Organic Materials in Civil Engineering
Yves Mouton
Copyright © 2006, ISTE Ltd.

Chapter 2

Organic Binders I. Bitumen and Road Construction

Organic binders have been known to humanity since the highest antiquity. With liana and interlaced ropes, they discovered the basic jointing technique, both for housing and for household furniture and objects of common use, even jewels. But whereas ropes functioned essentially by virtue of their mechanical properties and the entanglements that they formed, glue, excrements, pap, bitumen brought into play physico-chemical processes completely unknown to their users, though relatively well mastered in practice. Today's materials are certainly better known but adhesive bonding mechanisms have not yet revealed all their secrets. We will see further below (Chapter 4) how far we must go to give this mode of jointing the place that could be its in civil engineering.

In general, we call binder any substance used to bring together and maintain together particles that are generally solid. In civil engineering, we can distinguish:

– hydraulic binders, such as cement, so-called because they require water for setting;

– organic binders, such as bitumens or synthetic resins (polymers) so-called because they are made up of organic molecules.

We may note in passing that in road engineering, we refer to the former as *white binders* in contrast to *black binders* or more commonly *hydrocarbon binders* for the latter category.

The role of binder is particularly suitable for organic molecules. We will see about gluing (Chapter 4) that contact jointing, carried out by means of “natural” organic binders, is as old as the man. To limit ourselves to the field of current civil engineering, we will see that they are primarily used in three types of applications: road surfacing, products for the repair and protection of concrete structures and paints (protection of structures and road signaling).

The first of these applications represents a world in itself. It includes in reality the entire field road construction. Bitumen is in fact used primarily for the construction and maintenance of roads. In France, so-called industrial uses of this material (waterproofing, special paints) account for only 10% of the total production. This explains why its recent history and its evolution are closely related to the history and evolution of road construction.

This has not always been so, as it is one of the oldest materials used by man, not only for its adhesive strength, but also and perhaps especially for its hydrophobic qualities used in association with its gluing power to waterproof and caulk ships. It is also mentioned both in the epic of Gilgamesh and in the Bible: it was used to waterproof the floating cradles of Sardon and Moses, as well as Noah’s Ark. Its exceptionally long life explains why we can see testimonies of its use in the civilization of ancient Egypt, Assyria and Babylon: waterproofing of flooring of thermal baths, of reservoirs and waterworks, sculpted profiles, for instance. We can even add a peculiar use: bitumen was also used by the Egyptians to embalm bodies. The root “mum” of the word “bitumen” is the source of the term “mummy” [SAU 80].

All these uses refer to a *natural* material or, more precisely, a material extracted from relatively limited natural ores, which appeared at ground level in geologically unstable regions. This product was therefore considered as only exotic and without any significant importance in the field of construction. Even the caulking of ships required it only occasionally (Christopher Columbus at Trinidad, for instance) as the European market was chiefly dominated by the Scandinavians who used wood tar made from their immense forest resources.

Over the centuries, the use of mineral oil (the word “petrol” means oil from stone), various bitumens and tars gave rise to numerous uses where the notions of stabilization and waterproofing were generally confused. The brief history of road construction is quite fascinating [BIL 98]. It is said, for example, that following the accidental spilling of a barrel of tar on the Montgeron road near Paris, the author of the damage was ordered to remove the offending traces and, as he was unable to do so, everyone could not but admit that the road was more resistant at this particular place …

Things changed with the advent of the automobile whose development, from the outset, was seriously hampered by two drawbacks viz the state of the roads and the vehicle's suspension. After many ups and downs, the use of pneumatic tires solved the second problem, at least with respect to the vehicle, because if the condition of the roads limited the endurance of these machines and their speeds, it was primarily the dust caused by the dynamic contact of the wheel on the pavement that made the simultaneous circulation of the high-powered cars of that time unbearable.

In this context, we cannot forget to mention the name of Guglielminutti, a Swiss physician who became famous by his campaigns against this bane – dust – in the early years of the 20th century. He thus earned the nickname of Doctor Tar, a benefactor of humanity, medals and honors as well as a few caricatures in the newspapers [DES 35]. It is also because of him that even today we speak about tarring in connection with coating whereas the use of the tar for this purpose has practically disappeared.

The situation was different in 1901 when 20,000 m^2 were tarred in Paris. Three years later, it was 360,000 m^2 and very quickly all the available tar was exhausted. It then became necessary to come up with other solutions. Thus appeared a whole range of dust-guard products with picturesque names like Pulvicide or Pulvivore, but these were only palliative. Finally it was by using oil and particularly its heaviest cuts that the pioneers of the construction of modern roads discovered the solution. This was called "tarring and oil-coating of roads" and for three-quarters of the century, these two types of binders were used concurrently in road construction. Finally, tar disappeared gradually for economic and environmental reasons. The basic hydrocarbon binder used today is therefore bitumen.

It is true that today, dust control is no longer the primary concern of road manufacturers. The binding properties of bitumen are still topical, but are expressed differently. Thus, Figure 2.1 shows the profile of a standard pavement. The bitumen appears here primarily in the surfacing when it is coated or covered with a surface dressing. It can also be used in the base course if we use the technique of grave bitumen.

Before embarking on the study on bitumen itself, we need to clarify a few terminological elements, essential to all who are not familiar with the specific world in which this material is manufactured and developed.

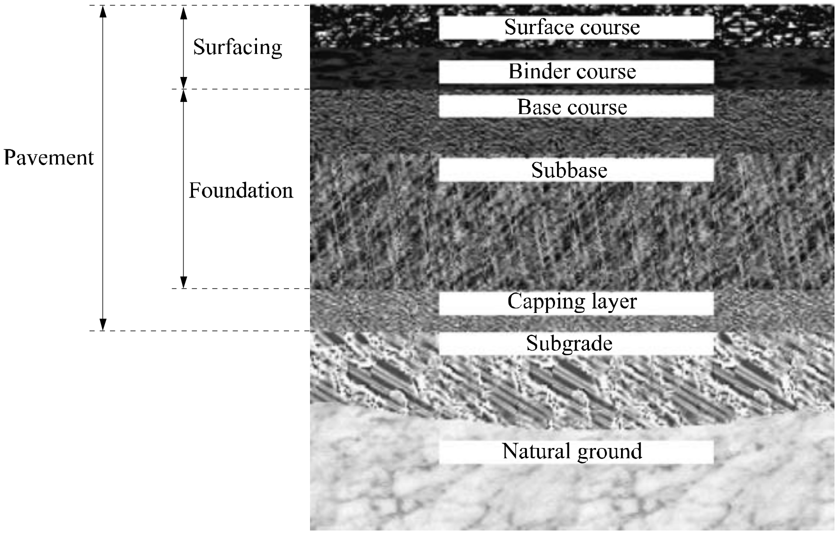


Figure 2.1. *Typical section of a pavement*

2.1. General terminology

We have seen that *hydrocarbon binders* are organic binders used in road engineering, because, as all organic materials, they are essentially made up of carbon and hydrogen with small proportions of oxygen, nitrogen and sulfur as well as trace metals. This family includes primarily:

– *bitumens*, derived from the distillation of certain *crude oils* of essentially animal origin (transformation of marine sediments accumulated in lagoons, lakes and seas of the secondary era). This origin is confirmed by the presence, in crude oil, of compounds like cholesterol, which is the sign of animal origin, but also of small quantities of porphyrins, which are compounds derived from chlorophyll; it may be noted that the French word "*bitume*" is *bitumen* in English and *bitumen cement (AC)* in American English. We must note here that "bitumen" has a more accurate sense than "asphalt" which often appears as ambiguous – this is why we will use the European terminology concerning bitumen technology;

– *tars*, prepared from *coal* or lignite by the destructive distillation in the absence of air, of plant origin (decomposition of plants and forests situated near marine banks and buried following the movements of the earth's crust);

– *naturals binders,* i.e.:

- *natural bitumens* which are in the form of a paste containing a high proportion of heavy hydrocarbons (40% at least) impregnated in shale or calcareous marls; the largest deposit is found in the West Indies, in the island of Trinidad,

- *bitumen rocks* or natural bitumens, made up of sand and fine calcareous and silicon particles, impregnated with 6–10% of bitumen; the mineral extracted according to the classic techniques of mining is then ground to yield natural bitumen powder.

Hydrocarbon binders have been classified based on their use into three main types, which are themselves sub-divided into various classes as shown in Table 2.1.

Types	**Classes**	**Comments**
Bitumens	Paving bitumen	No addition
	Oxidized bitumen	For particular uses
	Cut-back bitumens	Addition of relatively volatile thinner to decrease the viscosity of the binder
	Fluxed bitumens	Addition of a fluxing oil of low volatility (coal derived oil or oil) to soften the binder
	"Compound" bitumens	Tar-bitumen Pitch-bitumen
	Modified binder	Polymer modified bitumen (PmB)
	Special binders	Multigrades, etc.
Bitumen emulsions	Classifications according to: - ionic nature - stability - binder content	⇔ anionic or cationic ⇔ rapid setting, semi-rapid setting, slow setting, over-stabilised setting ⇔ 50, 55, 60, 65 or 70%
Tars (to recapitulate)	Pure tars	
	Modified tars	Addition of PVC or PS
	"Compound" tars	Bitumen content < 50%

Table 2.1. *Classification of hydrocarbon binders*

Tars today play, at least in France, only a marginal role in the road industry. The reasons of this almost complete disappearance are mainly economic but also because of health concerns: these products comprise in their composition a high proportion of condensed molecules which are particularly carcinogenic. Therefore, hydrocarbon binder and bitumen have become almost synonymous, regardless of the manner in which this material appears to the user.

Finally as regards the road binder terminology, we must discuss the modes of processing bitumen in road engineering.

Paving bitumen appears, depending on the samples, as a very viscous liquid or as a solid of pasty to hard consistency. Its processing modes are the same as those of thermoplastic polymers discussed in section 1.4, namely:

– by plasticizing at high temperature (140 to 160°C), this is the technique of *hot mixing*;

– by softening by the addition of a solvent, i.e. the use of thinners or fluxes, for surface dressings, for example;

– by emulsifying in water for surface coatings, cold mixes, treated gravel (garve-emulsion), repairs, etc.

Paving bitumen, formerly a by-product of oil refineries, has become thanks to the constant increase in road traffic a full-fledged standardized product, subjected to an increasingly precise regulation. We must however mention that to arrive here, significant research had to be carried out; such is the complexity of this material from its origin, as we shall see now.

2.2. Manufacture of bitumen

The production of bitumen can be schematized as below: a “crude bitumen” (i.e. rich in heavy fractions) or an in-line mixture containing this crude is sent to a distillation tower (also known as rectification tower) with atmospheric pressure. The distillation residue is then sent to another “vacuum” distillation tower (≈3 kPa). The residue of this second distillation can already be bitumen (called direct distillation bitumen or paving bitumen), or a soft base which yields a hard base after blowing (the sending of hot air which condenses light molecules with the elimination of water) or removing the bitumen (precipitation of the heavy fractions by pressurized liquid propane (propane precipitated bitumens)). *Semi-blown bitumens* are practically not used anymore for the manufacture of paving bitumens. The entire process is represented schematically in Figure 2.2.

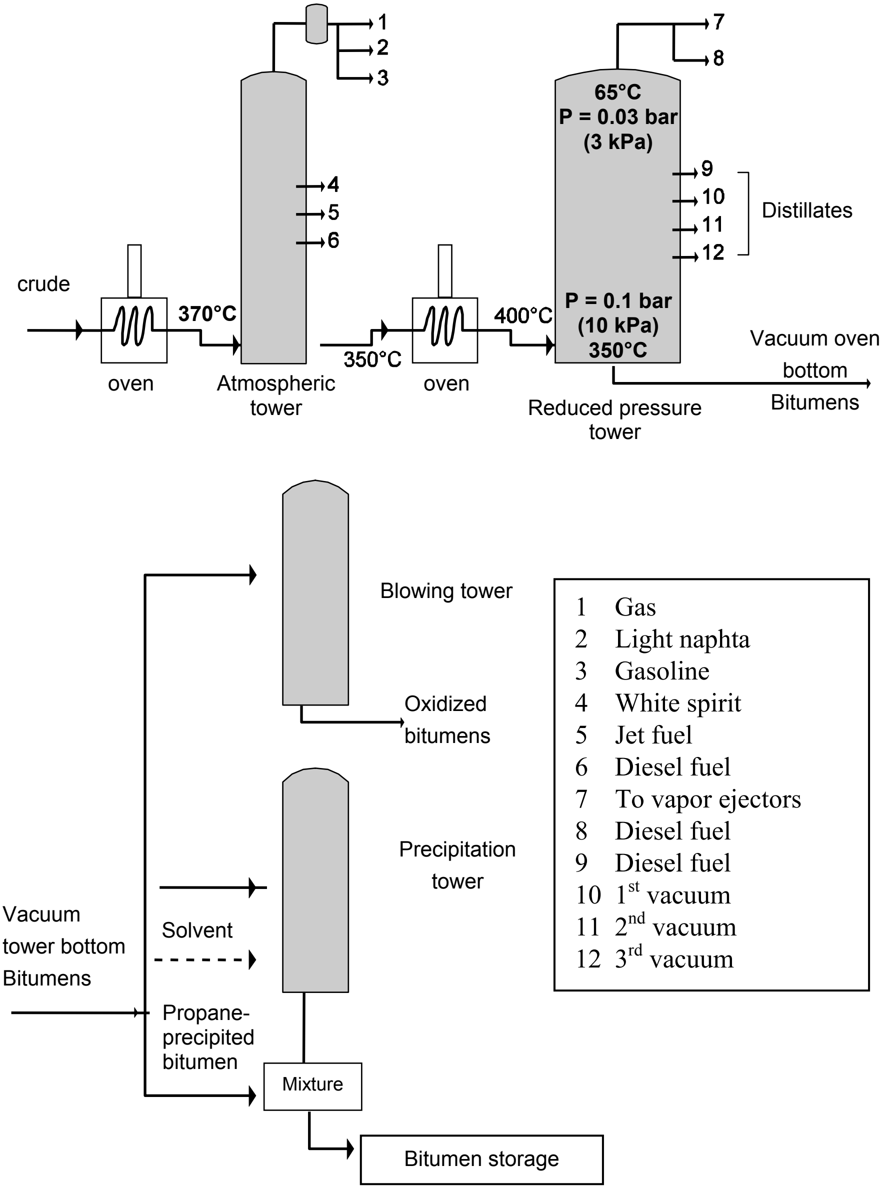


Figure 2.2. *Bitumen manufacturing (GPB documentation)*

2.3. Physico-chemical composition of bitumens

To study the usage properties of bitumen, the physicochemical approach has been practiced from the beginning by various researchers interested in the question. Many studies have been carried out on the subject and we can affirm today that we have a rather good knowledge of the relations between the chemical structure and the properties of these materials [BRU 86, RAM 00].

The flow chart for the manufacture of bitumens brings to light the extreme complexity of the finished product. It is perfectly illusory to envisage an exhaustive chemical analysis of this mixture, which can vary at the molecular scale from one sample to another, including on the same production line, although the product exhibits in general some constant properties. Eminent chemists have despite all odds embarked on the adventure, but with the idea to making significant groups, i.e. to propose a classification of the various components into physico-chemical families. We will mention in particular Corbett [HORN 69] who succeeded in defining “generic groups” according to SARA fractionation, thanks to techniques which will be developed with Chapter 5 (Figure 2.3).

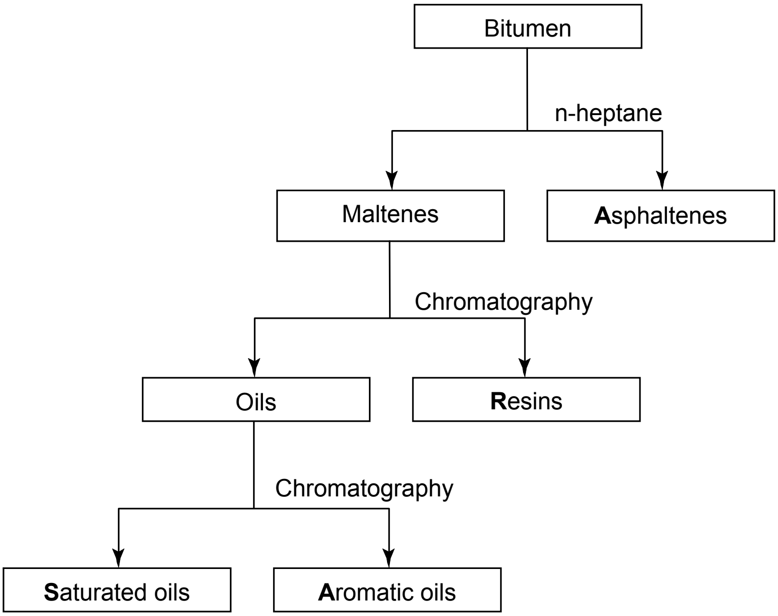


Figure 2.3. *SARA Fractionation diagram of bitumens*

Asphaltenes in the form of a solid mass, brown to black in color, with a molecular weight ranging between 800 and several tens of thousands $g.mol^{-1}$. Their structure (Figure 2.4) is marked by the presence of aromatic and saturated cycles (known as naphtenic-aromatic cycles) whose formation can be attributed to a process of pseudo-polymerization [BES 77].

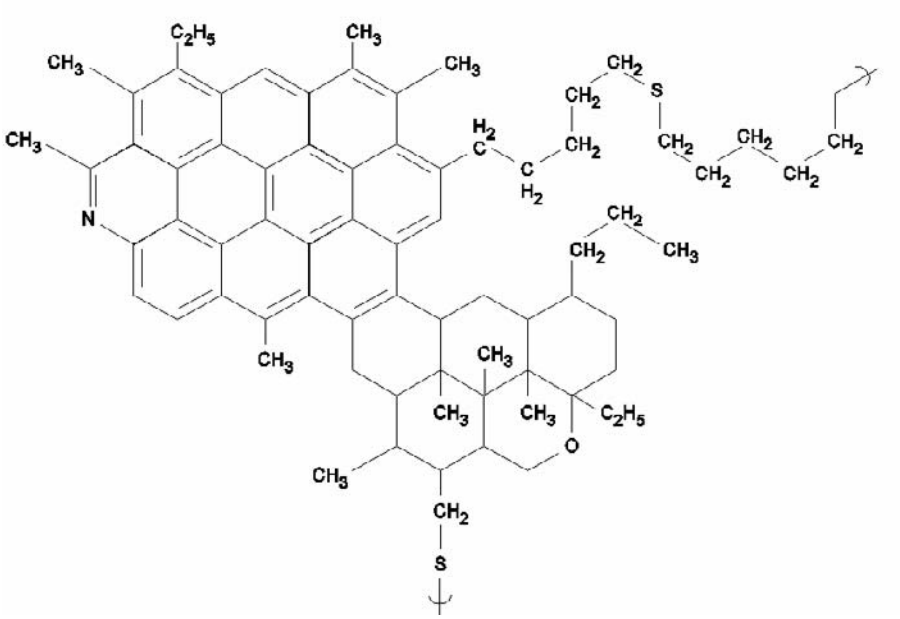


Figure 2.4. *Example of a hypothetical structure of asphaltenes (based on Yen [YEN 61])*

To clarify the role of maltenes, we must use the concept of the *colloidal structure* of bitumen. This interpretation has been consolidated by the study of the fractionation of maltenes by steric exclusion chromatography (also called gel permeation chromatography or GPC) according to an ultra-fast method [BRU 83]. Figure 2.5 shows that the bitumen is in the form of a system of agglomerates made up of micelles, which are themselves formed from asphaltene molecules peptized by the resins in the oily medium. In other words, the resins are adsorbed on the asphaltenes and allow their dispersion in the oily medium. If the asphaltenes are not peptized, they precipitate: this is called flocculation.

This interpretation explains in particular the great sensitivity of bituminous pavements to the discharge of organic solvents or mineral oils: the colloidal equilibrium of bitumen is locally destroyed irreversibly and the paving must be repaired.

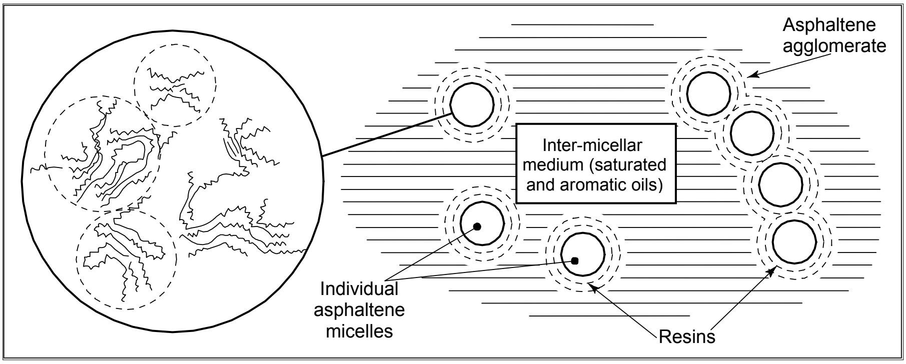


Figure 2.5. *Colloidal structure of bitumen*

By further developing this concept, we can define fundamental types of structures [KOL 73]:

– *the "gel" structure* which is characterized by the agglomeration of asphaltene micelles thus forming a continuous network in a slightly dispersing medium structured by resins. Bitumens having this structure are rich in asphaltenes. Their maltenes are poor in aromatic hydrocarbons. They exhibit an elastic behavior;

– *the "sol" structure* which is characterized by the total peptization of asphaltene micelles by the resins. The medium is in the form of a diluted and stable asphaltene solution in a strongly dispersing medium structured by the resins. The maltenes of the bitumens having this structure are rich in aromatic hydrocarbons. They exhibit a viscous behavior;

– *the "sol-gel" structure* which is intermediate between the two preceding structures and corresponds to the majority of bitumens. They are thus characterized by a viscoelastic behavior.

The stability of the bitumen in its environment largely depends on its micellar equilibrium. We have seen that the various types of structure bring into play the content of SARA fractions in the sample. The *colloidal instability index* I_C, based on these values, characterizes the type of bitumen studied according to formula [GAE 71]:

$$I_C = \frac{[\text{asphaltenes}] + [\text{saturated oils}]}{[\text{resins}] + [\text{aromatic oils}]}$$

where the terms between brackets represent the concentrations of the species considered. Thus, in a given oily medium, the greater the asphaltene content (in the case of the oxidized bitumens for instance), the more the bitumen is of gel type and the more unstable the structure is. This corresponds to a proportionally higher $\mathbf{I}_C$ value.

The thorough knowledge of the structure of bitumens has made great advances thanks to the development of specific chromatographic methods, which we shall now present briefly. They will be studied again and developed in their generality in Chapter 6.

Steric exclusion chromatography or GPC used in a traditional way, i.e. under optimal conditions such that the phases can always be considered as in equilibrium with one another, classifies the analyzed compounds according to their molecular size (according to their hydrodynamic volume). It thus gives an image of the composition of the medium, i.e. the description of the intermicellar phase on the one hand, of the dispersed phase (micelles and agglomerates) on the other hand; but the high dilution of the solution and the low rate of elution, which guarantee the equilibrium condition mentioned above, result in the almost complete dissociation of the structures. It is this observation that led to the idea of working outside the equilibrium, using a “fast” method and even an “ultra-fast” method.

Fast GPC highlights a bimodal distribution for asphaltenes, trimodal in the case of blown (or semi-blown) bitumens. The interaction between asphaltene micelles is hardly visible. It appears much more clearly when *ultra-fast GPC* is used. On the chromatogram, we can thus distinguish primarily three peaks: the molecules of the dispersing phase (which come out the last), the micelles which correspond to the dispersed phase with *sol* character, and finally the “interaction peak”, which comes out first and corresponds to the agglomerates, i.e. with the fraction of the dispersed phase, which gives the bitumen its *gel* character. The information drawn from this experiment must be compared with the rheological characteristics of the bitumen.

High performance liquid chromatography or *HPLC* perfectly complements the above method in the dispersing phase. Like it, it makes it possible to analyze the bitumen directly without precipitating the asphaltenes beforehand and separates saturated oils (eluted at dead volume), aromatic oils (detected by UV) and the resins (detected by inversion of the solvent flow) from one another.

Silica rod chromatography (IATROSCAN) is used to dose the fractions defined in SARA method: the asphaltenes are first separated by precipitation with N-heptane then the maltenes are analyzed by the apparatus. The resins do not migrate but oils are eluted by solvents of increasing polarity (n-pentane, toluene/chloroform 90/10 blend) and dosed by a flame ionization detector.

Despite its name, *simulated distillation* is in fact a gas chromatography applied to bitumens and derivatives. Modified according to the needs [WIT 91, MIG 92], it is based on the principle of the elution of the components of the sample in the order of their boiling temperatures. It thus makes it possible to:

– detect the presence of volatile fractions in a sample (commercial product, sample from a workshop following a disorder, etc.);

– analyze cut-back and fluxed bitumens;

– characterize regeneration binders;

– follow the evolution of binders during their aging.

All these methods allow a thorough and significant characterization of these complex materials [SUC 94]. We will see further below that other methods such as EES fluorescence are necessary when we study polymer-modified binders.

2.4. Various forms of bitumen

We have seen that bitumens can be processed in three ways: by plasticizing "pure" bitumen at high temperature (hot coating), by fluidification using suitable solvents or by emulsification. The last two processes are called cold techniques.

2.4.1. *Paving bitumens: characterization and classification*

When we admit that bitumen, although a finished product derived from the oil industry, cannot be qualified by the classic methods of characterization of chemical products, we must resort to physico-mechanical methods.

Thus, the classification of paving bitumens is still based on a *consistency* test whose origin is empirical. It follows the same reasoning as the Vicat needle test for the setting of cements: to appreciate the consistency or the hardness of the sample, the first thing that comes to mind is to press it with our fingers. For more accuracy, we inspect it with a needle.

The *determination of needle penetration* (EN 1426) is a measurement of the penetration, after 5 seconds, of a needle whose weight is 100 grams along with its support. The temperature must be rigorously controlled (and the sample stabilized at this temperature). The measurement is generally made at 25°C and is expressed in tenths of millimeter.

This test thus defines the various classes of paving bitumens (Table 2.2).

Classes	Primary uses
20/30	Sand asphalt
	High modulus grave-bitumen
35/50	Road base asphalt
	Asphalt concrete
	Porous asphalts
50/70	Grave-bitumen
	Asphalt concrete
70/100	Cut-back or fluxed bitumen manufacturing
	Bitumen emulsion preparation
160/220	Bitumen emulsion preparation

Table 2.2. *Classification of paving bitumens*

Among the other tests used for the characterization of the products, we must mention the determination of the *softening point by the Ring and Ball (R&BT) method* (EN 1427) which, along with penetration, informs us about the thermal susceptibility of the bitumen; in fact, this material does not have a clear-cut melting point – it is a blend – its consistency decreases when the temperature rises.

R&BT is the temperature for which a steel ball goes through a bitumen disk contained in a metal ring under standardized conditions, the temperature of the medium being increased by 5°C/min (the device is placed in a controlled temperature bath). It can be regarded as an isoconsistency temperature correspondent to a modulus of 0.01 MPa for a load time of 0.4 second or to a penetration of 800 tenths of millimeter.

The relevance and the validity of these tests will be studied in connection with the rheological properties of bitumen (section 2.7).

2.4.2. *Fluid binders*

Figure 2.2 showed the various ways of obtaining bitumen. Based on this, in addition to raw bitumen, we can formulate solutions – cut-back or fluxed bitumen together called fluid binders – and emulsions.

Cut-backs are formed from raw bitumen by adding an oil cut like kerosene. Their classification is still done using a consistency or rather pseudo-viscosity test, by a *flow time*, which resembles a measurement of kinematic viscosity, though it is not one strictly. They are used primarily for the development of surface dressings and minor repairs. The strong volatility of the solvent makes its quick evaporation after application easier, which is valuable for repair in service but requires much care.

Fluxed bitumen are formed from raw bitumen by adding a relatively heavy oil compared to the cut-backs and extracted, either from coal or from crude oil. They are characterized just like cut-backs by their pseudo-viscosity. The low volatility of the flux allows a slow stabilization of the granular mixture before its hardening consecutive to the departure of the solvent. Moreover, a part of this addition remains in the binder and gives it particular characteristics, especially in its adhesiveness.

In addition, it may be observed that if the viscosity of the binder is lower for cut-back than for fluxed bitumens, the same is true for their cohesion and their adhesiveness in general.

Lastly, we should not forget that when we use fluid binders, it is preferable to do so at the start of the season, precisely to allow the volatile parts to evaporate, rather than in autumn when disappointments may be in store ...

These recommendations are however just a formality insofar as the future of fluid binders has been strongly called in question by changes in the legislation concerning the use and discharges of organic solvents. If this does not have very serious consequences on cut-backs whose emulsion is an advantageous alternative, this is not the case with fluxed bitumens where replacement techniques based on “bio” emulsions or fluxes, are yet to prove themselves, particularly for taking into account of the maturing period which gives the mixture its stability and its particular qualities. But it is certain that new processes will be developed to fill this gap.

2.4.3. *Bitumen emulsions*

An emulsion is an intimate dispersion of two non-miscible liquids in one another, generally prepared in the presence of a surface-active agent called emulsifier. It thus comprises two phases: the dispersed phase in microscopic globules and the dispersing phase.

We can distinguish two types of emulsions: direct emulsions or “oil in water” and inverse emulsions or “water in oil”. Bitumen emulsions belong to the first category and, when by misfortune they are reversed for too long a time in a road construction site, the result is appalling – we will find bitumen everywhere, sometimes even on the walls of the surrounding houses!

2.4.3.1. *Formation of an emulsion*

In the art of cooking, it is well known that if we shake a bottle containing of oil and vinegar, we obtain an emulsion, but the two phases quickly separate and superimpose over one another. We say that this emulsion is unstable.

This example illustrates the principle that the internal energy of a liquid is minimal when its interface with the surrounding medium is minimal. That is why rainwater falls in the form of drops and emulsion globules are spherical. But it is also why, in the absence of other phenomena, the above dispersion of oil in vinegar tends to settle in two superimposed phases because the total surface of the globules is markedly higher than the interface between oil and vinegar after decantation.

In fact, in the formation of an emulsion, the system requires:

– a dispersion energy: this is the role of the emulsifying turbine creating contact between the phases by the laminating of two films;

– an emulsifier to ensure the stability of the globules formed.

How can we stabilize an emulsion? The simplest method consists of using bodies capable of creating repulsive electric charges on the surface of the globules. This is the role of emulsifiers, which are hypotensive surface-active agents, i.e. capable, at very low concentrations, of considerably lowering the interfacial tension between the bitumen and water.

Their molecular structure is amphiphilic or polar-non-polar, i.e. they are made up of a highly elongated molecule, comprising a hydrophilic end (thus polar in character and ionizable in water) and a hydrophobic or lipophilic chain (thus non-polar in nature and exhibiting strong affinity for the bitumen). Their effectiveness and their field of application depend on the equilibrium between these two effects, which is called hydrophilic-lipophilic balances (HLB) and which depends on the structure of the molecule.

The emulsifier can be of two types: anionic if it leads to negatively charged particles or cationic if it leads to positively charged particles. Today's bitumen emulsions are mostly cationic.

For cationic emulsifiers, the molecule type can be schematized by $R–NH_2$ where R corresponds to an aliphatic chain, therefore non-polar and lipophilic. It is an amine called fatty because of the aliphatic chain (also called fatty chain). The radical $–NH_2$ is not in itself hydrophilic but, if we salify the amine beforehand by a strong acid, usually hydrochloric acid, this radical becomes $–NH_3^+$ which is highly polar and hydrophilic. This is a cation strictly speaking.

The emulsion is in the form of a set of globules surrounded by a double layer of electrolytes, which serves as a screen with respect to the other globules and which prevents coagulation (Figure 2.6).

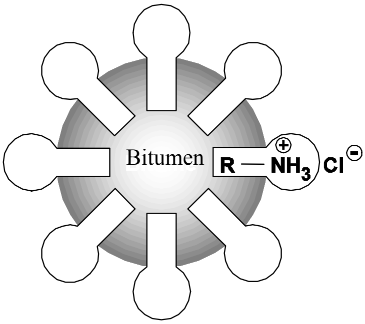


Figure 2.6. *Cationic emulsion globule*

2.4.3.2. *Failure of emulsions*

This phenomenon occurs in the presence of the aggregates. Two mechanisms can come into play: evaporation and a chemical reaction.

Evaporation occurs when, after the emulsion is spread, the surface to be covered is sufficiently large for the water to evaporate. We must mention that concentrated emulsions are spread at about 60-80°C. This is the main process in the failure of anionic emulsions. It has the big disadvantage of not automatically giving adhesiveness to the aggregate if this aggregate does not have any affinity for the binder, which is generally the case. This explains the unpopularity of anionic emulsions in France, except in the sunny Mediterranean region.

Cationic emulsions also give rise to a real reaction between the emulsifier and the mineral. This is a rather complex mechanism, which is based on chemical nature of the emulsifier, the granularity of the emulsion and the surface properties of the aggregates (cleanliness, surface electric charges, mineralogical nature). Here, the failure is brutal, very fast, and provides good adhesiveness. Emulsifiers for cationic emulsions also include products used as adhesive dopes.

It has been observed in workshops [LOM 03] that during the failure of an emulsion, the system imperceptibly goes through a phase of the water-in-oil emulsion: the binder is black, mat, without cohesion and it resembles wax. It then contains approximately 3% of water. The lifespan of this phase must be the shortest possible – and this is very generally the case – if not, it is a disaster ...

2.4.3.3. *Characterization of emulsions: applications*

The principal characteristics of an emulsion are:

– its concentration, which is measured by its complement, its *water content*; the test used to measure it consists of heating a sample in the presence of a bitumen solvent which carries away the water by azeotropy and by measuring the volume of water collected, whereas the bitumen remains in the recipient with the solvent;

– its *pseudo-viscosity*, measured using conventional apparatuses similar to those used for cut-back or fluxed bitumens; this characteristic is important for the proper functioning of spraybars;

– its *storage stability*, of obvious interest, but which sometimes conflicts with the requirement for a good failure rate;

– its *granularity* because the shape of the curve obtained informs us in particular about the stability and viscosity of the emulsion;

– its *failure rate,* which is indirectly given by a "failure index", the weight of siliceous filler necessary for the complete coagulation of a known quantity of emulsion;

– *adhesiveness* of the residual bitumen on various aggregates.

The applications of the emulsions classified based on the desired failure rates are summarized in Table 2.3.

Type of emulsion	**Applications**
Fast failure	Spreading
Semi-fast or slow failure	Penetration Precoating Pretreatment of aggregates Coating of materials containing little filler
Slow failure (stabilized)	Gravel emulsion Cold dense coating Impregnation

Table 2.3. *Applications of bitumen emulsions*

2.5. Usage properties of paving bitumen

Organic binders are used primarily for their adhesive properties in the broad sense of the term i.e. they must exhibit both good properties of physico-chemical *adhesion* on the support meant for them and specific *cohesion*. The traditional peeling test (also called pull-off test) can be easily transposed to the case of bitumen. In fact, let us try to extract an aggregate from a coating that has just been made. If the failure occurs in the interface, the adhesion is regarded as defective and this is called adhesion failure. If on the contrary the failure occurs in the bitumen, it is the cohesion of the bitumen that is blamed and we call this cohesion failure (Figure 2.7).

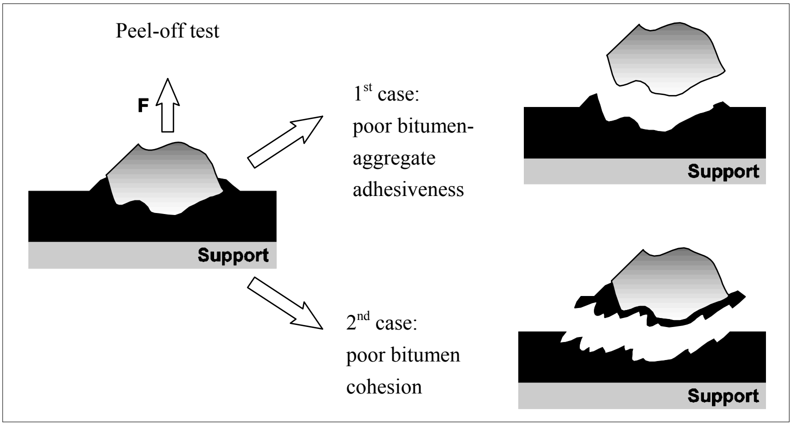


Figure 2.7. *Adhesion failure and cohesion failure*

The adhesion theories will be developed in Chapter 4, which deals more with adhesion bonding or gluing. We will see that this involves the wetting of the support by the binder. In the case of the coating of aggregates with the bitumen, the problem generally becomes complicated by the presence of water and the competition between the two liquids to cover the solid surface. This is the problem of *adhesiveness*. As for the specific cohesion of bitumen, we will see that it falls under the more general study of its *rheological properties,* which constitute the essential contribution of research on this material over the last 20 years.

2.6. Adhesiveness

The existence and maintenance of a contact bond between the bitumen and the aggregate suppose firstly that both the materials have been actually placed in contact and then that they preserve this contact. In this context, we must distinguish:

– coating, when we place the partners together and want to wet the aggregate with the bitumen; if the setting is done at high temperature (hot coating) on clean aggregates (and automatically dry), the fixing is generally done well, even if the aggregate and the binder do not have any particular affinity for one another; on the other hand, with fluid binders used in cold techniques, there can be competition between the binder and the water present on the aggregates and the success of the coating will depend on the *active adhesiveness* of the binder for the aggregates in question;

– stripping, when the coating in place undergoes the aggressions of water; this is called the *passive adhesiveness* of the binder for the aggregates of the coating.

In the above reasoning, we consider bitumen as a liquid. This reflects well the reality of the coating done at high temperature with paving bitumens or at ordinary temperatures with cut-back or fluxed bitumens. For stripping problems, we can however note that the actual consistency of the binder in place is generally a favorable advantage.

The concept of adhesiveness implicitly refers to the phenomenon of wetting, which will be developed in Chapter 5 in connection with the theory of adhesiveness (section 5.1.3.2). Figure 5.2 can be transposed as follows (Figure 2.8) where the values in question are:

γ_{GW}: aggregate-water interfacial tension

γ_{BW}: binder-water interfacial tension

γ_{GB}: binder-aggregate interfacial tension

α: wetting angle

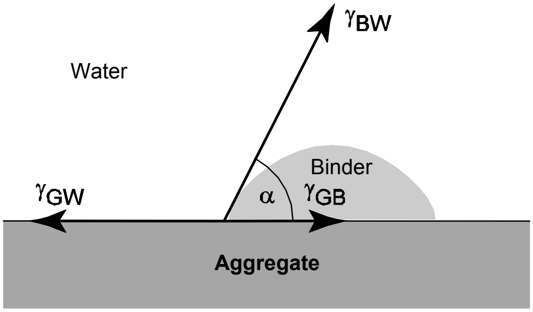


Figure 2.8. *Wetting of an aggregate by a fluid binder in the presence of water*

The equilibrium is expressed as:

$$\gamma_{GW} = \gamma_{BW} \cos \alpha + \gamma_{GB}$$

or:

$$\cos \alpha = \frac{\gamma_{GW} - \gamma_{GB}}{\gamma_{BW}}$$

To ensure the proper spreading of the bitumen, the angle α must be acute and therefore its cosine must be positive and tending as much as possible towards 1. This condition is generally not met as aggregates have greater affinity for water, which is a liquid with high polarity, than for bitumen. So the interfacial tension between the aggregate and water γ_{GE} is weak, the cosine is negative and the wetting angle is obtuse.

Experience corroborates the fact that the coating of a wet aggregate by fluid bitumen as such is impossible.

To solve this problem, we must significantly lower the interfacial tension between the aggregate and the binder. For this, we use surface-active agents called *adhesive dopes,* which are not very different from the emulsifiers described in connection with emulsions.

Dopes are primarily used in the following applications:

– doping in mass (coating and surface dressing);

– doping at the interface (surface dressing);

– pre-treatment of aggregates.

Moreover, in this representation, we have considered the phenomena at equilibrium. This is obviously a first approximation because coating as well as stripping is primarily dynamic. Let us consider the profile of a drop coming down an inclined plan. We note the dissymmetry between wetting in front of and behind the drop. We thus define the advancing angle and the receding angle (Figure 2.9). This phenomenon, which highlights the dynamic character of wetting, is sometimes called wetting hysteresis.

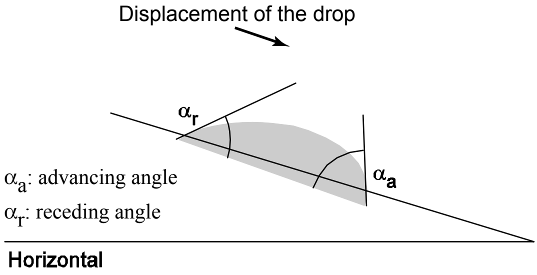


Figure 2.9. *Wetting hysteresis. Geometric manifestation*

The amplitude of this phenomenon, which is expressed here in the difference between the advancing and receding angles, depends primarily on the wetting rate, and therefore also on the viscosity of the liquid and the roughness of the support. As regards its applications in road engineering, we can say that it has practically no importance for hot mixing techniques in view of the setting conditions, and that it is even favorable for stripping because it then acts as a retarder with respect to the action of water given the high viscosity values of the binder at service temperatures. On the other hand, it is commonly used in cold mixing techniques where water is practically omnipresent.

Physically, hysteresis can be translated by the response of a tensiometer to which is attached a sample of the studied material immersed in and withdrawn from a container containing the liquid (Figure 2.10 based on [RAM 77]).

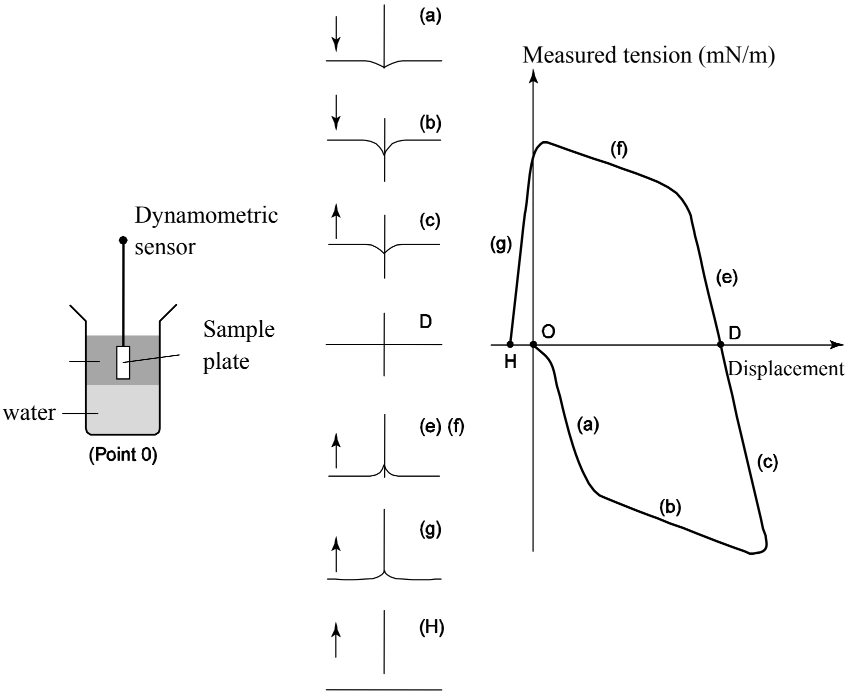


Figure 2.10. *Wetting hysteresis. Thermodynamic manifestation (the slopes of the segments (b) and (f) are due to Archimedes thrust)*

2.7. Rheological properties

The term “rheology” etymologically means the science of flows. Dealing primarily with viscous liquids, this discipline has gradually extended to all materials and sets of materials capable of exhibiting creep, from glaze putty that we mix with our fingers to the walls of Gothic cathedrals that have often acquired odd forms in the course of time, the difference between the two examples being only the time taken by the two sets of materials to become deformed.

In current usage, we directly associate the concept of rheology with the laws of the mechanical behavior of the materials or sets of materials considered.

The complexity of the composition of bitumens explains why they do not show a clear-cut transformation between the conventional solid state and liquid state. Rheological study therefore becomes a privileged means to characterize their cohesion depending on temperature, load time and the stresses applied.

2.7.1. *Viscosity*

The variable directly related to the rheology of a liquid material is *viscosity*. For a material that passes from the liquid state to various solid states in a complex manner, we have long understood this variable using empirical tests called *consistency* tests. Starting from low temperatures, we use:

– in the brittle elastic domain: *Fraass point*. The Fraass breaking point is determined using a specific apparatus in which a binder film of a thickness of 0.5 mm, deposited on a flexible steel strip, cracks when we fold this strip under defined conditions. We then carry out successive flexions, the temperature being decreased by 1°C/min. It is often believed that paving bitumens have, at the Fraass breaking point, a modulus of 100 MPa and a penetration at 25°C of 1.25 tenths of mm;

– in the viscoelastic domain: *penetration* (see section 2.4);

– at the start of the fluid domain: softening Ring and Ball Temperature (R&BT) (see section 2.4);

– in the fluid domain: *flow time* on the cut, considered as a pseudo-viscosity easy to measure or true *viscosity*.

We must say that the efforts towards the standardization of test standards made currently by the international community tend towards the return to fundamental variables. Viscosity is one of them but can be defined in two different ways:

– *Dynamic viscosity* η, ratio between the shear stress (F/S) and the shear rate (v/e) is given by the formula:

$$\frac{F}{S} = \eta \frac{v}{e}$$

where “v” is the linear flow rate and “e” is the thickness of the sheared layer.

It is measured using parallel plane (plan/plan mode), coaxial cylinder (annular shearing) or cone-plate rheometers or viscometers. It is expressed in Pa.s (old unit: poise; one centipoise is equal to one millipascal.second).

The measurements are performed in dynamic state as we will see about complex modulus or in laminar and permanent state.

– *Kinematic viscosity* ν, ratio between dynamic viscosity and density, is given by:

$$\nu = \frac{\eta}{\mu}$$

and is obtained using capillary viscosimeters where the variable measured is the flow time between two reference points. It is expressed in $m^2.s^{-1}$ (old unit: stokes; one centistokes is equal to one square millimeter per second).

2.7.2. *Viscoelasticity*

Based on these data, we can characterize *gel* bitumens and *sol* bitumens defined previously (section 2.3) and develop the concept of thermal susceptibility (Figure 2.11).

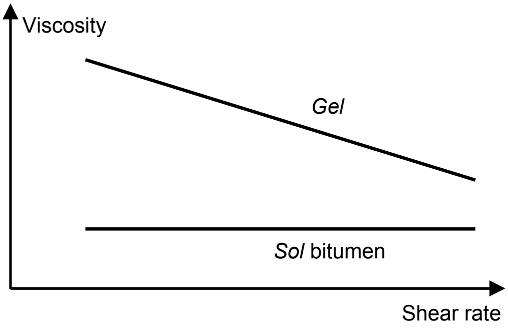


Figure 2.11. *Viscosity of sol and gel bitumens depending on the shear rate*

Bitumens are usually of *sol-gel* type. They exhibit a marked viscoelastic character. This property results in particular in the fact that for short load times, bitumen behaves like an elastic body and as the time of application of the stress is prolonged, it tends towards a viscous behavior by passing through a transition zone.

Bitumens are differentiated from one another by their viscous component and the transition zone. These two properties are in direct relation to the consistency of the bitumen and its thermal susceptibility (variation of the bitumen's viscosity according to temperature).

It can thus be observed that on roads, during fast traffic, the bituminous asphalts and bituminous coatings exhibit an elastic behavior. That is why this assumption is taken into account in most methods used to design pavements. Conversely, under prolonged stress that can result in a compaction of the supporting soil, bituminous materials exhibit a viscous behavior enabling them to follow its deformations without cracking.

This property is particularly appreciated for the construction of pavements with light structure. In areas of slow and channeled traffic or in parking areas that give rise to prolonged stress, it is advisable to choose the formulation judiciously in view of limiting the viscous character of the material and avoiding permanent deformations.

The stiffness modulus, generally denoted by S, ratio of the applied stress σ and the induced strain ε, characterizes this type of behavior: constant according to the load time for an ideal elastic solid material, linear in log-log co-ordinates for an essentially viscous body, it is in the form of a beam of curves where we find an elastic character for a short-term load application and at low temperatures and a viscous character under sustained loading and at high temperatures (Figure 2.12).

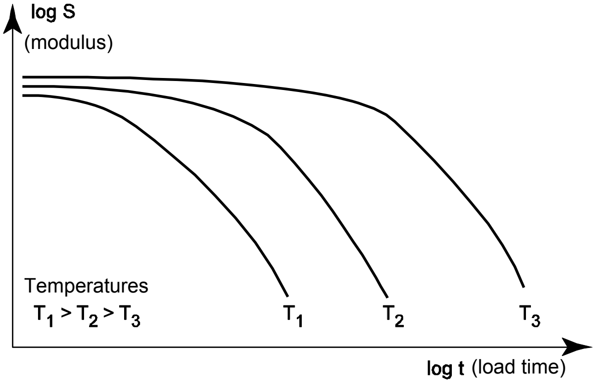


Figure 2.12. *Modulus of stiffness of bitumens*

To take into account all these data, we use more generally the concept of *complex modulus*.

2.7.3. *Complex modulus*

The study of the rheological behavior of pure bitumens is generally carried out using rheometers, which apply to the material a sinusoidal stress, under traction-compression or shear.

The response of the apparatus reveals a delay between the viscous deformation observed and the load application. The phase difference measured is called delay angle or loss angle φ. It appears in the definition of the complex modulus of stiffness S*:

$$S^* = \frac{\sigma}{\varepsilon} e^{i\varphi} = S^\circ e^{i\varphi}$$

where we come across S°, norm of the complex modulus, which effectively characterizes the stiffness.

In general, we denote the complex modulus by E^*:

$$E^* = E' + i\,E''$$

The real part E' is called *elastic* or *conservation modulus* because it corresponds to the part of the energy stored in the bitumen and likely to be restored at the end of the loading. The imaginary part E" is called *loss modulus* because it reflects the dissipation of energy by internal friction (entropic component of the system).

We also use the loss angle φ defined by its tangent, ratio of the above two modulii:

$$\tan \varphi = \frac{E''}{E'}$$

Thus, for a purely elastic body, φ = 0 and E" = 0, whereas for a purely viscous, Newtonian body, φ = π/2 and E' = 0.

This parameter is important because for φ = π/4 (or 45°), it separates the viscous domain from the elastic domain: below π/4 we are in the predominantly elastic domain. We can thus see that a material, which at 60°C has an angle φ < π/4, therefore exhibits an essentially elastic behavior, predicts greater elasticity and therefore greater brittleness at lower temperatures (which results in a tendency to crack) because it evolves in the same direction as the temperature.

If the measurement is performed under shear, we can define likewise the complex shearing modulus G* which, for an isotropic and incompressible body, is equal to the third of the tensile modulus:

$$E^* = 3\,G^*$$

The results are used to trace the isotherms of the modulus, modulus norm according to the frequency, from which it is possible to establish the *master curve*, directly and in the same coordinate system, in the same manner as for polymers (see section 1.8.6. and Figure 1.13) and to transpose it to a Black diagram (loss angle according to the modulus norm) or a Cole-Cole diagram (loss modulus G" according to the elastic modulus G').

All these results enable us to truly know the mechanical behavior of the binder in the temperature range considered, on the fundamental plane.

2.7.4. *Towards a rheological classification*

From a practical point of view, we understand the viscoelastic character of bitumen by its *thermal susceptibility*, i.e. the variation of its consistency with temperature. By measuring penetration at various temperatures, we note that the points are aligned in logarithmic co-ordinates according to:

$$\log_{10} \mathrm{Pen}_T = A\,T + B$$

Using this *penetration line,* it is possible to determine “A”, which is effectively the thermal susceptibility.

Besides, we define the *penetration index* (*PI*) using the formula:

$$\frac{d(\log_{10} Pen_T)}{dT} = \frac{1}{50}\frac{20 - PI}{10 + PI}$$

which becomes, if we have determined the thermal susceptibility “A”:

$$PI = \frac{20 - 500A}{1 + 50A}$$

The determination of the coefficient A differs according to the various schools. Thus LCPC method consists of effectively measuring the penetration at five temperatures (to verify the linearity of the distribution) and determining “A” using a linear regression. The Pfeiffer and Van Dormaal method uses penetration at 25°C and the Ring and Ball softening Point by estimating at 800 the penetration of the bitumen at this temperature.

PI is used to classify bitumens into three categories:

– *very susceptible*, with a highly negative PI (< -2);

– *moderately susceptible*, with a very low PI (close to 0); this category contains most direct distillation bitumens;

– *relatively unsusceptible*, with a markedly positive PI; this category includes blown bitumens, which however remain a school case (see section 2.12) and multigrade bitumens (see section 2.10.4).

The domain of significance of the PI does not however cover all the usage properties of bitumens, in particular at low temperatures.

We have seen that the brittleness of bitumen at low temperatures is characterized by the Fraass breaking point. We saw that at this temperature the maximum deformation undergone by the bitumen before failure was 1.64%. Further, it is generally admitted that at this temperature, paving bitumens have a modulus of 100 MPa and a penetration of 1.25 tenths of millimeter.

With high temperatures, i.e. above the Ring and Ball softening Point (R&BT), the fluid domain can be characterized by measurements of viscosity. Among the formulas suggested to describe the influence of temperature on viscosity, we have the Williams, Landel and Ferry formula (WLF) already discussed in connection with polymers and which can be written as below:

$$\log_{10}\frac{\eta(\mathrm{Ts})}{\eta(\mathrm{T})}=\frac{-\mathrm{C}_1(\mathrm{T}-\mathrm{Ts})}{\mathrm{C}_2+(\mathrm{T}-\mathrm{Ts})}=\log_{10}\mathrm{a}(\mathrm{T})$$

where Ts is the reference temperature, $\eta(\mathrm{T})$ is the dynamic viscosity at temperature T, C_1 and C_2 are constants related to the choice of Ts, and $\log_{10}$ a(T) is the *shift factor*.

For a polymer, we generally choose Ts in such a manner that the constants C1 and C2 have the conventional reference values, i.e. C1 = 8.86 and C2 = 101.6 K. This temperature is close to the glass transition temperature Tg of the polymer in question. For the bitumen, we will take for Ts a temperature close to its R&BT. This does not however mean that we must regard the softening marked by R&BT as a glass transition. The nature of bitumen is very different from that of a polymer. Likewise, the fact that it is possible to measure by DSC a glass transition temperature that is close to -20°C, i.e. not very far away from the Fraass Point, does not mean that the latter is an approximate measurement of a transition.

The existence of the two functions connecting penetration and viscosity to temperature (penetration line and WLF equation) led Heukelom [HEU 75] to design a scale diagram connecting the two domains by assuming that the R&BT

corresponds to the temperature giving a penetration of 800 tenths of mm (Figure 2.13) and on which we can plot the Fraass Point for a penetration of 1.25 tenths of mm.

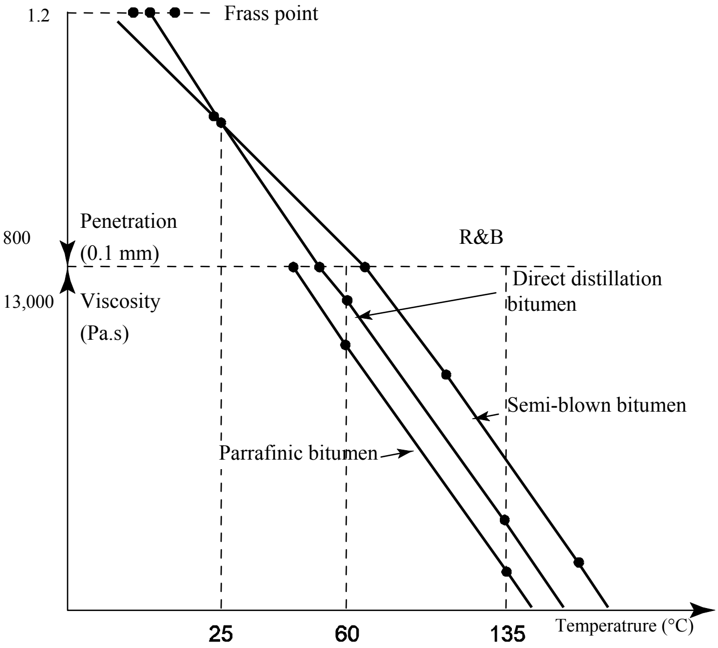


Figure 2.13. *Heukelom diagram of 3 types of bitumen*

Using this diagram, we can classify bitumens into three categories, which tallies rather well will those defined by the PI values:

– class D bitumens: all the direct distillation bitumens are represented by a line;

– class S bitumens: semi-blown bitumens present a diagram in two half-lines; at high temperatures, they behave like D bitumens with the same penetration; at low temperatures, they show a less susceptibility (positive PI);

– class P bitumens, i.e. paraffinic: they are represented by two appreciably parallel line segments whose connection brings into play the change of status of the paraffin.

This diagram is interesting insofar as it brings together vital information on the usage properties of the material in a simple manner.

We can thus combine in a single diagram the results of the various types of conventional tests used to characterize paving bitumen (Figure 2.14).

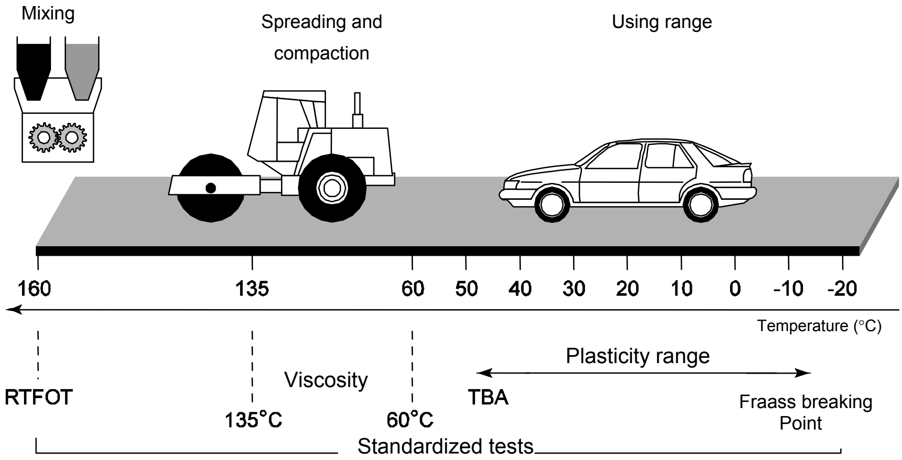


Figure 2.14. *Meaning of physical measurements*

This system (which also brings to light RTFOT, which will be clarified in connection with the aging of bitumens) has been extremely useful but has been insufficient to characterize the behavior of binders when, to meet the requirements arising from the increase in heavy traffic, manufacturers developed the use of increasingly hard bitumens. As a result, new cases of cracking in the surface courses appeared – this new type of deterioration was called *top-down cracking* – which could be attributed to thermal fatigue due to the temperature cycles undergone by the mixes or possibly to their behavior at very low temperatures.

However, if it is possible to establish correlations between the behavior of the bituminous concrete and certain characteristics of the binder used in the domain of high temperatures, this is not the case at low temperatures where Fraass point, for example, has never been sufficient to develop really satisfactory correlations. It has always been called into question for its poor reproducibility. It was therefore necessary to find a new test to overcome this obstacle.

It was then that the research carried out at the Institute of Transport of Pennsylvania within the framework of the SHRP (Strategic Highway Research Program) succeeded, for the study of the behavior of binders at low temperature, in recommending two new tests:

– a flexural creep test, using a specific equipment, the bending beam rheometer or BBR [BAH 92];

– a direct tensile test on dumb-bell shaped bitumen sample.

Before dealing with the BBR creep test and developing their contributions to the rheological knowledge of bitumens, it can be interesting to discuss the American SHRP method.

2.7.5. *The SHRP program – test methods and specifications of road binders*

In the face of serious problems arising from the deterioration of road pavements, the American administration launched in the beginning of the 1990s a large-scale research program – the SHRP – which in particular completely called into question the specifications on binders. The specifications proposed are primarily performance-oriented whereas the previous ones were mainly based on intrinsic characteristics, whether physicochemical or physicomechanical. They are based on a new set of tests, denoted by the term *Superpave*^{TM} [AND 94].

We must note that "binder" was primarily understood as "paving bitumen". Experience has indeed shown that modified bitumens deserve a few particular considerations before conforming to these proposed specifications.

The study leading to the choice of the variables to be measured brought to the foreground the rheological behavior of the binder because it reflects the need for the desired performances according to temperature and load time, in the operating ranges of the material. The method is based on four specific apparatuses:

– *viscosity* thus comes first with the choice of the *Brookfield viscometer,* which characterizes Newtonian fluids well and consequently bitumen at the mixing and compaction temperatures;

– for *behavior at low temperatures*, in particular those where the modulus of the binder exceeds 300 MPa, a specific apparatus was developed, viz. *bending beam rheometer or BBR*, which we mentioned above and which will described further below. It helps determine the modulus of stiffness directly at various temperatures and the susceptibility of the binder to load times;

– besides, the entire behavior of the *binder in the service temperature range* is well described by the law of variation of its shear modulus G*. For this purpose, we use a dynamic shear rheometer functioning between parallel plates;

– finally *aged binders* can exhibit their decrease in performances by a significant decrease of their resistance under *direct traction* and their evolution from a fragile rupture fracture to a ductile rupture.

In addition to these tests, two methods for the simulation of aging help formulate specific “aged binders” in sufficient quantity to be subjected to certain tests envisaged on “new” binders for the purpose of comparison. We will investigate them within the framework of the aging of bitumen further below (section 2.10).

The tests developed within the SHRP framework are taken into account in a rather complex specifications program, which involves a division into geographical or rather climatological zones. The comparison of this system with European specifications shows that [RAM 00]:

– the American specifications are in general stricter, in particular with respect to the evolution of bitumen during the mixing and more complete as they take into account *in situ* aging;

– the French specifications are generally satisfactory but must be completed;

– the European specifications can appear, in their current version, a little lax.

2.7.6. *Bending beam creep or BBR test*

Among the tests proposed by the SHRP program, we saw that the study of the creep of a bitumen beam at low temperatures (BBR test) was of great interest insofar as it seemed to fill a gap in the knowledge of the material’s rheology. The French scientific and technical community entrusted the Laboratoire Régional des Ponts et Chaussées of Aix-en-Provence with the task of transposing this test, specifying the operating procedure and determining its potential scope in the corpus of European standards in force or under harmonization. Among the results of this study which called for important research, [MIG 96], we will mention the following results.

The BBR test studies the deformation of a bitumen beam subject to a constant force applied for 240 seconds in its medium (Figure 2.15).

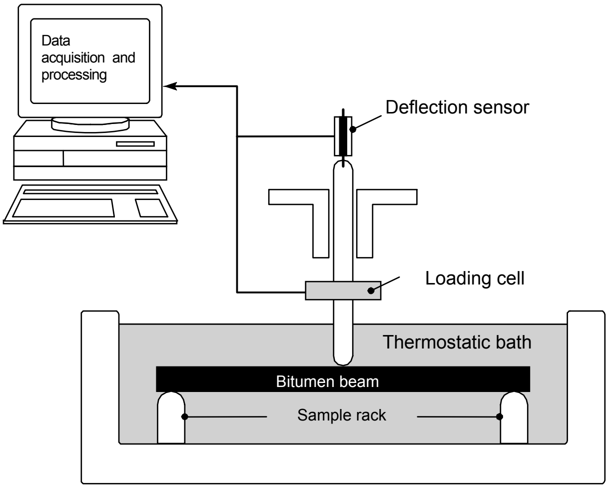


Figure 2.15. *Bending beam creep test – BBR. Equipment*

The expected results are:

– the *slope* ***m*** *of the creep curve*, i.e. the evolution of the bending or stiffness modulus S according to time, therefore the *susceptibility of bitumen to the load time* plotted in bilogarithmic coordinates (Figure 2.16); the characteristic value of m is the *load time of 60 seconds*;

– the *isomodulus temperature*, i.e. for which the bending modulus is equal to 300 MPa.

According to the specifications formulated by SHRP in the domain of low temperatures:

– at a temperature greater than 10°C at the minimal temperature likely to be reached by the pavement (hence the division into climatic zones), the stiffness modulus of the binder characterized by the BBR must be less than 300 MPa and m greater than 0.300;

– if the modulus is greater than 300 MPa but less than 600 MPa, the elongation at break measured by the tensile test must be greater than 1%.

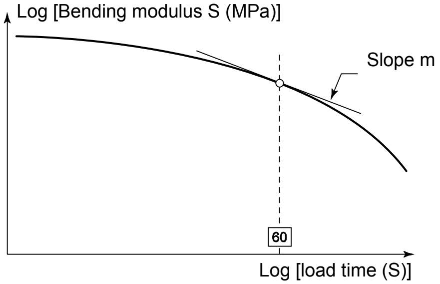


Figure 2.16. *Creep curve in BBR*

This approach is definitely advantageous and that is why the research in view of appropriating this test was undertaken. Among the results, we can mention in particular:

– a relatively good correlation between the isomodulus temperature 300 MPa and the Fraass Point (linear regression coefficient r = 0.911; T in °C):

$$T_{\text{Fraass}} = 1.38\ T_{\text{iso}} + 10.49$$

– a tendency of common evolution between this isomodulus temperature 300 MPa and the R&BT (linear regression coefficient r = 0.709), but not exactly a correlation.

However, in the SHRP, the test is performed at only one temperature according to the bitumen class and climatic conditions. This last parameter was not taken into account in France where it does not have the same importance as in the United States of America. It transpired that the most significant factor was the *susceptibility* measured by *m* and this resulted in choosing the following method.

The test is carried out at three temperatures, which allows us to make a linear regression and to calculate the values of the isomodulus temperature T(300 MPa) and susceptibility m. From this, we could deduce the *isosusceptibility temperature* T(m = 0.300), which seemed the most representative critical value after aging. In practice, if $m < 0.300$ it is this value that is taken into account, if not (if $m > 0.300$), we refer to the isomodulus temperature.

Additionally, we must point out that the problem of the top-down cracking of the bituminous concretes has given rise to a full-scale experimental study on various sites [GNB 99] and to a laboratory study on the cold behavior of hard bitumens [MAR 00] which confirm the results of the above study.

2.8. Aging of bitumen

Paving bitumen is used mainly to manufacture hot coatings. When it comes to studying its aging, we observe that the physicochemical evolution of the material comprises two distinct phases: *mixing aging,* which is its abrupt change following the thermal shock that it undergoes as a thin film in contact with hot aggregate, in the presence of atmospheric oxygen, and the *on-road aging* which is related to the aging of materials *in situ*. The former is fast and brutal, the latter occurs gradually.

To try to understand the phenomena brought into play in these two phases, we must start by defining what we normally mean by the aging of bitumens. We can indeed distinguish:

– *physical aging*, which results in an increase in the binder's viscosity without modification in the components but with changes in the colloidal equilibrium of the bitumen; this can be highlighted particularly by the evolution of chromatograms obtained by fast GPC;

– *chemical aging*, much more significant and much more complex, which corresponds to oxidation, cyclization and aromatization reactions; this is manifested particularly in infrared spectra with the appearance or reinforcement of carbonyl, sulfoxide or aromatic bands [PET 86].

Mixing aging, also called *hardening*, brings into play both types of aging but particularly its chemical aspect: the bitumen distributed as a thin film on aggregates heated at 160-170°C in the presence of air is under the best conditions to react chemically with oxygen and to carry out internal reactions impossible at service temperatures.

This compulsory stage in the technology of hot mixing has given rise to many simulation studies that have led to the development of a standardized method known as the Rolling Thin Film Oven Test, “RTFOT” [PET 89]. This test seeks to measure the combined effects of heat and air on a thin moving film of bituminous binder. For this, a small quantity of bitumen is placed in a rolling container in an oven so as to form a thin film (Figure 2.17).

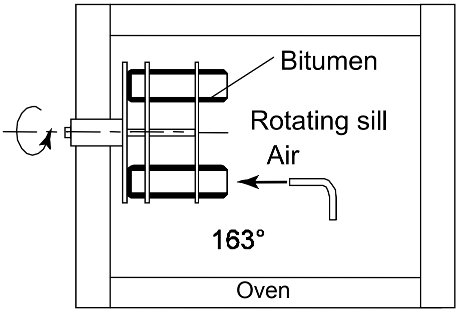


Figure 2.17. *RTFOT test. Block diagram*

According to the standardized test, the thin film of bitumen thus formed is subjected to a temperature of 163°C in the presence of air for 75 minutes to simulate the aging that the binder undergoes during mixing in a coating plant. The apparatus comprises 8 jars in order to allow the preparation of a sufficient quantity of "aged" bitumen so that it can be subjected to the series of tests indicated in the experimental design. We can then measure on the recovered bitumen the changes in certain characteristics, particularly those related to consistency (R&BT and Pen_{25}) and determine any one of the following "aging indices" (where the values measured before and after the RTFOT are respectively marked with the index° and an asterisk*):

– increase in R&BT: $\Delta R\&BT = R\&BT^* - R\&BT^\circ$;

– the minimal R&BT value after RTFOT (on 8 recovered samples);

– the remaining penetration after the RTFOT expressed in percentage:

$$\frac{Pen^* - Pen^\circ}{Pen^\circ} \mathbf{x}100$$

– the ratio of the viscosities at 135°C: η^*/η° or ν^*/ν°.

We can also conduct a rheological study using a dynamic rheometer on this "aged" product, which requires a considerable quantity of the binder.

The predictive capacity of RTFOT with respect to the coating behavior of current bitumens (i.e. except the modified bitumens and special bitumens) has been confirmed in France using full-scale tests [BAL 93]. It could thus be standardized (T 66 032 then EN 12607-1).

For *on-road aging*, or *in-service aging* strictly speaking, several approaches have been proposed. The most widely used method currently was developed within the framework of the American research program SHRP, which sought to establish new specifications for bitumens. A specific apparatus had to be designed, *Pressure Aging Vessel (PAV)*, which combines the action of air pressure and temperature to simulate the evolution of the material in time (Figure 2.18).

The validity, the scope and the adaptation of this test to the context of French and European specifications are being discussed and are still topical before this test can be introduced into the corpus of the standards under harmonization [MIG 98].

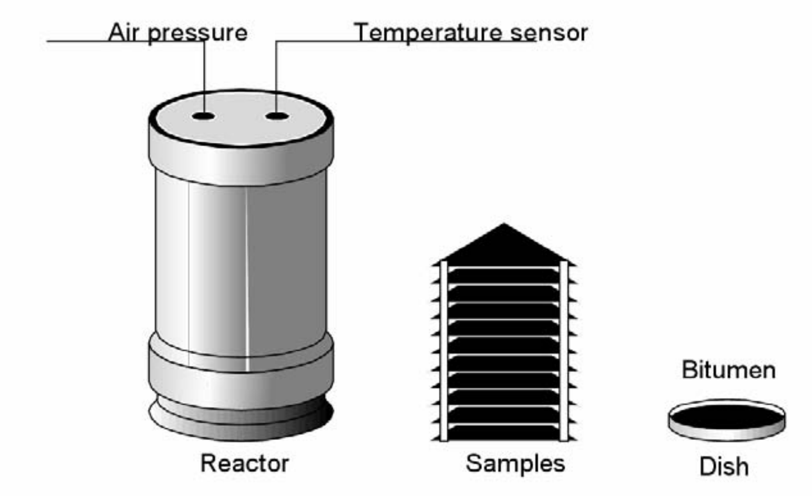


Figure 2.18. *PAV test. Equipment used*

Among the other on-road aging simulation methods, we can mention the use of a simple and fast test developed recently at the LCPC ([FAR 98]), which is based on the oxidation of the material in an oxygen cylinder, i.e. practically based on the same assumptions as PAV. Its use is still only theoretical as it requires as a prerequisite a full-scale trial campaign to validate it on bitumens other than those used for the development of the method. It has the advantage of only requiring the conventional material used in a chemistry laboratory but also the disadvantage of only treating samples of small sizes, which seriously limits its use for rheological tests after aging.

Finally, we must remember that these methods for simulating the evolution of the material have been developed for paving bitumens. They do not apply directly to modified bitumens and special bitumens, which will be dealt with further below.

All these tests available for the study of pure bitumens are recapitulated in Table 2.4.

Type of test	Name of the test	Variable measured	Standard reference	Comment
Conventional characterization tests	Needle penetration	Depth of penetration (in 1/10 mm)	EN 1 426	Reference for the classification of bitumens
	Ring and Ball softening point	Temperature (R&BT)	EN 1 427	
	Loss in mass on heating	Mass (in %)	NF T 66-011	
	Flash point	Temperature	EN 22 592	
	Solubility	Mass (in %)	EN 12 592	Toluene or xylene
	Paraffin content	Mass (in %)	EN 12 606-2	AFNOR method
	Crystallizable fraction content	Differential enthalpic analysis	test LCPC/Elf	AFNOR Draft
	Kinematic viscosity		EN 12 595	
	Dynamic viscosity		EN 12 596	
	Fraass breaking point	Temperature	EN 12 593	
	Ductility	Length	T 66-006	
Mechanical tests	Complex modulus: Tension/compression Annular shear Plane shear Isotherms of the modulus Master curve	Response of the rheometer in modulus and phase angle (or loss angle)	Complete study	Computer process incorporated into the rheometer
	Direct tensile test	Stress/strain	T 66-038	
	Determination of elastic recovery	Length	T 66-040	
	Bending beam creep test (BBR)	Response of the apparatus	M.O. LRPC Aix (Pr AFNOR)	Built-in computer process
	Cohesion with pendulum impact testing	Rising height	T 66-037	
Simulation of aging	Rolling Thin Film Oven Test (RTFOT)	All measurements on “aged” binder	EN 12 607-1	
	Paving Aging Vessel test (PAV)			
Chemical characterization	Silica rod chromatography			
	Infrared spectrometry			
	High speed chromatography on gel			
	High performance liquid chromatography			
	Simulated distillation (gas chromatography)			

Table 2.4. *Tests for the characterization and study of paving bitumen*

2.9. Limits in the use of bitumen: quest for an ideal binder

The advances made in the manufacture of bitumens and their modes of use have been considerable during the last few decades. Road engineering has won its spurs and paving bitumen, regarded in first half of the 20th century as a by-product of the oil industry, is now recognized as a material in its own right. This recognition does not however prevent users from demanding from it ever increasing performances, whereas, like all materials, it has its own limits. The characteristics of the *ideal bitumen* would then be:

– a very low *thermal susceptibility* in all ranges of services temperature, but very high in processing temperatures (consequently, of minimal *processing temperature*); this implies, according to the principle of time-temperature equivalence, a low susceptibility load time with resistance to permanent deformation, rupture and high fatigue;

– a minimal *sensitivity to aging* (both during processing and on-road);

– maximal *elasticity* and *cohesion*;

– maximal *adhesiveness.*

The first two characteristics have been represented on the diagram based on the Heukelom diagram (Figure 2.17).

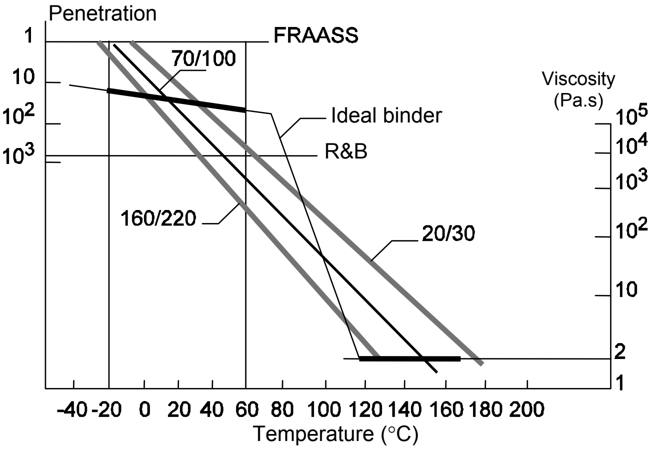


Figure 2.19. *Notion of ideal binder (based on Brûlé)*

To meet this expectation, the road industry has turned to new products, either by associating classic bitumen with polymers, or elaborating bitumen in refineries.

These are *modified bitumens*, *bitumens with additives* and *special bitumens* [CFT 02], which are presented schematically in Figure 2.20.

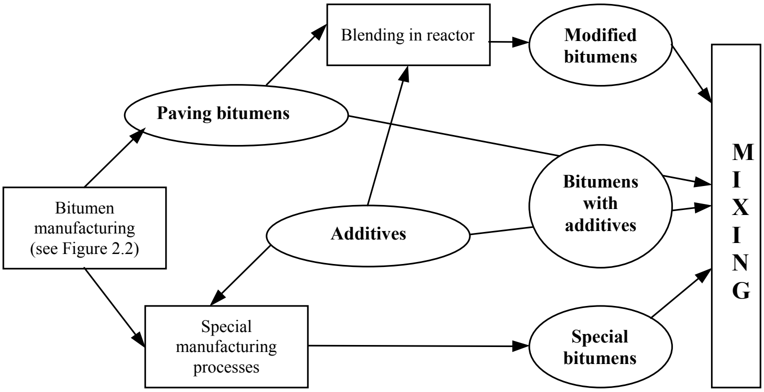


Figure 2.20. *Non-conventional bituminous binders*

2.10. Modified bitumens, bitumens with additives and special bitumens

The term *modified bitumen* applies strictly to a binder that has been modified (in factory or in a separate mobile unit), before use the mixing plant, by introducing an additive in order to modify their chemical structure or their physical and mechanical properties. This additive is generally a polymer. We often use the abbreviation PmB (polymer modified bitumens) to denote this family of products, or at least its principal terms (Figure 2.21).

The concept of modification refers in reality to the formation of a macroscopically homogeneous but microscopically polyphased medium. To clarify this concept developed in particular by Brûlé [BRU 75], we must return to the concepts of miscibility and compatibility discussed earlier in section 1.9. Thus, when we hot blend paving bitumen and a thermoplastic polymer, without taking particular precautions, we obtain as the case may be:

– *a heterogeneous blend*: the polymer and the bitumen are said to be *incompatible*, the components of the mixture separate and the system does not have the characteristics of a road binder – this is the general case;

– *a microscopically homogeneous blend*: the polymer and the bitumen are miscible in one another; this is also called *perfect miscibility* or solubility of the polymer in the bitumen, oils in the bitumen solvating the polymer perfectly; this case, occurring infrequently, has no practical interest, as even if the binder obtained is very stable, the modification of its usage properties is negligible compared to those of the original bitumen, only its viscosity is increased;

– *a microscopically heterogeneous but macroscopically homogeneous blend*, i.e. made up of two distinct phases, very closely overlapping in one another, which remains stable during the normal handling of the product and has markedly enhanced characteristics compared to those of the bitumen alone; this is called *compatibility* and this is the desired effect of the modification of the bitumen.

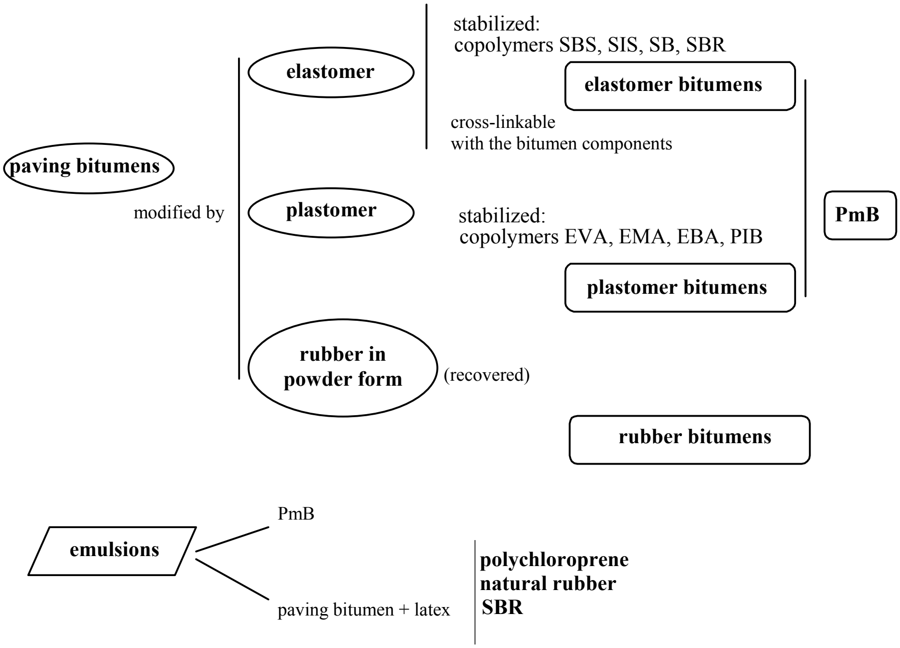


Figure 2.21. *Modified bitumens and binders*

In such a system, the polymer absorbs a part of the light oil fractions from the bitumen and “swells” by forming a phase distinct from the residual bitumen phase made up of the heavy fractions of the binder (the remainder of oils, resins and asphaltenes). The colloidal equilibrium of the bitumen is modified but not destroyed and the system remains a road binder.

This process highlights the structure of the bitumen and more precisely its aromaticity (Figure 2.22).

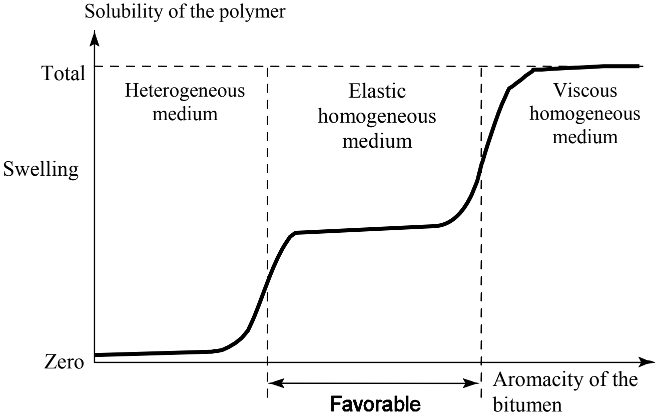


Figure 2.22. *Bitumen-polymer compatibility. Influence of the aromaticity of the bitumen*

The modifying polymers used have been classified under two types, elastomers and plastomers: in other words, we have taken into account the direction of the interval between glass transition temperatures and the ambient temperature, but the mechanism of modification is the same in both cases.

The most commonly used *elastomers* are copolymers like triblock or star polystyrene-polybutadiene-polystyrene (SBS) (Figure 2.23).

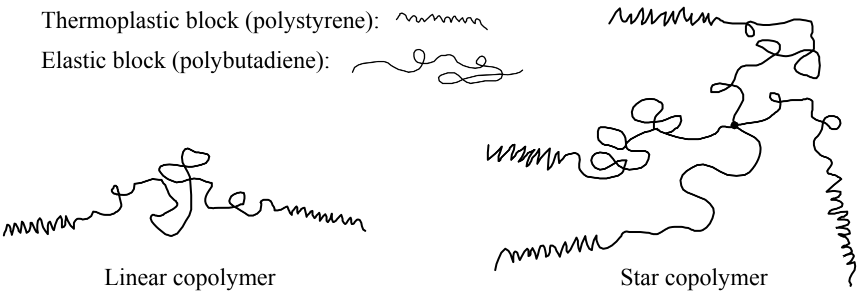


Figure 2.23. *Triblock and star SBS elastomers*

We can also find polystyrene-polyisoprene-polystyrene (SIS) triblocks, or partial blocks like poly(styrene-butadiene) (SB) or even statistical rubber-like copolymers like poly(styrene-butadiene) rubber (SBR). In these formulas, the polystyrene blocks do not exhibit any affinity for bitumen whereas there is swelling of the elastomeric polybutadiene blocks. The variations in their mechanical behavior according to temperature were discussed earlier (section 1.5) in connection with thermoplastic elastomers.

Another way of using elastomers is through a real chemical vulcanization by carrying out the corresponding reaction within the bitumen itself.

Various studies have been undertaken to modify the composition of the bitumen by reaction with polyfunctional organic compounds but the most interesting results come from the *in situ* cross-linking of SB copolymers grafted on judiciously selected bitumen asphaltenes (Figure 2.24).

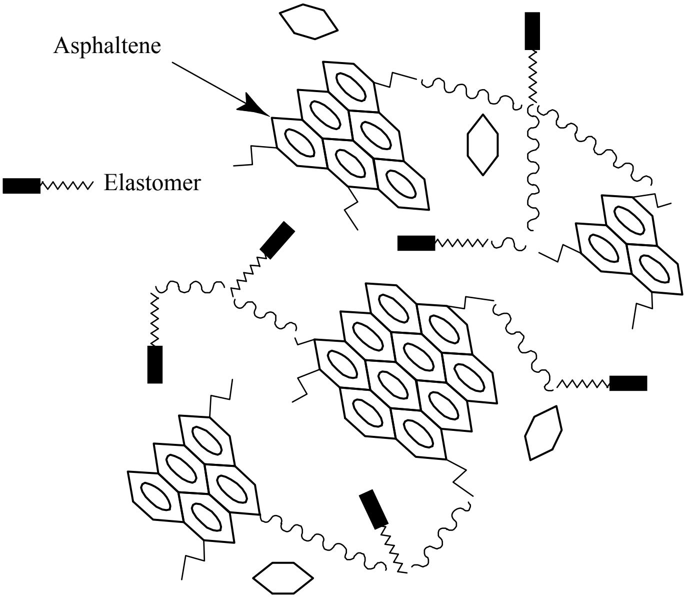
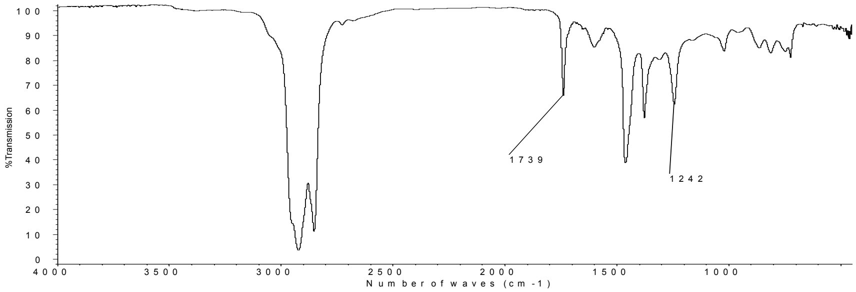


Figure 2.24. *Schematic structure of a cross-linked elastomer bitumen*

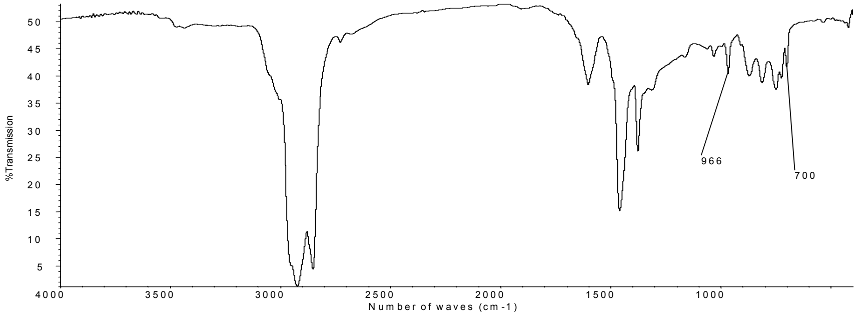
The *plastomers* used belong primarily to the family of ethylene vinyl acetate (EVA) copolymers. We also find EMA and EBA, ethylene methyl acrylate and ethylene butyl acrylate copolymers respectively.

2.10.1. *Physico-chemical characterization of polymer modified bitumens*

One of the questions raised to physicochemists is the verification of the presence and the dosing of the polymer in the bitumen. Infrared spectrometry is used in general to answer the first part of the question (Figure 2.25).



a) EVA copolymer (plastomer bitumen)



b) SBS copolymer (elastomer bitumen)

Figure 2.25. *Infrared spectra of typical modified bitumens*

We can thereafter carry out the dosing only if we have a suitable standard. We therefore use the polymer's characteristic band and proceed by the addition method. However, the use of infrared spectrometry is not limited to this quantitative aspect. It is also used successfully to characterize the evolution of the material during aging [MOU 03].

Additionally, two study methods specific to the modified binders are commonly used.

First, *microscopic observation techniques* that provide information on the dispersion state of the polymer in the bitumen:

– *Epifluorescence optical microscopy* [BRU 75] is the most widely used. It is based on the principle that the polymers swelled by certain components of the bitumen to which they are added are fluorescent when they are lit by an ultraviolet light. They re-emit a yellow-green light whereas the remaining bituminous phase appears black. The observation is made on opaque samples resulting from cold (temperature lower than - 20°C, i.e. T_g of bitumens) but rigorously plane fractures.

– For special cases where the analysis demands greater finesse (cross-linked elastomers bitumens, for example), we use techniques such as *scanning electron microscopy* (SEM) or *transmission electron microscopy* (TEM), if necessary, after the marking of the double bonds (butadiene for example) with the osmium tetroxide; we achieve even better results with environmental scanning electron microscopy (ESEM), or confocal scanning laser microscopy (CSLM) and atomic force microscopy (AFM).

Second, *storage stability*, i.e. information on the tendency of the blend to decantation, evaluated by the so-called “toothpaste tube” test, which consists of maintaining a tube containing the binder in a vertical position for a defined time, to cool it abruptly and then cutting it into three equal parts; the separation, if any, of the phases is then assessed by determining certain characteristics of the binder such as R&BT or density, on the upper and lower parts.

In addition to these physicochemical methods, we use physicomechanical tests such as the tenacity test – ductility or traction – ductility on dumb-bell shaped specimens, recovery test and elastic return, finally of the rupture tests (direct tensile tests or Charpy impact test). But the most interesting is the BBR test (bending beam rheometer) which is very relevant for the characterization of modified bitumens.

2.10.2. *Practical applications*

We generally consider that the advantages offered by associating polymers with bitumen are as follows:

– increase in the plasticity range (Figure 2.26; see Figure 2.14), which results in particular in enhanced performances at temperatures greater than 50°C;

– decrease in thermal susceptibility within the service temperature range;

– improvement in mechanical properties (elasticity, cohesion).

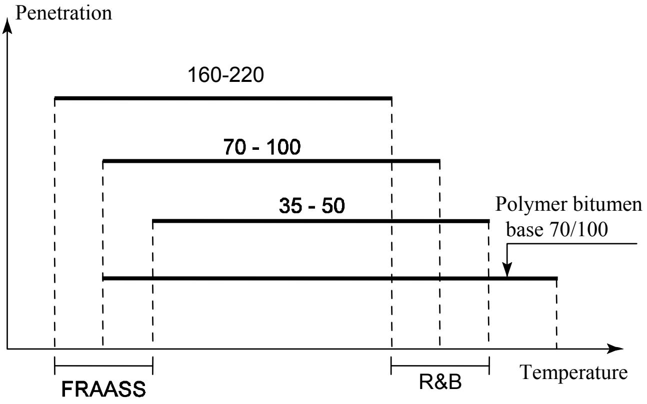


Figure 2.26. *Variation in the plasticity range with the bitumen grade*

We will not be able to develop these advantages here (along with a few disadvantages, of course). For this, we will refer to the recent study carried out under the aegis of the PIARC and presented in the form of technical guide [AIP 99]. We will only point out that these products have allowed, by complementing the range of paving bitumens, the development of techniques which would have remained marginal without them: mixes in thin or very thin layers, high performance surface dressings on high-traffic pavements, etc.

It remains however that even if these binders are used, a contractor in a hurry cannot just ignore factors essential for the proper completion of the works (choice of components, work conditions, including bad climatic conditions before and after the normal season of work). The use of a modified binder does not exempt him from taking the normal precautions in using a road binder, failing which he will damage its reputation.

Finally, we must point out that the durability of these binders is still the subject of particular research because the techniques used for the study of mixing and on-road aging of traditional paving bitumens are not often suitable for these types of binders, particularly because it is very difficult to recover aged binder by traditional stripping techniques. We must not forget that the binder itself is a sensitive colloidal medium.

2.10.3. *Bitumens with additives*

The additives considered here are products introduced during the manufacture of the surfacing or the processing of the mixing. These include:

– polymers added in the mixing plant (EPDM, polyolefines);

– polymers and plastics thus recycled (PE recovered from telephone cable wastes, recycled polyolefines);

– reground rubber (recycling of rubber from used tires);

– fibers of various types – natural (cellulose), synthetic organic (polyesters, polyethylenes, polypropylenes, acrylics), mineral (glass, rock wool) or metallic (cast iron, steel);

– bitumens and natural bitumens (Trinidad bitumen, gilsonite).

The interactions between these additives and the bitumous phase are generally conventionally physical in nature. When the additive is organic, there can be a slightly stronger interpenetration of the molecules than for mineral or metallic additives, but we are far from solubility or even the compatibility described above.

2.10.4. *Special paving bitumens*

Besides traditional binders manufactured in view of meeting the specifications in force, manufacturers are developing bitumens resulting special particular production processes for specific uses in road engineering as well as for industrial or hydraulic uses. These are called special bitumens.

We can distinguish [CFT 02]:

– *hard bitumens*, i.e. with penetration lower than standardized bitumens, 15/25 and 10/20; 5/10 grade is still in its experimental phase; they are used mainly in base courses or binder courses but some 15/25 binders can be used in wearing courses under certain conditions;

– *multigrade special bitumens* characterized by a markedly positive penetration index ($0 < IP_{\mathrm{Pfeiffer}} < 2$); they are used to address the risks of rutting and cracking in view of their wide range of application temperature;

– *pigmentable special binders* allowing colored coatings (in beige, red, white, green or blue); they are used mainly for urban roadways and signaling of dangerous zones in general; they owe their name more to their use than to their chemical origin.

2.11. Regeneration binders

This is the name given to products used in processes of recycling mixes, formulated specially from oil cuts to decrease the consistency of aged (therefore hardened) bitumen and correct the chemical composition of this binder, particularly by adding aromatic fractions.

It has in fact been observed in the analysis of the binder extracted from a bituminous coating in service for several years (10 years) that the rheological properties of the original bitumen have changed, in particular in several characteristics such as softening point, penetration, Fraass breaking point, dynamic modulus. On the whole, by aging, bitumen becomes harder, more viscous and less fit for self-repair.

From the point of view of composition, the modifications are seen in the increase of asphaltene content and of their average molecular weight as well as in the decrease of naphtenic-aromatic resin and oil contents. That leads to an increase in the colloidal instability index (see section 2.3).

To give a second life to the bitumen, formulators have shown that it is enough to add to the aged bitumen a specially prepared binder, containing a high proportion of naphtenic-aromatic resins and oils.

In this connection, there are two schools of thought. The first proposes a “fluid” regeneration binder to obtain the correct maltene content. The second recommends, in addition to the rebalancing of maltenes, the introduction of small quantity of low molecular weight asphaltenes in order to give the regenerated binder a wider spectrum of the molecular weights of asphaltenes. The binder thus obtained has a colloidal equilibrium very close to that of “new” bitumen.

2.12. Other uses of bitumen in civil engineering

In this context, we are referring primarily to waterproofing materials that are discussed in depth in Chapter 3. We will however point out here that the nature of bitumens used for this purpose is different from that of road binders: they are mostly blown bitumens also called oxidized bitumens, recalling the origin of their manufacture. We also find *jointing products*, generally made up of PmB with a high dose of elastomer, used in the structures (section 4.4.2) or the repair of cracked coatings.

All these products may be found in the contribution of B. Lombardi in Chapter 7 (section 7.2).

2.13. General conclusion

The development and research carried out on bitumen over the last 50 years have been considerable. From a by-product spread on the road to stabilize it, a whole new family of materials has been born and has become indispensable in today’s society.

Bitumen is an industrial product resulting from the refining of oil, made from “bitumen crudes”, an adhesive used mainly in road construction.

It is an organic binder but not a polymer, a mixture that is extremely rich in various components whose organization forms a colloidal structure. This characteristic explains its sensitivity to the discharge of hydrocarbons that irreversibly destroy the colloidal equilibrium. This organization also makes the material mechanically self-repairing.

Mechanically it is a strongly viscoelastic material. This property explains the flexibility of bituminous surfacing.

The performance level of this material – mechanical and durability – can be enhanced by internal modification using specific polymers. These treatments, like the optimal use of existing products, require the contribution of physicochemists, both for rheological studies and for the design and development of new products.