Organic Materials in Civil Engineering
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Chapter 3

Organic Binders II. Materials for the Conservation of Heritage and Safety

The preceding chapter was devoted to the first application of organic binders used in civil engineering works. We will now focus on the two last applications: products for repair and protection of the concrete structures on the one hand, and paints for the protection of structures and road marking on the other hand.

It may be noted that these concerns cover almost all the components of sustainable development applied to civil engineering works.

3.1. Concrete repair and protection products

The management of the heritage of civil engineering structures includes in particular their maintenance and repairs that can be generated by an attentive surveillance or an accident. Thus arises the need for products especially formulated to meet the requirements of project managers, whether for repair strictly speaking or the protection of concrete, for servicing or after repair. It is true that in almost all cases, these products contain organic macromolecules.

The repair market made great strides in developed countries during the last quarter of the century and particularly in France where civil engineering structures that are part of the national heritage were systematically inspected. Many repair, rehabilitation and maintenance projects were undertaken in the wake of these series of assessments whose repercussion on the market resulted particularly in the appearance of new products and the evolution of traditional formulas. Thus the products belonging to the chemical industry (synthetic resins) that appeared in the 1960s experienced a boom for about 20 years before suffering from what could be called the "wonder product complex": the remarkable results obtained with epoxy resins, for instance, stimulated the development of a lucrative and not very scrupulous market where companies with just three or even two employees offered products that appeared efficient during demonstration but had a durability in the same order as that of the company in question ... Users therefore reacted by condemning this entire family of products, whereas in fact there were interesting promises of progress.

It should be said that they could find a substitute solution: in the face of this invading phenomenon, the industrial mortar industry succeeded in reacting with a remarkable dynamism. It understood the stakes involved and invested accordingly in research effort so that it could offer a whole family of new products whose active principle remained cement matrix but which included organic macromolecules as additives to give the product qualities that cement alone could not provide, particularly adherence and flexibility. Organic matrix materials however continued to be used where they could not be replaced or when the formulators could sustain sufficient technical and commercial dynamism.

It is always interesting to meditate on history. It yields several insights both into the design and feasibility of the processes.

Firstly, it should not be imagined that "the repair product does the repair", whatever the intrinsic qualities of the product in question may be. Aspirin has proved itself to be an excellent drug but has never repaired bone fractures. On the other hand, this product could be used successfully to bring relief to patients after the reduction of a fracture.

When a project manager uses a repair product, he is in fact buying a service. The rejection of resin materials at the end of the 1980s is partly because this concept had not been well understood by both the parties involved: formulator of products and contractor in charge of the application, after which the key-audience came to a conclusion a little too quickly ...

The use of new products is often accompanied by modifications in the processing practices. In this case, resin materials are not applied in the same manner as classic cement products. This leads to problems related to the qualification of the personnel in charge of this process, which should never be underestimated.

Finally, the use of a repair product is part of a larger framework, viz. the "repair project", where the mechanical aspect is essential: as the deteriorations to be repaired are often caused by displacements or unexpected stresses, it is these causes that we must address in priority before repairing the structure. This being said, the choice of the repair product is not secondary as it is of vital importance in the development of the repair project. The method can be represented by a diagram (Figure 3.1), which places the processes in their correct context [MOU 83].

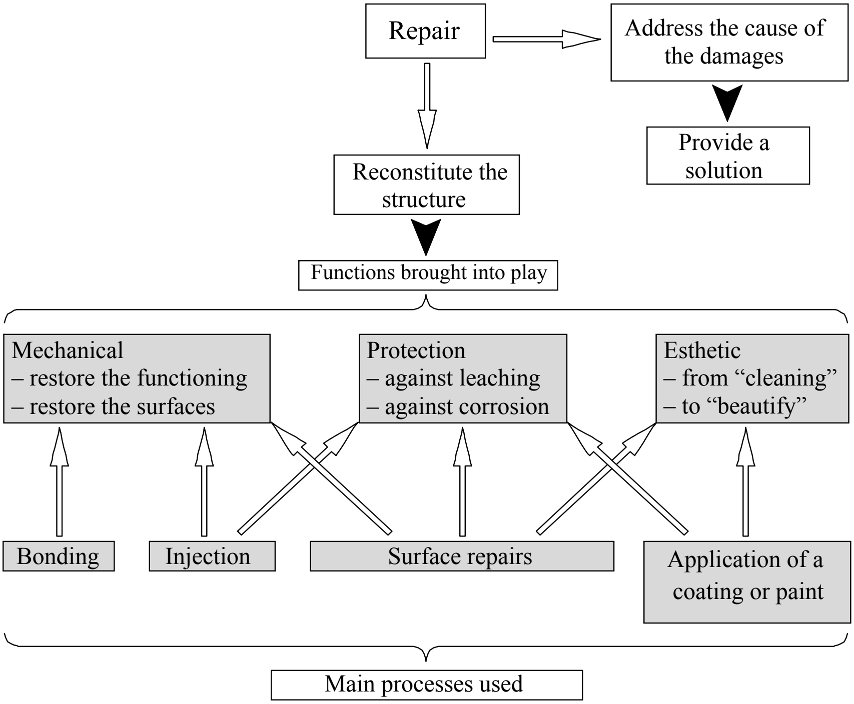


Figure 3.1. *Concrete repair and protection processes. Origin of the method*

We can distinguish three essential functions:

– *mechanical function*, which covers practically what is usually called repair, i.e. giving a new integrity to the structure, primarily from a mechanical viewpoint; it is for this that we use repair products strictly speaking;

– *protection function*, which primarily seeks to preserve as long as possible the structure in the state to which it has been restored after the repair, by preserving it particularly from environmental aggressions, rains and various pollutants; *protective products* are associated with this function;

– *esthetic function* finally which ranges from the minimum – "cleaning", treatment of the invisible parts of the structures – to the creation of veritable works of art; *paint* is used in particular for this function. It may be noted that in the case of paint, choices can range between restoring the original state of the structure and creating a new state in view of its new environment.

The processes and materials used to meet all these needs have been studied in view of standardization; in this context, repair and protection products were grouped together on the one hand and paint on the other hand. This distinction has dominated the studies undertaken in France since the seventies. These studies resulted in the preparation of technical guides which served as basis for this corpus of standards. These guides were updated [MOU 96], [BOU 99] and are often easier to read than the standards themselves, which is in fact in line with French tradition. We will therefore follow the same distinction i.e. paints for concrete will be treated with other types of paints for civil engineering, in section 2.3.3. We may add that the recent publication of a technical guide specific to the protection of concretes by application of products to the concrete surface [MAH 02] will complement all this usefully because this subject had only been touched upon in the 1996 guide.

3.1.1. *Products and systems for the protection and repair of concrete structures: normative definitions*

The plethora and multiplicity of the offer in this field compelled the European Standardization Committee to carry out a significant work of definition, which is the object of EN 1504-1, which distinguishes:

- surface protection systems;
- structural and non-structural repair products and systems;
- structural bonding products and systems;
- concrete injection products and systems;
- anchoring and reinforcing steel bar products and systems;
- products and systems for prevention against the corrosion of armatures (Reinforcement Corrosion Protection).

In this study, we call “products” *compounds formulated for the repair or protection of concrete structures* and “systems” *two or more products that are used together, or consecutively, to carry out repairs or to protect concrete structures*.

These definitions draw from the concepts of monocomponent and bicomponent introduced in Chapter 1 (section 1.4.2) but are specific to the application in question. We will see that for paints (section 3.2) the concept of system is used in a different sense, which we will also find in connection with waterproofing (section 4.1).

We can also distinguish “non-structural repairs” intended to *restore the geometrical or esthetic aspect of the structure* from “structural repairs” intended to *replace the damaged concrete and to restore to the structure its integrity and its durability.*

3.1.2. ***Physicochemical classification of repair and protection products***

From the physicochemical point of view, we can classify the products used for the repair of concrete structures into three categories depending on whether the binder that ensures the cohesion of the system is hydraulic (cement), reactive organic (synthetic resin) or mixed, i.e. both hydraulic and reactive organic. This is the approach adopted in the guide of 1996. It may however be noted that this classification departs slightly from the one proposed by Omaha in his *Handbook* [OHA 95] insofar as it stresses the important difference between reactive polymers and non-reactive polymers, but in the final analysis, it is only a question of presentation.

Products based on hydraulic binders, which are subdivided, according to whether the binder in question is modified or not by an organic polymer, into:

– *produced based on hydraulic binders with additions,* which are primarily made up of a binder (cement), aggregates (rolled or crushed) and additions if necessary (other than organic polymers). Water is added at the time of use. These products can be prepared on the worksite from ready-to-use dry industrial mortars (it is enough to add the necessary quantity of water without any other additive) or prepared *in situ* by mixing the various components, for instance, for shotcrete;

– *produced based on hydraulic binders modified by organic polymers*, which use polymers called “miscible resins” (i.e. in stable dispersion in water – latex for example) and can be classified into large families, such as polyvinyls (acetate, propionate, laurate), polyacrylics, and poly(styrene-butadiene). They are in either of the two following forms:

- monocomponent: the polymer is present in the form of a powder premixed with the hydraulic binder, or

- bicomponent: the component A contains the polymer and the water necessary for hydrating the cement; the component B contains the cement, sand and inert fillers, as well as additives if any (fibers, silica fume, for example); the product is prepared on the worksite by mixing components A and B, without any other addition.

Products based on synthetic resins, i.e. based on reactive organic binders, are defined by their original chemical family.

Mixed matrix products, also called *hybrids* whose active binder is made up of both cement and reactive synthetic resin, bring into play both the setting and hardening of the hydraulic binder and the cross-linking of the organic polymer.

The organic materials act as modifying agents in modified hydraulic binders and as such in the last two categories that will be studied specifically in the rest of this chapter. The study of the modification of cement matrices by the incorporation of organic polymers is not discussed here because it would be too lengthy and especially because it has been dealt with in the recent handbook by Omaha cited above.

3.1.3. *Products based on reactive organic binders: general introduction*

Generally speaking, *products for the repair and protection of concrete structures* based on reactive organic binders differ from one another according to the physical and chemical transformations that occur during their processing and according to the structure of polymer obtained finally (linear or cross-linked).

The synthetic resins in question are reactive organic polymers that can be:

– monocomponent polymeric systems, admixtured or filled; they become reactive when the temperature is raised or react with atmospheric humidity; they belong to the polyurethane family;

– bicomponent polymeric systems, available in predosed packages, where the components, admixtured or filled, must be mixed at the time of use; they are primarily epoxy resins;

– tricomponent polymeric systems: an accelerator and a catalyst must be added to the resin at the time of application; they are mainly polyester and methacrylic resins.

Organic binders occurring in the formulas of repair and protection products are therefore mainly *epoxy resins*, which are used both in repair products and in paints for the protection of concretes and steels, *polyurethanes*, which are primarily used for the protection of sidings or all kinds of surfaces, to a lesser degree, *methacrylic resins*, which were unpopular for a long time because of the odor of the monomers present but which seem to be developing now thanks to new more favorable components, *unsaturated polyesters*, which are used primarily in anchoring systems or anti-corrosive protection coatings of metal parts, and lastly *acrylamides*, used usually in geotechnonolgy for sluices but also in some cases for repairing concretes in constantly humid atmospheres.

Each of these families has specific characteristics but offers a wide range of possibilities to the formulator to vary the properties of the desired materials, either by acting on the formula of the monomers used or by a careful “formulation”; as a result, we must show extreme caution when we speak about their general properties.

3.1.3.1. *Epoxy resins*

Epoxy resin materials used in civil engineering are in the form of bicomponents reacting in the ambient temperature, to be mixed at the time of processing using the fluidity of the mixture during its practical duration of use [MOU 78].

The epoxy resin family is vast and offers many applications in various technological fields. Those related to the field of civil engineering are mainly of *amine-epoxies*, primarily because these mixtures are capable of reacting in ambient temperature (between 5 and 25°C).

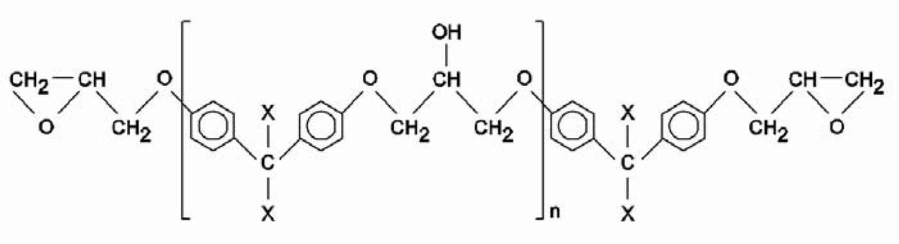
Chemically, these are polyethers that are formed by a reaction between a polyepoxy “base” and a “hardener” comprising active hydrogen atoms.

It must be pointed out that the expression *epoxy resin* is ambiguous because it indicates both the component called *base* as well as the result of the reaction of this *base* with the *hardener* associated with it.

The *base* is made up of a mixture whose most widely used reactive part is a monomer (oligomer) denoted by the abbreviation DGEBA or DGEBF, commonly represented as below:

$$\nabla — \mathbf{B} — \nabla$$

to denote the following developed formula:



where n ranges between 0 and 1, and X = H for DGEBF; X = CH_3 for DGEBA.

The most common base (see above formula with X = CH_3) is obtained by the reaction of bisphenol A (dihydroxy-4.4' diphenylmethane) on glycerol epichlorhydrine (chloro-1 epoxy-2.3 propane).

The *hardener* is also made up of a mixture whose reactive part is a polyamine (or a mixture of polyamines) with the general formula (highlighting the active hydrogen atoms):

$$H_2N — \mathbf{D} — NH\text{ - }Y$$

where **D** is a generally aliphatic unit and Y is a aliphatic radical or a hydrogen atom.

They are primarily aliphatic polyamines such as diethylene triamine (DETA), which are highly reactive, and their derivatives, amino condensates (adducts), polyamino amides, imidazolines, etc.

We must add to this family polysulfides, molecules containing active hydrogens, which are used as flexible hardeners, generally in association with aliphatic polyamines. They furthermore have the advantage of reacting at low temperatures (below 0°C) but also the disadvantage of releasing a very unpleasant odor.

It may be recalled that the cross-linking of epoxy resins can be also achieved with carboxylic acids or their anhydrides, but at high temperatures (150-200°C). These systems can thus be used only for reactions in workshop. Their reactional mechanism is very different from that of epoxy-amines.

The reaction between the two active components of the mixture, the base and the hardener, is a *polycondensation* (see section 1.3.1) which can be written as below:

$$— \mathbf{B} — \nabla \; + \; HNH — \mathbf{D} — \; \longrightarrow \; — \mathbf{B} — CH(OH) — CH_2 — NH — \mathbf{D} —$$

The polymer obtained is highly cross-linked. As the *base* monomer is generally difunctional, this property is explained by the fact that the *hardener* used is at least trifunctional as can be seen in the formula used previously where mobile hydrogen atoms correspond to the reactive amine functions.

The chemical mechanisms of these reactions are complex but they are well understood now. Thus we can describe the general outline as follows: after an initiation stage where the presence of tertiary amines acts as an accelerator, the primary amines react first, then the secondary amines according to their environment (inducer effects and steric hindrance). It first forms a linear chain and thereafter the system cross-links thanks to the remaining secondary amine functions.

The reaction is highly exothermic (about 400 $J.g^{-1}$) and the stoichiometry is ensured between the epoxy functions and the number of reactive hydrogen atoms. It is therefore not enough to directly compare the epoxy index of the base with the basicity of the hardener (see section 6.5) to be assured of a good cross-linking. We must take into account the number of effective reactive functions. Finally, we must remember that commercial products are always mixtures and that some components present in negligible quantities can also intervene and distort the calculations.

We have said that the most widely used *bases* have DGEBAs or DGEBDs as their main component. This is because their synthesis is significantly more economical than that of others di- or tri-epoxies. But this nevertheless enables formulators to prepare a wide range of mixtures which however remain generally difunctional as regards their reactivity. *Hardeners* are selected from several types of polyamines according to the reactivity required for the reactional mixture and properties desired for the polymer.

The starting of the reaction requires a certain activation energy which is acquired after some time thanks to the heat released by initiation reactions. This gives the user the time to set up the material (called *usual practice time* or *DPU* in France and little different from the *pot-life*). It is however possible to decrease this time by using catalysts, or by replacing the original polyamine by another, more reactive polyamine. But we must not forget these reactions are temperature-sensitive. This explains why there are for certain products a “winter” formula and a “summer” formula comprising the same bases and whose hardeners differ only by the catalyst or the chain length of the polyamine.

The influence of temperature on the polymer formation reaction, polycondensation, has several consequences depending on whether we are looking at the original mixture or the finished product:

– more or less fast start of the reaction, as we have just seen, with impact on the *usual practice time*;

– more or less fast and more or less complete curing (or hardening) of the resin *in situ*, which we can characterize by its *in situ cross-linking time*.

The *in situ cross-linking time* is the time necessary for the monomer mixture to react as completely as possible and to acquire the mechanical properties expected from it in the practical conditions in which it is processed [MOU 78]. This parameter is not taken into account explicitly in the specifications but must not be forgotten in its principle because it directly determines the time need for restoration of serviceability and indirectly the working conditions (ambient temperature to be maintained in difficult cases). It can be compared, with all the caution appropriate in this kind of exercise, with hardening time of hydraulic concrete. It is however markedly shorter than the latter: about 10 days at the usual worksite temperatures for classic epoxy systems against one to three months for hydraulic concrete. Practically, it can be determined approximately by the Shore D hardness of a specimen placed under the conditions of the structure in progress.

Isocyanates also react on the hydroxyl functions of the epoxy resins to create urethane bonds. We can thus obtain *epoxy-polyurethane* polymers, with the epoxy functions not affected by the reaction with isocyanates, which are then cross-linked by polyamines [BRU 75].

Likewise, it has been possible to develop *epoxysilicones* used for the protection of mineral surfaces or the improvement of the bonding between polymer and concrete [BRU 76].

The properties of the obtained materials can be summarized as follows: high mechanical resistance, strong bonding to usual materials, high chemical resistance, excellent dielectric properties, high dimensional stability and very low hardening shrinkage, excellent resistance to thermal cycles and good abrasion resistance.

3.1.3.2. *Polyurethanes*

Polyurethanes form a very vast family and as their chemistry is rather complex, we will limit ourselves to the main reactions that we must know to understand the functioning of these products [MAR 00].

The urethane bond is obtained by the reaction of the alcohol function with the isocyanate function according to the diagram below:

$$\underset{\text{isocyanate}}{\mathbf{Y}-N=C=O} \;+\; \underset{\text{alcohol}}{HO-\mathbf{R}} \longrightarrow \underset{\text{urethane}}{\mathbf{Y}-NH-CO-O-\mathbf{R}}$$

If we disregard the secondary reactions, we can see here that the reaction of a diisocyanate with a diol according to the above schema results in the formation of a linear polyurethane. If, on the other hand, we use a polyol or a polyisocyanate with functionality > 2, we obtain a cross-linked polyurethane. This reaction is often called polyaddition but, from the thermodynamic point of view, it is a polycondensation without elimination of any volatile compound.

In fact there are always secondary reactions. They result primarily from the fact that the isocyanate function is very sensitive to the presence of active hydrogen atoms such as the amines or quite simply water.

Thus, *amines* can react with isocyanates to yield ureas (and polyamines with polyisocyanates to give polyureas) according to:

$$\underset{\text{isocyanate}}{\mathbf{Y}-N=C=O} + \underset{\text{amine}}{H_2N-\mathbf{M}} \longrightarrow \underset{\text{substituted urea or ureine}}{\mathbf{Y}-NH-CO-NH-\mathbf{M}}$$

This reaction is interesting because it brings into play an amine that can be used also as a hardener of an epoxy resin (see section 3.1.3.1). It has therefore been possible to prepare epoxy-polyurethanes copolymers (double cross-linked networks) [BRU 75].

As regards *water*, it takes part most often in a parasitic reaction. It reacts with isocyanates releasing gaseous carbon dioxide CO_2, which could be advantageous to obtain foams but on the contrary is generally considered a drawback because the bubbles formed are not easy to control and give the material mechanical disturbances. The continuation of the reactions is written as:

$$\underset{\text{isocyanate}}{\mathbf{Y}-N=C=O} + H_2O \longrightarrow \underset{\text{carbamic acid (unstable)}}{\mathbf{Y}-NH-COOH} \longrightarrow \underset{\text{reactive amine}}{\mathbf{Y}-NH_2} + CO_2 \nearrow$$

$$\mathbf{Y}-NH_2 + \mathbf{Y}-N=C=O \longrightarrow \underset{\text{urea (symmetric)}}{\mathbf{Y}-NH-CO-NH-\mathbf{Y}}$$

The latter reaction with water limited a long time the use of polyurethanes in external structures or on wet surfaces.

This problem was solved by using a fluid epoxy resin anchoring primer. This reaction has however been used for the formulation of paints as *monocomponent reactive system cross-linking with atmospheric humidity*. This obviously supposes that the deposited coat is sufficiently thin for the reaction to be as complete as possible and that the formation of bubbles imprisoned by the polymer film is minimal.

In addition, the rate of the reaction of isocyanates with the 0H function varies with the class of the alcohol, as well as with phenols, in the following order:

$$R-CH_2\,OH > R,R'=CH\,OH > R,R',R''\equiv C\,OH > Ar\,OH$$

As regards phenols (denoted Ar OH), the reaction is a reversible equilibrium at average temperature such that this property can be used to prepare *blocked systems*, i.e. mixtures where the isocyanate has been blocked by reaction with a phenol and reacts with polyol only after being released by heating at the temperature of its manufacture. This is therefore another kind of monocomponent which however needs to be heated to initiate the reaction.

The *isocyanates* used in practice are generally *prepolymers* because the usual basic monomers are toxic and volatile. For example, a derivative of toluylene diisocyanate (TDI) is used: $C_6H_3\ (CH_3)\ (NCO)_2$, obtained by reaction of this product with a trivalent alcohol like trimethylolpropane:

$$CH_3 - CH_2 - C\ (CH_2OH)_3$$

The triisocyanate obtained:

$$CH_3 - CH_2 - C\ [CH_2 - O - CO - NH\ - C_6H_3\ (CH_3)\ NCO]_3$$

is no longer volatile. It is a prepolymer as a polyol is made to react with a diisocyanate but the proportions of the original mixture (1/3) are such that the reaction cannot result in complete cross-linking.

MDI (4.4'-méthylène *bis*-phenylene diisocyanate) is also used:

$$OCN - C_6H_4 - CH_2 - C_6H_4 - NCO$$

It is less toxic than TDI.

However, aromatic polymers tend to turn yellow when exposed to light. Therefore, we use aliphatic isocyanates like HMDI (hexamethylene diisocyanate):

$$OCN - (CH_2)_6 - NCO$$

or IPDI (isophorone diisocyanate) for all works where the polymer is exposed to light.

This is why, in the paint industry in particular, it is believed that polyurethanes resist UV better that epoxies (which are almost always formulated from aromatic bases as we have seen above).

With regard to polyols, we still use prepolymers, generally polyesters or polyethers containing free OH functions (bifunctional for thermoplastic polyurethanes, tri- or poly-functional for cross-linked polyurethanes). Their average molecular weights range between 150 and 4,500 $g.mol^{-1}$ for polyethers, and 1,500 to 4,000 $g.mol^{-1}$ for polyesters.

As organic binders, polyurethanes are used in construction for the formulation of non-structural repair products, protection and paint systems, industrial floors, waterproof coating and joints. Theoretically, they offer an infinite range of polymers, which gives free course to the proliferation of various products called simply "polyurethanes". We must therefore specify the type we are referring to when we use this term in a market.

3.1.3.3. *Unsaturated polyesters and derivatives*

With unsaturated polyesters, we enter the specific field of chemistry because they are skillful mixtures that react at the right time and up to a certain point, in a context where we find all the concepts discussed previously [CAN 93-1, CAN 93-2].

Thus the product that must be processed on the worksite is already a polyester, linear (therefore soluble in a suitable solvent), but with a relatively low molecular weight in general. It reacts *in situ* by radical polymerization, using a peroxide added to the "monomer" at the time of use, by forming a three-dimensional network whose density depends on the nature of the monomers used in the mixture.

This mixture contains the above-mentioned linear polyester (containing double bonds) as well as a reactive solvent (by its own double bonds), generally based on styrene. The system copolymerizes by forming a network whose density depends largely on the proportions of the various ingredients.

The oligomer itself results from a polycondensation between several acids and a diol, most often ethylene glycol. This reaction is carried out in the workshop where it is possible to regulate the polycondensation and to stop it when necessary. All this can be summarized by a diagram (Figure 3.2).

1. Manufacturing of the product

Chemical reaction:

$$\begin{array}{c}\text{Mixture}\\ \text{of}\\ \text{diacids}\end{array} + \begin{array}{c}\text{Diol}\\ \text{(or mixture}\\ \text{of diols)}\end{array} \xrightarrow[\textit{elimination of water}]{\textit{heating}} \begin{array}{c}\text{Linear unsaturated polyester}\\ \text{(copolymer)}\end{array}$$

(Polycondensation reaction with elimination of volatile compounds)

Dissolution of the above copolymer in a mixture of reactive solvent(s) + various additives

$$\longrightarrow \begin{array}{c}\text{Reactive base}\\ \text{(mixture of “monomers”)}\end{array}$$

2. Processing

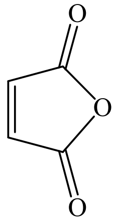
Addition to the base of a “catalyst” (polymerization initiator) then if necessary an accelerator, at the last moment

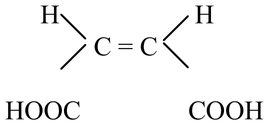
$$\longrightarrow \begin{array}{c}\text{Material } \textit{in situ}\\ \textit{(polymerization reaction and}\\ \textit{creation of three-dimensional network)}\end{array}$$

Figure 3.2. *Unsaturated polyesters*

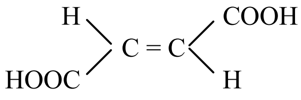
The mixture of *diacids* is made up of:

– an unsaturated diacid strictly speaking, maleic acid, presented generally by its anhydride, or sometimes its *trans* isomer, fumaric acid:





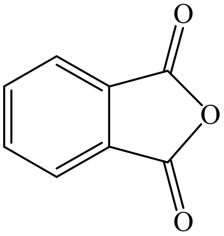
Anhydride and maleic acid



Fumaric acid

– saturated diacids used particularly to modify the mechanical properties of the final product, such as:

- phtalic anhydride widely used because it is very economical:



corresponding to orthophtalic acid: o-$C_6H_4\ (COOH)_2$

- or isophthalic acid, meta isomer of the above: m- $C_6H_4\ (COOH)_2$
- or adipic acid: $HOOC - (CH_2)_4 - COOH$

Diols include in particular the compounds given in Table 3.1 among which the most common is propylene glycol.

Name	**Chemical formula**
Propylene glycol (PG)	$CH_3 - CH(OH) - CH_2OH$
Ethylene glycol (EG)	$HO - CH_2 - CH_2 - OH$
Diethylene glycol (DEG)	$O\ (CH_2 - CH_2OH)_2$
Dipropylene glycol (DPG)	$O\ (\ CH_2 - CH(OH) - CH_3)_2$
Neopentyl glycol (NPG)	$(CH_3)_2\ C\ (CH_2OH)_2$

Table 3.1. *Main diols used in the formulation of unsaturated polyesters*

Solvents are generally styrene-based to which we add variable quantities of other products comprising single or double bonds, indicated in Table 3.2.

The *in situ* polymerization reaction is not instantaneous; it comprises a first phase of initiation corresponding to the formation of the active sites then the temperature rises – this is gelation (the gelling point corresponds to the inflection of the curve representing the change in temperature according to time) – up to the exothermic peak, specific to the product and then goes down again, causing a shrinkage, which is also specific to the mixture that has reacted. The entire process is rather fast but there is certain latitude to play on the formulation and to modulate the first phase for instance in order to allow the time necessary for a good setting.

Name	Formula	Comments
Styrene (to recapitulate)	$C_6H_5 - CH = CH_2$ or $Ph - CH = CH_2$	Base solvent, present almost always
α-methyl styrene	$Ph - C(CH_3) = CH_2$	Decreases the temperature of the exothermic peak during a cold polymerization
Vinyl toluene	*o*-Ph $(CH_3)\ CH = CH_2$	Increases the flash point, temperature resistance and => decrease of the shrinkage
Divinyl benzene	*o*-Ph $(CH = CH_2)_2$	Increases the flash point, reactivity, toughness, T temperature but also brittleness
Methyl methacrylate (MAM)	$CH_2 = C\ (CH_3)\ COO - CH_3$	Used in 50/50 coupling with styrene, enhances the wettability of the glass and resistance to aging and shocks
Diallyl phthalate	*o*-Ph– $(COO - CH_2 - CH = CH_2)_2$	Improves the mechanical characteristics of the resin

Table 3.2. *Main reactive solvents used in the formulation of unsaturated polyesters*

The essential difference with resins cross-linking by polycondensation is the fact that after the exothermic peak and the cooling of the product, the reaction can be regarded as completed. It is no need to wait for any curing.

However these resins have two important drawbacks that prevent them from being used extensively in civil engineering: their shrinkage and especially their sensitivity to hydrolysis.

Shrinkage can be decreased by adding various fillers but still remains significant. This parameter already poses problems in the hydraulic concrete industry, i.e. it does not encourage innovation in not well-known materials having this same drawback.

But it is *sensitivity to hydrolysis* in particular that is the stone stumbling block for the user of polyesters in most civil engineering works [MOR 89]. It results from the ester function itself.

It may be recalled that the ester function results from the following equilibrium:

$$\text{acid} + \text{alcohol} \leftrightarrows \text{ester} + \text{water}$$

This equilibrium is displaced to a basic medium, for example, in the presence of wet concrete (but concrete is always humid in our climate …) according to:

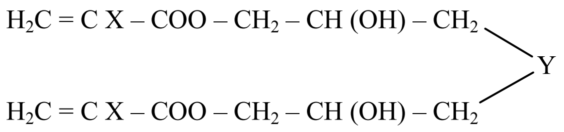
$$\text{ester} + OH^{-} \rightarrow (\text{anion})^{-} \text{ of the salt} + \text{alcohol}$$

This *saponification* reaction (pure “soap” is chemically a salt of fatty acids extracted from the glycerides of oilseeds, which are glycerol esters) is active as long as the pH is alkaline.

As the ester bonds are in the middle of the chain, it is believed that their attack compromises the durability of the material. This reaction is however hampered by the compactness of the medium – the product is in solid phase – but it can develop with the least defect in the structure.

It has been observed that isophthalic polyesters are more resistant to hydrolysis than their ortho counterparts. Other products, with similar structure and similar use, are more efficient in this respect, namely *vinyl esters* or *vinylesters*.

This family can be situated in a certain manner between unsaturated polyesters and epoxies, and is therefore also called *epoxyvinylesters*. They are obtained by reaction of an epoxy base with acrylic or methacrylic acid. For example:



where X = H for acrylic esters and X = CH_3 for methacrylic esters and Y corresponds to a bisphenol unit or a novolac unit.

The possibilities of the use of unsaturated polyester and vinyl ester resins in civil engineering depend on the study of their resistance to mechanical stresses and chemical aggressions, in particular that of water.

By comparing the water absorption of the various samples of these resins at various temperatures, it has been possible to highlight hydrolytic degradation and its kinetics [SPI 93]. The influence of the molecular structure has been confirmed and the methods have been proposed to predict the “risk-free” lifespan and the shelf-life of these materials for a specific use.

3.1.3.4. *Methacrylic resins*

Methacrylic resins used in civil engineering form a very small part of the family of the acrylic adhesives whose variety and applicability are extremely vast. The products that interest us here are structural adhesives and therefore reactive products [COL 88].

The term “methacrylic” is a contraction of “methyl acrylic”, the radical methyl replacing the hydrogen atom in α of the carboxylic function:

Acrylic acid: $CH_2 = CH - COOH$

Methacrylic acid: $CH_2 = C\ (CH3) - COOH$

Thus, the monomer of PMMA (for *polymethylmethacrylate*) is MAM (for *methylmethacrylate monomer*) with the formula:

$$CH_2 = C\ (CH_3) - COO - CH_3$$

The direct polymerization such monomers can thus yield only linear, and therefore thermoplastic, polymers. To obtain chemically cross-linked products, we need di-unsaturated monomers like the ethylene glycol dimethacrylate with the formula:

$$CH_2 = C\ (CH_3) - COO - CH_2 - CH_2 - O - CO - C\ (CH_3) = CH_2$$

which plays the role of a cross-linking agent when added to MAM and copolymerized with it.

The polymer formation reaction is here a *chain polymerization* where the acrylic double bonds come into play (see section 1.3.2).

Initiation is generally ensured by a peroxide (generally called “catalyst” in common practice) which is formed at the time of use by thermal or photolytic dissociation (UV radiation) or by oxidation-reduction (Fe II/Fe III system, for instance).

The current applications of these products in the repair of structures are very few. The repair of an airport runway was carried out successfully on an experimental basis but the technique did not develop thereafter. However, it remains potentially interesting. These products are rather used for the manufacture of shock-resistant and weatherproof parts – rain, sun, various industrial atmospheres – for road safety equipment or street furniture, for example.

3.1.3.5. *Other acrylic derivatives*

Acrylamides have found an original application in the field of civil engineering: stopping seepages into underground works. Similarly, they have been used as expanding plugs in cavities when the concrete is exposed to permanent humidity: injected into the cavity, the product acts like a sponge and hardens in the presence of water. However, unlike the sponge, it acts as a plug.

They are usually in the form of a tricomponent system:

– an acrylamide base in aqueous solution, generally colorless and with a viscosity equivalent to that of water (1 mPa.s or 1 cPo at 20°C);

– a polymerization initiator;

– a polymerization accelerator, generally ammonium persulfate.

The main advantage of these polymeric systems lies in the fact that the gel formed during polymerization is very hydrophilic and can thus imprison large quantities of water, thus giving rise to a significant swelling (from 100 to 500% in volume depending on the formulation). It is the "plug" function referred to above.

These gels however exhibit low mechanical resistances and can be used only in permanently wet mediums because they also have the property to retract in dry air and, as this behavior is not strictly reversible, their plug effect then disappears.

These products have been widely used in civil engineering works but the acrylamide base had to be discarded because of its carcinogenic properties. We now use derivatives of acrylic salts of sodium, magnesium or calcium for example, which have similar properties with regard to the formation of hydrophilic gels.

3.1.4. *Repair produces based on reactive organic binders: usages and required characteristics*

Depending on the type of deteriorations to be repaired or the type of structure to be reinforced, we can once again refer to the classification proposed by the technical guide. The products and systems concern:

– surface repairs (structural or not);

- structural bonding;
- injection (cracks);
- anchoring (sealing and wedging).

3.1.4.1. *Surface repair products*

Also used for the partial reconstitution of structural elements, these products concern:

- crazing and surface cracking;
- defects without apparent reinforcements: bug holes, honeycombing, holes and cavities, misalignments of the formwork or flatness, excessive porosity, surface wear of the concrete, spalls and surface deteriorations, etc.;
- defects with apparent reinforcements: holes (concreting defect), bursting of the concrete, corroded or broken reinforcement, possibly accompanied by traces of rust on the concrete.

In this type of application, we generally use mortars based on polymer modified hydraulic binder, particularly because they are intrinsically passivating for metal reinforcements (highly basic pH in the presence of water). The use of resin mortars generally requires the preliminary application of a passivating agent also called a corrosion inhibitor (see further below). This constraint is however not a major obstacle because these mortars can offer interesting solutions for singular points, for example, when a fast setting is required and when the adhesion with the support is particularly precise.

The repair of disorders affecting the weight of the massive structure and resulting from an internal chemical reaction such as an alkali-aggregate reaction or sulfatic reactions is part of a comprehensive approach, which can be completed by the application of a surface repair product, but which is not treated as such in the corpus of the standards on concrete repair and protection products.

3.1.4.2. *Structural bonding and structure reinforcement products*

This is a field where the organic binders, in this case, epoxy resin formulations, are incontestably the most efficient. It concerns:

- reinforcement by bonding of metal sheets or composite materials;
- reinforcement by addition of metallic reinforcement elements;

– the bonding of concrete which includes both construction joints (where cheap formulations such as latexes or acrylic emulsions are used) and an original construction method: the *in situ joining of prefabricated voussoirs*.

The construction of a concrete civil engineering structure by joint voussoirs requires a good conjugation of the surfaces involved. It was proposed to use the surface of the voussoir n-1 as a mould for voussoir n. The system is then glued using an epoxy adhesive specially formulated for this purpose, which plays the role of a lubricant for the placement, a waterproof material to prevent subsequent water flows and an adhesive to prevent displacements in the coupling during the assembly. The resistance of the system is finally assured by prestressing.

In this list, we can observe that *reinforcement by bonding of composite materials* has not been mentioned in the Guide because these products were recent at the time and the feedback was not yet sufficient to enable the experts to standardize the rules for their use. However, this application became most important for organic materials in the repair of structures because composites are progressively replacing metal sheets. These materials and the reinforcement process will be studied in Chapter 5 (section 5.2.4.1).

3.1.4.3. *Injection products*

Here the typical materials are epoxy resins, but we should not forget ultra fine cement grouts, which have been specially developed for this application. The question is to know what we can expect from an injection: a restoration of the monolithism of the damaged structure or a simple weatherstripping, i.e. a kind of waterproofing.

The answer is obviously qualified but the experience provides us some general guidelines:

– if we want to treat an active breathing crack, it is useless to inject; the best option is weatherstripping by bridging with a flexible product;

– when the crack has stabilized and the concrete reinforcements do not seem to be particularly corroded, a reactive resin injection executed correctly, with qualified personnel, yields very good results quickly and easily, i.e. it ensures at least a weatherstripping effect and a partial restoration of the monolithism. Besides, the repaired structure acquires a very slightly viscoelastic behavior, the old cracks playing the role of shock absorbers [MOU 78];

– the question is more delicate when we want to treat a concrete where the reinforcements are corroded and where it is difficult to be certain that the treated part is not likely to undergo new attacks because the entire part to be repaired cannot be completely weatherstripped.

This is the stumbling block of all concrete repair techniques using reactive resins: it is certain that in itself a resin does not have any passivating power, as it is the case for cement, but a good resin putty plays its role very well as a barrier to prevent water from attacking the concrete and its reinforcements. Therefore, saying that the injection of a resin is ineffective, even harmful (in comparison with other processes such as injection of an ultra fine cement grout, which in fact does not provide the same adhesion with the adjoining concrete) because it cannot prevent the corrosion of a concrete is only begging the question. Everything depends on the state of the concrete and the accessibility of the part to be treated and on the environment of this part. If we can create the barrier and if the aggressiveness of the ambient medium is not too great, resin injection is the simplest, most practical and most effective technique.

To limit risks of corrosion, we often use *reinforcement protection products*, generally epoxy organic primers, containing corrosion inhibitors, based on zinc or phosphate salts, for instance.

We can mention another problem: if the injection is executed badly, it is very difficult intervene “to repair the repair”. Will chemists be able to find powerful and reversible products to solve this problem?

Lastly, if we add to these potential drawbacks the fact that injection represents a relatively modest market in terms of tonnage, we can understand why manufacturers hesitate to invest in a certification procedure whose test and management expenses, justified *per se*, are not easily compatible with the expected sales volume.

These reservations should not mask the considerable and very significant successes of these techniques for the repair of concrete structures and the important role that they play – and continue to play, as corroborated by their stable sales volume – in this field where they are generally indispensable.

3.1.4.4. *Anchoring or sealing or wedging products*

Sealing products use reactive systems, generally based on epoxy resins or unsaturated polyesters. For the latter, the choice of the system must take into account the nature of the anchorage block. We know that polyesters are sensitive to hydrolysis (see section 3.1.3.3). If it is hydraulic concrete, there is a risk insofar as the alkalinity of the medium strongly increases this sensitivity (saponification).

These reservations are, however, relative. There are currently formulations based on top-of-the-range polyesters and vinylesters which give a long life to anchorings but we must be prudent in this regard as the price of the product varies very quickly with the choice of the basic monomer. The result is in direct proportion with this choice.

We can associate with these products or systems wedging products (reactor turbines for example) which also follow the same general method.

3.1.4.5. *Required characteristics*

The choice of products must take into account both the characteristics of the materials in question and the loads to which the area of the structure to be repaired is subjected. For this, we have a corpus of standards for tests and definitions which have enabled to set up a NF Certification mark (NF 030) for “Special products intended for hydraulic concrete constructions”.

Table 3.3 gives the effectiveness tests used in the various cases. The standards referred to are still national standards pending the constitution of the complete “package” of European standards which, after its adoption, will replace all the standards constituting EN 1504.

Other tests are recommended on a purely optional basis: liquid permeability tests on sawn or rough surfaces, shock resistance on sawn or rough surfaces after freezing-thawing cycles and UV radiation resistance for surface repair products, resistance test in vertical surface for structural bonding products, adhesion test after aging by mechanical fatigue and adhesion resistance test under water circulation for injection products, tests for resistance to sea water or high sulfate content water for sealing and wedging products.

Test		**Reference**	**Hydraulic binder**	**Reactive binder**	**Mixed binder**
Surface repair products		**P 18-840**			
	Adhesion to sawn or rough surfaces	P 18-852/58*	X	X	X
	Adhesion after thermal cycles on sawn or rough surfaces	P 18-853/59*	X	X	X
	Shock resistance on sawn or rough surfaces	P 18-854/60*	X	X	X
Products for structural bonding between two concrete components		**P 18-870**			
	Direct traction in sawn and reconstituted cylinder	P 18-871	X	X	X
	Compression-shear on sawn and reconstituted cylinder	P 18-872	X	X	X
	Bonding limit time	NF P 18-874		X	X
Injection products		**P 18-880**			
	Sand column injectability	P 18-891	X	X	X
	Splitting of specimens from sand column	P 18-892	X	X	X
	Brittleness on shock	P 18-893		X	X
	Adhesion before and after thermal cycles	P 18-894	X	X	X
	Polymerization shrinkage	P 18-896		X	X
	Shrinkage	P 18-361	X		
	DPU (usual practice time) on 500 g	P 18-810		X	X
Wedging and sealing products		**P 18-821/22***			
C	Aptitude for placement	P 18-832/33*	X**	X	X
C	Bleeding in confined volume	P 18-834	X		
C	Compression creep	P 18-835		X	X
S	Tearing**	P 18-831	X	X	X
S	Tensile creep	P 18-836		X	X

* The first number refers to products based on hydraulic binders and the second on reactive organic binders or mixed binders

** The test method includes an exemption to the standard included in the regulation of the certification mark

Table 3.3. *Efficiency tests required by the NF certification mark special products intended for hydraulic concrete constructions*

It may be noted that these lists take into account the strains arising from the state of the support. Surface preparation is a very important concern that is necessary for all concrete repair and protection operations. It is developed in the guide of 1996 but we will speak about it more precisely further below in connection with protection and paint works.

Apart from these effectiveness characteristics, we must mention identification tests, essentially physicochemical, used in inspections. We will not detail them here because this aspect will be developed in Chapter 6.

All these criteria and characteristics rely on mechanical as well as physical and chemical concepts. The person in charge of the application, who has broken away from the usage practices of a given product, ends up transforming his knowledge into "experience". But if he must change the type of material and uses this experience incorrectly, he risks serious trouble. This partly explains the relative conservatism of the profession – and we cannot blame it for some caution – as well as the success of cement derivatives whose setting is essentially rather traditional.

It is, however, true that a number of repair products formulated based on an organic binder can meet needs where they remain unequalled, even irreplaceable.

3.1.5. *Concrete protection products and systems*

The *functions expected* from the application of protection products or systems are primarily to prevent water from entering the concrete, whether it is pure water – and it is already aggressive even then – or charged with aggressive ions: primarily HCO_3^- (dissolved carbon dioxide), Cl^- (chlorides) or SO_4^{--} (sulfates). The 2002 guide thus defines a qualification reference frame for the following "qualifiable" functions:

– protection against the penetration of water;

– protection against chlorides;

– protection against carbon dioxide;

– protection against swelling reactions (alcali-aggregate reaction and sulfatic reaction);

– protection against scaling due to frost;

– protection against water pressure;

to which it adds the capacity of cleaning resistance.

The products and systems proposed to meet these requirements can thus be classified under the following families:

- *dampproofing agents*;
- *mineralizers*;

which can be grouped under the term *impregnation products*,

- *paints*, with which we can associate *woodstains*;
- thin coatings based on modified hydraulic binders;
- thin coatings based on synthetic resins;
- thick plastic coatings.

The entire range of products, whether qualifiable or not, is quite varied as we will see now.

3.1.5.1. *Corrosion inhibitors*

These are products applied to the concrete surface and which migrate up to the reinforcements to protect them. They are primarily phosphate or amine compositions. Their migration inside the concrete can reach several centimeters. They cannot be qualified in the current state of knowledge because their efficiency has still not received a sufficient consensus.

These products should not be confused with passivators or passivation agents used for the treatment of reinforcements before resurfacing (zinc salts for instance) mentioned in connection with epoxy resin patching mortars.

3.1.5.2. *Impregnation products*

The purpose of the *dampproofing agents* is to decrease the wettability of the support while allowing it to breathe. They are generally siliconized or fluorinated derivatives.

Mineralizers were designed based on the idea that it is possible to reconstitute damaged cement matrix by the application of silicates as such or associated with organic molecules. Their effectiveness depends on the rate of penetration into the damaged support and consequently on its porosity. It also depends on the mineralogical characteristic of the cement matrix in question.

3.1.5.3. *Paints and derivatives*

Paints and *woodstains* will be studied further below, in section 3.2.3. With the various types of coatings discussed below, they form most of the "barrier" systems used to stop water in its destructive work.

Thin coatings based on modified hydraulic binders are in general bicomponent systems made up of cement added with specific fillers to which a hydrodispersed polymer is added at the time of use (SBR latex, for example).

Thin coatings based on synthetic resins are systems made up of several resin coats in order to obtain a thickness ranging between 0.5 and 2.5 mm. We thus use mono- or bicomponent polyurethanes, bicomponent methacrylic resins, monocomponent linear or photoreticulable acrylic resins.

Thick flexible coatings have the same composition as traditional paint (see section 3.2.1) and are generally formulated with acrylic emulsion binders. They are distinct from them by their consistency particularly due to the presence of fillers. Applied at dosages of 1.5 to 3 kg/m^2, they give "thick" coatings compared to paints, and which are a protective and highly rough in nature.

3.1.5.4. *Required characteristics*

To help the project manager to make his choice, the 2002 guide [MAH 02] recommends the method summarized in Table 3.4. For qualifiable systems, it recommends a qualification reference frame defined with respect to the functions listed above (at the beginning of section 3.1.5) based on a combination of performance levels at basic tests.

Thus, a system qualified for a given function can be qualified as class 2 or 1 according to its degree of efficiency: class 2 corresponding to systems very efficient in performing the corresponding protective function, and class 1 to efficient systems.

The qualified products and systems are described in an identification record, which can be used for subsequent inspections.

Characterization of the support		
↓	Mechanical characteristics	Sound or correctly repaired support
	Geometric characteristics and surface texture of the supports	Absence of specific defects: - not flatness, lips, non-rectilinear edges - variations of colors, blooms, black spots, traces of rust, sweating, laitance, dapples, sand holes or honeycombs, bubbles, cracks, etc.
	Physical characteristics	Porosity, humidity rate State of the concrete with respect to the gel
	Chemical characteristics	Alkalinity Presence of various stains (oils, curing compound, calcite, rust run-outs, micro-organisms, etc.) State of the corrosion State of the concrete with respect to an internal swelling reaction: alkali-aggregate reaction or sulfatic reaction
Determination of aggressing agents		
↓	Gel + salt	Use of non-destructive tests for: open porosity, coating and rusting of reinforcements, resistivity and corrosion rate, cracking Sampling for carbonation analyses and measurement, Cl^- ions permeability, bubble rate, mechanical characteristics, density and porosity, a petrographic analysis, swelling potentiality, chemical analysis
	Alkali-aggregate reaction	
	Sulfates	
	Rainwater	
	Carbon dioxide (CO_2)	
	Chlorides	
List of constraints		
↓	Climatic constraints	Temperature, hygrometry, rain, dew point, before and during application and service
	Mechanical constraints	Thermal expansions, presence of cracks, etc.
	Chemical constraints	Acid rains, salt water, etc.
	Local constraints	Arising from access and placement conditions Arising from the orientations of the support, vertical surfaces, ceiling
	Esthetic constraints	
Choice of products and systems		

Table 3.4. *Method preceding the choice of protection products or systems (based on [MAH O2])*

Lastly, we must say a few words about the *preparation of supports*. The techniques that can be used are:

– *brushing and dedusting* which help to remove only non-bonding particles;

– *sandblasting,* which corrects geometric defects;

– *leaching,* which removes localized stains (oils or exhaust gas residues);

– *acid washing,* which is allowed only for non-reinforced concretes;

– *spraying of abrasives,* which is a general and efficient technique (laitance and various stains) but must be well controlled to avoid creating geometric defects and must be followed by dedusting;

– *spraying of pressurized water* which can be used to clean soiled zones (15 to 40 MPa), to descale the supports (40 to 100 MPa), while pressures greater than 100 MPa are not advised (disbonding of the concrete);

– *treatment of micro-organisms* with suitable products such as biocides;

– *resurfacing* when surface is particularly deteriorated.

3.1.6. *Mixed matrix products (modified binder)*

The idea of manufacturing hydraulic binder mixed matrix products – reactive organic binder is not recent but the products derived from it, epoxy-cement mortars or concretes (ECC), remained for a long time inexhaustible subjects of laboratory research before finding an industrial opening in flooring. They are now venturing out of their original field of application.

The system comprises three components: the first two are the base and the epoxy binder hardener, presented separately as emulsion in water, and the third is the granular mixture containing cement. It is often considered that the epoxy system reacts first and quickly gives a certain consistency to the mortar while the hydraulic binder develops its hydration more slowly. This continues and it is believed that the C–S–H crystals formed in this second phase get entangled through the network formed by the epoxy system. Eventually, the mechanical resistances of the mortar are primarily due to the cement network.

These characteristics were taken into account for the treatment of the mixed binder products in the regulation of the NF certification mark s*pecial products intended for hydraulic concrete constructions*.

But this is only an initial approach and H. Van Damme will show in the last chapter that it is very promising for the development of new materials.

3.2. Paints for civil engineering

In civil engineering fields, paints play a very important role. They are used both for the protection of metal structures against corrosion and for the protection and restoration of concrete surfaces or even for road marking intended for the safety of users. They represent considerable stakes and markets for which physicochemical knowledge has been called upon to control their use, because they are also products resulting directly from the chemical industry [GRA 85].

3.2.1. *General definitions*

A paint is a film-forming product in liquid or powder form made up of an opaque and complex mixture of powdery materials – pigments and fillers, binders, additives and generally of a solvent called also vehicle more generally. The opacity of dry film, ensured by the powdery materials, makes the difference between a paint strictly speaking and a woodstain (see section 3.2.3).

It may be remarked that "paint" indicates the original product as well as the result of its processing. The corresponding relation:

$$\begin{array}{c}\text{Liquid paint}\\ \text{in container}\end{array} \xrightarrow[\textit{drying}]{\textit{application}} \begin{array}{c}\text{dry paint on}\\ \text{the substrate}\end{array}$$

highlights the importance of the application and drying phases in the success of a paint operation. It also reflects the general recommendations made earlier for the processing of organic binder materials.

3.2.1.1. *Constituents of paints*

We generally distinguish four types of constituents in the formulation from a paint, which are as follows:

– *Powdery materials*

Pigments primarily provide opacity (masking power), color (esthetic function) and possibly an anti-corrosion power (see section 3.2.3).

Fillers have the function of providing physical and rheological characteristics (by granulometric filling, in particular) adapted to the required use: appearance, abrasion resistance, thixotropy, etc.

In the absence of powdery materials, the composition is denoted by the term *varnish.*

– *Binder*

Sometimes called resin, it is the noble part of the mixture. It ensures the coating of the powdery materials and the formation of the film during drying. It is therefore responsible for the resistance of the paint in time and to a large extent for the success of the application. It is also generally the most expensive constituent (except when the pigment is titanium dioxide, as is the case of road marking paints) and consequently the one with the most economic weight in a mass distribution market. It therefore deserves the user's greatest attention. It is generally an organic polymer which gives its generic name to the paint itself: we speak about vinyls, glycerophthalics, polyurethanes, epoxies, silicones, etc. In each case, we are referring to families of products that offer a wide range of properties where the user must make a careful choice according to his particular usage.

– *Additives*

Added in small quantities, these are generally organic materials. They can have multiple functions: wetting agents, thixotropic agents, "anti-skinning" agents, fungicides, etc.

– *Solvent*

This term refers both to solvents strictly speaking as well as the water which tends to replace them and which does not play strictly the same role, hence the use of the term *vehicle*, which is more general but not widely used yet. However, it enables to make a classification between:

– solvent phase paints, where we distinguish between traditional paints and high dry extract paints (higher than 75%);

– water phase paints, where we distinguish solutions (water-soluble paints), dispersions (water-dispersed paints) and emulsions (water-emulsified paints);

– paints from which the solvent is completely absent, as is the case of systems with hot processing or many bicomponent products (solventless paints).

We thus have here three of the four processing modes of organic binder materials mentioned in section 1.4.2: solution, dispersion in water, mixture to be made at the time of use (bicomponents). In this last case, the binder used for application is not yet strictly a polymer since the purpose of the chemical reaction between the two components is to create it. This is therefore called *reactive paint*. The fourth mode, softening by heating, is used only for certain marking coatings, which are not strictly paints but related products.

3.2.1.2. *Paint drying modes*

The above classification is based on the solvent type. If we are interested in the mode of drying, which essentially concerns the binders, we can distinguish the following:

– Binders with drying by oxidation (oils, stand oils, alkyds)

This is the method of “old-fashioned” painting, i.e. with unsaturated oils. The mechanism includes essentially four stages: the departure of the solvent, the opening of the double bonds (where exposure to UV rays is desired to catalyze the reaction), the fixing of oxygen and finally the formation of oxygen bridges to cross-link the system and to harden it. These two last steps are catalyzed by siccatives. The system lasts quite long in our climates ...

– Binders with physical drying (thermoplastic resins: acrylic resins, chlorinated rubber, etc.)

This is the classic mode of processing thermoplastics or monocomponents: evaporation of the solvent and formation of the film by coalescence. The mechanism is physical and reversible.

– Binders with drying by cross-linking: epoxies, polyurethanes

This time, it is the mechanism of processing bicomponents cross-linking by polycondensation, chemically and irreversibly. It comprises three (or two) steps: mixture of the two components before application, departure of the solvent in the case of solvented products, chemical reaction between the two components creating the network (cross-linking).

– Binders with drying by coalescence

The mechanism associated with this class of binders resembles that of physical drying but differs from it by the role of the vehicle: the equilibrium of the dispersion must first break by the departure of water and its evaporation; then coalescence occurs according to the same principle as for solutions. It must be noted here that the mechanism is not reversible.

3.2.1.3. *Characteristics of the dry film*

After investigating liquid paint in its container and the drying mechanisms, we must now focus our attention on dry film.

Its characteristics depend primarily on two factors:

– the proportion between the powdery materials and the binder or rather the pigment volume concentration (PVC):

$$PVC = \frac{V(P+C)}{V(P+C)+V(L)}$$

where V(P+F) is the volume in the film occupied by the powdery materials (pigments + fillers) and V(B) is the volume in the film occupied by the binder;

– the nature of the binder (and therefore its drying mode).

The respective influences of these two factors are summarized in Table 3.5 and Figure 3.3.

Family of products	**Products drying by**			
	Oxidation	**Evaporation**	**Cross-linking**	**Coalescence**
Presentation	Monocomponents	Monocomponents	Bicomponents	Monocomponents
Long term recoverability	Good	Excellent	Low (except modified EP)	Excellent
Water resistance	Low	Good	Excellent	Good
Chemical resistance	Low	Good (except solvents)	Excellent	Variable
Mechanical strength	Variable	Variable	Excellent	Variable
Drying Low T/high H%	No	Yes	No (except modified EP)	No
High thicknesses	No	Yes	Yes	Yes

Table 3.5. *Characteristics of the dry film depending on the binder*

As a comment to this table, we can add that, during painting, we must also take into account the potential toxicity of the various formulas: the first three families because of the presence of the solvent, and in the third, the presence of amines in the hardener. This reservation plays an important role primarily for works in confined environments.

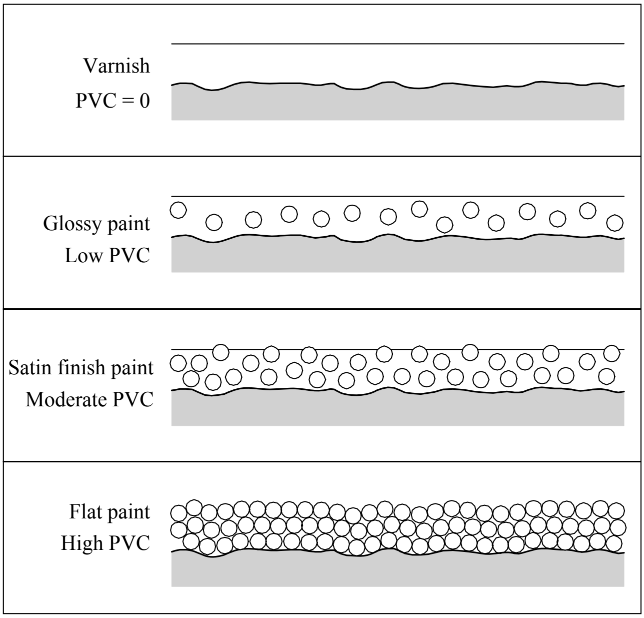


Figure 3.3. *Appearance of the dry film depending on the PVC*

3.2.1.4. *Paint systems*

The painting of a structure, whether for the anti-corrosion protection of steel or of concrete, requires several coats, each of which has different roles. We thus create a *paint system* that is made up of:

– a *primer or priming coat* to ensure adhesion of the complete system to the support; it can also reinforce the surface cohesion of the substrate, which is very necessary (for concrete, for instance) or perform a particular function (anti-corrosion, for steels);

– an *intermediate coat*, perfectly compatible with the two other coats, which confers on the system the desired thickness; it fulfills the protection function;

– a *top coat* which is used to resist external aggressions and fulfill an esthetic function.

Each one of these coats can be multiplied to reach the desired thickness, depending on the desired performance level.

3.2.2. *Anticorrosion paints for metal structures*

The application referred to here corresponds to the oldest use of paints in civil engineering. Iron and steel, when they become building materials and are subjected directly to the aggression of their environment – atmospheric oxygen and water (atmospheric, running or stagnant, or even impregnating the supporting base) – tend to return to the oxide state, i.e. their state of natural equilibrium, in the absence of protection against corrosion. Paints were used very early as a defense against this fate, a simple passive barrier against the corrosive agents first, then rather quickly, an active barrier, helping to increase the durability of the treatment significantly, with specific formulations adapted to the problem.

3.2.2.1. *Corrosion*

The phenomena brought into play are primarily electrochemical in nature. They can be summarized schematically in the formation of galvanic cells between sound metal and an impurity, where the metal plays the role of anode and dissolves according to the reaction:

$$\mathrm{Fe} \longrightarrow \mathrm{Fe}^{++} + 2\,\mathrm{e}^-$$

The functioning of this cell requires an electron collector and an electrolyte. The former is the atmospheric oxygen which is active when it is dissolved in water according to the reaction (in the cathodic zone):

$$\tfrac{1}{2}\,\mathrm{O_2} + \mathrm{H_2O} + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{OH}^-$$

The corrosion of the immersed metal structures is all the more active as the water is more acidic and in motion. Tidal zones are particularly exposed to the phenomenon. For atmospheric corrosion, the atmospheric moisture acts both as electrolyte and to dissolve the oxygen. The reaction continues as long as there is metal and sufficient moisture (higher than a critical value) because of the depolarizing nature of oxygen. The steel surface is in the form of a system of cells where the steel is anodic and dissolves while the impurities play the role of cathodes.

The above mechanism in fact describes the case of pitting corrosion, but can be generalized to all of the phenomena bringing into play the corrosion of steel and that of metals in general. However, it supposes a hierarchy between the metals, which determines for each couple the one that plays the role of an anode and the one that plays the role of a cathode. We are referring to electrochemical potential, which is an intrinsic data of matter. Table 3.6 shows where iron is located in the scale of the potentials of other metals or compounds intervening in the corrosion of metal structures.

Couple	**E° (V)**	**Galvanic zones for ferrous metals**
Al / Al^{+++}	- 1.76	Anodic
Zn / Zn^{++}	- 0.76	
Cr / Cr^{+++}	- 0.74	
Fe / Fe^{++}	**- 0.44**	**Reference**
H_2 / H^+	Reference	Cathodic
Calamine*	+ 0.30	
Cu / Cu^{++}	+ 0.34	

Table 3.6. *Standard potentials at 25°C of a few redox couples related to the corrosion of metal structures*

Note: the electrochemical potential used for the oxidation of calamine (mill scale) is actually a measurement whose interpretation is complex. In fact, we consider that calamine, which is not a pure substance with a well defined composition, consists of three laminar layers of iron oxides (more or less in the form of silicates or other salts) all the more richer in oxygen as they are closer to the surface of the steel. Therefore, we should start from steel and go towards FeO (wustite) then Fe_3O_4 (magnetite) and then Fe_2O_3 (hematite) surface. The mechanical characteristics, the coefficients of expansion and electrochemical potentials of these layers are different from those of steel. Thus, from the point of view of oxidation-reduction, calamine is "noble" compared to steel, i.e. it behaves as an anode vis-à-vis steel (cathode) which is then attacked. It is therefore absolutely necessary to eliminate calamine before applying a coating.

3.2.2.2. *Anticorrosion protection processes*

From the above, we can think of protecting steel by making the cells function contrary to the corrosion mechanism thanks to the presence of more electronegative metals, which then play the role of a cathode with respect to anodic steel. In civil engineering, it is primarily zinc that is chosen to play the role of the sacrificial metal. The booklet 56 of the C.C.T.G. thus recommends various processes with specific frameworks for use:

– *hot galvanization* where the metal part is immersed in a tank of molten zinc;

– *painting*;

– *metal spraying followed by painting*;

– *hot galvanization followed by painting.*

Painting takes us back to organic materials. The products used are obviously specific to the expected function.

3.2.2.3. *Anticorrosion paints*

The specificity of anti-corrosion paints primarily lies in their capacity to play the role of an active barrier. The components in question are therefore the binder (barrier if it is sufficiently impermeable) and the pigments (inhibitors or metals playing the role of a cathode).

The *pigments* used can be classified as below:

– pigments with a cathode effect, the main (and practically the only) representative of which is zinc powder;

– pigments with inhibitor effect: phosphates zinc, barium metaborate;

– pigments with barrier effect: aluminum powder, micaceous iron oxide, glass scale, etc.

Binders that play the role of barrier must have two essential qualities: adhesion and impermeability. The former corresponds to the usual qualities required from a binder, with the additional characteristic that because in this case we are considering a paint system, adhesion involves not only the interface between steel and the anchorage paint, but also several interfaces between the paint coats. The influence of processing parameters – atmospheric conditions, the environment and execution of the project – has a great importance. The latter insists on the specific cohesion of the system and refers to the compatibility between coats described in connection to interfaces.

The paint formulator is thus confronted with highly complex physicochemical problems. The certification method has considerably reduced the use of “à la carte” formulations (which would not be very profitable commercially) but compels each manufacturer to offer a wide range of products to meet the various needs of his customers.

3.2.2.4. *Criteria for the choice of the protection paint system*

The anti-corrosion paint market is large, both in terms of production and with respect to the safety of structures. We can say today that it affects the sustainable development of steel constructions. This is why it has given rise to thorough studies for standardization and certification purposes. Thus, in France, the *Association pour la Certification et la Qualification en Peinture Anticorrosion* (ACQPA) was created in 1994 in view of certifying paint systems, the qualification of paint operators and inspectors of protection painting [AND 96]. It regularly publishes lists of systems certified as conforming to the “high durability” class of EN ISO 12944 standard

[ACQ 01]. Without considering that the use of a certified system is compulsory – it is the specifications that must decide this – it is not possible to be unaware of the existence of this document which, moreover, recalls in its introduction the principal codes of practice.

Thus, the project manager must select from the list of protection systems at his disposal the one that corresponds best to his needs, both in terms of the lifespan of the protection and ease of organizing the worksite for the application in question. To make his choice, he first takes into account the following criteria:

- the number of coats;
- the mode of application of the coats;
- the drying time of each coat;
- the minimum and maximum recoating time of each coat;
- the dry thickness of the application;
- the atmospheric conditions during the application and the product's drying time.

As a general guideline, ACQPA considers, for the certification of various paint systems, the following criteria:

- The *environment classes* characterized by their aggressiveness according to the NF EN ISO 12 944-2 standard and divided into C2 (low), C3 (moderate), C4 (high), C5M (very high, marine), which is itself divided into C5Ma and C5Mm, depending on whether the part of the structure is subject to sprays only or to tides and lastly Im2 (submerged in seawater or brackish water).
- The *substrate type* with three reference surfaces:
  - A for steel stripped by dry spraying of abrasives with the care degree Sa 3 or Sa 2 ½ according to ISO 8501-1 and a roughness "Moderate G" according to EN ISO 8503-2;
  - Z for metallization by hot spraying, according to EN 22063 with minimum 120 µm zinc or zinc/aluminum alloy 85/15 or 200 µm at least of aluminum;
  - G for hot galvanization by immersion, according to EN ISO 1461, with steels conforming to A 35-503 in a molten bath of normal type Z7 according to NF A 55-101;
- The *project type* depending on whether we have new (N) or maintenance (M) works;
- *Exposure* depending on whether we have visible (V) or invisible parts (I).

The last parameter essentially concerns the colorimetric stability tests of the finishes of "V" systems, carried out in Florida for one year.

The application conditions also conceal problems such as: the protection of a new structure is done in two stages, first in the workshop of the metal manufacturer, just after abrasive stripping, by the application of the anti-corrosive primer; the following coats are applied, either partly in the workshop and partly on the site, or entirely on the site, after reconditioning of the zones deteriorated during transport and assembly. These deteriorated zones are always prepared by abrasive stripping before application of the paint but the reconditioning of the coats applied in the workshop before the application of the top coats on the site is very often nothing but simple washing with pressurized water. Therefore, there is a rupture in the "normal" application of the coats of the system and while making the choice, we must check whether this rupture is compatible with the technical possibilities of adaptation of the system.

The paint system must therefore be selected both for its intrinsic protective qualities and for its compatibility with the application conditions specific to the site in question.

We can thus draw general rules regarding the individual performances of the products constituting the paint system:

– the drying time of each coat must be the shortest possible; for the primers applied in workshop, the aim must be the rapid shipment of the structural members; for the finish on the site, we must avoid pollutions by external agents present on the site;

– the last coat applied in the workshop must moreover allow great ease of cleaning so that the elimination of all the stains due to transport and assembly is easy;

– the maximum recoating times between coats must be the longest possible to allow better flexibility in the organization of work;

– it must be possible to retouch easily on the site, preferably with monocomponent products whose use is relatively unhampered by atmospheric conditions;

– the part of the system left below the top coats must have a sufficient strength to ensure a good protection of the metal for a period that can go up to 12 months, even more.

These rules show that the initial concept of the choice of the protection of a civil engineering structure based solely on its anti-corrosive performances has become obsolete and that the choice of the system must include criteria related to the application of the coats, cleaning and the ease of retouching on site.

3.2.2.5. *Surface preparation*

The success of paintwork depends largely on the preparation of surfaces to be covered [MIG 96]. In this case, several scenarios can arise:

– new works with three possibilities:
  - painting of stripped steel;
  - painting after metal spraying;
  - painting after hot galvanization;

– maintenance works for repainting:
  - structures previously stripped and painted;
  - galvanized structured, whether painted or not;
  - painted metallized structures.

Each of these cases requires special attention and call for the application of precise rules which we cannot enumerate here. We will however point out that the surface preparation methods range between:

– *naked stripping* when the protection is planned for a particularly aggressive environment, an expensive operation requiring special precautions for the protection of the environment of the site itself; and

– *polishing* which consists of removing the old paint up to the level where it exhibits a sufficient bonding adherence with the support [AND 93].

3.2.2.6. *Main protection coatings*

The formulation of current systems is changing constantly, in tune with the regulations that had to take into account increasingly serious environmental and health concerns. New products have appeared on the market and others still are being explored. We can however give some general indications on products currently used [MIG 94].

The typical system comprises three coats with a total dry film thickness of at least 180 to 210 µm depending on the environment, distributed as below:

– epoxy anti-corrosive primer rich in zinc;

– epoxy or modified epoxy intermediate coat; this coat must dry quickly, have the longest possible recoating time, a sufficiently waterproof and resistant pigmentation for on-site risks, particularly while waiting for the application of the finish;

– polyurethane, acrylic resin or acrylic-polyurethane top coat, easy to apply on site and great color stability.

The systems' minimum thicknesses to be recommended depend primarily on:

– aggressiveness of the surrounding atmosphere (C2, C3, C4, C5, Im2);

– type of work (new or maintenance).

This example is given only as a general guideline. Other families of products can be used such as chlorinated rubber paints, monocomponent polyurethane hardening with atmospheric moisture or, for invisible parts, epoxy pitch paints, but the constraints pointed out above almost always call for three coat systems for visible parts and two coats for invisible parts.

3.2.3. *Paints for concrete*

Many manufacturers consider that a concrete structure or building can do very well without paint or similar coating, its physical and esthetic properties being sufficient to give it the entire lifespan desired. It is indeed possible to create a beautiful and durable concrete structure, but it can be also necessary to paint a structure, either at the time of construction because it is the architect's project, or subsequently, because it has aged badly or for other reasons such as an improvement of the following aspects:

– esthetics, case of certain structures in urban environment or classified site, anti-noise walls;

– security, case of the red and white marking of pylons or beacons where paint has a precise signaling function;

– comfort, ease of cleaning and energy saving, case of the treatment of the tunnels by light color and non-dazzling coatings, washable to facilitate maintenance (cleaning with pressurized water);

– protection strictly speaking of the concrete material, more precisely of its impermeability, i.e. a slowing down of the penetration of external moisture from run-off or condensation.

The paints used to meet these needs fall within a system whose specific vocabulary must be clarified.

Thus, the term *painting* means a protection operation by application of paints, woodstains or anti-graffiti products, with a total dry film thickness ranging between 20 and 600 µm.

A *woodstain* – this term comes from wood technology – has a composition comparable to paint; it can be colorless or colored, but is *non-opacifying* with a more fluid consistency such that it impregnates the concrete well. It is made up of a binder (acrylic or polyurethane), a vehicle (content ranging between 40 and 80%), possibly fillers, pigments and dyes.

An *anti-graffiti function* can be provided by paint, a varnish or a woodstain.

The particular characteristic of binders used in these systems lies in their resistance to the basicity of the substrate. We saw previously that when the concrete is wet, it has a high pH (between 12.6 and 13.6). Thus, oil-based paints and glycerophthalic paints are absolutely unsuitable for use here. Therefore, the main constituents are epoxies, polyurethanes, acrylics and vinyls, chlorinated rubbers and certain oil resins.

The basic tests used for their qualification are given in Table 3.7.

Quality test	**Test methods**
Practical application and surface drying time test	LCPC NF T 30-037 / NF EN ISO 1517
Pull-off test adhesion test	NF T 30-062 / NF EN 26624 / ISO 4624
Water permeability test	NF T 30-801
Washability test	LCPC
Artificial aging strength	NF T 30-049
Colorimetric characteristics	NF ISO 7724-1, 2 and 3 / NF X 08-014 / NF T 34-554-1 and 2

Table 3.7. *Quality tests used for the choice of paints for concrete*

This set of tests can be supplemented by complementary tests required by particular conditions: resistance to steam (NF T 30-018), micro-organisms (NF X 41-520), hydrocarbons (NF T 30-053-1/NF EN ISO 2812-1 and 2), salt + gel couple (procedure of the LRPC of Lyon), to backpressure water (procedure based on NF P 18-855), fire resistance (decree of 20/08/1991), etc.

Based on the experience gained since 1978, the writers of the guide of 1999 [BOU 99] have drawn the following lessons, which must be understood as trends and not as certainties:

– in all cases, when durability is the decisive selection criterion, epoxy or polyurethane systems are the best;

– when constancy of the color is sought primarily, systems comprising an aliphatic or acrylic polyurethane finish give the best results;

– epoxy and polyurethane systems have moreover the advantage of exhibiting good chemical inertia, which makes them particularly advantageous when the structure is in an aggressive environment or in contact with polluted water or soils;

– these systems are also appropriate for the painting of tunnels because of their good leaching resistance necessary for the maintenance of the structure; there is no significant deterioration of colors but on the other hand as the processing of these products is done in a confined environment, we must choose systems in an aqueous phase or without solvent;

– vinyl systems are suitable for car park ceilings, at very interesting costs;

– lastly, we must never lose sight of the fact that the best results are always achieved when the processing is done with the utmost care and by following the codes of practice indicated in the technical guides.

3.2.4. *Road marking paints and products*

Pavement markings form an integral part of road equipments. Compulsory in France on motorways and expressways as well as on all networks for certain transverse marks, it has became in a few decades an all the more indispensable complement to the safety of the driver as the traffic is denser and moves at higher speeds.

The products used for markings are all based on organic binders.

3.2.4.1. *Road marking*

Pavement markers are part of the entire road equipment. Depending on the case, they fulfill either one of the three main functions [COR 98]:

– a *regulatory function*. This includes the continuous longitudinal lines, the transverse markings supplementing the "stop" signs and "yield right of way", directional arrows, the parking and public transport markings, pedestrian crossings.

– a *warning function*. This includes direction arrows, roundabout arrows, changes in the modulation of the discontinuous longitudinal lines, advance ground signaling "yield right of way", zebra crossings and removal of the emergency stop line.

– a *guidance function*. Here we find the marking of axis and stringers as well as the marking for delimiting specialized ways.

The essential properties required from marking products are summarized schematically in Table 3.8.

Properties in question			Variables measured
Visibility	By day By night	In dry weather In wet weather In rainy weather	Trichromatic components Coefficient of luminance under diffused light Retroreflective luminance coefficient
Mechanical properties	Sliding resistance		SRT coefficient
	Resistance to wear during traffic		Full-scale test
Technological properties	Capacity for prolonged storage		
	Drying time		
	"Removability" (for temporary products)		

Table 3.8. *Criteria entering into the specifications of marking products*

Among these criteria, the wear resistance and the retroreflection are original. The former concerns the durability of the marking. It requires a full-scale test, relatively rare to be underscored here, which is taken into account mainly for certification purposes. The latter refers to physical concepts, which will be presented now briefly.

3.2.4.2. *Retroreflection*

When a ray of light meets a surface, it gives rise to several types of reflected rays whose energies depend on the texture of surface in question. Thus we can distinguish (Figure 3.4):

– specular reflection, like a mirror, very intense on a smooth surface;

– diffuse reflection, scattering in all directions and the more so as the surface is rough;

– retroreflection, where the light meets an obstacle, for example glass beads correctly embedded in the surface considered, which enables it to return in its direction of incidence.

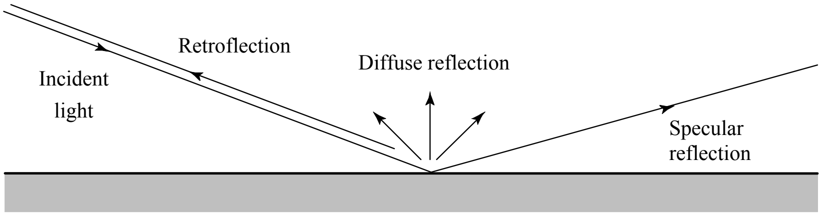


Figure 3.4. *Different types of reflection*

The way in which the glass beads are embedded into the marking product has great importance because this affects the output of the retroreflection (Figure 3.5).

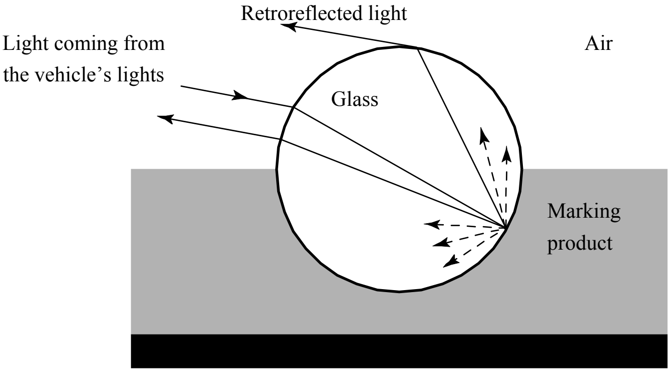


Figure 3.5. *Phenomenon of retroreflection at the scale of a glass bead*

We can thus see that:

– if the bead is embedded too little, the ray can cross it and continue in its way; additionally, the bead in question will tend to be ejected by the vehicles;

– if the bead is embedded inserted too deeply, the angle of incidence increases and a phenomenon of total reflection occurs at the air-glass diopter level with the result that the light makes a specular reflection on the bead's external surface, increasingly intense as we approach the limit angle and the retroreflection dies out little by little.

The above principles explain the functioning of retroreflection on dry surfaces. We can deduce from them that when the beads are covered with a water film, the retroreflection disappears. We must find a process where a significant part of marking exceeds the height of the water film. This is called visible night marking in rainy weather (VNTP).

One of the processes used for this purpose consists of using micro-beads of various diameters, the largest acting during rainy weather while the finest are fully efficient in dry weather. These beads must further be surface treated (oiling) to be correctly wetted by the paint and remain attached there. Lastly, their density also affects the homogeneity and stability of the paint at the time of processing. This gives an idea of the importance of this component and the care required for its manufacture and explains why a certification procedure has been associated with them.

The retroreflection is appreciated by the *coefficient of retroreflected luminance* RL which is measured using specific apparatuses (luminance meter, retroreflectometer, Ecodyn) by the ratio between the luminance and the orthogonal illumination at a given distance (NF EN 1436).

3.2.4.3. *Choice of the products*

As for anti-corrosive paint systems, the markings used on the French road network are the object of a certification. *L'ASsociation pour la QUalification des Equipements de la Route* (ASQUER) has developed a certification reference frame and governs the NF certification mark dedicated to "Road equipments". This reference frame comprises appendices both on the procedure to be followed by the manufacturer and tests and performance thresholds required by the products to be compliant with the certification mark.

As regards products, there is a certification procedure for powdering products (glass beads, mixture of glass micro-beads and aggregates) and a procedure for the temporary (worksites) or permanent marking products (retroreflective products or not, VNTP products).

Certification starts with the full-scale *durability test* mentioned above: the manufacturer is called upon to apply his products to one of the two road sites selected for this purpose by the certification mark committee, within the framework of an annual campaign. The measurements indicated schematically in Table 3.8 and adapted on request are performed at the time of processing and are reproduced after six months for temporary products or one year for permanent products.

3.2.4.4. *Main products available*

Road marking primarily uses paints but also hot or cold coatings and various prefabricated tapes or objects.

Paints are primarily based on acrylic binders: the trend is to use derivatives of acrylic acid for temporary marking and methacrylics for permanent marking. This is practically always true for water dispersion products and true to 90% for organic solutions. The old products used as solvent toluene, then xylene and now the trend is to formulate water dispersions.

White pigment is titanium dioxide. It is the most expensive component in this type of paint.

The incorporation of glass beads is generally done by powdering at the time of application. It obviously requires much care and workmanship, which shows the importance of specialized teams.

Hot coatings, also called thermoplastics, are generally manufactured using thermoplastic polydienic resins. They are processed at temperatures close to 200°C in melters and brought to the pavement in hollow shoes, with thicknesses in the order of a millimeter. The product "sets" quickly by cooling (1 min approximately).

Cold coatings are based on methacrylic resins, aqueous monomer solutions which polymerize *in situ* after evaporation of water, by action of a peroxide. They are used in particular for setting the "yield right of way" mark with thicknesses of about 2 mm.

Prefabricated or preformed tapes are manufactured industrially and are ready for use. They can be self-adhesive, heat-reactivatable or require the use of adhesive. Once placed, they are immediately usable. Their composition is generally based on polyurethane what gives them a long life and makes them easily removable, provided they are not too old ... The problem encountered here is the texture of the pavement (roughness, porosity). The fastening type to be chosen – self-adhesive or gluing – depends mainly on this parameter.

It may be noted that prefabricated tapes are especially used in temporary marking, but that there is no major obstacle in using them for permanent marking.

3.3. Conclusions

This second chapter on organic binders was dedicated to the maintenance of heritage and safety. The following main ideas can be retained.

With regard to the maintenance of heritage, products for the repair and protection of concrete structures call for the use of two types of materials: mortars based on polymer modified hydraulic binders where the polymers contribute interesting characteristics such as flexibility and adhesion on the one hand, synthetic resins, which are products for specific use, very efficient resins like epoxy resins, polyurethanes, unsaturated polyesters and acrylic resins on the other hand. Synthetic resins are often little known, could be misused sometimes and as a result have earned the mistrust of those in charge of the application because their technology requires a minimum effort to be controlled.

It should also be remembered that all these processes have been the object of standardization where the technological aspect has a dominant part.

The case of steel is particular because its maintenance and the very life of the structures that it constitutes call for the careful application of paints adapted to its problems. Paint technology also includes a considerable set of standards and application rules all the more strict as it affects the safety of the structures.

Lastly, in the specific field of road safety, marking products primarily paint and coating technology. They have an interesting particularity: to be approved in France, a product must have successfully undergone a durability test included in a full-scale test run on a trunk road for six months or one year.