassociates at temperatures above 150°C to give a number of reaction options. It is therefore described as a true *latent* curing agent because it is essentially non-reactive at room temperature.

Dicyandiamide or 1 cyanoguanidine

$$H_2N - \underset{\underset{\underset{H}{|}}{\overset{\overset{NH}{||}}{C}}}{} - N - \overset{\overset{NH}{||}}{C} - NH_2$$
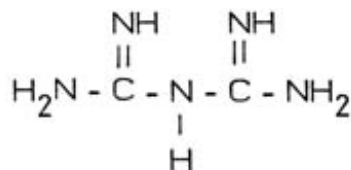
Figure 2.

Even at elevated temperatures, the reaction rate is very low, and so the curing agent could be incorporated using a Z-blade mixer, which was 'state of the art' equipment before the introduction of extrusion compounding. The optimum concentration of dicyandiamide is in the order of 4 to 5 parts per hundred of resin.

Dicyandiamide melts at 211°C and, as a result, does not dissolve in the resin, reducing its effectiveness. To overcome this, it had to be micronised before compounding to ensure adequate dispersion. Stoving schedules in the order of 200°C for 30 minutes were necessary, so that, as soon as the faster extrusion method became available, dicyandiamide was quickly replaced with curing agents that were more reactive.

The rate of cure of dicyandiamide may be dramatically increased by the incorporation of *accelerators* such as *tertiary* or *quarternary amine* compounds. Manufacturers normally supply two or more such curing agents with different quantities of a given accelerator. These may be blended together as well as with dicyandiamide itself to give a range of possible curing speeds. It is essential to remember that the blends should be made only from curing agents incorporating the *same* accelerator, to avoid possible synergistic effects.

The concentration of curing agent will depend on the resin used and will be recommended by the supplier. Curing schedules from 10 minutes at 180°C to 15 minutes at 150°C may be achieved with accelerated systems.

To achieve good appearance and high levels of gloss, one still had to overcome the disadvantages of the high melting point and insolubility of dicyandiamide. This was achieved by the development of *substituted dicyandiamide* where typically, a tolyl group replaces one of the hydrogen atoms on the amine group, as shown in Figure 3.

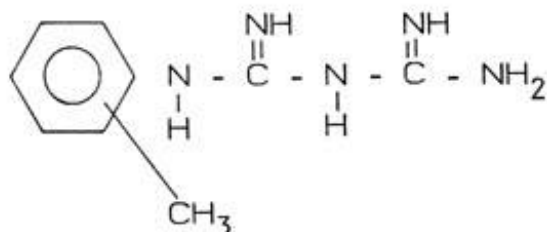## Substituted dicyandiamide : tolyl biguanide

Figure 3

These soluble curing agents are not quite so reactive as the fastest accelerated systems but may still yield compounds that can be cured by stoving for 30 minutes at 150°C. For low-temperature cures under these conditions, it is advantageous to use a resin with a low melt viscosity.

A very important class of amine curing agents are those based on *cyclic amidines* as manufactured by Hüls. Hardener B31, for example, is highly reactive and can produce epoxy powders which cure at temperatures below 130°C. This makes them of particular interest for coating objects with soldered joints. B31 may also be used as an accelerator for dicyandiamide cured epoxies as well as for epoxy-polyester hybrids. Other Hüls hardeners of special interest are B55 and B68. These are salts of a polycarboxylic acid with a cyclic amidine and produce coatings with matt finishes. Using various combinations of either curing agent with B31 gives a range of surface finishes from matt to gloss.

In general, the amine curing agents give powders with good storage stability and excellent flow, producing smooth coatings with superior mechanical properties and good chemical resistance. They have the disadvantages of yellowing badly on overbake and of staining in contact with copper, which catalyses the reaction.

Another class of curing agent which once found favour but has now been superseded, is the boron trifluoride amine complexes, an example of which is shown in Figure 4.

Boron trifluoride - amine Complex

Figure 4

The complex dissociates at elevated temperatures, allowing both the boron trifluoride and the amine to initiate the cross-linking. The resulting coatings exhibit superior resistance to yellowing but have poor mechanical and chemical resistance properties.

Anhydride Cure of Epoxies

The polycarboxylic acid anhydrides react with epoxy resins at elevated temperatures to yield a complex cross-linked structure. In Figure 5, trimellitic anhydride is given as a typical example. Reaction rates are normally slow but may be dramatically improved by incorporating suitable catalysts such as *stannous octoate*. The resultant coatings have excellent hardness, very good mechanical and electrical properties and superior resistance to water and alkali. In contrast to the amine curing agent, the resistance to yellowing on overbake is excellent, and they do not stain when in contact with copper.
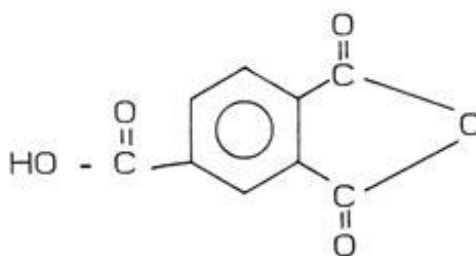
Structural Formula of trimellitic anhydride

Figure 5

A major drawback of anhydrides is their irritant nature and potential hazard to health. In addition, they are susceptible to hydrolysis by atmospheric moisture, which leads to poor curing properties and gritty appearance due to premature cure.

Attempts have been made to overcome these disadvantages by encapsulating the curing agent in a carboxylic acid terminated polyester resin or by forming anhydride adducts. However, owing to restrictions on their use imposed by health & safety regulations, limiting their allowable concentration in the workplace atmosphere, most of these developments have now largely ceased.

Phenolic Cure of Epoxies

Phenolic hydroxyl terminated curing agents are used where coatings with high reactivity and very good chemical resistance are required. The formula is shown in Figure 6, and it is not too surprising that the structural similarity to epoxy resins ensures a ready compatibility, producing blended finishes with high flow and good gloss.

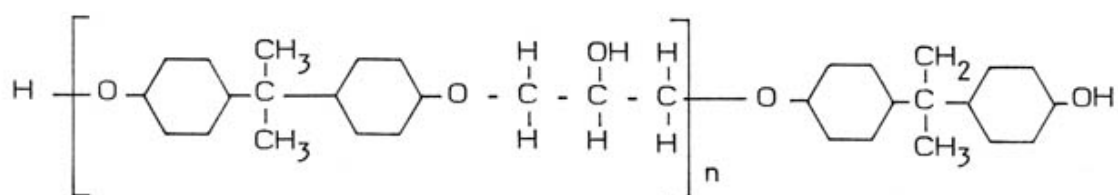Structural Formula of phenolic hydroxyl terminated curing agent

Figure 6

When used with basic accelerators such as *2-methyl imidazole (2-MI)* the formula for which is shown in Figure 7, systems are capable of being cured at temperatures as low as 130°C.

Methyl imidazole
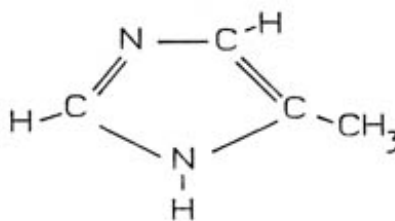
Figure 7

At higher temperatures, the curing reaction can proceed very rapidly indeed and in such applications as pipe coating, the residual heat from the components alone may be sufficient to effect complete cure. By using *epoxy novolac* resins, very high cross-linking densities may be achieved with consequent improvement to both chemical resistance and heat resistance. In addition to pipe coating, such systems are used to coat reinforcing bars used in concrete.

The presence of an aromatic ring in the *bisphenol A* structure of the chain leads to one of the main weaknesses of epoxy resins: i.e. their tendency to yellow under the influence of heat and outdoor exposure. Although alternative polymeric epoxy systems with superior non-yellowing properties are known, their physical properties render them unsuitable for use as coating powders. Fortunately, certain grades of saturated polyester resins are available which are entirely suitable at elevated temperatures. Therefore, polyesters have replaced epoxies in many such applications.

SAQ 1 - What were the main advantages of substituted dicyanamide over the unsubstituted form?

1.3. Polyester systems

Generally, polyesters are defined by the polymer structure shown in Figure 8 and are produced by the condensation reaction of an organic acid group and an hydroxyl group. In one form or another, they are now the most commonly used resin medium for coating powders.

Reactive hydroxl or carboxylic end groups

X _/\/\/\/\/\/\/\/\ R – C – O – R' /\/\/\/\/\/\/_X

‖

O

Polymer backbone made up of repeated units
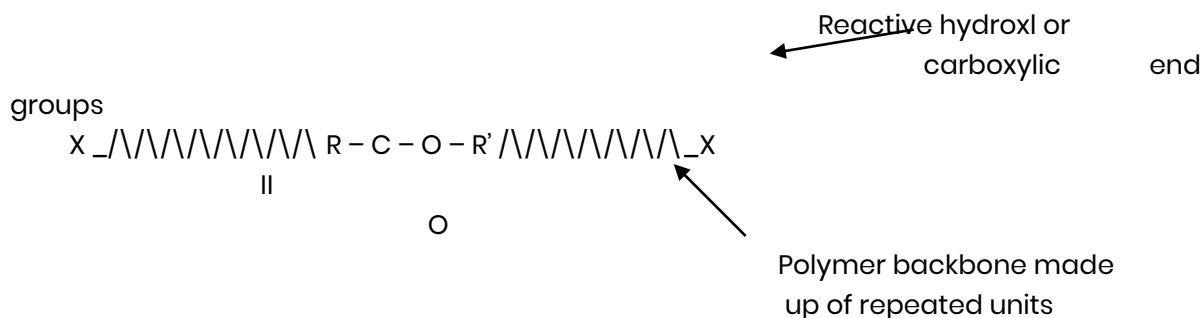
Figure 8

In Module I11, we saw how the polyesters used in coating powders fall into two distinct categories, where the reactive groups (shown as X in the diagram,) at each end of the polymer chain are either *carboxylic acid* or *hydroxyl* groups.

As with the epoxies, manufacturers of polyesters are able to produce resins with widely differing characteristics, by varying the average molecular weight, molecular weight spread and degree of branching. The formulator has the choice of resins of differing functionality, glass transition temperature, softening point and melt viscosity which can be combined to produce a wide range of properties.

Epoxy-Polyester Hybrids

An important application of carboxylic polyesters is their use as a curing agent, or more accurately, as a *co-curing agent* with epoxy resins to produce the so-called hybrid or mixed resin powders. A wide range of polyester resins is available, and so, in combination with different epoxy resins, the precise characteristics of the product can be varied substantially.

Stoichiometric proportions of the resins are generally recommended. These can be calculated from the acid value of the polyester and the epoxy equivalent weight. Some latitude in the ratios used is allowed, but higher proportions of polyester tend to reduce chemical resistance and film hardness, whereas an excess of epoxy can lead to reduced resistance to yellowing on long-term ageing. By varying the proportion of resins, the formulator may, therefore, adjust the properties of the coating to optimise specific performance.

There is continual economic pressure to increase the proportion of the cheaper resin (usually polyester) in the mix. If this is taken to an extreme, the properties of the final film may be adversely affected. The respective melt viscosities of the two resins must also be taken into account, as a wide difference can lead to insufficient mixing during compounding, resulting in poor dispersion.

In general, the epoxy-polyester powders cure at moderately rapid rates and at temperatures between 180°C and 200°C. The resultant films have very good flow and gloss. Their resistance to yellowing on overbake and to prolonged exposure at elevated operating temperatures is superior to that of unmodified epoxies. Resistance to outdoor weathering conditions is better than for straight epoxies but, for prolonged exposure, the polyester systems described later in this Section are preferable. Mechanical properties are generally excellent and, with the exception of some solvents, the hybrid powder coatings have satisfactorily chemical resistance. In particular, they have excellent detergent resistance. Like the anhydride-cured epoxies, epoxy-polyesters do not stain on contact with copper.

Systems that cure at lower temperatures may be obtained by using basic accelerators such as 2-methyl imidazole (2-MI). This allows stoving schedules of 170°C for 10 minutes. The introduction of more reactive epoxy resins allows the curing temperature to be reduced even further, to below 150°C. Under these conditions, care must be taken to ensure that the medium has sufficient melt flow to maintain a good appearance

Properties	Epoxy-Polyester	Epoxy-Amide
Cost	Polyester resins are cheaper than epoxies – hence cheaper powder	Epoxy resins are more expensive
Over-stoving colour	Less yellowing on over-	Yellowing occurs on

stability	stoving	over-stoving
Chemical resistance – e.g. to detergents	Greater resistance to detergents	Fair resistance but do not meet trade specifications
Copper staining resistance	No staining from welded areas	Amine hardeners can give staining from weld deposits

Figure 9

Epoxy-polyester hybrid powders now account for over 50% of the coating powder market and seem set to maintain their importance. Figure 9 summarizes the properties of these materials in comparison with the conventional, amine cured epoxy powders, and Figure 10 lists some of the polyester resins that are used commercially with epoxy resins to produce hybrid systems.

Typical Polyester Resins for Hybrid Systems

Supplier	Polyester	Glass transition temperature (^{o}C)	Acid value (mg KOH/g)	Acidity (Equivalent per kilo)
EMS-CHEMIE	Grilesta P7205	46	68	1.29
EMS-CHEMIE	P7401	60	36	0.64
UCB	Crylcoat 314	60	73	1.30
UCB	1022	52	50	0.89
DSM	Uralac P2065	73	83	1.47
DSM	P3042	55	78	1.38
DSM	P4250	52	35	0.63

Figure 10

SAQ 2 – What are the advantages that the epoxy-polyester system has over the conventional amine-cured epoxy powders?

TGIC Cure of Carboxylic Polyesters

As you may have realised, the polyester component in hybrids acts to dilute and inhibit the yellowing inherent in the epoxy resin. To eliminate it would require an epoxy molecule that does not contain aromatic groups. Such a material is available as the multifunctional epoxy compound triglycidyl isocyanurate, commonly called TGIC. This

material reacts with carboxylic acid functional polyester resins as shown in Figure 11 to give coatings with superior heat-resisting properties. These coatings will resist continuous exposure to temperatures up to 140°C and intermittent exposure to temperatures up to 160°C. This contrasts with the better hybrid systems, which discolour at temperatures above 170°C.

TGIC reacted polyester coating powders may be used to coat oven sides and radiators and similar objects that operate at high temperatures. In addition, these systems have excellent weather resistance and are used extensively for coating architectural items, in particular, window frames. Other outdoor applications include the trim on motor cars.
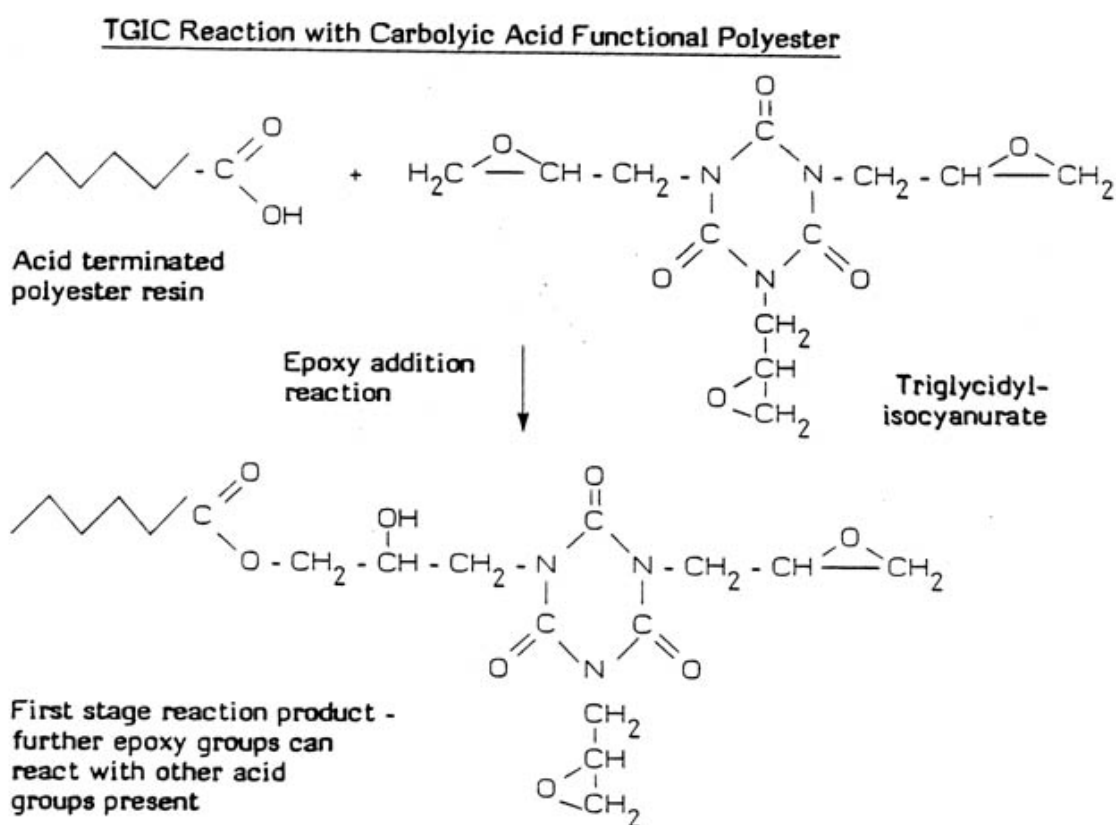
Figure 11.

As you can see from the structural formula, TGIC is a tri-functional curing agent, promoting cross-linking through its three epoxide ring structures. Because of this multi-functionality, we can, therefore, use polyester resins with lower functionality than we would need in, for example, the hybrid systems. This is an advantage, as TGIC is a very expensive material and we need a lot less with such resins. This financial benefit is offset to some extent by the fact that the resins are of higher molecular weight. This means increased melt viscosity, with a consequent reduction in the flow-out properties of the film.

Systems are available which require only four parts of TGIC for every 100 parts of resin. The common ratio of polyester to TGIC is in the order of 100 to 8. Stoving schedules for these systems are typically 10 minutes at 200°C. Amine catalysts can be used to reduce curing temperatures down to 170°C but at some risk to performance. This is because the curing reaction takes place only slowly below 150°C but very rapidly above it. Just as the melt viscosity drops to a value where wetting of the substrate becomes effective, the film rapidly begins to gel. For this reason, accelerated systems need to be formulated with care to avoid reducing their performance.

TGIC is a fine white crystalline powder that melts in the range of 85 °C to 95°C. So, under normal processing conditions, it is fully compatible with polyester resins. As the melting range indicates, TGIC should not be considered as the pure chemical shown in Figure 11. It does form isomers so, to calculate stoichiometric proportions, an epoxy equivalent of 107 grams of TGIC per mole of epoxy should be adopted. This is equivalent to an epoxy content of 9.3 moles per kilogram.

Polyester-TGIC coatings have excellent mechanical properties and very good chemical resistance. They exhibit good gloss, which is retained even after years of outdoor exposure. The evidence for higher molecular weight resins being used is indicated by the tendency for the finish to show a slight orange peel effect.

TGIC has been shown to exhibit mutagenicity. It can also be a skin irritant. Manufacturers and users of powders containing TGIC should make themselves aware of its hazards and follow the safety guidance accordingly. It is thought that the resin partially reacts with the curing agent during the compounding stage and that it effectively encapsulates the TGIC, reducing the hazard in the powder form.

Typical Polyester Resins for TGIC Systems

Supplier	Polyester	Glass transition temperature (°C)	Acid value (mg KOH/g)	Recommended TGIC content (parts per 100 resin)
EMS-CHEMIE	Grilesta P7307	62	34	7.6
EMS-CHEMIE	V73-8	60	22	5.3
UBC	Crylcoat 307	63	30	7.6
UBC	E2514	60	50	11.1
DSM	Uralac P2400	63	32	7.5
DSM	P3800	58	20	4.2

Figure 12

In Figure 12, you will find a list of polyester resins which are suitable for use in TGIC systems. For interest, compare these with the list of polyester resins used in the hybrid systems

shown in Figure 10. Figure 13 compares the properties of hybrid powders, TGIC-based polyesters and amine-cured epoxy powders.

Comparison of Properties of Different Powder Types

Property	Epoxy - DICY	Epoxy-Polyester	Polyester
Stoving conditions	180°C/10 mins	185°C/10 mins	200°C/10 mins
Specific gravity range	1.2 - 1.6	1.2 - 1.6	1.2 - 1.5
Scratch hardness BS 3900 E2	Excellent - pass 4 Kg	Excellent - pass 4 Kg	Excellent - pass 4 Kg
Cross-hatch adhesion BS 3900 E6	Excellent	Excellent	Excellent
Flexibility BS 3900 E1	Good - pass ¼" bend	Good - pass ¼" bend	Good - pass ¼" bend
Impact resistance - BS 3900 E3	Excellent pass 220"/lbs	Good - pass 220"/lbs some micro-cracking	Excellent - pass 220"/lbs
Abrasion resistance (Taber Abraser Test)	Excellent	Excellent	Excellent
Surface Hardness Pencil Test	Pass 3H	Pass 3H	Pass 3H
Heat Resistance - White and pale colours	Intermittent 100°C Continuous 80°C	Intermittent 120°C Continuous 110°C	Intermittent 160°C Continuous 140°C
Chemical and solvent resistance Acids Alkalis Oils Most solvents Ketones and Chlorinated Solvents	Excellent Excellent Excellent Moderate Poor	Excellent Excellent Excellent Good Poor	Excellent Poor Excellent Good/excellent Poor
Salt spray resistance BS 3900 F4 (1000 hrs.)	Excellent	Excellent	Excellent
Humidity resistance BS 3900 F2 (1000 hrs.)	Excellent	Excellent	Excellent
Exterior durability	Not recommended for continuous outdoor exposure	Suitable intermittent exposure - but not continuous outdoor exposure	Very good - gloss and colour retention very good

Figure 13

Standard polyester powders are usually based on a polyester resin derived from terephthalic acid (see Figure 14) whilst the new generation of "super-durable" polyesters are instead based on isophthalic acid, (see Figure 15) in which the meta-configuration of

the carboxylic groups on the benzene ring confers greater chemical stability on the final coating.
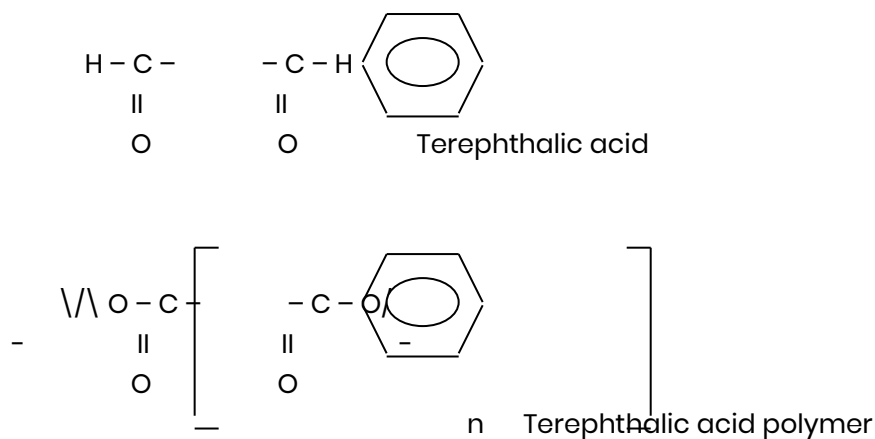
H – C –   – C – H
   ‖   ‖
   O   O   Terephthalic acid

\/\ o – C   – C – O
      ‖   ‖
      O   O
                           n   Terephthalic acid polymer

Figure 14

O
‖
H – C   O
                 ‖
              C – H
              Isophthalic acid
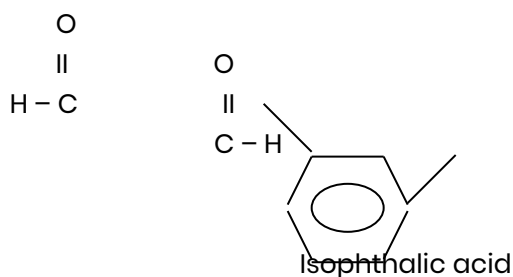
Figure 15

Isocyanate Cure of Hydroxyl Polyesters

Polyesters containing hydroxyl groups react with isocyanates to form urethanes, as shown in Figure 16. A number of isocyanates are available, but only a few are suitable for use in coating applications. These include hexamethylene di-isocyanate (HDI) and isophorone di-isocyanate (IPDI). The latter is preferred in coating powder due to its relatively low volatility at stoving temperature.

Reaction of Hydroxyl Group with Isocyanate

$$\text{—\hspace{-0.2em}\wedge\hspace{-0.2em}— OH} \quad + \quad O = C = N - R \quad \longrightarrow \quad \text{—\hspace{-0.2em}\wedge\hspace{-0.2em}— } O - \overset{\overset{\displaystyle O}{\|}}{C} - \underset{H}{N} - R$$

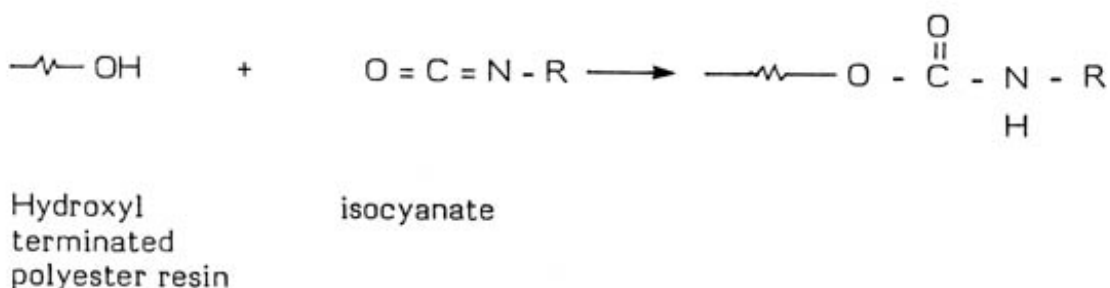Hydroxyl   isocyanate
terminated
polyester resin

Figure 16

Isocyanates are too reactive to be used alone and they are always handled in powder coatings in a *masked* or *blocked* form. This is based on the principle of reacting the isocyanate to produce an unreactive addition compound or *adduct*, which will dissociate at higher temperatures to free the . The isocyanate is then free and is available to react with the hydroxyl polyester. Nowadays, the blocking agent is almost invariably ⬚caprolactam, which can comprise up to 5% of the binder. At the stoving temperature, caprolactam volatilises and is lost from the film.

The hydroxyl polyester has a significant influence on the quality of the polyurethane coating. Thus, the degree of branching will determine the flexibility, hardness and toughness of the final film. The reactivity of the system will also be determined by the choice of resin and curing agent. Figure 17 lists hydroxyl polyesters and Figure 18 shows a selection of isocyanate adducts.

The influence of the resin and adduct on the reactivity of the system, as determined by gel time, is shown in Figure 19. The components are generally used in stoichiometric proportions.

Typical Hydroxyl Polyesters

Supplier	Polyester	Glass transition temperature ($^{\circ}$C)	Hydroxyl value (mg KOH/g)
UCB	Crylcoat 2383	68	50
UCB	2392	63	30
DSM	Uralac P2115	48	38
DSM	P2504	64	35
DSM	P4215	53	40

Figure 17

Typical Isocyanate Adducts

Isophorone diisocyanate adduct (Hüls)	Block isocyanate content	Splitting temperature (^{o}C)	Melting range (^{o}C)
B1065	10.5	175	75-83
B1530	15	170	85-90
BF1540*	15	160	105-115
Note : BF1540 is an internally blocked system. The other two are $\mathcal{E}$-caprolactam adducts.			

Figure 18

Reactivity of Polyester - Adduct Systems

Polyester type	Gell time at 200°C		
	B1065	B1530	BF1540
Crylcoat 2383	> 300s	136s	> 300s
2392	> 300s	180s	> 300s
Uralac P2115	> 300s	190s	153s
P2504	> 300s	280s	217s
P4215	> 300s	210s	158s

Figure 19

The isocyanate adduct dissociates at temperatures in excess of 170°C, which represents the lowest curing temperature. Curing schedules of 10 minutes at 200°C or 30 minutes at 175°C are common. Suitable catalysts, such as dibutyltin dilaurate or stannous octoate accelerate the cure by lowering the temperature of dissociation of the blocking agent in the isocyanate adduct. Care should be taken when using this method as it can reduce the storage stability of the powder and lead to yellowing of the film.

During the curing process, the blocking agent is lost from the coating. As this represents a significant proportion of the original powder, it can lead to considerable problems for the coater. Care must be taken to ensure that the cooler parts of the oven exhaust system are not blocked by condensate and that neighbours are not inconvenienced by the emissions.

Another difficulty arising from the volatility of the blocking agent is the formation of pinholes in the coatings as it is driven from the curing film. For films of thickness in excess

of 80 microns, this can be a severe problem. However, in thinner coatings, the addition of up to 1% of benzoin can alleviate the problem.

The presence of the blocking agent does have one beneficial effect as it acts as a solid solvent, holding the film open to allow gases to escape and promoting improved flow. This effect, along with the particular surface tension properties of the system, explain why polyurethanes have such high gloss, generally excellent finish and are relatively free of surface defects.

The introduction of internally blocked isocyanates (uretdiones) overcomes the problems associated with the volatile blocking agents such as ⬚caprolactam. These products have the structure shown in Figure 20, which unblocks during the curing process, to form reactive isocyanate molecules.
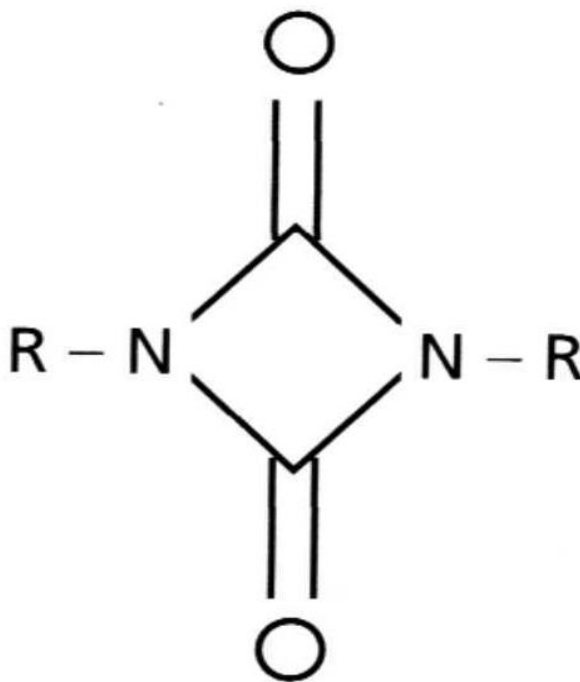

Figure 20 – Internally blocked isocyanate - Uretdione

In addition to excellent appearance and good mechanical properties, the polyurethanes exhibit outstanding resistance to the effects of outdoor exposure. Therefore, they are used extensively in external applications in the USA, Asia etc. whilst in the UK the polyester-TGIC systems are preferred for this purpose. The reason for this divergence in technology is not altogether clear, but one thought is that differences in the design of ovens in the UK seriously inhibited the use of materials such as polyurethanes, because of the volatiles emitted.

The reaction between isocyanate and hydroxyl groups can be used to enhance the properties of epoxy-polyester hybrids. The adduct can provide additional cross-linking by reacting the isocyanate with the pendant hydroxyl group already present in the epoxy resin molecule and with the hydroxyl formed by the carboxyl-epoxy reaction.

The additional cross-linking improves the solvent resistance of the powder and its resistance to boiling water and boiling the detergent solution. The use of the adduct is only recommended for those systems which cure above 175°C – the de-blocking temperature of the adduct. The extra performance is achieved at the cost of some discolouration of the film.

SAQ 3 – What is the main disadvantage of a blocked isocyanate cross-linking agent, and how could this be overcome?

TMA cure of hydroxyl polyesters

Hydroxy functional polyesters have been successfully cross-linked with anhydrides - typically with trimellitic anhydride (TMA). However, the same hazards to health, which were described earlier in the Section regarding the reactions between anhydrides and epoxies, apply here. Consequently, these systems are no longer used.

Hydroxylamide cures of carboxyl polyesters

For over 20 years, TGIC was used almost exclusively as a curing agent for exterior durable, carboxyl-terminated polyesters. During that time, no other curing agent could equal its unique blend of properties. The first serious rival to TGIC came on the market just as major concerns were being expressed about the potential health hazards associated with TGIC.

The new product was Primid XL 552 - a member of a group of chemicals known as β-hydroxyalkylamides (HAA). Figure 21 shows the structure of another member of this family of products - Primid QM 1260.
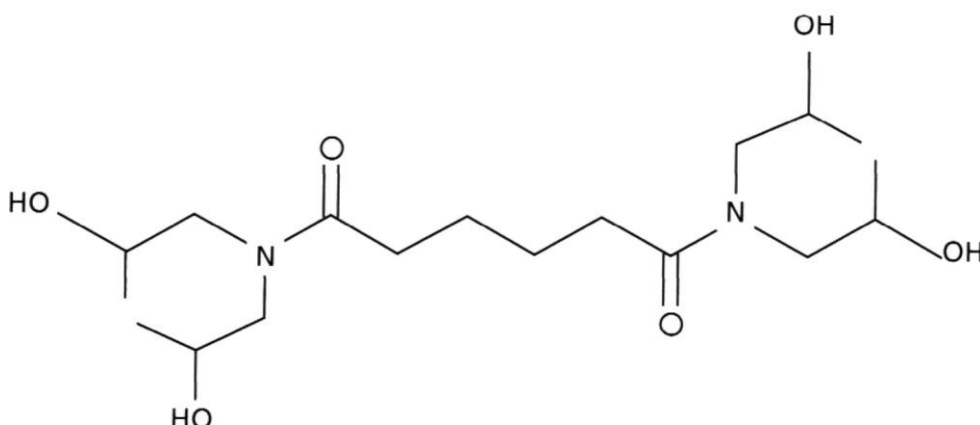
Figure 21 – Primid QM1260 Structure

Primid contains no epoxy groups, has a relatively "clean" toxicological profile and reacts with carboxyl-functional polyesters to yield products with weathering characteristics similar to those of polyester-TGIC systems. Water is eliminated during the reaction, which has proven to give some problems when these coatings are applied as thick films (i.e. over about 130μm), as some of the water may become trapped in the film during curing. Custom-built resins were specially produced for use with Primid, partly to complement its tetra-functionality and partly to help stabilise the system against yellowing, particularly in direct-fired gas ovens. Q1260 was developed to help overcome this problem.

To date, no method has been found to catalyse the HAA-polyester reaction and cure rate has to be influenced purely by functionality. So, polyesters with a high Primid demand tend to cure more rapidly than those with low demand. Mixing the resultant products together produces low-gloss systems, and this remains the most widely used technique to reduce the gloss of polyesters. Unfortunately, the final gloss can vary slightly, depending upon the relative reactivities of the resins supplied. With TGIC, reduction of gloss is achieved by catalysing one component of the blend.

Primid-cured polyesters have good electrostatic properties compared to TGIC, due to the higher polarity of the HAA and lower inherent curing temperature than uncatalysed polyester-TGIC. Most formulators agree, however, that it is not a total potential replacement for TGIC and it is unlikely that one single curing agent will achieve this in the foreseeable future.

During the search for TGIC alternatives, other epoxy chemistry was evaluated, culminating in the launch in the mid-1990s, of a product from Ciba referenced Araldite PT910. This is a mixture of epoxy compounds similar to TGIC but without its potential mutagenicity. It is, like many low molecular weight epoxy compounds, a potential skin irritant and must be handled with appropriate care.

One of the components of PT910 is liquid at room temperature, which depresses the softening point of the formulated coating. It, therefore, became necessary to produce resins having a higher softening point than normal, to allow formulators to make coatings with acceptable storage properties. This can lead to dispersion problems during extrusion, as the low viscosity curing agent and the high viscosity polyester do not readily mix unless the conditions in the extruder are modified to suit this type of formula.

When properly formulated, the finished products have similar characteristics to polyester-TGIC in terms of weathering properties, resistance to foul oven conditions, etc. As cross-linking is by addition rather than by a condensation reaction, thick films can be applied without the risk of the foam entrapment found when using Primid systems. Catalysts used with TGIC react in a similar way with PT910. In view of this, the use of PT910 is growing, despite the potential storage stability issue.

It is expected that, when TGIC eventually disappears from the market, Primid and PT910 will take over most of that volume. Nevertheless, new developments are in the pipeline, and unless a true alternative is found for TGIC, the market will fragment further over time.

Oxiranes

Further development in the area of polyester resin chemistry involves the use of *aliphatic oxiranes*, marketed by their originator, DSM, in the mid-'90s as "Uranox". These products are not classified as hazardous chemicals.

They are produced by synthesis of a carboxyl functional polyester and an aliphatic oxirane based upon epoxidised organic oils, in two separate reactors. The molten resin and cross-linker are pumped through a continuous mixer to get a homogeneous blend. The binder/cross-linker blend is metered on to a cooling belt to solidify and is then crushed to the correct form for delivery. Obviously, it is important to control the ratio of resin to the cross-linking agent during this process. Cross-linking does not readily take place under "normal" curing conditions, so a catalyst has to be added in the form of a masterbatch when formulating coatings based on this chemistry. The catalyst which works best is not one normally associated with polyester powder coatings and was found only after considerable development work.

The oils chosen for the cross-linker are blends rather than single compounds, selected for their degree of unsaturation in order to ensure optimum cross-link density in the finished product. Figure 22 shows a schematic representation of the polymer.
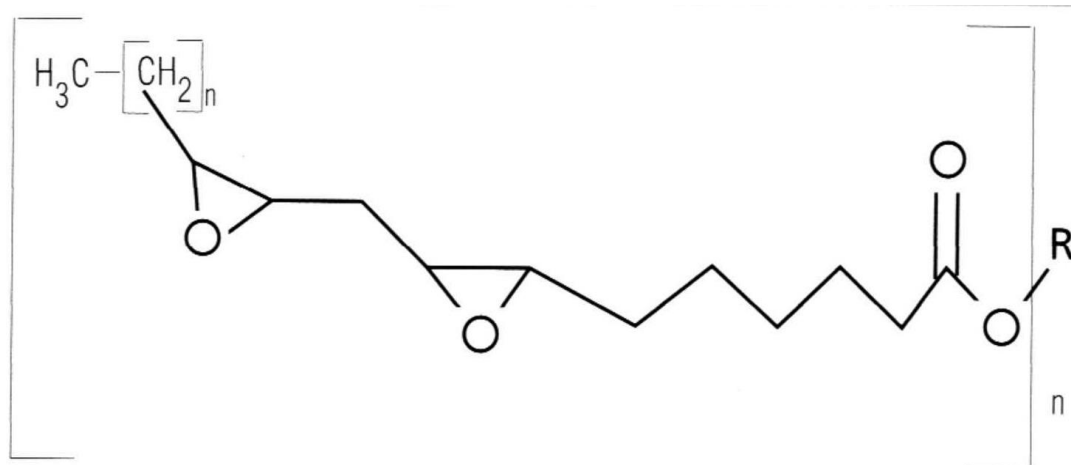
Figure 22 - Oxirane polymer structure

After addition of a carboxylic acid to an epoxide group, a hydroxyl group is formed. This can react with another epoxide group to give a tetra-hydrofuran ring. This prevents the last epoxide group from networking, which can result in many "dead ends", i.e. poor cross-link density. This would happen if, for instance, only epoxidised linseed oil were used. Oils with mono unsaturation, such as olive oil, will react in a 1:1 ratio and improve the cross-linking potential. By blending oils, the optimum cross-link mechanism can be derived.

Powder coatings made from such resins have been shown to have properties similar to those of polyester-TGIC, though they tend to yellow more on overbaking and there are some problems associated with gloss reduction. They have not yet found market acceptance for these and other reasons associated with formulation flexibility. Suggestions for using Uranox in combination with other systems, such as Primid, PT910 or urethanes, has given the coatings formulator an increased range of options in non-TGIC chemistry.

1.4.   Acrylic systems

The general chemical definition of an acrylic polymer is one derived from *acrylic acid* $(CH_2=CHCOOH)$. One such derivative, *methacrylic acid* $(CH_3CH=CHCOOH)$, is a common starting point for variants and gives a typical polymer structure, shown in Figure 23, widely used in powders.
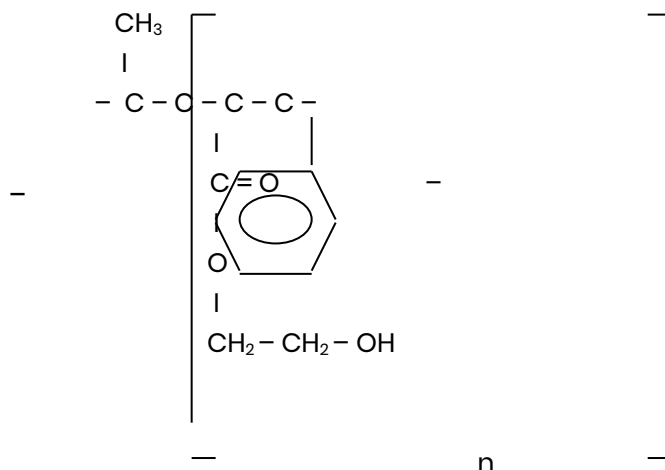
Figure 23 – Typical structure of an Acrylic resin

When powder markets first began to develop, the excellent weathering properties of acrylic paints were already well-known and so the incentive to develop coating powder versions was strong. The chemical structure of acrylics makes them highly resistant to degradation by UV light. Any UV degradation or hydrolysis that does occur takes place at the side chains of the polymer.

As we saw in Module I1, despite this superiority over polyester systems, acrylic powder resins have found only limited application in the UK. There were two main reasons for this: the early resins were based on *Glycidyl methacrylate (GMA)* chemistry and (a) had poor storage stability and - more importantly perhaps - (b) were totally incompatible with all other thermosetting powders, restricting both their manufacture and application.

These materials can be cured with aliphatic di-acids, in a similar reaction to that of TMA/epoxies, discussed earlier. The resins can also cross-link with acid functional polyesters, to produce materials analogous to the epoxy-polyester hybrid or polyester/TGIC systems.

Recent work has led to the development of *hydroxy functional acrylics (HFAs),* which are compatible with other resin systems but which retain the excellent weathering and corrosion resistance associated with acrylics. These products can be cross-linked using blocked isocyanates.

It is possible for resin manufacturers to produce resins with dual functionality - i.e. GMA resins with some hydroxy functionality built-in, so that the material can be cross-linked with a mixture of carboxylic polyester and blocked isocyanate.

An important advantage for the acrylics is that the materials can be modified to produce powders with a wide range of gloss options, all with smooth finishes, in a single component. This contrasts starkly with the problems of reproducibility encountered when

manufacturing low gloss polyesters. Here, it is necessary to make two materials with differing reactivity and then to dry-blend them. Even then, the resultant finish has a micro-textured, grainy appearance.

GMA Acrylics

Despite the limitations of compatibility described above, the excellent weathering properties of these materials, and their potential for use in the automotive finishes field, means that they cannot be totally ignored.

The general structure of GMA acrylic resins is shown in Figure 24.

$$
\begin{array}{c}
\left[\begin{array}{c}
CH_3 \\
| \\
-CH_2-C- \\
| \\
C=O \\
| \\
O \\
| \\
H_2C \\
| \quad O \\
H_2C \diagup
\end{array}\right]_n
\end{array}
$$

An acrylic polymer-based on glycidyl methacrylate
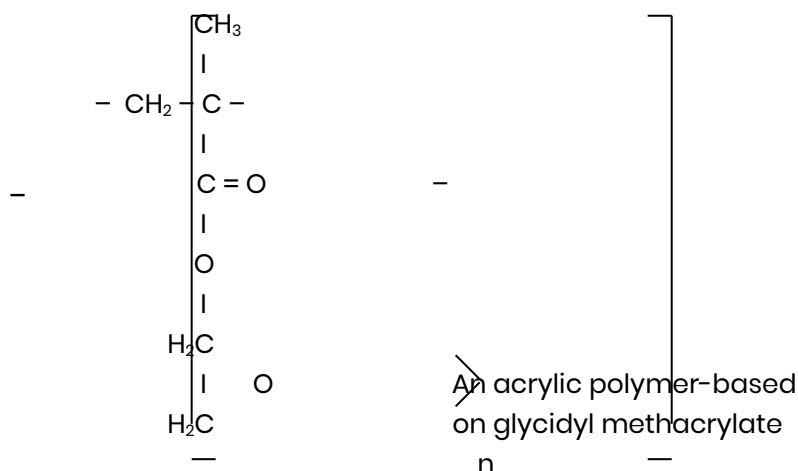
Figure 24 – glycidyl methacrylate acrylic (GMA) polymer

Note the epoxide ring, which is the reactive component in cross-linking of GMAs.

HFA Acrylics

These resins are based on *hydroxy ethyl methacrylate (HEMA)*, as shown in Figure 25. The reactive component here is - as their name implies - the hydroxy group on the side chain. The powders made from HFA acrylics to not exhibit the contamination problems associated with the GMA type, either in production or during application.

```
              CH₃
               |
  ⎯ CH₂ ⎯ C ⎯
               |
  ⎯          C = O              ⎯
               |
               O
               |
              H₂C              An acrylic polymer-based
               |                 on hydroxy ethyl meth-
              H₂C ‑ OH            acrylate (HEMA)
              ⎯                      n        ⎯
```

Figure 25 – hydoxy functional acrylic (HFA) polymer

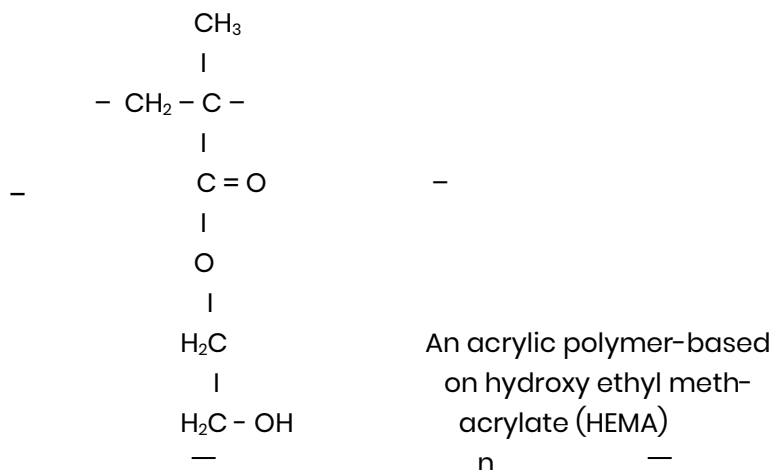The HFAs have extremely good weathering properties. (see Figure 26). Also, it is claimed that, unlike other acrylic systems, they present no more cross-contamination difficulties when changing from polyester to acrylic and back again than there would be in switching from one polyester to another.

XENON ARC WEATHEROMETER
SAE J1960 Cycle
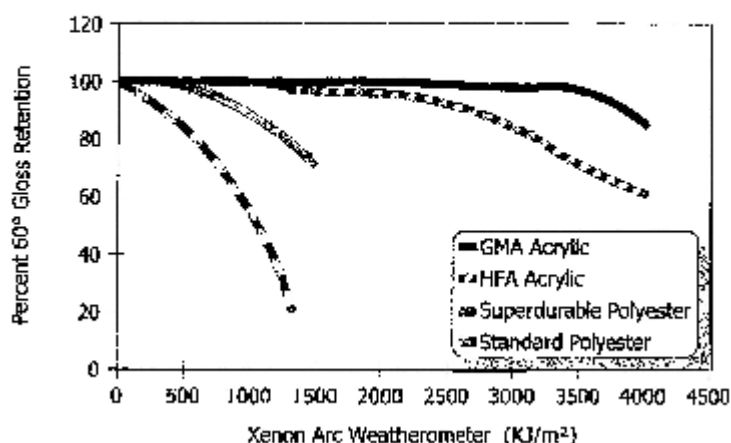
Figure 26 - A comparison of the weather-resistance properties of powder coatings made from standard polyester, super durable polyester, GMA acrylic and HFA acrylic, on exposure to Xenon Arc.

The graph shows that HFA acrylics have far superior durability than even the best polyesters but that they are themselves outperformed by the GMA types. Typically, in Florida durability tests, standard polyesters would be expected to pass 1 to 2 years exposure, with the superdurable types perhaps surviving for up to 5 years. The HFAs

would normally be expected to last 5 years or more whilst the GMAs would last for between 5 and 10 years.

HFAs also have excellent scratch and mar resistance plus good flow and appearance. This combination of properties currently seems to offer the best opportunity for powder coating to eventually penetrate the vehicle finishing market.

Automotive manufacturers now using polyesters are contemplating increasing their coating performance specifications in anticipation of these new options. Existing polyester powders will probably be allowed "grandfather rights" for the moment. (i.e. existing approvals will stand, they are slowly phased out, on new models.)

SAQ 4 - Write down some of the factors you would consider when selecting the resin binder for a thermosetting powder coating.

Section 2. Additives

So far, in this module, we have discussed the resins and curing agents that go together to make up binder systems. Now, we will consider those ingredients that alter the way in which the medium behaves - the *additives*.

Additives include flow control agents, accelerators, wetting agents and other materials that induce special effects. These are far too numerous to list individually, and in detail so, we offer the following examples and general concepts, to help you appreciate the sorts of modifications that can be made to the basic properties of powder media.

We would point out that pigments and extenders (*fillers*) also exert some influence over such properties as flow characteristics. We would refer you to other modules in the series, where these are discussed in detail.

2.1.   Flow Control Additives and Wetting agents

There is a range of additives available that helps the medium to wet the surfaces of the substrate and the pigment, to promote adhesion and pigment dispersion, respectively. In addition, virtually all coating powders need an additive to equalise and reduce the surface tension forces in the film at the melt stage, thus promoting levelling and preventing the formation of craters.

As mentioned in earlier modules, there are usually conflicting requirements in terms of surface dynamics. For example, low surface tension may improve surface wetting and spreading power, but high surface tension is needed to achieve coalescence and

levelling of the molten film. This is just one of the paradoxes presented to the formulator, who must experiment to achieve the optimum result.

The materials most widely used for this purpose are a group of *alkyl acrylate* polymers and copolymers, having relatively low molecular weights. Typical examples are (a) *n-butyl acrylate* polymer and (b) *ethyl acrylate* / 2-ethyl hexy acrylate copolymer. Figure 27 is a table giving the trade names of some of the more common agents on the market.

These acrylate polymers are not completely compatible with the binder and tend to migrate to the surface. There, the polar backbone remains dissolved in the resin whilst the alkyl chain tends to concentrate on the surface. The consequence is that the surface tension equalises due to the organized material structure over the surface. In powders, a significant amount of the additive remains in the bulk of the material, which means that we need to add an excess to achieve the required result. An addition of between 0.5 and 1 part per hundred of resin is normally used.

Types of Flow Agent

Flow Agent	Composition	Usual Addition % on Resin	Supplier
Modaflow	1:1 Copolymer of ethyl acrylate and 2-ethylhexyl acrylate	0.5-1.0	Monsanto Chemical Co.
Modaflow II Powder	As above carried on extender to give dry powder handling	1.0-1.5	Monsanto Chemical Co.
Acronal 4F	n-butyl acrylate homopolymer	0.6-1.0	BASF Ludwigshafen
Perenol F3	Copolymer of n-butyl acrylate and 2-ethylhexyl acrylate	0.5-1.0	Henkel & Cie GmbH Dusseldorf

Figure 27

It is extremely important that the additive is dispersed evenly throughout the bulk of the material. If not, variations between particles of finished powder may lead to severe disruption of the film. As acrylate flow control agent is a very viscous liquid, dispersion is difficult when using conventional mixing methods.

In the early days of powder manufacture, it was the practice to dissolve the flow agent in a solvent, such as toluene, which aided dispersion. However, different methods are used now. One common method is to prepare a *masterbatch*, normally at the 10% level, in one of the more commonly used resins.

This technique of master batching is useful in a number of instances, helping to ensure uniform dispersion of small quantities of important ingredients. For example, dry blended 'dilutions' of pigments in extenders can be used to accurately control the addition and dispersion of small amounts of tinting pigments.

In making a masterbatch, you should be aware that, if there is too high a concentration of a low melting point additive, the mixture might begin to *sinter* (i.e. stick together in a block,) during storage. Also, it will need to be added to the premix as particles of similar size to the rest, to avoid 'demixing' when feeding into the hopper of the extruder feed system.

The resin manufacturers now supply flow control agent already dispersed, in masterbatch form. The concentrations may vary from product to product. The main disadvantage in using these materials is that the base resin that the supplier has chosen may not be suitable for your purpose. Flow agent is also available in the form of a fine powder, where the acrylate polymer has been absorbed into an inorganic base. This powder can be incorporated directly at the premix stage. The quantities used must take into account the dilution of the flow agent.

Although the acrylate flow control agents are the most widely used, there are many other types available. Among these are the fluorocarbons and the silicones, both of which are used in masterbatch form. The silicones tend to have varying properties depending on the resin used and can also have adverse effects, causing defects such as severe *cissing* or *fish-eyes* on other coatings used in the vicinity. With particles of powder it is even more important to avoid cross-contamination and so silicones have virtually disappeared from the range.

Another early levelling agent is a low viscosity version of *polyvinyl butyral* (PVB). This continues to be used, particularly in fluidised bed applications, where edge coverage is of great importance. Typical quantities range between 3 and 6 parts per 100 of resin. Polyvinyl formal has similar properties.

Other materials that have been used to lower melt flow of the powder coating include ethyl cellulose or epoxidised oils. To increase viscosity, finely divided minerals such as silica and talc can be used.

A material widely used as a solid solvent in coating powders is *benzoin*. This additive reduces melt viscosity, allowing entrapped volatiles (including air,) to escape and so greatly improving film appearance. Typically we would use additions in the order of 0.2 to 0.5 parts per 100 parts of resin.

All these materials should be added with discretion to ensure that the optimum quantity is used. Too much flow control agent can be as troublesome as too little, leading to poor storage properties and poor edge coverage. Similarly, excess benzoic will sublime from

the film when heated, forming a dusty deposit on the cooler parts of equipment such as the oven entrance and the conveyor.

The use of these various surface-active agents and their effect on the flow, levelling and wetting must be taken as a whole and requires close investigation to achieve the best results.

SAQ 5 – The preparation of a masterbatch of flow additive was described. What are the advantages of using such a technique?

2.2.   Reduced gloss effects

Matt finishes

In Section 1, we drew attention to the salts of polycarboxylic acids with cyclic amidines that could be used to produce a range of matt finishes. Although these curing agents are extensively used for this purpose, other additives have been used in the past and still have some application. These include varieties of *polythene wax* which are incompatible with the binder and migrate to the surface reducing gloss. The surface layer also acts to increase surface slip, improving the mar resistance of the coating.

In paint manufacture, extenders are commonly used to reduce the gloss of a film. Although the same can be done with powders, there is less scope because it is relatively difficult to wet the pigment particles efficiently with molten resin, during the short time available extruder. Extenders such as talc, coated carbonates and some silicas (all of which have high oil absorption,) are used for reducing gloss. These can also be used in textured finishes (qv) as they usually also have an influence on the melt viscosity of the coating. However, excessive use can slow down extrusion rates and will affect the physical properties of the applied coating.

Polyester / TGIC systems can be made to produce a matt finish by incorporating accelerators such as *zinc mercaptobutyl thiazole (ZMBT)*, giving gloss levels of 35% to 40%. To reduce the gloss further in polyesters, we usually have to resort to a different method, involving the production of two powders with different reactivity and then dry blending them. This technique - which is effectively 'controlled contamination' - is commonly used to produce powders with gloss levels as low as 5% to 10%.

During cure, such a mixture effectively forms two phases - a continuous phase of the slower reacting material into which the faster curing powder is dispersed. The reason for this is that the more reactive powder cures so quickly that it does not have the time to diffuse into the continuous phase. The greater the difference in reactivity between the two blended powders, the greater is the reduction in gloss, so in some systems, it is

possible to control the gloss level by accelerating one component or the other. Differences in surface tension will also play a part, as each powder interferes with the other's flow. The result is micro-textured, granular effect that can be clearly seen under magnification. This disruption of the surface scatters reflected light, so lowering the gloss.

Some acrylics can be produced in matt finish, from a single component, avoiding the granular, textured effects of the polyesters, whilst exhibiting excellent exterior durability.

2.3.   Special Effects

Another area where additives are used in formulating is in the manufacture of special effects such as *textured* and *hammer finishes*.

Structured finishes

Structured coatings are characterised by surface patterns and profiles that come under the general heading of '*textured finishes*'. Included in this category is the special effect known as '*hammer finish*'. The degree of texture may be coarse or fine, rough or smooth and gloss or matt. These variations can also be coupled with clear coatings and metallic pigments, to provide a wide range of finishes.

Essentially, there are four basic means of producing a textured finish:

•   the powder can include coarsely ground material which, on stoving, does not flow out sufficiently to form a smooth coating. This is sometimes referred to as a '*spatter*' finish.

•   solid material can be added to the powder, and this remains proud of the surface when the coating levels and cures.

•   the viscosity of the powder melt can be increased sufficiently to prevent a smooth flow-out. In extreme form, this produces a surface like sandpaper.

•   the coating can be contaminated in a controlled fashion. This gives rise to localised surface craters that form the textured pattern.

Although the particle size of the powder plays some part in achieving the desired finish, the principle of using large particles alone to form the structured finish is no longer favoured. The reason lies in the application of the powder. On spraying, the coarser particles tend to follow different trajectories to the finer powder. This means that it is very difficult to achieve a consistent appearance. Furthermore, over-sprayed powder usually has a quite different particle size distribution to the original, which means that reclaimed powder gives very unreliable results.

The second method of forming a texture, by using a material that does not melt, can be carried out either by dry blending the additive or by compounding it into the powder. Dry blending can be used to incorporate from between 5 to 20 per cent of a thermoplastic material, such as nylon or polypropylene, to produce a rough wrinkle finish. Care has to be taken that the polymer is capable of withstanding the high stoving temperatures. This technique suffers from the same disadvantage as using large particles, namely the difficulty of using reclaim powder. Consequently, strict control of the blend of recovered and virgin powder is needed for its reproducible application.

The alternative is compounding the texturing agent into the powder, which helps to alleviate - but does not completely overcome - the problem of reclaim. A typical example of the technique is the use of mineral fillers that can be incorporated to produce a very attractive wrinkle or crinkled finish. The degree of texture depends on the quantity of agent used, which can vary from 5% to 15%. The viscosity of the powder melt also has a marked effect on the final appearance. Suitable materials include talcs and micas.

The increase in melt viscosity through the use of extenders can produce a texturing effect, particularly if some thixotropy is induced in the melt. The quality of finish obtained is often described as 'leatherette'. It is not usually a pronounced texture but rather resembles orange peel. An example, is the use of 30% of a stearate-coated calcium carbonate. The desired thixotropic effect can be achieved using a relatively a small quantity of filler. A similar result can be obtained by using, for example, only 0.2 to 1.0 per cent of a colloidal silica.

CAB is a texturing agent of the 'contaminant' type and will produce a very attractive patterned finish. This technique of obtaining a textured finish - by the controlled used of a contaminating agent - has wide application. Essentially, it involves contaminating a base formulation with some ingredient that has a local surface activity.

There are two distinct techniques used:

(a) the texturing agent is incorporated into the premix. If necessary, more of the additive can be blended in, after grinding. Here the texturing agent is of a type which has very low surface tension and a melting point *above* that of the extrusion process but *below* that of the curing temperature. The particle of texturing agent will, therefore, pass through the manufacturing stage unchanged and will only melt to produce local surface activity during the final cure.

(b) the base is extruded and ground before the texturing agent is dosed into it. Here, it is possible to use the normal flow agents, such as Modaflow, which melt in the extruder. Also, any reject material can easily be re-processed to produce another powder. A disadvantage is that the more the material is processed, the more likely it is to pick up extraneous contamination.

The texturing agent is usually added at concentrations as low as 0.1%, with each particle creating its own small ciss mark. In both methods, the base formulation contains little or no flow agent, so it is extremely prone to general contamination. As a result, quality complaints are more frequently received about these products. Contamination levels of 1 part in 100,000 are sufficient to cause rejection. These are 'normal', endemic levels found in any spraying area, laboratory or application plant. Formulators are advised to carry out controlled contamination tests on these and conventional, gloss films (especially polyurethanes and acrylics,) to convince themselves of the nature of the contamination to be expected.

Control of the texture pattern can be effected in several ways:

- increasing the concentration of texturing agent will increase the number of active sites until the optimum is reached, after which the pattern will become more and more fine and smooth. Reducing its concentration will allow the active sites to flow out more, producing deeper, wider patterns.

- the base formulation will have an effect: the lower the melt viscosity of the base formulation, the more the surface action will be able to take effect. The lower the inherent surface tension of the system, the stronger the activity of the additive will need to be to produce a texture. Polyesters are particularly difficult media for the production of textured finishes. Similarly the amount of flow agent in the base will change the structure. For example, increasing the concentration of flow agent in the base will *reduce* the relative effect of any texturing in it. In this way, one can, for example, reduce the depth of an individual ciss, preventing penetration through to the substrate.

- the coarser the particle size of the texturing agent (i.e. the more active ingredient there is in one spot) the larger will be the pattern of the resulting texture. If the additive used is extremely fine, it will begin to act like a normal texturing agent, smoothing out the film.

- different types of texturing agents have different effects, depending on their surface tension properties. Examples are the Modaflows, and grades of Cellulose acetate butyrate (CAB), Plexigum and fluorocarbon.

- Whilst the particle size distribution of the powder coating will affect the texture to some small degree, coarse powders will generally lead to problems in application and recovery.

By adding metallic pigments, which are far more mobile in the film than other pigments and which orientate to give iridescent effects, we can produce a wide range of effects. This is the basis of the hammered finishes, which are based on only lightly pigmented or dyed media. The extra mobility of these media and the effects of the surface-active

agents in moving the metallic pigments into swirls, gives rise to the classic hammer effect.

A highly filled base with a comparatively high melt viscosity will give a much tighter finish. Fully pigmented bases are used in conjunction with metallic pigments to produce the so-called '*antique*' finishes. In these products, the more mobile metal particles are pushed away from the texturing agent to form a web pattern, which is superimposed on the textured base colour.

Apart from the natural attractiveness of the final textured coating, these finishes are very useful for hiding imperfections in the substrate. They are used, for example, to cover unsightly areas such as weld lines and metal defects very effectively. To achieve the full texture effect, coating thicknesses of at least 75 micrometres are usually needed.

Again, care must be taken when reclaiming textured, and hammered powders, particularly the latter, as changes in appearance can easily result from re-using the sprayed material. If the very fine metallic particles are not bonded to the bulk powder, the after filter will preferentially capture them. Such changes in particle size distribution and in the concentration of metallic pigment will affect the final appearance.

By their nature, textured coatings lack the protective qualities of conventional powder coatings. The low spots of a coating can easily penetrate to the substrate, and this usually prohibits the use of these coatings outdoors or in hostile environments. However, they can show remarkably good resistance to abrasion and generally retain their appearance even after considerable wear. This makes them a favourite choice for such applications as office furniture.

Another novel additive is Powderlink 1174 (tetramethoxy methylglycouril) which, when accelerated with Crylcoat 120, can be used to produce a wrinkle effect.

> **SAQ 6** – List the various ways of producing a structured surface finish in a powder coating.

Section 3. Formulation

We have mentioned several times that the more versatile a material is and the more scope it allows for modification, the more useful it will be to the powder formulators. In this section, we will give examples of how the various systems are used in formulating coatings with particular properties.

The examples are not meant to portray specific formulations but rather to act as guides and to illustrate the very wide choice that the manufacturer has when it comes to

formulating a suitable coating powder. You should realise that there is not enough time and space in this module for an exhaustive survey of all the variables that can be explored when making a suitable coating, so we will only consider the more important factors.

We have used the specific grades of commercially available raw materials when listing the various components to be used in a premix. Although these will always be suitable for the particular purpose, other materials may be found to perform equally well or, in certain circumstances, even better. To decide which is best for your purpose, you will have to look first at the copious technical literature that the manufacturers of the raw materials happily supply. Practical experience will also lead to a greater awareness of the range of finishes which it is possible to produce from coating powders.

## 3.1.	Epoxies and Epoxy-Polyester Hybrids

In Figure 28A, you will find the first formulation. This is an old-fashioned example, using micronised dicyandiamide. Its curing schedule is 20 to 30 minutes at 200°C. A high proportion of barytes is used in this example. This would not detract too much from an already poor appearance, although flexibility may be compromised a little. Modaflow is one of the acrylic flow agents that we mentioned in Section 2.

By accelerating the dicyandiamide, a much faster cure is possible, as illustrated in Figure 28B, which incorporates one of the Shell range of curing agents. This formula will cure in 10 minutes at 180°C. In this white compound (which contains a rutile titanium dioxide made by the chloride method) you will see that some of the pigment has been substituted with barytes. Also, the shade has been subtly altered by the addition of very small quantities of pigment, incorporated using the master batching technique described for controlled additions of flow agents.

Epoxy Cured with Dicyandiamides

	A	B	C	D
Epikote 1055	100	100	100	100
Dicyandiamide (Micronised)	4.4	-	2.5	-
Epikure 108FF	-	4.8	-	-
Epikure DX143	-	-	2.5	-
Epikure 147	-	-	-	4.2
Barytes	70	20	20	-
Modaflow	0.5	0.5	0.5	0.5
Carbon black Regal 400	1.0	-	-	-
Tioxide R-TC4	-	50	50	70
Benzoin	-	-	-	0.3
Carbon black Regal 400 1% Master batch	-	0.04	0.04	0.04
Violet RL 5% Master batch	-	0.04	0.04	0.04

Figure 28

An even faster curing agent in this range is DX143 which we have used in formulation 28C to accelerate dicyandiamide itself. The cure schedule of 28C would be similar to that of 28B.

The next formulation (Figure 28D) illustrates the use of a substituted dicyandiamide. These curing agents are capable of producing very high gloss coatings so, in this example, to maintain surface quality, barytes has been excluded. In fact, the inclusion of *micronised* blanc fixe would not significantly affect the gloss.

To aid melt flow and to ensure a smooth finish by eliminating any trapped air, a small quantity of benzoin has been used. The substituted dicyandiamides are not as reactive as the accelerated grades, and the formulation will take 15 minutes to cure at 180°C.

An alternative curing agent for glossy coatings is the cyclic amidine B31 which is made by Hüls. The two formulations shown in Figure 29, illustrate the effect of using epoxy resins with different epoxy equivalent weights. Here Dow's DER 664U has an epoxy content of about 1100 whereas DER 663U has about 1300 millimoles per kilogram. So, the latter needs an additional curing agent to satisfy the greater number of epoxy groups. This leads to a higher density of cross-linking and the coating would, therefore, be harder and more resistant to chemical attack. However, the flexibility would tend to be inferior. A curing schedule of 15 minutes at 140°C would be suitable for both materials. A slightly different acrylic flow agent is used in these examples and another rutile titanium dioxide.

Epoxy cured with Cyclic Amidine

DER 664 U	100	-
DER 663 U	-	100
B 31	6.25	7.5
Arconal 4F	1.0	1.0
Kronos CL 220	70	70

Figure 29

Highly reactive systems are also obtained by using phenolic hydroxyl terminated curing agents of the type shown in Figure 30, where a series of Ciba Geigy products are used as examples. Formulations 30A and 30B can both be cured in 12 minutes at 150°C. Here we have taken the opportunity to use alternative techniques to incorporate the Acronal 4F flow agent using masterbatches: Araldite GT 1942GB already contains 1% of flow agent and XB2874 has 10%.

Phenolic Hydroxyl Curing Agents

	A	B	C	D
Araldite GT 7004	100	-	-	-
Araldite GT 1942 GB	-	100	-	-
Araldite GT 7220	-	-	100	100
XB 2874	7	-	-	-
Modaflow Powder II	-	-	1.4	1.4
Polyvinyl butyral B 30 H	-	-	3	-
XB 3082	33	31	45	45
2-methyl imidazole	-	-	1.0	-
2:4:6 tris (dimethyl amino methyl) phenol	-	-	-	1.0
Fine silica (5 micrometres)	-	-	30	-
Red iron oxide	-	-	1.5	-
Carbon black	-	-	-	0.2
Tioxide R-TC4	70	70	-	10

Figure 30

Coatings produced from these materials will have good mechanical strength and excellent chemical resistance. Resistance to yellowing is inferior to alternative systems, and outdoor performance is relatively poor. They are, therefore, recommended for their technical rather than decorative properties.

Instead of conventional epoxies, epoxy novolac resins can be used. These produce very high cross-linking densities, making coatings which are suitable for tank linings, pipe coatings and reinforcing bars.

A pipe coating formulation is shown in Figure 30C, and it includes an accelerator to enable the film to gel extremely rapidly at coating temperatures of around 220°C. Formulation 30D shows a similar material suitable for drum lining. In any formulation work, you need to bear in mind the end use of the coating. Here, for example, in a drum that might come into contact with food, 2-methyl imidazole would not be a suitable accelerator. An appropriate alternative is given in Figure 30D.

The pipe coating formulation also contains fine silica, which, together with polyvinyl butyral helps to control the melt flow. Modaflow Powder II is used here as the main flow control agent. Because it incorporates an inorganic base, extra is required to ensure that enough flow agent is present in the mix.

Redundant Epoxide Formulations

	A	B
Araldite GT 1946	100	100
*TMA adduct	20	-
Boron trifluoride - amine complex	-	6
Modaflow II	1.5	1.5
Benzoin	0.5	-
Tioxide R-TC4	75	50
Violet RL 5% Master batch	0.03	0.02
*Adduct - Trimellitic anhydride	50%	
- acid terminated polyester	50%	

or Grilonit H 88083

Figure 31

For the sake of giving you the whole picture, you will see two formulations in Figure 31 that are no longer used. 31A is an anhydride-cured system, which will give excellent hardness

and superior resistance to water and alkali. The irritant nature of the anhydride, even in encapsulated form as shown in the figure, prevents its use. The stoving schedule for this system is 10 minutes at 180°C. Formulation 31B includes the boron trifluoride amine complex as the curing agent. The physical and chemical properties of these systems are always poor, even after stoving for 30 minutes at 200°C.

So far, we have only considered epoxy systems, which give finishes which are reasonably glossy. Now, let us turn to the methods that are available for making reduced gloss finishes.

Reducing gloss levels.

In Section 1 we mentioned the salts of carboxylic acid with a cyclic amidine that are marketed as curing agents by Hüls. Two grades are available - B55 and B68, each of which gives finishes with greatly reduced gloss.

In Figure 32A you will see a formulation which uses B55 with a reflectance value in the range of 20 to 25, whereas formulation 32B uses B68 which has a considerably lower reflectance of between 5 and 10.

By combining these hardeners with the Hüls gloss hardener B31, a complete range of different gloss levels can be produced. Thus, formulation 32C has a reflectance of around 50.

Matt Epoxy Powders - Huls hardeners

	A	B	C
Grilonit L1204	100	100	100
B55	6.25	-	2.25
B68	-	9.1	-
B31	-	-	2.25
Modaflow	0.9	0.9	0.9
Tioxide R-TC4	70	70	70
Carbon black 1% Master batch	0.01	0.01	0.01

Figure 32

Although these materials have low reactivity, necessitating a cure temperature in excess of 180°C, these systems are used extensively because of the control they give the formulator over gloss. However, they tend to yellow at 200°C, and they are expensive.

An alternative means of producing matt finishes is by mixing powders of differing reactivity. In Figure 33, you will find a formulation that incorporates dicyandiamide curing agents. In this example we have taken the opportunity to add some French chalk filler,

which also acts to reduce gloss. Remember, with this particular formulation you must ensure that the half containing dicyandiamide is properly cured, so a stoving schedule of 20 minutes at 200°C is needed.

Matt Epoxy Powders – Mixed reactivity

Epikote 1055	100	100	
Modaflow II	1.5	1.5	
Dicyandiamide	4.4	-	Manufacture separately.
Epikure 108FF	-	4.8	Then dry blend 50:50
Talc IT Extra	5.0	5.0	
Carbon black Regal 400	1.0	1.0	

Figure 33

Next, we show some examples of hybrid systems, where epoxy is co-cured with a carboxyl-polyester resin.

Figure 34 illustrates the effect of using polyester resins of different acid values in combination with Dow epoxy resin DER 664U, which has an epoxy content in the range 1050 to 1140 millimoles per kilogram. Notice how the properties of the coatings change depending on the ratio of polyester to epoxy. Formulation 33C, which has the highest polyester content, has such improved non-yellowing characteristics that it can be used for limited exterior exposure.

Epoxy - Polyester Formulations

	A	B	C
DER 664 U	50	40	30
Uralac P2127 (Acid value = 70-85)	50	-	-
Uralac P2228 (Acid value = 47-57)	-	60	-
Uralac P2450 (Acid value = 28-38)	-	-	70
Perenol F3	1.0	1.0	1.0
Benzoin	1.0	1.0	1.0
Tioxide R-TC4	50	50	50
*Pigment Master batch	0.5	0.5	0.5

*Pigment Master batch:

Tioide R-TC4	100
Violet RL	1.0
Carbon black Regal 400	0.8
Blue BLP	1.0
	——
	102.8
	——

Better yellowing resistance   ——————————————▶

Increased hardness   ◀——————————————

Improved chemical resistance   ◀——————————————

Cheaper   ——————————————▶

Figure 34

In Figure 34, you will see that small quantities of tinting pigment have been incorporated using a dry-blended, colour masterbatch. In these formulations, we have used Perenol F3, which is another acrylic flow agent.

None of the systems in Figure 34 are particularly reactive, so they need 15 minutes at 180°C to cure.

To achieve faster curing times, systems have been developed which incorporate lower molecular weight epoxy resins with an epoxy content in the range of 1300 to 1600 millimoles per kilograms. These resins have lower melt viscosity and hence have excellent flow characteristics. They suffer from the disadvantage of lower softening point and care is needed to ensure that storage stability is adequate. Typical examples are Dow's DER 692H and Ciba-Geigy XD 4143. Both these resins already incorporate a flow agent. Typical cure times range from 15 minutes at 160°C to 7 minutes at 180°C.

In Section 1, we described the use of an isocyanate curing agent to improve chemical resistance of a mixed system, albeit at the expense of some discolouration. Figure 35 gives a typical formulation using a caprolactam blocked isophorone diisocyanate adduct, which cross-links with the hydroxyl groups present on the epoxy resin. A minimum

curing temperature of 170°C is needed to ensure that the adduct dissociates. In this example a stoving schedule of 15 minutes at 180°C is recommended.©

Hybrid Powder with Isocyanate Curing Agent

DER 664 U	45
Crylcoat 344	55
Adduct B1530	8
Modaflow	0.5
Benzoin	1.0
Kronos Cl 220	50

Figure 35

As with the epoxy powders, the polycarboxylic acid/cyclic amidine salts can be used to achieve a matt finish with these hybrid systems. This is achieved by reducing the proportion of polyester and curing the excess epoxy resin with the hardener, as we have shown in Figure 36. In these examples, the reflectance values are respectively 100, 55 and 20. These systems suffer from the disadvantages of tending to yellow on cure and being expensive.

An alternative strategy for reducing gloss is to use special waxes such as Grilonit MA68021 and MA68022. Waxes can also be used to promote slip. An example is modified micronised polyethylene wax such as Lancowax TF 1780.

Matting Hybrid Systems

	A	B	C
Epikote 1055	50	60	70
Crylcoat 314	50	40	30
Perenol F3	0.5	0.5	0.5
Benzoin	1.0	1.0	1.0
Tioxide R-TC4	50	50	50
B68	-	2.0	5.0

Figure 36.

We suggest you learn more about the astonishing range of materials

SAQ 7 – By studying the current technical literature, compile a list of the range of materials on offer to coating powder formulators.

3.2. Polyesters

As we mentioned in Section 1, for superior weathering and heat resistance, coatings based on polyesters are used in preference to those containing epoxy resins.

In Figure 37, you will find formulations in which Ciba-Geigy's Araldite PT 810 - a triglycidyl isocyanurate or TGIC - is used to cure two polyester resins. Each of these has a different acid value.

TGIC Cured Polyester

	A	B
Grilester V 73-9	100	-
Grilester V73-8	-	100
Araldite PT810	7.5	5.3
Modaflow	1.0	1.0
Tioxide R-TC 60	70	70
Violet RL 5% Master batch	0.06	0.06

Figure 37

In formulation 37A the resin has an acid value of between 30 and 36, whereas the resin in formulation 37B has an acid value of between 20 and 24. The latter therefore needs significantly less TGIC, and this can represent a considerable cost saving, as the curing agent is expensive. However, the cheaper material will need a longer curing time - 12 minutes instead of 7 - at 180°C, and its weathering resistance will not be as good, although still adequate for most purposes. The rutile titanium dioxide pigment is a special grade with good outdoor durability. The tinting masterbatch should preferably be made using a polyester base and not epoxy.

Polyesters containing TGIC are frequently used as clear, weather-resisting topcoats, and a typical example is shown in Figure 38. To ensure the best possible dispersion, the flow control agent is incorporated as a masterbatch. You may have noticed that benzoin has been used to improve the surface appearance.

Crylcoat 430	90
Crylcoat 2455 Master batch	11
Araldite PT810	7.6
Benzoin	0.4

Figure 38

The alternative use of hydroxyl-terminated polyesters for outdoor application, by cross-linking with isocyanates to produce polyurethanes, is illustrated in Figure 39. Here, the resins used in formulations A and B have hydroxyl values of respectively 50 and 35. Thus, different levels of the isophorone diisocyanate adduct will be needed in each case, to achieve a satisfactory cure. The proportion of adduct in formulation 39A results in a coating with outstanding flow.

	A	B
Crylcoat 2383	100	-
Crylcoat 2392	-	100
B1530 (Isophorone diisocyanate adduct)	25	15
R-TC60	75	75
Modaflow	1	1
Benzoin	0.6	0.6
Stannous octoate	0.5	0.5

Figure 39

Benzoin is an essential ingredient in these systems to ensure that volatile blocking agent - in this case ⊠caprolactam - escapes into the atmosphere.

Stannous octoate is used here as an accelerator. This material should preferably be incorporated in masterbatch form to ensure uniform distribution. It is a matter of judgment whether the resulting reduction in storage stability and the increased tendency to yellow is justified by the increase in reactivity. Both these accelerated systems will cure after 10 minutes at 200°C.

It is possible to achieve a matt finish by mixing together two polyester powders having different rates of reactivity. However, it is more common to blend together TGIC and isocyanate-based polyester powders. This gives more significant and reliable reductions in gloss.

Special matting agents for TGIC systems such as zinc mercapto butyl thiazole (ZMBT) and XB3329 have been developed to produce a single component, reduced gloss polyesters. The latter example was developed by Ciba Geigy. You will find a typical formulation in Figure 40. Here, a calcium carbonate filler has been used to replace a percentage of the TiO_2 pigment. The gloss level of this system is about 32%, but this has been achieved only by sacrificing physical properties such as impact resistance.

Matt Polyester

Uralac P3800	100
Araldite PT810	4
XB3329	8.3
Benzoin	0.8
Modaflow Powder II	1.5
Tioxide R-TC60	33
Durcal 3 - ($CaCO_3$)	33

Figure 40

Using this technique, consideration must also be given to the respective melt viscosities of the resin and hardener as too wide a difference can lead to insufficient mixing during compounding, with consequent poor dispersion.

3.3.   Acrylics

Because of their reactivity, acrylic systems offer a great deal of formulating flexibility, as in Figure 41:

Raw Material Reference	Polyester Acrylic	Acrylic Primid	Polyester Acrylic	Acrylic PT910
Crylcoat 810	490	542.5	–	–
Grilesta 7806	–	–	493.5	550.6
Crylcoat 700 (acrylic)	210	147	206.5	123.9
Primid XL-552	–	10.4	–	–
Araldite PT910	–	–	–	25.5
Kronos 2160	300	300	300	300
Resiflow PV5	10	10	10	10
Benzoin	4	4	4	4
Gel time @ 200°C (s)	98	93	70	100
Gloss - 60 ° Head (%)	3	15	3	18

Figure 41 - Examples of GMA curing agent and polyesters to produce low gloss finishes
Here we see examples of the use of an acrylic polymer curing agent with exterior durable polyester resin, to produce a, 'one-shot', dead-matt finish. Between the extremes shown for each type of medium, the gloss will increase progressively with increasing additions of the Primid XL-552 or PT910 hardeners.

3.4. Structured Finishes

One of the simplest texturing agents is an acrylic flow control agent master batch - an example is given in Figure 42.

Texturing Master Batch

Epikote 1055	95
Modaflow	5
	100

ground to 200 mesh

Figure 42

The application of the texturing agent is illustrated in Figure 43, where the base formulations produce a blue gloss and a matt, black-textured coating respectively.

Textured Epoxy Coatings

	A	B
Epikote 1055	100	100
Epikure 108FF	5.5	1.0
B55	-	5.0
Modaflow II	1.5	1.5
Barytes	100	100
Winnofil S. (CaCO$_3$)	12	-
Tioxide R-TC4	5	-
Phthalocyanine blue	3	-
Regal 400 carbon black	-	2

ground to 150 mesh. Dry blended with 0.5% texturing master batch

Figure 43

Added to each of these is 0.5% of the texturing agent, dry-blended into the powder. The particle size of the base will determine, to a large degree, the fineness of texture. In these examples, a medium texture is required. Notice, too, that quite large quantities of filler have been used, including fine calcium carbonate in the gloss formulation, to ensure that the base has reasonably high melt viscosity. A low viscosity base will flow out too much and, in consequence, the texture will be less pronounced.

Reducing the amount of Modaflow in the extruded base will make it more susceptible to the effect of the texturing agent, exaggerating the profile of the texture pattern. In these examples, we would expect that the gloss texture containing the extra filler would produce a finish with a more pronounced structure than the matt material.

Hybrid coatings are textured using exactly the same principles, as shown in Figure 44. In this example the base should produce a fine texture as it is ground in order to pass through a 200 mesh sieve. As we mentioned earlier, the coarser the texturing agent, the more pronounced its local effect would be, i.e. giving deeper and broader patterns.

Hybrid Powder - texture

Epikote 1055	50
Grilester P7205	50
Modaflow II	1.5
Barytes	100
Winnofil S	12
Tioxide R-TC4	70
Blue 5% master batch	0.1

ground to 200 mesh. Dry blended with 0.5% texturing master batch

Figure 44

Although this method allows the manufacturer to modify the appearance at the end of the process, in general, the blending technique is not to be recommended, since every handling operation increases the risk of cross-contamination.

The manufacture of hammer finish coating powders follows the same general principles of controlled contamination as those used with the other structured coatings. There are, however, some variations. Hammer finishes contain metallic pigments that are generally included in both the base and in the hammering masterbatch. These metallic pigments can be extremely fine and need to be well dispersed, so it is usual practice to incorporate them in masterbatch form.

The appearance of the hammer finish depends on the coating being transparent to allow the metallic pigment to be seen. Opacifying pigments are therefore excluded, organics being preferred. Further, the melt viscosity of the base has to be low as the structure of hammer finishes is much flatter than most other textures, so fillers are also left out. Particular care has to be taken that the hammering masterbatch is carefully screened to ensure the absence of any large particles.

Hammer coating powders tend to be significantly more expensive than other structured coatings so the efficient recovery of overspray is very important. However, changes in the pattern of the finish can easily arise when recovered powder is used and careful blending with virgin material is essential for control of both cost and quality.

Figure 45 shows how these two masterbatches are incorporated to produce a typical hammer coating powder. You will notice the complete absence of filler and the low concentration of pigments used.

Epoxy Hammer Finish

Epikote 1055	100
Epicure 108FF	5.5
Hammer master batch No. 68A	10
Phthalocyanine blue	0.05
Organic yellow	0.1
Carbon black Regal 400	0.4

ground to 150 mesh

Dry blended - 100 parts hammer base
            0.75 parts hammer master batch 68B

Figure 45

SAQ 8 – What are the factors that affect the degree of texture in a structured coating?

3.5.   **Metallic effects,**

There are three basic methods of obtaining a metallic finish:

Compounding the metal into the medium in the conventional way. This approach invariably results in a loss of metallic lustre because of the abrasive action in the extruder. A typical example is shown in Figure 46. Here, an attempt has been made to encourage the metal particles to migrate to the surface by incorporating stearic acid and wax. Despite these aids the resulting finish still resembles a conventional grey rather than a metallic.

Compounded Silver

Epikote 1055	100
Epikure 108FF	5.5
Modaflow II	1.5
Tioxide R-TC4	5
Aluminium powder Al 755	10
Stearic acid	2
Microwax	1

Figure 46

Dry blending the metallic pigment into a clear base, as we have illustrated in Figure 47. The 'gold' pigments are in fact copper bronzes. The resultant finish is better than that produced by compounding, but it still lacks the lustre associated with metals.

Dry-blended Gold

Epikote 1055	100.00
Epikure 108FF	5.50
Modaflow II	1.50
Organic yellow	0.25
Organic Red	0.06

Ground to 170 mesh (90 microns) and dry blended:

Base	100.0
Puregold 10990	7.5
Gold 412	2.5

Figure 47

Bonding – where the base and metal pigments are subjected to controlled heat treatment, to enable the pigment particles to stick to the ground powder base. The base powder may be pigmented or clear.

A wide range of novelty finishes can be produced using metal pigments, and Figure 48 demonstrates the versatility of coating powders:

Pewter Finish

Black base:	Epikote 1055	100
	Epikure 108FF	5.5
	Modaflow II	1.5
	Barytes	70
	Carbon black Regal 400	1.2

ground to 170 mesh (90 micrometres)

Dry blend –	Black base	90
	Bonded silver powder	10
	Texturing master batch (Fig. 65) (106 mesh - 150 micrometres)	0.5

Figure 48

A black and a silver powder have been blended with a coarse texturing agent to give a finish known generally as 'pewter'. Such finishes are used extensively to produce antique effects, and they are used in such applications as fire surrounds.

3.6. Factors affecting the choice of formulation

Apart from the actual materials used, there are a number of other factors that will have a bearing on our final choice of formulation. Good formulators will make themselves aware of these and should take them into account. Some we have already mentioned during the course of this module.

Apart from the basic raw material cost of a product, we should understand the costs involved in its manufacture. For example:

- Different types of equipment may behave differently with a given formulation. This is particularly true of different types of premixers and extruders, where the variation in colour development and dispersion may slow down manufacture.

- A highly pigmented formulation may take much longer to extrude. Cost-cutting by increasing the extender content of a formulation may prove to be counterproductive.

- Certain additives or resins may adversely affect the storage properties of the product.

- A more resilient resin system may take longer to grind, slowing down production and adding cost.

- Certain combinations of resins may not melt uniformly in the extruder, giving a non-homogenous product, which could lead to hazing or poor physical properties.

- Significant differences in particle or granule size between the various raw materials can lead to de-mixing. Vibration in the feed system into the extruder can cause larger granules (e.g. larger flakes of resin or masterbatch) to rise to the top of a mixture, whilst very fine particles (e.g. pigments or flow agents) filter down to the bottom. This can lead to variations in appearance and performance throughout the batch.

A company's willingness to accept these costs and variances may depend on policy, but the formulator should point out the likely difficulties, where these are foreseeable.

Modules 501 to 505 in this series, deal with factors affecting the formulation of coatings generally.

ASG 1
Please carry out ASG 1 in Appendix 2, before continuing with the next Section.

Section 4. Special Developments

When embarking on new developments, always consider the alternatives, including those outside your own technology. Ask yourself "Why?. Even if a new potential development did work, would it necessarily be better than the alternatives already available in other fields? Remember, new products have to be commercially viable to succeed. Most of the time, the driving force for development is cost, but it could also be legislation or production capacity, for example.

4.1. Thin film powders

Thermosetting powders are used extensively as direct replacements for stoving paints. Powders are normally applied by electrostatic techniques. Originally, this would have given rise to films of around 75 microns or more, but improvements in formulation and resin systems have given rise to films of 50 microns.

In comparison, paints can be applied at film thicknesses of 10 microns or even less, if necessary, and there is pressure from customers to do the same with powder.

As a result of further innovations in manufacturing and the properties of raw materials, it is possible to powder coat to consistent films of 25 microns or less.

Three main features affect the ability to form thin films:

- particle size

- flow characteristics

- surface wetting and dispersion

Particle size

Application properties are greatly affected by particle size and distribution. Current application equipment is designed for particles with an average size of 40 microns. Finer particles tend to be more difficult to fluidise, convey through pipework. They are also more difficult to electrostatically charge.

There is a school of thought that the particle size of a powder is what ultimately determines the final film thickness so that, the smaller the particle, the thinner the film. Whilst this is certainly, partly true, it is by no means the only factor.

Flow characteristics

The flow and cure characteristics of the particle will have a bearing on the spreading and coalescing properties of the film in the molten state.

New resin systems are constantly being developed. For a thin film powder, we need a medium with:

- resins showing improved melt flow and lower melt viscosity, combined with

- additives which lower the viscosity and surface tension in the molten phase, allowing the more mobile film to spread more easily.

Surface Wetting and dispersion

Modifications for thin films can have a dramatic effect on the formulation of a powder, with serious implications. For example, the *mileage* or *coverage* of a coating powder is determined by the equation:

$$\text{Coverage in } m^2\,kg^{-1} = \frac{1000 \times \text{efficiency factor *}}{\text{film thickness in microns} \times SG}$$

$$\text{Cost in £. } m^{-2} = \frac{\text{Cost in £. } kg^{-1}}{\text{Coverage}}$$

* Where efficiency is the percentage of powder used and incorporates a number of other factors such as recovery efficiency or the ability to actually achieve the average, specified film thickness on the components in hand.

Obviously, all other factors being constant, if we halve the film thickness, we can halve the cost of the coating. But things are not quite that simple. Thinner films will require increased pigment content, with less scope for the addition of cheaper extenders. In general, this will increase the specific gravity of thin film powders, (especially in lighter colours dependant on titanium dioxide, for example,) reducing their coverage and so, increasing their cost per unit area.

The side effects of such changes, whilst not impossible to overcome, present some development problems. In particular:

- finer particles will mean slower output, using conventional grinding and sieving techniques. This obviously adds to production costs.

- flow additives and lower viscosity resins may mean an increased risk of sintering and possibly the emission of more fume during cure.

- low surface tension for spread and flow may adversely affect other factors, such as edge coverage or coalescence.

- in addition to the higher pigment loadings already mentioned, we may need to improve pigment dispersion, to produce finishes with good gloss and opacity.

- Improvements will need to be made to application equipment, to overcome the fluidisation, charging and transport difficulties associated with fine particles.

- If more flow leads to lower melting point and T_g of resins, storage facilities will need to be improved, perhaps even refrigerated.

4.2. Radiation curing

Infrared radiation

In most cases, powder coatings that are made to be cured in convection ovens can be also cured by *infrared radiation (IR)*. There is an enormous choice of IR equipment on the market, powered either by electricity or gas:

- shortwave - usually as electric lamps - capable of extremely rapid, high energy emissions.

- medium wave - the most common types - either as gas burners or as electrical elements in glass tubes.

- 'black-body', long-wave emitters - usually as heater wires embedded in ceramic mouldings or in mineral-insulated, metal sheaths.

For optimum effect, the emitted wavelength needs to be in a range easily absorbed by the coating. All three types have been used at one time or another. However, mediumwave is the most commonly used and most successful type,

The mechanism of IR cure is similar to that of a conventional cure, though the following points need to be taken into account:

(a) radiation is directional, and areas shaded from the source will not melt or cure, except through the slower effects of conduction and convection.

(b) the rate of absorption of radiation energy is inversely proportional to the distance of the object from the source. Areas closer to the source may begin to overcure before those further away have cured.

(c) the rate of absorption of energy will be affected by the colour of the coating and the nature of its medium.

(d) Rapid cure from the surface inwards may impair the surface wetting of the substrate, leading to poor adhesion.

(e) because of the high temperatures of the emitters, skin temperatures on the coating increase rapidly on exposure, which can lead to severe discolouration in some areas. The time between cure and overcure can be much shorter with IR.

IR is now more commonly used to simply melt the coating, rapidly reducing its viscosity and increasing the opportunity for flow, before it is cured in a convection oven.

Ultra Violet radiation

UV curing systems rely on the formation of highly reactive chemical groups, created when high energy UV radiation attacks and breaks bonds within certain molecules. These unstable groups instantly react with materials around them - the whole scission/reaction process may take less than a thousandth of a second. The mechanisms can often be triggered by Electron Beam radiation too.

Resin chemists used this process to develop liquid systems suitable for use as surface coatings. The technology used photo-initiators to forming free radicals. Often these coatings do not usually contain solvent, which is a distinct advantage from an environmental point of view, but there are safety issues to be taken into consideration too.

One technical drawback is that the UV light is readily absorbed within a few microns of entering the film, limiting the film thicknesses that can be cured. Most pigments and some of the other components in the coating also absorb, further limiting the technique. Therefore, it was seen as useful only for clear or lightly tinted, thin films. However, the technique has been widely adopted for printing and marking processes, where thin films are *de rigeur.*

Recently, new systems have been produced that use cationic photo-initiators to bring about polymerisation. These systems allow for thicker films to be applied and cured. Absorption problems are less pronounced than for the free radical systems. This has allowed the development of a range of UV curable coating powder resins. In these cases, the powder must be melted first, usually in IR, before exposing it to the curing radiation. Recent developments by Ciba Geigy and others have shown that it is possible to produce solid, bisphenol-A based epoxy resins, which, in the presence of chain transfer agents, are suitable for use as powder coatings that can be melted and cured with a combination of IR and UV. The curing process takes place through photoinduced cationic polymerization and gives powders reported to have improved caking resistance, flow and adhesion.

One of the main advantages of such systems is that they offer the possibility of developing coatings suitable for application to temperature-sensitive substrates such as wood, paper, MDF and plastics. The storage stability and chemical properties of such powders would be similar to normal, thermally cured products.

Components are sprayed with powder and passed under IR lamps, to melt the powder. Rapid cure is then brought about by irradiation with standard, medium pressure mercury lamps, which trigger the cationic polymerization.

Like all radiation, UV only travels in straight lines, so coated surfaces need to be exposed directly to the radiation source to cure properly. The UV absorption properties of the materials in the film will have a bearing on the degree of cure. Raw materials used in these powders need to be carefully selected for their absorption characteristics. In the same way, too thick an applied film may also limit the through-cure, as mentioned earlier. To overcome this, it is often necessary to apply two coats for optimal results

Figure 49 shows the properties of two Ciba-Geigy development products designed for application to wood. These are intended as a two coat system: primer LMB 6191 and topcoat LMB 6192. In this example, priming with LMB 6191 gives strong adhesion, but limited flow and LMB 6192 gives good flow and durability.

	LMB 6191 Primer	LMB 6192 Top coat
Melt viscosity (mPa.s)	3400 at 175 °C	2500 at 125 °C
Hoeppler viscosity	1441 mPa.s	300 mPa.s

Softening point	130 ºC	96 ºC
Tg of coating powder	55 ºC	35 ºC
Caking resistance of powder	40 ºC / 1 month	25 ºC / 1 week
Adhesion to primer	–	good
Adhesion on wood	Good	moderate
Epoxy Resin	Type 8	Type 4, high flow resin
Acetone,	2	0-1
Flow (0 = best, 5 = worst)	2	1

Figure 49 – typical characteristics of a UV system for application to wood

.
After melting with IR, each film is irradiated with UV, which releases the photosensitive catalyst, initiating the cationic polymerization process. Adding a second coat of LMB 6192, either with or without sanding, results in a very smooth surface,

SAQ 10 – Metal casings, each with a surface area of 3.2 square metres, are coated with powder to an average film thickness of 55 microns. 13% of the material is usually wasted and dumped. If the powder costs £4.35 per kilogram, what is the cost of coating each item?

That is the end of the study material. When you are satisfied with your understanding of the work, carry out the CMA and submit it for marking.

After that, you will be ready for the End Test, which will be arranged in the near future.

Appendix 1

SELF ASSESSMENT QUESTIONS (SAQ's) & ANSWERS

NOTE: If you have had any difficulties with any of the SAQs, read through the relevant Section again to ensure you understand the work. Discuss any problems with your counsellor.

SAQ 1: What were the main advantages of substituted dicyanamide over the unsubstituted form?

Answer to SAQ 1: The substituted compound had a lower melting point and was more readily soluble in epoxy resins, making the curing reaction more controllable and allowing the formulation of powders with improved appearance and gloss.

SAQ 2: What are the advantages that the epoxy-polyester system has over the conventional amine-cured epoxy powders?

Answer to SAQ 2: - see Figure 9

SAQ 3: What is the main disadvantage of a blocked isocyanate cross-linking agent, and how could this be overcome?

Answer to SAQ 3: The main disadvantage is that the blocking agent will need to be removed from the film, quickly, to avoid it becoming entrapped, leading to yellowing and pinholing of the film. Additives like benzoin can assist the release of these products. An internally blocked isocyanate would avoid those problems.

SAQ 4: Write down some of the factors you would consider when selecting the resin binder for a thermosetting powder coating.

Answer to SAQ 4: You should consider what type of object is to be coated, what temperature it can withstand and where it will be used. You should then take into account the customer's application, and stoving facilities from this determine the necessary melt-flow temperature and rate of cure.

SAQ 5 - The preparation of a masterbatch of flow additive was described. What are the advantages of using such a technique?

Answer to SAQ 5 – Masterbatches are useful tools for:
- Adding small but critical amounts of raw materials more accurately.
- Assisting in uniformly dispersing small quantities of materials throughout a premix.

- The preparation of solid mixtures from liquid components, either by compounding the material in a resin or by adsorbing it onto an extender.

SAQ 6 - List the various ways of producing a structured surface finish in a powder coating.

Answer to SAQ 6 - The four methods given in the text for producing a textured finish are:

- The incorporation of coarsely ground material, which, does not flow out sufficiently on stoving
- Solid material like polyethylene beads which do not melt at all.
- The use of high the viscosity or fast curing resins, which restrict flow out.
- The controlled addition of contaminants having surfactant properties.

SAQ 7 - By studying the current technical literature, compile a list of the range of materials on offer to coating powder formulators.

Answer to SAQ 7 - The variety of products available is enormous. Here are just a few of the materials you may have listed:

- *Pigments*: including titanium dioxide; organics; inorganics; metallics; Masterbatches.
- *Resins*: Epoxies; Epoxy novolac; hydroxyl and carboxyl reactive polyesters; glycidyl and hydroxy reactive acrylics.
- *Curing agents:* Dicyanamide (including accelerated and substituted types); Phenolic hydroxyl; Cyclic amidines (e.g. B31); Matting additives (e.g. Hüls B55 or B68); Primid XL-552; Araldite PT910; TGIC; Isocyanates; uretdiones; Acrylates (e.g. Crylcoat 700)
- *Flow agents:* Acrylic polymers (e.g. Modaflow II) in adsorbed or masterbatch form; polyvinyl butyral; hydrogenated castor oil; benzoin.
- *Fillers:* various grades of barium sulphate, calcium carbonate, talc and silica.
- *Miscellaneous*: Accelerators (e.g.2MI; ZMBT); dry powder flow promoters; polyethylene waxes; organic texturing agents (e.g. nylon)

To be an expert at formulating powders, you will need to understand something of the individual effects of and the interactions between the various components in the complex mixture you intend to create.

SAQ 8 - What are the factors that affect the degree of texture in a structured coating?

Answer to SAQ 8 - In coarse, "matchbox" like textures, particle size and the melt-flow characteristics, (especially the viscosity and cure rate of the powder,) will determine the degree of texture.

However, in powders showing hammer finish and the "antique" effects, the texture pattern is determined largely by the relative surface tension characteristics of the base mixture and the texturing additive (e.g. CAB, Plexigum.). The bigger the difference, the deeper will be the pattern and the broader it's spread (amplitude). The particle size of the powder plays only a minor part here, but the particle size of the *texturing additive* will have an effect on the spread of the pattern. The concentration of the texturing agent will have an effect too – At a critical level, the pattern will start to become tighter as the centres of low surface energy begin to interfere with each other.

SAQ 9 - The formulations mentioned are for illustrative purposes and will look increasingly old fashioned as new materials and processes are developed. What changes might you expect to see in the future?

Answer to SAQ 9 - There are always changes going on in the industry. At present developments include:

- Improvements in the compatibility of acrylic resins, allowing the increased use of these very useful materials.
- New rapid-cure systems, some capable of being cured by radiation sources such as ultraviolet light, infrared or electron beam.
- Resin systems capable of producing thin film in the order of 25 microns, mainly for their economy – in practice, this capability is also dependent on new techniques of manufacture and application.

Higher reactivity and better flow may mean that resins with lower molecular weights become the norm. Storage of such materials will need to be better controlled.

SAQ 10 - Metal casings, each with a surface area of 3 square metres, are coated with powder to an average film thickness of 55 microns. 12% of the material is usually wasted and dumped. If the powder costs £4.30 per kilogram and has a specific gravity of 1.60, what is the cost of the powder used to coat each item?

Answer to SAQ 10 - Coverage of the powder is 10 square metres per kilo, and the cost per square metre is 43 pence per square metre. Therefore the cost of the powder applied to each unit is £1.29. (See coverage calculations in item 4.1.)

Appendix 2

NOTE: *This is a Tutor Marked Assignment. Before you begin work on the Assignment, please read the general instructions and guidance, which you will find in the Introductory pamphlet issued with each Module.*

Assignment – ASG 1

Choose a thermosetting powder system for each of the following end uses:

1.   Computer VDU casings

2.   Bicycle frames

In each case, justify your choice as fully as you can.