# ANCIENT BINDING MEDIA, VARNISHES AND ADHESIVES

# L. Masschelein-Kleiner





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Translated by Janet Bridgland Sue Walston A.E. Werner



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Editor's note: The place names included in this volume are not necessarily a reflection of current geopolitical reality, but are based on the historical trade names under which various products and substances have come to be known.

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## **INTRODUCTION**

The materials used as binding media, adhesives and varnishes are all film-forming substances. These are liquid plastic materials that are capable of forming a solid skin called a film when applied in a thin layer on several materials that are called substrates [1].

The use of film-forming materials is doubtless as old as man himself. Nevertheless, the history of the discovery of these materials is not well known. Ancient technical treatises are rare and often difficult to translate. The terms used to describe the materials are imprecise and sometimes they have changed their meaning in the course of time. A comprehensive review of these treatises was published in 1969 by Alexander [2].

Modern methods of analysis are gradually revealing more detailed information about ancient techniques [151, 152, 153, 157, 178]. Still, many unanswered questions remain; these include, for example, the date when oil painting first came into use [3,4], the composition of the well-known binding media of the Flemish Primitives [5], the nature of the varnish used in the past for musical instruments, etc.

This book will deal with the physical and chemical properties of film-forming materials. Knowledge of their properties will help conservators understand phenomena encountered in their work that would otherwise be difficult to master.

The principal characteristics of the natural film-forming materials used in the past will then be discussed.



#### **Chapter One**

## PHYSICAL AND CHEMICAL PROPERTIES OF FILM-FORMING MATERIALS

#### I. LIQUID STATE

Film-forming materials must be used in a state that is sufficiently liquid to permit easy application. With the exception of fresh drying oils which are naturally liquid, this state is most frequently obtained by the addition of solvents. The resulting mixtures are solutions, dispersions or emulsions.

#### Solution

A solution is a homogeneous mixture of two or more finely divided substances in which the particles are present at a molecular scale, i.e., *having a diameter of the order of* 0.001  $\mu$ m ( $\mu$ m = one micron, which is one millionth of a metre).<sup>1</sup> Examples include varnishes and certain adhesives.

#### • Dispersion

A dispersion is a suspension, in a fluid, of relatively fine particles of matter, which have no apparent propensity to dissolve in or combine with the fluid. This fluid is referred to as the external phase or dispersion medium.

When the particles are colloidal substances, the dimensions of the colloids vary between 0.0001 and 0.2  $\mu$ m in diameter.

These colloidal dispersions have the property of diffusing visible light, giving them a milky appearance. This is the Tyndall effect. Such suspensions can be formed, for example, by mixing proteins (eggwhite, egg-yolk, casein, gelatin, etc.) or polysaccharides (gum tragacanth, starch, etc.) in water. As will be seen later, these same substances can act as protective colloids for stabilizing pigments.

In dispersions of non-colloidal materials, the diameter of the particles varies between 10 and 500  $\mu$ m (e.g., ground pigments, dust, etc.).

<sup>1</sup> 

In this publication, three units for very small distances are used in various contexts. The fact that there are three reflects the various disciplines that overlap in this area, and each discipline has its own preferred unit! Thus angströms (Å), nanometres (nm) and microns ( $\mu$ m) are all used. Their absolute values are: 1 Å = 10<sup>-10</sup> m; 1 nm = 10<sup>-9</sup> m; and 1  $\mu$ m = 10<sup>-6</sup> m. The interrelationships are: 10 Å = 1 nm; 1000 nm = 1  $\mu$ m; 1000  $\mu$ m = 1 mm; and 1 000 000  $\mu$ m = 1 m.



#### Emulsion

Emulsions are dispersions of two liquids that are insoluble in each other. One liquid forms the *external phase* or *dispersion medium* and the other is reduced to fine droplets constituting the *internal* or *dispersed phase*.

Emulsions are not very different from dispersions and show the same Tyndall effect.

The external phase determines the properties of an emulsion: Thus, in an "oil-in-water" emulsion, it is the water that determines the viscosity and character of the emulsion.

The "oil in water" emulsion is a *lean emulsion*: i.e., one that can be thickened with the addition of more oil (as with mayonnaise) and made more fluid with the addition of water or an aqueous solvent (such as vinegar).

The "water-in-oil" emulsion is a *fatty emulsion*: i.e., one that can be thickened with the addition of more water and liquified with the addition of more oil or an oil solvent (fig. 1).

These emulsions are unstable. For example, when water is progressively added to oil, while being shaken, the droplets of water come closer and closer together and finally coalesce at a critical point. This critical point is reached when the emulsion contains 74.04% water. It will be seen that emulsions can be stabilized by the addition of surface active agents (surfactants) and by protective colloids.

#### I. 1 Surface phenomena and wetting [6,7,8,9]

When pigments are to be mixed with a binding medium or a panel is to be glued using an adhesive, it is clear that one of the conditions necessary for achieving a successful result is that the binding medium or the adhesive must adequately *wet* the solid pigment particles or the substrate (fig. 2).

For a liquid to wet a solid, it is necessary for the forces of attraction between the molecules of the solid and the liquid to be stronger than the intermolecular forces within the liquid.

Fig. 2



Consider a liquid contained in a vessel (fig. 3): within the liquid mass, the interactions between the molecules take place equally in all directions and cancel each other out. However, at the surface, i.e., at the liquid/air interface, the attraction outwards – toward the molecules in the air – is weaker than the attraction inwards – toward the other liquid molecules; there is thus a resultant force directed toward the interior of the liquid. The surface of the liquid can be compared to an elastic membrane, like a balloon, which tends to revert to its minimum surface area. Drops of water also demonstrate this phenomenon.

Thus there exists, at the surface of a liquid, a force that tends to reduce the surface area to a minimum. This is the *surface tension*.

Fig. 3



The high surface tension of water explains why it is difficult to obtain uniform applications of watercolour unless the painting surface has been previously wetted [10]. This also explains why it is difficult to achieve a smooth gradation of colour, because the paint stops at the end of the brush stroke and does not spread out. The Italian Primitives solved this problem in the painting of shadows by using hatching, spaced more or less closely together.

Oil, on the other hand, tends to spread because it has a low surface tension. The greater the surface tension of a liquid, the less easy it is for it to wet a solid.

Surface tension at 20°C in dynes/cm [9]		
Mercury	485.0	
Water	72.75	
Gelatin 1%	8.3 (5°C)	
Glycerol	63.4	
Oleic acid	32.5	
Ricinoleic acid	35.8 (16°C)	
Linseed Oil	37.5	
Turpentine	31.5	
White spirit	between 29.0 and 31.5	

#### Wetting agents

There are compounds that are able to reduce the surface tension of liquids to which they are added. These are called *surface-active agents* or *surfactants*.

The molecules of these compounds contain both a hydrophilic part and a lipophilic component (fig. 4).

Fig. 4



In a binary system (oil/water or binding medium/pigment), the surfactant molecules are arranged at the interface so that each end of the molecule is oriented toward the substance to which it is attracted. The surface tension at the interface is thus greatly reduced and wetting is improved [11].

Example 1. Oil/water/alkaline soap (fig. 4)

Example 2. Grinding of pigments; some pigments, such as Prussian blue or phthalocyanine blues are difficult to grind in oil. They do not wet readily and tend to cake.

Because these pigments are very hydrophilic, they contain a layer of water adsorbed on their surface. Also, the action of mechanical grinding induces electrical charges – equal in number and of opposite polarity – on opposite sides of the particles. While as a result there is no overall charge, the particles do tend to cake (fig. 5a)



A small percentage of surfactant (0.1% to 0.25%), e.g., ox-gall, lecithin of egg-yolk, or simply the use of an acid oil, will enhance wetting. The molecules of the surfactant are attracted to the surface of the pigment, forming a film around the particles so that they take on the same electric charge and repel one another (fig. 5b).

When it is necessary to add a diluent to a paint, this should be done at the end of the mixing procedure because it will compete with the binding medium for adsorption onto the pigment particles. It is thus necessary to allow enough time for the binding medium to form a coating around the particles [12].

#### I. 2 Stabilization of pigments

Once the pigments have been well wetted and mixed with the binding media, they should remain in a homogeneous suspension. Their weight, however, tends to cause them to settle to the bottom or to float to the top of the paint layer, depending on their density (fig. 6).

Fig. 6





Some binding media (proteins, glucides [polysaccharides]) are able to counteract this undesirable effect. These are *colloidal* molecules, i.e., molecules that are larger than other molecules, having a diameter of 0.001 to 0.3  $\mu$ m instead of some 10 Å. They increase the viscosity of the medium, which slows down the movement of the pigment particles, and such binding media also interact with the particles.

It has been observed that when an electric current is passed through a colloidal suspension some of the particles will move toward the positive pole while others will move toward the negative pole. According to the generally accepted theory, this takes place as though each particle were surrounded by a layer of so-called protective colloids. These colloids selectively adsorb certain ions present in the surrounding liquid, which appears to give rise to an electric charge.

This explains why these particles become electrically charged, repel each other and, therefore, remain suspended in the liquid medium [7].

During the last decade, considerable work has been done by the coating industry to develop polymeric wetting and dispersing agents for solvent-based paint systems. They are high molecular weight polymeric wetting agents with numerous hydrophilic centra and they impart a positive charge to the pigments. They can thus wet the pigments and stabilize them as well [163].

#### I. 3 Rheological properties [13]

Apart from the forces of gravity and surface tension, there are other physico-chemical reactions that help to keep the film spread out on the substrate. In fact, if it were not for these reactions, the film would collect into globules because of surface tension, and these would run down vertical surfaces because of the force of gravity.

The study of the phenomena associated with the flow and deformation of liquids when certain constraints are applied to them is called *rheology*. Many important properties of paint are involved, which include its brushability, its tendency to maintain deformation, the way in which it spreads and its ability to settle into wave formations or to run, etc. One of the measurable criteria characterizing these phenomena is *viscosity*, i.e., the resistance of a liquid to flow. From a physical point of view, viscosity can be visualized by imagining a fluid contained in a vessel, e.g., paint in a pot. The more viscous the paint, the more difficult it is to empty the pot. When the paint flows as soon as the pot is tilted and the rate of flow is proportional to the tilt of the pot, the paint (i.e., the fluid) is said to be "Newtonian."





Many paints behave differently. Some are said to be "plastic," and in this case one must exceed a certain critical force, called the *flow limit*, before the paint starts to flow.

The so-called *thixotropic* paints behave in yet another manner, similar to that of quicksand: when at rest quicksand is firm, but when it is agitated a victim will sink into it because movement causes the sand mass to behave like a liquid. The same is true of an aqueous solution of gelatin. It stays put after it has been laid down, but becomes fluid by the action of brushing. This phenomenon is due to a reversible change taking place in the fluid, which passes from the state of being a *sol* to that of being a *gel* and vice versa, depending upon whether it is being agitated or is at rest. The rate of the change varies a great deal. The gel structure re-establishes itself at different rates after stirring. The rate at which this change takes place is a predominant factor in determining the efficacy of a thixotropic paint in hindering the sedimentation of pigment and in opposing the flow and spreading of the paint (fig. 9).

Fig. 9



In thixotropic fluids, the time factor is very important. The viscosity of the system depends on the length of the preceding period of rest, the duration of agitation and even on all of the other factors to which the fluid has been subjected. The change from sol to gel is associated with a rate of change in viscosity on the upward change that differs from that on the downward or return. There is in fact a hysteresis loop [15] (fig. 10).



TORSION VISCOMETER

It is almost certain that the Old Masters, from van Eyck to Rubens, had managed empirically to produce a thixotropic paint; this phenomenon, in fact, made it possible for them to superimpose layers of paint  $\hat{a}$  frais, without having successive layers intermixing [16, 17]. Thus Rubens was able to paint "La Kermesse" in 24 hours. Examination of the painting shows that the superimposed layers are distinctly separated, since the brush strokes are visible in the underlying layers [18]. After Rubens, the composition of thixotropic paint seems to have been lost.

An understanding of this phenomenon of gelation should, therefore, permit a rational approach to this secret of the Old Masters. Unfortunately, the explanation is still only in the hypothetical stage. It is certain that the interaction between pigments and binding media plays a determinant role. It is possible that some pigments have specific attraction for colloidal micelles present in the binding medium. The binding medium might form voluminous envelopes around the pigments which become entangled in a more or less reversible manner.

In cases where the pigments react with the binding medium, the explanation is clearer. It is known, for example, that white lead and zinc oxide react with oil to form soaps of fatty acids, the micelles of which are absorbed at the interface of the pigment/binding medium [19].

In practice, it is possible to make a thixotropic paint by adding certain compounds to it. In an organic medium, use is made of heavy metal soaps, waxes, calcium and magnesium alginates, and polyamide resins. In an aqueous medium, casein, albumin, gelatin, dextrin, various polysaccharide gums, sodium or potassium alginates, etc., must be resorted to. Some of these substances are mentioned in old recipes. De Mayerne describes the heating of raw oil with litharge, powdered bone or lead-rich Venetian glass. These compounds lead to the formation of calcium and lead soaps. The same applies to the medium used by Van Dyck, which, according to Eastlake [20], was composed of nut oil gently heated with ceruse to which was added mastic dissolved in turpentine.

Thixotropy influences various properties of paints. The *brushability* or ease of application of a paint depends on the pull of the hairs of the brush and on the number of brush strokes needed to achieve a given coverage of the paint. During this operation, the thixotropic structure is being repeatedly destroyed and restored in accordance with the alternating periods of deformation and rest.

The quality of *flow* (spreading) is the ease with which irregularities in the surface, caused especially by the hairs of the brush, will disappear with the natural flow of the paint. This property depends on the force of gravity and surface tension as expressed by Waring's formula [21]:

Fig. 11



where

h = the depth of the striations made by the brush, d = their width,  $\gamma$  = surface tension and f = limit of flow.

The weaker the limit of flow, the more easily the paint spreads. This formula takes into account both the influence of the brush hairs and the thickness of the paint layer.

With a non-thixotropic paint, the deformation observed is proportional to the force exerted by the brush. On the other hand, with a thixotropic paint, at each stroke of the brush, the gel structure is broken down and then restored during the interval between brush strokes.

In the case of varnishes, their capacity for flowing is extremely important. In fact, as will be seen later, the evenness of the varnish surface is predominantly responsible for its *gloss*.

#### I. 4 Oil index and critical concentration [22]

When a binding medium is gradually added to pigments, each pigment particle is progressively covered by a film of *adsorbed* binding medium. After that the voids between the pigment particles are filled up; this is referred to as *interstitial* binding medium.

The sum of the adsorbed and interstitial binding media thus constitutes the minimum amount of binding medium (for a given pigment) that will confer a normal degree of cohesion to the paint film. This combination, which is specific for each mixture of pigment and binding medium, is known as the *critical pigment volume concentration (CPVC)*. Any additional binding medium beyond this value is superfluous. This concept of CPVC now replaces the old empirical oil index, i.e., the amount of linseed oil needed to wet 100 g of pigment completely.

In fact, the oil index cannot be measured accurately and does not give reproducible results. The mixing sometimes causes acicular pigments (those having protruding parts) to crumble, and the use of certain binding media can cause deflocculation that does not occur with oil. Furthermore, the result obtained may also depend on the speed of rotation of the mixer.

Also, the film that oil forms around the pigment particles is monomolecular and is only a few ångströms thick. It is quite different in the case of high molecular weight polymers that build up multilayered films that can easily reach a thickness of 1000 Å.

The CPVC has certain definite advantages over the oil index system, and the concept is based on a definite physical reality. Thus, when the quantity of pigment in a paint film is progressively increased, it may be seen that the permeability and opacity [23] increase sharply, while the gloss decreases for a given volume of the pigment [24]. Increases in this value (the CPVC), therefore, correspond to sharp increases in the porosity of the film.

Fig. 12



Unfortunately, the technical literature does not give enough measured CPVC values for the pigments used in artists' paints, so it is still necessary, for the time being, to use the old oil indices [25], as in the following table.

PIGMENT	OIL INDEX	
Zinc oxide	14 to 16% (non acicular) 25% (acicular = needle-like)	
Vhite lead 12%		
Chrome yellow 10 to 20%		
Yellow ochres ? 30% or 75%		
Red ochres	d ochres ? 25% or 65%	
Burnt sienna	t sienna 50 to 60% (calcined)	
Umber	60 to 75%	
Ultramarine	Ultramarine 35%	
Prussian blue	? 56% or 90%	
	USE IN ART [26] (units not specified)	USE IN BUILDING [26]
Ivory black	110	60
Raw sienna	175	82
Burnt sienna	175	45
Cyan blue	75	50
Raw umber	100	48
Burnt umber	90	47
Yellow ochre	75	28
Ultramarine	37	28
Chrome orange	32	20
Vermilion	20	14
Ceruse	15	10

#### **II. SOLID STATE**

#### II. 1 Film formation [27]

The formation of a film involves the conversion of a liquid phase, in which the film-forming material may be present in solution or as an emulsion or be in the molten state, into a solid laminar system.

Depending on the nature of the compounds involved, the formation of the solid system may be the result of a physical change or a chemical reaction, or a combination of both.

#### **II. 1. 1** Film formation by physical change

If pre-formed macromolecules are in solution or in a dispersion, the film is formed by *evaporation*, and if they are in the molten state, the film is formed by *solidification*.

#### Evaporation of solvents from a solution [28]

This phenomenon is involved in film formation with the terpene resins (page 64). These are film-forming materials which yield solutions that can be dialysed and do not show the Tyndall effect. They behave like large, more or less globular molecules.

The evaporation of the solvent involves the loss of a certain quantity of molecules at the air-solution interface. This loss of solvent molecules causes voids that are immediately filled by horizontal and vertical displacements of neighbouring molecules, resulting in the formation of small vortices that gradually encroach on the whole surface of the liquid.

Fig. 13



The viscosity of the solution increases and the rotation speed of the vortices decreases. If this decrease is too rapid, a hexagonal pattern (the "vortex") is formed on the surface of the film. This is the "orange-peel" effect and causes a reduction in the brilliance of the film. Stresses appear at the angles of the hexagons, and these constitute potential points of weakness where the film will break [27].

A paint layer is rarely more than 25  $\mu$ m (25 000 nm) thick. The size of the pigment particles varies from between 30 and 3 000 nm; there are, therefore, between 8 and 800 particles in the layer [29]. Since the length of a single carbon-carbon bond is about 0.15 nm, there can be only about 170 000 such bonds in a layer of 25 000 nm.

Accordingly, macromolecules that are highly twisted or have a low molecular weight rarely number more than a hundred through the thickness of the film. The size of the constituents is thus a significant factor regarding to the nature of the film that is formed. Each discontinuity or specific orientation has an effect on the structure of the film. Thus, the choice and quantity of the solvent will influence the quality of the dried film.

Katz and Munk [30] showed the importance of this by measuring the permeability to water vapour of different films formed from solutions in a number of solvents.

The films that are the most dense, and that are the least permeable, are obtained when it is possible for the molecules of the film-forming substances to arrange themselves in a particular manner. This can occur when the increase in viscosity resulting from loss of solvent does not reduce the mobility of the molecules too quickly and if there are interactions between the solvent and binding medium that assist their orientation.

In addition, the film often has a different permeability on the surface facing the substrate from that on the surface facing the air. Indeed, it may often be observed that the substrate has had an influence on the orientation of the molecules in the film.

Accordingly, it is usually possible to distinguish three levels in the thickness of the film: the lowest layer, where the molecules are directed toward the substrate or an adjacent layer; the central layer, where there is no specific orientation; and the uppermost layer, where the molecules are oriented toward the film-air interface or toward the interface with a subsequent paint layer.

Fig. 14



SUBSTRATE

Molecular orientation at these interfaces is even more pronounced when there is good wetting between successive layers.

The rate at which the viscosity increases before drying also influences the optical properties of the film. This phenomenon has been very well described by Feller [31].

Fig. 15



Natural resins remain fluid for a long time, even when there is very little solvent left (up to 80% solids content). When solutions of these resins are applied as varnishes on an irregular paint layer, the resins fill up the depressions as the solution dries and the resultant varnish film is almost perfectly smooth.

Most of the synthetic resins, on the other hand, form very viscous solutions, even when there is still about 50% of the solvent remaining. The flow is checked much more quickly, and the surface of the dry film is not as smooth as in the case of the natural resins. This characteristic explains the difference in gloss between these two types of varnish.

During evaporation, the film is subject to contraction caused by its decrease in volume due to loss of solvent. This is a crucial phase in the formation of the film.

Keck [32] has described particularly well the mechanical defects that can result from poor paint formulation: the use of solvents that are either too volatile or not sufficiently volatile, or are present in excess; poor adhesion of the film to the support; or too thick a layer. Such defects will show up during drying by the formation of a number of fine cracks in the paint – a result commonly referred to as "premature cracking." Usually these fine cracks do not extend through the whole thickness of the paint layer. Their formation depends on the binding medium. They vary in width and may even appear as fissures. Cracking that is due to age is much narrower and more uniform.

The volume concentration of the pigments also influences the resistance of the film to cracking. The lower the concentration of pigments, the less resistance there is to the stresses that cause breakdown of the paint film. Thus, the dark, pure tones, without added white pigment, are the most sensitive [29].

#### Drying of emulsions [33, 34]

Emulsions are dispersions: a mixture of two immiscible liquids (e.g., oil and water) in which one is dispersed throughout the other in small droplets (though not as small as in a colloid). These emulsions are often stabilized by the addition of a wetting agent, a protective colloid, or both (see page 4). The drying of emulsions is influenced by these additives.

In considering drops of a dispersed liquid surrounded by surfactants, it can be seen that, during evaporation of the external phase, they will come closer together until finally they touch. There is a pressure being exerted on the wall of the drops due to surface tension, and this is responsible for their spherical shape. At the moment when they touch, the presence of a layer of surfactant prevents them from coalescing. It can be assumed, however, that, as the drops crowd together, some of them will compress and deform the neighbouring drops. The convex curvature of some compressed drops will become concave and the surface tension forces will assist this deformation rather than counteract it. These forces become strong enough to break the double layer of emulsifier, and the drops combine (fig. 16).

The surface-active agents are expelled and migrate toward the surface and toward the substrate where they compete with the film-forming material for adhesion.

Fig. 16



Since the aggregation is less pronounced at the surface, the external surface of the dry film thus formed is always less solid than the deeper layers.

In cases where the emulsion is stabilized by protective colloids, these remain adsorbed on the surface of the drops of dispersed liquid. The cohesion of the film is entirely dependent upon the extent, great or small, to which the colloids are able to act as a kind of cement between the grains. The film is much less homogeneous than in the former case, and as a result the dry film usually has a milky appearance and very poor transparency.

#### Observation

It is sometimes difficult to determine whether a substance is dissolved or dispersed in a liquid. If the intermolecular attraction of the solid and liquid is greater than the attraction between molecules of the solid, a true solution is formed. But if the molecules of the liquid are only attracted by some active groups of the solid's molecules, then only swelling will occur [35]. Thus, the long linear molecules of gelatin form micelles in which there are crystalline parts through which water can penetrate and cause unlimited swelling, leading finally to solubility. The formation of a film goes through the following reversible phases:

COLLOIDAL SOL 
$$\leftarrow$$
 COLLOIDAL GEL  $\rightarrow$  DRYING

#### Solidification of a molten substance

The number of film-forming materials that can be applied in the molten state is somewhat limited. Among natural materials these include wax, shellac and bitumen.

The films formed are much more compact than those formed by evaporation from solution and the layers can be thicker without giving rise to defects.

#### **II.1.2** Film formation by chemical reaction

The chemical reactions involved are mainly those of oxidation and polymerization. They are responsible for film formation in the case of drying oils, and to a certain extent also in the case of the terpene resins. In the latter case the reaction is preceded by evaporation of the solvent. The ability of drying oils to form a film depends on the number and relative positions of the carbon-carbon double bonds contained in the molecule. These double bonds are responsible for both the chemical reactions: oxidation and polymerization.

These reactions lead to the formation of a three-dimensional network [36, 37]. Oxygen, light and metallic salts are the catalysts (fig. 17).

Fig. 17



The main metallic driers are salts of lead, manganese and cobalt. In the past one used lead linoleate, which was prepared by reacting linseed oil with litharge. These compounds seem to act essentially as transporters of oxygen [38]. In the presence of air, they are converted to a higher state of oxidation, and then return to their original state, transferring oxygen to the surrounding oil. This process continues until all the reactive double carbon-to-carbon bonds in the oil have been oxidized. The cobalt and manganese salts react mainly on the surface, the cobalt salts being more active. On the other hand, lead salts react in depth and they produce a film of superior quality. If oxidation of the surface takes place too rapidly, there may be a sharp increase in surface area. The surface wrinkles and the underlying layers do not dry properly. Sometimes the top layer loses its flexibility when it dries too fast. Any movement that occurs in the soft underlying layers can cause cracking of the film.

The addition of driers in carefully prescribed amounts can, nevertheless, be advantageous. A film of linseed oil exposed to south light becomes "touch-dry" in two days. The addition of 0.1% of a cobalt drier reduces the drying time to seven hours [62]. It should be noted that the "touch-dry" state means that one can touch the surface with the finger without its sticking to the surface, but this in no way signifies that the film has dried throughout its depth. The drying reaction will continue for many years. During reticulation of the film, there is shrinkage of the network, and substances that are still in a fluid state migrate either toward the surface or toward underlying layers:

this is the phenomenon of "synaeresis." An exudation occurs and this plays an important role in the smoothness of the film surface and in its optical qualities [17].

As reticulation proceeds there is a progressive hardening of the film. This hardening, however, is moderated by the simultaneous production of small molecules which act as plasticizers; these are the result of degradation reactions. Thus the mechanical properties of the film can be harmed if these small molecules are removed by excessive leaching with solvents during the removal of the varnish from a painting [39].

Japanese lacquer (from *Rhus vernifluca* syn. *Rhus vernicifera*) forms a film in a somewhat exceptional manner. There is an enzymatic oxidation that, in the presence of moisture, converts the liquid extract from the plant into a completely insoluble film.

#### **II.2** Optical properties [40]

When a light falls on a paint film or on a varnish, some of the light is returned at the film-air interface. This is called *reflection*. The greater the amount of reflected light, the glossier the film appears to be. The rest of the light penetrates the film. When passing from air into a medium with a different *refractive index*, the direction of the light rays is altered. This is called *refraction*.

Some of this light is *absorbed* by the pigments and by the binding medium, and the rays of light also undergo *multiple diffusion* on the surface pigment particles.

Sometimes there is still enough light so that it can be reflected from the substrate, passed back through the film and emerge into the air. This then gives the observer information about the colour of the ground. The paint is then said to have a poor covering power.

#### II. 2.1 Gloss

Light falling on a perfectly smooth surface is reflected by that surface so that the angle of incidence is equal to the angle of reflection. The surface behaves like a mirror, and this is known as *specular reflection* (fig 18).

If there are broad irregularities in the surface, the rays of light are reflected in various directions, but at each point the angle of incidence is still equal to the angle of reflection. This is referred to as *semi-specular reflection*.

If the irregularities in the surface are so small that their dimensions approach those of the wavelength of visible light (400-700 nm), reflection takes place in all directions. This is known as *diffuse reflection*. Much less light is returned in the direction of an observer, and there is a loss of *gloss*. The *glossiness* of a surface is defined as the ratio of the *specularly* reflected luminous flux to the incident luminous flux [41, 42, 43].

A surface appears to be even glossier when the amount of specular and semispecular reflected light is high in comparison with the amount of diffusely reflected light. This condition is more closely followed if the surface is flat. It is necessary to





take into account not only the small irregularities but also those of larger size. In fact, convex irregularities reflect light in various directions, some of which are lost to view. Any defect in the smoothness of a surface, such as "orange-peeling" or wrinkles, makes the surface appear matt. This quality can be deliberately achieved, for example, by adding wax to a varnish, which produces a granular surface, as shown by De Witte [52].

Fig. 19



MATT SURFACE

GLOSS SURFACE

The gloss depends not only on the viewing angle but also on the kind of lighting; a point source of light provides an impression of brightness greater than that observed with a diffuse light source.

The refractive index (see definition p. 20) of the film is also an important factor; the higher the refractive index, the greater the intensity of the reflected light [40]. By choosing a material of sufficiently low refractive index, it is possible to decrease the amount of reflected light considerably. This is the effect obtained with an anti-reflection surface layer. In this way a thin coat having a thickness equal to one-quarter of the wavelength of the incident light and a refractive index of the value of  $\sqrt{n}$  almost cancels out all specular reflection from a layer having a refractive index of n. Feller [44] has pointed out the importance of viscosity and refractive index in relation to the gloss of natural and synthetic varnishes. Also, De Witte has carried out systematic research at the Institut Royal du Patrimoine Artistique (IRPA), Brussels, to determine precisely the nature and relative importance of various factors responsible for the optical quality of varnishes, so as to select the best type of varnish.

#### II. 2. 2 Opacity - hiding power

The opacity or hiding power of a paint layer is its ability to mask the support on which it has been applied.

Light travels back and forth through the paint film, during which time it undergoes refraction, diffusion and absorption. The paint layer is accordingly more obscured if the loss of light in the course of its travel is significant, resulting in less light being returned to the viewer (fig. 20).

Fig. 20



#### Refraction

When a ray of light passes from a medium with a refractive index  $n_1$  into a medium with a refractive index  $n_2$ , the direction of the refracted ray is given by Snell's Law:

Fig. 21



The refractive index is the ratio of the speed of light *in vacuo* (300 000 km/sec) to the speed of light in the given medium.

The amount of light transmitted by the paint layer is also dependent upon the difference in the refractive indices of the binding medium and the pigments. When a ray of light passes from the binding medium onto a pigment grain, it is deviated to a greater extent when the difference in the respective refractive indices is large. The more it is bent, the less chance there is of its return to the viewer (fig. 22).

Fig. 22



It is well known that oil paintings become less opaque with age [58]. Fresh linseed oil has a refractive index of 1.48. Old linseed oil can reach a refractive index of 1.57 which is close to the refractive index of many pigments [59]:

Ultramarine	1.50 - 1.60	Gypsum	1.52 - 1.59
Prussian blue	1.56	Ivory black	1.65 - 1.70
Smalt	1.49 - 1.52	White lead	1.94 - 2.09
Malachite	1.65 - 1.90	Zinc White	2.02
Kaolin	1.56	Silica	1.55

This property can also be used to determine the refractive index of crystals. The crystals are placed successively in liquids of different refractive indices and the liquid in which the crystals become transparent is noted.

Rees Jones [158] applied the Kubelka-Munk theory when studying the changes in appearance of oil paintings during aging. When the reflectance of the underlayer is zero and the paint is white, the formula is:

$$\boldsymbol{R} = \frac{e^{Sd\left(\frac{1}{R_{\infty}} - R_{\infty}\right)} - 1}{\left(\frac{1}{R_{\infty}}\right)e^{Sd\left(\frac{1}{R_{\infty}} - R_{\infty}\right)} - R_{\infty}}$$

where:

R: reflectance

S: characteristic scattering power per unit thickness of the paint (in cm<sup>-1</sup>)  $R_{\infty}$ ; reflectance of the paint film when the underlayer is totally obscured d: thickness of the film

S and R have certain values in new paint which diminish on aging, and this promotes an increase in the transparency.

The contrast between mid-tone and light is increased while that between mid-tone and dark is reduced. When the artist uses thick painted layers and dark grounds some distortions in the rendering of forms may occur.

Rees Jones also studied varnished oil paintings [196]. Some de-saturating white light can be reflected from the air-varnish and varnish-oil interfaces.

The degree of dispersion (page 9) is governed by the pigment volume concentration, PVC. As noted earlier, the opacity changes abruptly when the critical pigment volume concentration (CPVC) is reached. At that moment, there is just enough binding medium to fill the voids between the pigment particles. When, however, the amount of pigments in relation to the binding medium increases beyond these proportions, voids are formed between the particles: voids that are filled with air. The binding medium has a refractive index of about 1.5, whereas the refractive index of the voids is that of air, i.e., 1.0. The difference in the refractive indices of pigments and voids is high and therefore the deviation of the light by refraction also increases, which explains the increase in opacity [42, 61, 161].

In the same way, it is possible to explain the so-called "regeneration" that is achieved by getting old paints and varnishes to absorb solvent vapours. The voids caused by the breakdown of the film-forming material are temporarily filled by the solvent and by the swelling of the binding medium. This rejuvenation is only temporary, as it disappears when the solvent evaporates [62].

#### • Diffusion

When light penetrates a paint layer, it encounters a large number of small particles of pigment suspended in the binding medium. These particles disperse light rays in all directions many times: this is *multiple diffusion*. If the particles or molecular aggregates are less than one-and-a-half times the wavelength of the light, they diffuse the light. Particles that are larger in size reflect the light.

In the ultraviolet and visible part of the spectrum, the diffusing particles have colloidal dimensions (from 0.001 to 0.2  $\mu$ m). The intensity of diffusion is spatially symmetrical for particles smaller than  $\frac{1}{10}$  or  $\frac{1}{20}$  the wavelength of light: this is known as Rayleigh's diffusion. Larger particles give off less intense diffusion backwards [56].

If the layer has a lot of pigment particles diffusing the light, the greater part of this layer will, as a consequence, be opaque.

According to Rayleigh's Law,  $I_o = I \frac{inc}{\lambda^4}$ , the short wavelengths (blue) are

diffused to a greater extent than the long wavelengths (red). Light from the sun passing through the atmosphere loses some of its blue component, and, therefore, appears yellow. Red light is diffused to a lesser extent, and it is this light that penetrates the paint layers more deeply, provided it has not been absorbed [57]. In this way it is possible to study the drawings that underlie paintings using infrared light with a

wavelength of 2  $\mu$ m, where the covering is of maximum thickness, as has been shown by van Asperen de Boer [141].

The shape of the pigment grains and their degree of dispersion also have an effect on the diffusion of light. It is possible to predict, for a given refractive index, which shape of particle will produce the most diffusion [24, 60] (fig. 23).

#### Fig. 23



The factors influencing opacity have been particularly well studied for titanium dioxide pigments [162]. The amount of transmitted light obviously depends on the thickness of the layer and equally on the colour of the ground. A black ground will absorb more light than a white one. Accordingly, it can again be seen that the choice of a white ground by the Flemish Primitives tended to ensure that the paintings would have a maximum luminosity.

In this connection it should also be noted that *transparency*, a quality opposed to opacity or hiding power, will be greater the more the layer allows light to pass in and out. The nature of the surface must also be taken into account; hence the importance of the process for laying down flaking paint, which "... restores to a painting its lost depth...," as the Philippots [63] have remarked.

#### II. 2. 3 Colour

Some of the light penetrating a paint layer is absorbed by the materials present: pigments and binding medium. The absorption of the visible part of the spectrum, from 400 to 700 nm, produces the visual effect of colour.

All the colours of the solar spectrum can, as is known, be reproduced by additive mixing of the three primary colours: red, blue and green. This phenomenon can be made visible by projecting these colours onto a screen from three separate projectors.

In paintings, the colours observed are not the result of the additive mixing of the three primary colours, but are instead a subtractive mixing of the three secondary colours: yellow, magenta and cyan blue [54].

Yellow absorbs blue light and transmits greens and reds. Magenta absorbs green light and transmits red and blue light. Cyan absorbs red light and transmits blue and green.



If the white light from a projector is intercepted successively by two filters of secondary colours, it can be seen that the addition of yellow and magenta by the filters will give rise to the colour red that is then transmitted. The addition of yellow and cyan gives green; the addition of magenta and cyan gives blue.

If the three secondary colours are superimposed, the result is black, since none of these colours are transmitted. To darken a colour it may be noted that: red to which some cyan is added gives a brown; adding magenta to green gives rise to olive, etc.

It is, therefore, certain that if a blue pigment is mixed into a medium that yellows with time, it will gradually darken in the course of time.

These rules seem to have been perfectly understood by the Flemish Primitives. Not only did they bind their blue pigments such as lapis-lazuli with an aqueous medium that does not yellow, but also they were past masters in the juxtaposing of thin monochromatic paint layers so as to obtain maximum luminosity. According to Rubens, the mixing of pigments will lead to the darkening of paintings [55].

A great number of defects that appear on the surface of paintings can be explained by the phenomena that have just been described. Such defects include sinking, bloom, blushing, chalking, etc.

There is a certain confusion about the precise connotations of these terms. It may well be useful to reproduce some definitions taken from various sources.

*Sinking*, sometimes also called *sinking-in*: A dull spot on the surface of an oil-painting caused by the absorption of the pigments by the ground.<sup>2</sup> Uneven dullness caused by the support's absorbing the oil.<sup>3</sup> Tone, the matt appearance of a painting that exhibits 'sinking-in.' Marijnissen [81] proposes the following definition (in French): "By 'sinking-in' we mean the premature and localized dullness of the paint layer of an oil painting. The phenomenon is explained by the rapid or excessive absorption of the binding medium by an underlying layer ..."

<sup>2</sup> New Shorter Oxford English Dictionary

<sup>3</sup> Translated from the French definition in Petit Robert

*Bloom*: Marijnissen defines this (in French) as being "... a veil, often slightly bluish, that forms on the surface of varnish and is like the bloom on some fruits or the misting on glass..." An English definition has: A cloudiness on a shiny surface (akin to the delicate powdery deposit on grapes, plums, etc.<sup>4</sup>

*Blushing*: In *Petit Robert*, it is defined (in French) as being the compost on which mushroom mycelium grows; the French verb means "to show traces of fungi." As Marijnissen notes, this term can be "... used in a derogatory way by painters and restorers to describe any phenomenon that produces a veiling on the uniform appearance of a varnish, except for bloom."

*Chalking*: [69, p. 465] "... formation of a friable powdery coating on the surface of a paint film by disintegration of the binding medium..."

However this may be, it seems more logical to classify these defects according to their causes, whenever this is possible.

*Humidity* seems, for example, to be an essential factor in bloom. The presence of hydrophilic groups in the varnish, such as acid groups, clearly favours the formation of stains. Majewski [50] and Thomson [51] have identified ammonium sulphate on bloomed surfaces. Hill [49] has shown that ammonium sulphate can be deposited on paintings when the panel is colder than the surrounding environment, a difference of 1°C being sufficient. Ammonia and sulphur dioxide will form this compound by oxidation in the presence of light.

The presence of minute crystals on the surface of a varnish will always tend to diffuse light, and this could explain the veiling that is observed. This defect can often be cured by simply rubbing the varnish with a soft cloth.

Thomson offers another possible explanation of bloom: that it may be an exudation from the varnish, but this theory has not yet been confirmed.

A third explanation could be that the hydration of film-forming substances causes swelling, even a change in refractive index that would favour the diffusion of light. In this regard it should be noted that natural resins, which are very sensitive to bloom, are extremely hygroscopic: some of them can absorb as much as one-fifth their weight of water.

The *degradation of the medium* causes an appearance of chalkiness that is much more serious. Colling and Wilkinson [48] have put forward the hypothesis of a phase of degradation where the surface would be more severely broken down because it receives more dangerous radiations. The degraded medium becomes powdery and falls away, leaving the pigments more and more exposed. When the ratio of pigments to binding medium reaches the CPVC (see page 10), there is an abrupt loss in gloss [45]; the irregular exposed surface strongly diffuses the light. Feller [46, 47] uses this concept to explain the chalking of some retouchings made with dammar and zinc white that were formulated too near to the CPVC.

4 New Shorter Oxford English Dictionary

Fig. 25 [46, 47]



Numerous studies have been undertaken about the mechanisms of medium weathering when titanium dioxide is present [161]. Titanium dioxide is photoactive and, as a result, it can catalyse the breakdown of the binder. When rutile titanium dioxide is irradiated with UV light having a wavelength shorter than 405 nm, OH<sup>•</sup> and HO<sub>2</sub>• radicals are formed which initiate the decay of the medium. To reduce the degree of photocatalytic degradation, pigment manufacturers dope the TiO<sub>2</sub> crystal with transition metals such as zinc or aluminium and they coat it with oxides such as alumina, zirconia or silica.

The impoverishment of medium that occurs with *sinking-in* leads to the same optical phenomenon.

A new coat of varnish or oil is equally well able to fill the voids that cause the light diffusion, but this practice is debatable. The original medium or old varnish is no better off, and it contains chemical substances that can accelerate the ageing of newly applied materials.

#### • II. 3 Mechanical properties [64]

The mechanical properties of paintings play an essential role in their behaviour during ageing. *Permeability* and *porosity, toughness, flexibility* and *adhesion* will each be treated separately.

#### II. 3. 1 Permeability - porosity

The *permeability* of a film is its ability to allow the passage of a fluid (gas, vapour, liquid). The collection of holes, pores, fissures, breaks and cracks present in a film is responsible for its *porosity*.

The two properties, permeability and porosity, are caused by many factors, the principal ones being the nature of the materials in the paint layer (pigments, binding media, solvents – see page 13), the way in which the film is formed and the processes that take place during ageing.

The permeability of a film to water vapour plays an important role in conservation. It has an effect on the swelling and contraction of moisture-sensitive supports (wood, linen), and favours degradation by hydrolysis.

Film-forming materials	Water vapour permeability [141] g/m <sup>2</sup> /day
paraffins	0.17
gum lac	8.9
rosin	19.7
stand oil	50
linseed oil	104
gelatin	126
ethyl cellulose	537

The chemical composition of the film-forming material is a predominant factor in determining water vapour permeability. The most permeable materials contain many hydrophilic groups. These groups can be formed in the course of the oxidation of drying oils; this explains the superior behaviour of the stand oils, which are oxidized to a small extent during drying (see page 38).

The relative porosity of adjacent layers plays an important role in their good adhesion. According to Garcia [179], the best way to promote a good fastening of the different layers with each other without sinking, is to obey the "law of decreasing porosities." The old rule "fatty upon lean" is but a particular case.

It is also possible to achieve decreased porosity by progressively enriching the layers with the same binding medium.

#### II. 3. 2 Toughness

The toughness of a paint layer is its capacity to resist penetration by hard objects.

This is a very complex quality that depends on several factors. The inter- and intramolecular interactions within and between the molecules of a binding medium can cause differences in toughness. Thus the molecules of thermoplastic resins are only bound to each other by Van der Waals forces and polar bonds. They are less tough than the thermosetting resins, which are bound by covalent bonds [65].
Feller [66] has measured the toughness of various natural and synthetic resins. Generally speaking, the natural resins were found to be tougher than the synthetic resins used in conservation.

Resins [66]	Sward hardness
Dammar, mastic	81
Polyvinyl acetate (PVA)	63
n-butylmethacrylate	30

This toughness can be explained by the molecular structure of the natural resins. They form very rigid molecules having strong polar attraction for each other. According to results obtained by X-ray diffraction analysis [67], the toughness increases when intermolecular distances decrease and when the molecules are oriented in an orderly manner. The presence of very hard pigments or fillers also has an influence on the toughness of the paint layer. Such is the case with Prussian blue and colcothar (English red).

Interaction between pigments and binding medium can also be significant. Some pigments, such as red lead, white lead and zinc white, react with oil to form very hard soaps.

# II. 3. 3 Flexibility

The flexibility of a film is measured by the maximum elongation it can undergo (by stretching, bending or twisting) without breaking [64]. Flexibility is related to the *elasticity* and to the *plasticity* of the film [68, 69].

The *elasticity* of a film is its ability to stretch and orientate the macromolecular chains, of which it is formed, in the direction of the applied stress.

Every material has an *elastic limit*; if the applied stretch is below this limit, the film undergoes an *elastic deformation*. This deformation is instantaneous, completely reversible and proportional to the applied force, as expressed by Hooke's Law:

Fig. 26

$$\frac{L}{F = E \lambda} F$$

F = APPLIED FORCE  $\lambda = DEFORMATION = \frac{dL}{L}$ E = YOUNG'S MODULUS If the stretching force exceeds the elastic limit, the film can still undergo a more pronounced elongation, but this is no longer reversible. This is *plastic deformation* and it is proportional to the time period over which the force is applied.

The difference between the two kinds of deformation can be explained at the molecular level. Most film-forming materials are built up of long chains of methylene (CH<sub>2</sub>) groups. These groups are arranged in a zig-zag manner, forming chains that can easily bend and stretch, since the carbon atoms can rotate freely about the single bonds joining them.

Fig. 27



In the case of paint films, elastic deformation essentially corresponds to the stretching of these linear chains. On the other hand, plastic deformation involves the complete macromolecules' sliding along each other [68]. It is, therefore, understandable that ageing often brings about a decrease in flexibility. Cross-linking and the formation of the three-dimensional network hinders all these movements.

In practice, the two kinds of deformation generally occur together. If too sharp a blow is given to the film, plastic deformation will predominate, provided, of course, that the force is not sufficient to break the film. If the force is applied more gently, the film first suffers an elastic deformation that changes progressively into a plastic deformation. The film can be elongated to a much greater extent before breaking than is the case when the force is applied quickly.

## Plasticizers

Many natural film-forming materials lack flexibility. Some, such as terpene resins, are made up of rigid molecules. Others, such as proteins and carbohydrates, show strong intermolecular attractions that tend to prevent the molecules from sliding over each other.

It is possible to overcome this defect by adding certain substances known as "plasticizers." Glycerol and honey can act in this capacity for aqueous binding media, and elemi functions as a plasticizer for terpene resins.

These plasticizing substances are relatively non-volatile liquids or soft solids that are retained in the dried film. They increase the space between the chains of the binding medium, thus decreasing the intermolecular forces and improving flexibility. Fig. 28

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ADHESIVE BREAK

#### COHESIVE BREAK

# II. 3. 4 Adhesive power [64, 70, 71, 72]

By definition, *adhesive power* is the ability of a coating to adhere to its substrate. *Adhesion* is the ability of a coating to remain attached to its substrate. In a paint, the binding medium joins the pigments together and causes them to adhere to their support. In a join, the adhesive forms a bridge between two supports. The adhesion of a film to its support is most often measured by the force necessary to break the glue bond. This breaking can be either *adhesive* or *cohesive*.

# · Sources of adhesive power

# a) Mechanical causes: mechanical adhesion

The liquid film may penetrate irregularities in the surface of the substrate and remain anchored there after drying. At the beginning, the film must be sufficiently liquid to be able to wet the substrate. The substrate should be porous and the film should not shrink on drying.

# b) Physico-chemical causes: specific adhesion

Mechanical causes are not, in fact, sufficient in themselves to explain the phenomenon of adhesion; this becomes apparent when it is a question of gluing two smooth surfaces.

Adhesion brings into play a complex ensemble of different forces of attraction (Van der Waals forces, polar bonds, electrovalent bonds, covalent bonds, hydrogen bonds, etc.) that act in differing degrees, depending on the nature of the substrates and the adhesives. These same forces are responsible for the wetting of a support by a liquid film and for the strength of the adhesive bond between the dry film and the substrate itself. A layer that does not wet well will not adhere. Adhesion nevertheless requires more energy than is needed for wetting: 1 to 2 Kcal more.

Non-polar compounds such as paraffin waxes have very low adhesive power, because they can only exert Van der Waals forces. The adhesive strength of beeswax is better, because it contains some polar components. To obtain the adhesive strength required in relining, it is, however, necessary to add a terpene resin that has much more pronounced polarity.



Generally speaking, it is evident that the adhesion of a film to a polar substrate increases with the number of polar groups present in the film-forming material. Molecules with linear chains will have lower adhesive strength than those having branching chains, particularly if these are regularly arranged. This, of course, has to be related to the structure of the layer in which the interactions take place. This layer has, in fact, very special properties. Its thickness hardly exceeds some tens of Angstrom units, because *the range of the forces of attraction is short* and their effect decreases rapidly over distance.

The structure of the layer in which interactions takes place often exhibits molecular orientation, leading to an increase in toughness. The macromolecules of film-forming materials are arranged more or less perpendicularly or obliquely to the surface of the substrate, according to the arrangement and number of the chain's branches (fig. 29a).

It has been shown that some contaminants, among them the fatty acids, are oriented toward the surface of glass or metal (fig. 29b). The polar groups are directed toward the substrate and the non-polar methyl groups are directed outwards. This assemblage cannot be wetted by a polar liquid or an adhesive. This explains why it is necessary to degrease surfaces thoroughly before they are glued together. The same phenomena of directional attractions are apparent in the reaction of silicones with glass and paper, which makes the latter non-wettable by water.

Fig. 30



The presence of plasticizers and solvents can interfere with the formation of the layer in which interactions between adhesive and substrate take place, because they compete for a position on the substrate. Moreover, the use of excessive amounts of solvents should be avoided, because this induces shrinkage on drying. Thixotropic glues, such as animal glue, have important advantages in this regard. They are liquids that wet well as soon as they are applied, they set quickly and allow easy alignment of the two pieces being glued together.

In conclusion, a good glue joint demands thorough cleaning of the two substrates; the adhesive layer should be as thin as possible but also as continuous as possible to ensure maximum effectiveness of the forces of attraction.



# **Chapter Two**

# DESCRIPTION OF THE MAIN NATURAL FILM-FORMING MATERIALS

The natural film-forming materials are so numerous and so diverse that it is essential to group them into large categories. This book will follow the classifications put forward by the biochemists [73]:

I. Lipids or fatty materials

II. Carbohydrates, particularly sugars

III. Proteins or albuminous materials

To these will be added a very important family of film-forming materials derived from the vegetable kingdom:

IV. Terpenes or resinous materials

In addition to the above compounds obtained from the animal and vegetable kingdoms, there is a further category of mineral substances which must also be included [74, 75]. We shall finish with:

V. Empyreumatic materials: tars, bitumens

# I. LIPIDS OR FATTY MATERIALS [76, 77]

These materials, referred to as oils if they are liquids, and waxes or fats if they are solids, are difficult to describe briefly. One characteristic they have in common is their ability to produce translucent stains on paper. These fatty substances are insoluble in water and their density is less than that of water. In general they are soluble in aromatic and chlorinated solvents, in ether and in carbon disulphide.

Most of the lipids contain esters of various straight chain organic acids having a high molecular weight, and are referred to as *fatty acids*.

These acids can be divided into three classes:

# I.1 Normal saturated fatty acids

They have the general formula, where n = total number of carbon atoms in the molecule, of:

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CH3-(CH2)n2-COOH
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e.g.: palmitic acid  $C_{16}H_{32}O_2$ 

stearic acid C18H36O2

cerotic acid C<sub>26</sub>H<sub>52</sub>O<sub>2</sub> melissic acid C<sub>30</sub>H<sub>60</sub>O<sub>2</sub>

These acids are very stable. Only their weak acidic function confers some reactivity. Their salts are known as *soaps*.

# I.2 Unsaturated fatty acids

These acids contain one or more carbon-to-carbon double bonds. e.g.:

- oleic acid  $CH_3$ -( $CH_2$ )7-CH = CH-( $CH_2$ )7-COOH
- linoleic acid CH<sub>3</sub>-(CH<sub>2</sub>)<sub>4</sub>-CH = CH-CH<sub>2</sub>-CH = CH-(CH<sub>2</sub>)<sub>7</sub>-COOH
- linolenic acid CH<sub>3</sub>-CH<sub>2</sub>-CH = CH-CH<sub>2</sub>-CH = CH-(CH<sub>2</sub>)7-COOH

The carbon-to-carbon double bonds react with atmospheric oxygen, and this oxidation is one of the principal reasons that fats become rancid. The complex oxidation process also involves degradations that produce foul-smelling products (acids and aldehydes).

The presence of more than one C=C bond (linoleic and linolenic acids) makes the molecule especially reactive. These double bonds are responsible for the drying of oils.

# I.3 Hydroxy acids

As the name implies, these acids contain hydroxyl (OH) groups, e.g.:

ricinoleic acid CH<sub>3</sub>-(CH2)<sub>5</sub>-CHOH-CH<sub>2</sub>-CH = CH-(CH<sub>2</sub>)<sub>7</sub>-COOH

All these fatty acids are, for the most part, present in the lipids as esters, i.e., combined with an alcohol. Depending on the type of alcohol the lipids can be divided into three groups:

## A. GLYCERIDES

The alcohol is glycerol : CH<sub>2</sub>OH–CHOH–CH<sub>2</sub>OH.

This class is by far the most extensive. It includes the majority of animal and vegetable fatty substances, oils, butter, tallow, etc.

# **B.** CERIDES

In this case the alcohol is a linear alcohol of high molecular weight, e.g.:

- myricilic alcohol CH3-(CH2)28--CH2OH
- cerilic alcohol CH<sub>3</sub>-(CH<sub>2</sub>)<sub>24</sub>-CH<sub>2</sub>OH
- cetyl alcohol CH<sub>3</sub>-(CH<sub>2</sub>)<sub>15</sub>-OH etc.

These compounds are the main components of waxes. The esters usually consist of an acid and an alcohol having the same number of carbon atoms.





### C. STEROIDS

Here the alcohol is a sterol, i.e., a compound having a tetracyclic structure. One of the commonest is cholesterol (fig. 31).

Steroids are found in ox-gall, oil from egg-yolk, gallstones, and also in some vegetables such as rye, from which ergosterol is obtained.

# A. GLYCERIDES

In the literature dealing with glycerides there are frequent references to the terms *saponification*, *hydrolysis* and *hydrogenation*. These can be explained as follows:

Saponification

When an oil or a fat is heated with potassium or sodium hydroxide, glycerol and an alkaline salt of a fatty acid (i.e., a soap) are formed. The *saponification index* is the number of milligrams of potassium hydroxide needed to saponify one gram of the sample. At first sight, it might seem that the saponification index would be smaller, the greater the molecular weight of the glyceride; however it is also necessary to take into account the neutralization of free fatty acids that might be present in the sample.

Hydrolysis

The hydrolysis of glycerides leads to the formation of glycerol and free fatty acids. In former times, hydrolysis by sulphuric acid at 110°C was used in the manufacture of candles made from a mixture of stearic and palmitic acids. Nowadays, these fatty acids are obtained by the oxidation of paraffins derived from petroleum.

### Hydrogenation

Hydrogenation involves the conversion of the double C=C bonds into saturated C-C bonds by the addition of hydrogen. This process is of great industrial importance as it enables solid fats to be made from oils, and is used in making margarine. Also the hydrogenation of castor oil is important in the manufacture of alkyd resins.

### **ANIMAL FATS - TALLOW**

Animal fats are generally obtained as slaughterhouse by-products from domestic animals: cattle, sheep and pigs.

• Composition

The glycerides contain oleic acid ( $\approx 40\%$ ), palmitic acid ( $\approx 25\%$ ), stearic acid ( $\approx 20\%$ ), myristic acid ( $\approx 5\%$ ) and linoleic acid ( $\approx 2\%$ ). In addition there are small amounts of cholesterol and other fatty acids (arachidonic acid, elaidic acid, vaccenic acid, etc.).

• Properties

Besides being used as foodstuffs, these fats are used as lubricants, especially in the treatment of leather.

#### **VEGETABLE FATS**

Solid fats also occur in the vegetable kingdom, e.g., coconut butter, palm butter. These are primarily foodstuffs.

Vegetable fats differ from the animal fats in that they contain lower molecular weight fatty acids, C<sub>6</sub> to C<sub>14</sub>, principally lauric acid CH<sub>3</sub>–(CH<sub>2</sub>)<sub>10</sub>–COOH.

#### DRYING AND SEMI-DRYING OILS [76, 77, 78, 79, 80]

Animal oils, such as whale oil and fish oil, are only of interest as foodstuffs and have no drying properties, so this section will deal mainly with vegetable oils. These are found in the seeds, skins, kernels and fruits of certain plants [76].

Drying oils have been by far the most popular medium for many centuries. About AD 1550, Vasari spread the opinion that Van Eyck discovered oil painting [188]. Actually, Heraclius (10th century) and Theophilus (early 12th century) had already described how to extract the oil from the seeds and how to boil it then with white lead [2].

The solid film presents very different aspects: matt or shiny, porous or glazed following the quantity and the nature of the pigments or of the coating technique. Its excellent flexibility decreases on ageing.

An oil is said to be "drying" when, after being spread out in a thin layer, it forms a continuous film within a reasonable time (a few days) [37].

The drying power is related to the concentration of polyunsaturated fatty acids in the oil, because their C=C double bonds enable polymerization and oxidation reactions which promote the formation of the film. For an oil to be regarded as a drying oil this concentration should reach at least 65%. The presence of linolenic acid is essential for rapid drying. Oils also contain saturated fatty acids that are so stable that their concentration hardly changes on ageing. Mills [79] has proposed a method of analysis by gas chromatography based on the ratio of palmitic acid to stearic acid. This ratio remains constant over the course of time and is characteristic for each oil, as shown in the following table:

Oil	linoleic acid (%)	linolenic acid (%)	% total polyunsat.	ratio palm.: stear.	Refractive index <sup>(1)</sup> at 25°C
Linseed	15	52	67	1.4-1.9	1.4800
Рорру	76		76	4.2-5.0	1.4770
Nut	61	12	73	2.7-3.0	1.4770
Soya	54.4	7.3	61.7		1.4813
Safflower	75.8	1	76.8		1.4744
Sunflower	63.5	_	63.5		1.4796

### Note 1: Source: [9, 80]

Oleic acid, often present in large amounts, is also much more stable than the polyunsaturated acids.

### Linseed oil

Linseed oil is extracted from the seeds of the flax plant (*Linum usitatissimum*), from which linen is prepared. It dries faster than other oils used in painting, owing to its high concentration of linoleic acid.

Composition

The composition depends on a number of factors such as the quality of the seeds, the climate and the soil, and also on the methods of extraction and refining.

High temperatures must be avoided during extraction, because they cause the products to become coloured, and modify the composition of the triglycerides.

It is necessary to remove the phospholipids, mucilages and any other impurities present in the extract from the seeds. Mucilage will flocculate in the presence of small amounts of water. Coloured matter is removed by passing the oil over clay.

### • Properties

The way in which a drying oil forms a film has already been described (pages 15-16). The film has particular properties which will be examined below [37].

A film of linseed oil that is touch-dry is often referred to as linoxyn. The porous network of the partially oxidized and polymerized glycerides encloses in its interstices some molecules of unchanged glycerides. The phenomenon of shrinkage associated

with the formation of the three-dimensional network can also lead to the exudation of liquid substances toward the surface of the film and toward underlying layers. This is known as *synaeresis*.

This explains why a tacky film often appears at the surface of an oil painting when it is drying. When it begins to dry the oil film is soft and has low mechanical and chemical resistance. The structure is very porous, and a liquid can easily diffuse through it, for example the still-liquid oil from an overlying layer. This period is therefore critical to the occurrence of sinking-in [81]. The weak mechanical resistance could be due to the fact that the high molecular weight structure is, at this stage, being built up by means of weak secondary bonds such as hydrogen bonds, rather than by covalent bonds.

As ageing proceeds, oxidation and polymerization reactions occur. The film becomes tougher, and acidic compounds are formed: propionic acid, azelaic acid, etc. The acidity of oil increases and this can be dangerous for some materials such as cellulose. It is therefore advisable to prime paper and cellulose canvas (linen or cotton) with glue before painting with oil.

Certain sensitive pigments, such as ultramarine, can sometimes be altered as well.

Acidity of oils and resins is also responsible for the degradation of tracing-papers [174]. The refractive index increases and can approach that of certain pigments, resulting in an increase of transparency. Townsend has shown recently [201] that the presence of lead driers enhances the change in the refractive index.

There are various ways that the rate at which the oil dries can be increased.

Thus, by heating to 150-160°C, usually with a small amount of salts of lead, cobalt or manganese, *boiled oil* is obtained. This procedure induces the start of oxidation and polymerization. The material formed is more viscous and dries more quickly.

A similar result is obtained by blowing air through heated oil, giving *blown oil*. Both these procedures lead to the formation of unsaturated ketones that are responsible for yellowing of the oil.

Products with less colour can be obtained if conditions favour polymerization rather than oxidation: this is the way *stand oil* is formed. The heating is carried out at temperatures between 280°C and 310°C, in the absence of air. The polymerization increases the drying power of the oil and also enhances the lustre and water resistance of the film that is formed, which is less coloured [82]. On the basis of the work of Koller and Burmester [185], the use of stand oil should explain the blanching of some modern paintings by Serge Poliakoff. After heating in the absence of air, some unsaturated acids like linoleic acid are only isomerized but not oxidized. When the pigments do not promote oxidation, these substances remain liquid and migrate towards the surface. In the present case the bad formulation of the painting was probably the cause of the phenomenon. Indeed, the authors measured a high proportion of medium (more than 50%) in every sample taken from the blanched areas.

In fact, the action of light on linseed oil is very complicated. Thus, while light usually causes yellowing, it has often been observed that an oil painting kept in the dark will darken more, but then regain its original hue when once again exposed to light [77, 83]. This apparently contradictory behaviour might be explained by the oil's producing, in the dark, mostly coloured, conjugated, unsaturated ketones that are unstable to light.

The effect of pigments on the ageing of linseed oil has recently been studied [146]. In particular, it was shown that vermilion accelerates the degradation of oil in ultraviolet light whereas verdigris seems to have a stabilizing effect.

# Poppy oil

This is extracted from the seeds of the opium poppy, Papaver somniferum.

Composition

Poppy oil contains a smaller percentage than linseed oil of the very reactive unsaturated acids (no linolenic acid), and therefore dries more slowly than linseed oil.

• Properties

Poppy oil yellows less than linseed oil, but it does not dry nearly as readily. The film remains porous for almost three months and has a tendency towards synaeresis.

### Nut oil

This oil is extracted from walnuts, the fruit of the walnut tree, Juglans regia.

• Composition

Nut oil contains about 12% of linolenic acid which gives it a drying power somewhat greater than that of poppy oil.

• Properties

Nut oil was apparently used in the past for the clear tones in a painting, as far as can be judged from the old treatises. Laurie [84] proposed a method for increasing its drying power: the oil would be spread out in a thin film on water and exposed to air and light.

# Egg-yolk oil

Egg-yolk contains between 17 and 38% of lipids, which can be extracted by chlorinated solvents or by ether. The glyceride fraction contains the saturated fatty acids, palmitic and stearic, and the non-saturated acids, oleic, linoleic and clupadonic.

Since these compounds have a very low drying power, the egg-yolk itself dries only with great difficulty. If it is added to linseed oil it will hinder the hardening of the latter. This oil can nevertheless act as a very beneficial plasticizer for egg-tempera painting.

# **B. WAXES**

Waxes – sometimes called cerides – are solid substances that melt easily and are difficult to saponify using alkalies. They contain esters of long chain acids and alcohols.

The sources of natural waxes are very diverse: animal, vegetable and mineral.

The following table gives the properties of some waxes.

Waxes .	Melting point (*C)	Toughness	Acid Index*	lodine Index**	Refractive Index		
Mineral		I		1	-1		
Ceresin	54-77		0	7-9	1.4415-1.4464 (60°C)		
Montan	76-92	hard-brittle	25	10-16			
Ozocerite	58-100	variable	0	7-8	1.4415-1. <b>4464</b> (60°C)		
Vegetable							
Candelilla	65-69	hard	16	14-37	1.4555 (71.5°C)		
Carnauba	83-91	very hard, brittle	4-8	13.5	1.463 (60° <b>C)</b>		
Animal	Animal						
Beeswax	62-70	not very hard	17-21	8.5-11	1.4398 (75° <b>C)</b>		
Chinese	65-80	hard	13	1.4-2	1.4566 (40°C)		
Spermaceti	41-49	powder	0.5-2.8	2.6-3.8	1.440 (60°C)		
Lanolin	38-42	soft			1.4781-1.4822 (40°C)		

GENERAL PROPERTIES OF NATURAL WAXES [80-85]

\* The acid index refers to the amount of free acids present. It is the quantity in milligrams (mg) of potassium hydroxide (KOH) required to neutralize the acids in 1 g of the fatty material.

\*\* The iodine index indicates the amount of double bonds (C=C) present. It is the quantity, in milligrams, of iodine that will react with 1 g of the fatty material.

Auger [177] proposed the following definition of wax:

- Drop point above 40°C without decomposition. This distinguishes a wax from an oil or fat.
- Has a solid consistency at room temperature.
- Translucent to opaque in appearance. This reflects the amorphous-to-crystalline structure.

- Relatively low melt viscosity above the drop point. This differentiates a wax from a resin or plastic.
- Consistency and solubility are strongly dependent upon temperature. This relates to properties such as melt viscosity, hardness, etc.
- Capable of being polished under slight pressure. A typical characteristic of most waxes although temperature dependent.

# MINERAL WAXES

#### WAXES EXTRACTED FROM PETROLEUM

#### Paraffin and microcrystalline waxes

These two kinds of waxes are obtained from petroleum, but the methods of extraction differ. Paraffins are separated by distillation, whereas the microcrystalline waxes cannot be distilled without decomposing. They are extracted with the aid of a complex series of solvents.

Composition

The paraffins consist mainly of long-chain saturated hydrocarbons, with a molecule containing 26 to 30 atoms of carbon.

The microcrystalline waxes also contain long-chain saturated hydrocarbons, but, in contrast to the paraffins, there is a high proportion of hydrocarbons having branched and cyclic chains. Their molecular weight is higher and they contain 41 to 50 atoms of carbon.

• Properties

When the paraffins solidify, either from solution or from the molten state, they develop large, well-formed crystals. In contrast, the microcrystalline waxes form only very small, misshapen crystals, and then only from the molten state.

# COMPARISON OF PROPERTIES OF PARAFFIN AND MICROCRYSTALLINE WAXES

Property	Paraffins	Microcrystalline waxes
Melting point	50–60°C	70°C
Flexibility	brittle	resistant and very flexible
Toughness	low	hard
Transparency	good	opalescent
Gloss		less gloss
Shrinkage		low
Adhesive power		better

### WAXES EXTRACTED FROM COAL, LIGNITE, BITUMEN OR PEAT

#### Montan wax

Montan wax is extracted from lignite, principally in Germany and in the western United States, using a mixture of solvents (e.g., benzene:ethanol – 85:15).

Composition

The composition of the wax differs according to its source and is still not well known. It contains a mixture of long-chain esters, acids, alcohols and hydrocarbons.

Properties

Montan wax is brown to black in colour and this limits its use. It is very hard and can be scratched by the fingernail only with difficulty. It melts at about 80°C and is soluble in aromatic and chlorinated solvents, in methyl ethyl ketone and in dioxane.

It is used for the manufacture of carbon paper and for making floor polishes.

### Ozocerite

Ozocerite is generally found in bituminous deposits of Miocene age, and near oil-bearing deposits in eastern Europe. It is extracted by melting the bituminous earth in boiling water: the wax floats to the surface and can then be separated.

Composition

The wax appears to contain a mixture of saturated and unsaturated hydrocarbons of high molecular weight, some liquid hydrocarbons and some unidentified compounds containing oxygen.

• Properties

Ozocerite is resistant to the action of acids and alkalies. It is soluble in aromatic and chlorinated hydrocarbons but not in alcohols. It shrinks more than beeswax on solidification and becomes harder on ageing.

### Ceresin

Ceresin is purified ozocerite. Nowadays paraffin (up to 80%) and even rosin are added to it to give it the appearance of beeswax.

#### VEGETABLE WAXES

#### **Candelilla** wax

This wax comes from a shrub, *Euphorbia antisyphilitica* (syn. *E. cerifera*), which grows mainly in southern North America and in Mexico. The wax is separated by plunging the plant into boiling water to which a small amount of sulphuric acid has been added.

### Composition

The main constituent of candelilla wax is a hydrocarbon, hentriacontane. There is also myricilic alcohol, amongst others.

• Properties

Candelilla wax is yellow to brown in colour. It is very hard and brittle. For this reason, it is chiefly used to harden other waxes. It is soluble in acetone, oils, hot chlorinated solvents and turpentine.

### Carnauba wax

This wax exudes from the pores of the leaves of a Brazilian palm, *Copernicia* prunifera (syn. C. cerifera). The wax is collected by beating the dried leaves.

Composition

The composition of this wax is not well known. Its most interesting properties, namely its hardness and lustre, are due to the presence of unsaturated hydroxy acids containing 12 atoms of carbon.

• Properties

Carnauba wax is a hard, greenish solid which melts at about 82-85°C while giving off a pleasant odour. It is resistant and has a high gloss. It is added to other waxes to increase their melting points, hardness, resistance, lustre, and to decrease their tackiness, plasticity and tendency to crystallize.

At room temperatures, the wax is soluble only with difficulty in fat solvents. The solubility improves at about  $45^{\circ}$ C.

## ANIMAL WAXES

### Beeswax

Beeswax is collected by melting the honeycomb in hot water. It is then strained and can be bleached with oxidizing agents such as potassium permanganate or potassium dichromate. In former times, beeswax was bleached by exposing it to the sun. The oxidation products that are formed should always be carefully removed by washing and filtering.

• Composition

Beeswax consists mainly of esters of long-chain acids and alcohols having 21 to 36 carbon atoms. There is also a glue, *propolis* (bee glue), as well as pigments and other, as yet unidentified substances.

Properties

Beeswax is virtually insoluble in water. It is, however, permeable to water vapour, unlike the paraffins [14, 86]. Nevertheless, a recent study by Brewer [167] shows that beeswax is an efficient moisture barrier for several kinds of wood panels:

mahogany, oak, lime-tree and poplar. Beeswax is soluble in aromatic and chlorinated hydrocarbons and in hot alcohol.

# **Chinese wax**

This wax is secreted by the insect *Coccus ceriferus* which lives on the branches of the ash tree in western China.

Composition

The main constituent is ceryl cerotate.

• Properties

Chinese wax is whitish, hard, lustrous and crystalline, odourless and tasteless. It is insoluble in water but easily soluble in aromatic hydrocarbons, and slightly soluble in alcohol and ether.

It is used chiefly for the manufacture of candles, the formulation of wax mixtures for leather and floors, the finishing of silk and cotton textiles, and for glazing paper.

# Spermaceti wax

This is a wax found in the skulls of sperm whales and related cetaceans.

• Composition

The wax consists chiefly of a cetyl palmitate.

• Properties

Spermaceti wax is found as a whitish, translucent substance that is relatively brittle. It is soluble in boiling alcohol, chloroform, carbon disulphide and oils.

It has been used extensively in the cosmetic industry, for example in making emulsions with egg-yolk and almond oil. It has also been used for making candles, soaps, wax mixtures and in the finishing of textiles.<sup>1</sup>

# Lanolin

Lanolin occurs in the fleece of sheep, and is extracted by washing the wool with a detergent. The lanolin is separated by centrifuging, and purified by treating with water to which some alkali has been added so as to remove free acids and impurities.

Composition

1

Lanolin is a complex mixture of esters of long-chain fatty acids and alcohols. The latter are aliphatic alcohols, steroids or triterpenes, which makes it hard to classify this material.

[As a result of recent bans on the hunting of large whales, it is no longer available in commerce.]

#### Properties

Lanolin contains nearly 30% water. It has a greasy consistency and is whitish or yellowish in colour. It is insoluble in water but soluble in chlorinated and aromatic hydrocarbons and in hot alcohol. It can absorb up to twice its weight in water.

It is used in the cosmetic industry, mainly because of its ability to retain water. Some people use it to restore flexibility to old woollen textiles, but others prefer to avoid its use for this purpose because it retains dust.

### C. STEROIDS

Steroids are esters of fatty acids and of a special class of alcohols, the *sterols*. These compounds are secondary cyclic alcohols containing between 27 and 29 carbon atoms [87]. They are solid at room temperature, their melting points lying between 100 and 200°C. The name sterol is derived from the Greek work "stereos" meaning solid.

The sterols are widespread in the animal kingdom (zoosterols) and in the plant kingdom (phytosterols), and also occur in fungi (mycosterols).

#### Cholesterol

Cholesterol is one of the most widespread sterols. Its name is derived from the Greek word "chole" meaning bile. It is, in fact, found not only in bile secretions, but also in most animal tissues. A normal person weighing 70 kg contains about 140 g of cholesterol, of which approximately 11.3 g are in the blood, 30 g in the muscles, 12.5 g in the skin and 32 g in the brain, nervous system, etc. [88].

Egg-yolk contains about 2% cholesterol. Ox-gall contains cholesterol, but also a number of other components including sodium salts of various bile acids (i.e., sterols with 24 carbon atoms and having an acid carboxyl group COOH), an amino acid, glycine, together with derivatives of choline and lecithin that give it surface-active properties.

#### Vegetable sterols

Vegetable oils also contain sterols amounting to between 45 and 80% of their non-saponifiable fraction (see page 34). The main constituents are  $\beta$ -sitosterol, which makes up 50-90% of the sterol fraction, stigmasterol and campesterol. All the vegetable oils have practically the same qualitative composition of sterols, but the relative amounts differ. It is, however, very debatable whether the oils can be differentiated by this means, because, as shown by Mills and White [89], the sterols disappear on ageing. This is also true of cholesterol which indicates that it would have been eliminated from old paint layers in which egg-yolk was used as the medium.

#### **Saponins**

Saponins are vegetable substances containing either sterols or triterpenes associated with sugars [87]. Their aqueous solutions lather easily. They form oil-in-water emulsions and act as protective colloids.

They are dangerous to some degree, in that they have a powerful haemolytic effect when injected into the bloodstream. Ingestion by mouth is, however, harmless to humans.

#### II. CARBOHYDRATES, PARTICULARLY SUGAR COMPOUNDS

*Carbohydrates* – sometimes known as *glucides* – are composed of polyhydroxaldehydes or polyhydroxy ketones. For example:

- glucose CHO-(CHOH)4-CH<sub>2</sub>OH
- fructose CH2OH-CO-(CHOH)3-CH2-OH

The carbohydrates can be classified as mono-, di-, tri-, or polysaccharides.

The monosaccharides are

- pentoses C5H10O5 such as arabinose, xylose, ribose ... or
- *hexoses* C<sub>3</sub>H<sub>12</sub>O<sub>6</sub> such as glucose, galactose and fructose.

The *disaccharides* are formed by the union of two sugar units that can be hydrolyzed:

#### C12H22O11

such as sucrose or cane sugar (glucose and fructose), lactose (glucose and galactose) and maltose (glucose and glucose).

The trisaccharides contain three sugar units:

### C18H32O16

This is the case with raffinose (galactose, fructose and glucose).

*Polysaccharides* are formed by the union of many sugar molecules. Among them are polysaccharide gums, mucilages, starch, cellulose.

These substances are hygroscopic and many of them are soluble in water, at least up to the trisaccharides. They are generally insoluble in organic solvents, with the exception of pyridine. Many important film-forming materials are found amongst the polysaccharides. These plant-derived materials are found worldwide (see Map 1).

Analysis of polysaccharide gums and mucilages can be made by several chromatographic and spectroscopic methods [91, 107, 160, 166].



Map 1. – Origin of the most important polysaccharide gums and mucilages [202]

COMPOSITION OF MAJOR PLANT GUMS AND MUCILAGES [90, 202]

	uronic	acid	mannan	
PLACE	+ glucuronic	+ galacturonic	gluco-	galacto-
EUROPE	<i>Prunus</i> spp: cherry, plum, peach, almond	flax seed		
AFRICA	Acacia senegal, A. sudan, A. seyal, A. drepanalobium, A. karoo Marike	flax seed okra		carob
ASIA	Acacia arabica, A. modesta, Prunus spp., marike or ghatty	tragacanth, karaya, kutira, jeol	konjaku Iles mannan	guar
AMERICA North Central South	mesquite angico, sapote	cholla chagal	cashew	guar brea
OCEANIA	Acacia pycnantha	·	·	

## A. POLYSACCHARIDE GUMS

These vegetable materials all have a similar molecular composition, namely sugars and sometimes uronic acids.

The *polysaccharide gums* are secreted by certain plants, essentially in response to being wounded. They serve to seal the wound so as to stop the destruction of the tissue and prevent drying out. Actually, the mechanism by which the gums are produced is not well known. The exact place where they are formed has not yet been identified: Is it near the wound, or are the gums brought from somewhere else to the place where exudation is occurring?

Some people believe that the gums are produced as an infection product by micro-organisms, moulds, bacteria, etc.

Whatever the case may be, it has been observed that the production of gum increases when the environmental conditions do not favour the plants: high temperature, lack of water, poor soil, etc. [90].

The structure of the polymers in polysaccharide gums is very complex. There is a great variety of constituent sugars and numerous irregularly distributed side chains of highly variable length and composition.

# B. VEGETABLE MUCILAGES

The *vegetable mucilages* are polysaccharides produced by the normal metabolism of certain plants. They serve as a nutritional reserve, stored in the bark, roots, leaves, seeds and even the flowers. They sometimes act as agents for the retention of water, as in the case of aloes and euphorbia.

The macromolecular structure is normally simpler than that of polysaccharides.

• Properties

The structure of a polysaccharide influences solubility and adhesive properties. Sugars and the uronic acids are compounds containing a large number of hydroxyl (OH) groups. These groups are very hydrophilic, and this is why most of these materials are more or less *soluble* in water, or will *swell* in water. Some of them form gels with water; it seems probable that these substances have side chains distributed in a regular manner, allowing development of the three-dimensional network required for gel formation.

Others cannot form a gel because the structure is too irregular; they form true aqueous solutions.

In the case of carbohydrates, the *adhesive power* is mainly due to the presence of hydrogen bonds. The strength of the join is more a product of the very large number of these bonds, involving numerous OH groups in the molecule, rather than the actual strength of individual bonds.

The *film* is formed by simple evaporation of water. The resulting films are brittle, and for this reason plasticizers are often added, as well as agents that retain water and prevent too pronounced a drying-out; these include glycerol, sorbitol, urea, ethylene glycol.

As ageing proceeds, the macromolecules are broken down into smaller fragments, and this increases their susceptibility to water. The films are also very liable to be attacked by fungi and other micro-organisms.

# A. POLYSACCHARIDE GUMS

# Gum arabic or acacia gum

There are more than a hundred different species of acacia, all of which produce a gum. *Acacia senegal* (syn. *A. verek*) is the main one exploited commercially. This acacia grows over a wide territory extending from Senegal to the Red Sea and the Indies. It is found in almost all dry tropical and sub-tropical areas of the world.

The exudation of the gum is stimulated by making incisions of about 5 to 10 cm in the bark of the trunk. The tree should be between six and thirty years old when this is done.

#### Composition

Gum arabic is composed of the calcium, magnesium or potassium salts of an organic acid, arabic acid. Analysis shows that this acid is, on average, composed of L-arabinose (30.3%), D-galactose (36.8%), L-rhamnose (11.4%) and D-glucuronic acid (13.8%). The presence of rhamnose seems to vary with the species of acacia from which the gum is obtained.

#### • Properties

The macromolecules of gum arabic have a molecular weight of between 250 000 and 300 000. The molecules are almost spherical, being about 100 Å long and with a diameter of 110 Å. The gum dissolves slowly, but completely, in twice its volume of water. The viscosity of an aqueous solution of gum arabic depends on its pH: maximum viscosity is reached at the neutral point (pH 7).

It appears that the macromolecules readily change their shape and dimensions in solution, and this indicates that the forces of attraction between the constituent sugars are weak. This confirms the hypothesis of a highly branched structure. This also supports the theory that the macromolecule is formed by the assembly of fragments made up of D-galactose and D-glucuronic acid with a molecular weight of between 10 000 and 20 000, bound together with labile fragments such as L-arabopyranose.

When the solution is heated, there is a decrease in viscosity and the macromolecules start to break down, as shown by the liberation of sugars. This molecular degradation can also be brought about by a number of other factors, such as the presence of acids, salts, ultraviolet light or even by simple mechanical grinding. The ageing of gum arabic has recently been studied [200]. The medium remains soluble. Only a heating to 100°C makes it brown and insoluble.

Gum arabic is an excellent protective colloid, and for this reason it is often used to stabilize emulsions or dispersions and as a thickening agent.

An aqueous solution of the gum is used as a binding medium in watercolours and gouaches, and it serves as an adhesive for paper and cardboard. It is also the gum used on envelopes and stamps. Gum arabic was also the binding medium of miniatures on ivory [165].

The analysis of the mural paintings in the tomb of Nefertari, the wife of Rameses II, identified a gum arabic without rhamnose which could have come from a local acacia species still growing in the Luxor region [168].

#### **Gum tragacanth**

This gum is produced by various species of *Astragalus* (of which there are more than 1 600 different species known), leguminous plants found in Greece, Iran, Syria and in general throughout Asia Minor. The usual commercial source is *A. gummifer*.

The gum exudes from freshly cut incisions in the stem, but a better yield and a higher quality gum is obtained by making incisions in the roots. The gum exudes in the form of thin ribbons that are almost colourless and that dry in one to two days. Astragalus has an average life of six years and the gum appears to be produced only every second year.

Composition

The gum consists of the polymerization products of L-arabinose, D-xylose, L-fructose and D-galacturonic acid.

• Properties

Gum tragacanth has the extremely interesting property of forming very viscous solutions, even at low concentrations. Its molecular weight is greater than that of gum arabic, namely 840 000, and the macromolecules have an elongated shape, being 4 500 Å in length and 19 Å in diameter: this explains the high viscosity of its solution. Gum tragacanth is only partially soluble in cold water and forms a gel in concentrations above 0.5%. Although there is at present no explanation for it, the solution reaches a maximum viscosity after 48 hours at 40°C. The viscosity otherwise depends on the pH; it reaches its maximum at pH 8, and appears to be proportional to the amount of methoxy ( $-O-CH_3$ ) groups in the molecule.

Gum tragacanth is an excellent protective colloid, and is used to stabilize emulsions and dispersions and also as a thickening agent. It is also extensively used in the cosmetic and pharmaceutical industries.

# Fruit tree gums

Some old recipes record the use of these gums as binding media, especially in the illumination of manuscripts. They are undoubtedly mostly gums from cherry, plum or peach trees [91]. Their production is spasmodic, the yield often small, and the brownish colour is a disadvantage.

# **B. VEGETABLE MUCILAGES**

# Starches

Starch is the main carbohydrate reserve of plants. It is found as small, concentrically layered granules of highly varied shape and size (from 0.005 to 0.15 mm in length).

It is found in seeds, roots, bulbs, sap and fruits, etc. The sources that are commercially exploited are principally maize, wheat, rice, potatoes, tapioca, arrowroot, bananas, etc.

Composition

Starch contains two polymers, *amylose* and *amylopectin*,, and their respective proportions differ greatly depending on the origin of the starch. Rice starch contains a small amount of amylose (between 16 and 17%), maize starch contains between 22 and 28% amylose, and pea starch between 34 and 70% [92].

Fig. 32



Amylose is a linear polymer of 1,4-anhydroglucose joined by  $\alpha$ -linkages (fig. 32), with a molecular weight varying between 150 000 and 2 400 000.

Fig. 33



Amylopectin is a polymer having many side chains formed by short linear chains of the same 1,4-anhydroglucose units, attached at the 1,6- position (fig. 33), with a molecular weight varying between 1 and 60 million.

Properties

Amylose and amylopectin have different properties, and the proportion in which they are present influences the properties of any given starch.

Amylose has a helical structure. With iodine it forms a blue complex compound in which the iodine atoms are situated inside the helix. Amylopectin or degraded starches form different complex compounds with iodine that are red or violet in colour.

Amylose is not very stable in solution, and tends to form irreversible gels, so-called "retrogression," and very hard films. Amylopectin, on the other hand, makes very viscous solutions that are more stable, and either do not gel or else give rise to reversible gels.

In all cases, starch films have rather mediocre mechanical properties. They can be plasticized by the addition of urea, ethanolamine, glycerol or castor oil. Starch is hydrolyzed by acids or enzymes such as diastase into products of lower molecular weight, and finally into glucose. This hydrolysis can also occur during the process of ageing.

Starch is an excellent glue for paper. It has been used in Japan for numerous centuries for relining painted silk. A special flexible glue is used for kakemonos [silk or paper scrolls] because they must be rolled up. Therefore, the starch undergoes an enzymatic hydrolysis lasting ten years. We succeeded in reproducing a similar quality of glue by a controlled acid hydrolysis which can be achieved in some hours in the laboratory [189].

# Dextrins [93]

Dextrins are products obtained from the breakdown of starch by heating it to between 180°C and 250°C, often in the presence of alkaline or acidic catalysts.

Composition

The heating brings about a change in structure. It appears that the 1-4 linkages are broken and the structure re-forms 1-6 linkages, with the result that dextrin contains many side chains.

• Properties

The dextrins retain some of the properties of the starch from which they are derived. They are usually more soluble in water than the original starch, because the molecular weight is lower and the intermolecular rearrangement gives rise to groups of atoms that make them more soluble.

Some starches are more easily converted into dextrin than others. Thus potato starch and tapioca starch are more easily converted to dextrins than is wheat starch.

Films formed from tapioca dextrin are transparent and lustrous, whereas those based on wheat dextrin are more opaque, doubtless due to partial retrogression.

To counteract the lack of mechanical resistance of dextrin films, humidifying agents are often added, as these retain atmospheric humidity and prevent too pronounced drying of the film. Among such substances are urea, D-glucose, sorbitol, glycerol and ethylene glycol.

Dextrins are mainly used as glues for paper and cardboard, and also for starching textiles.

### Galactomannans

These mucilages, composed of D-mannose and D-galactose, are most commonly found in the seeds of various leguminous species.

Guar from *Cyamopsis tetragonolobus* has a mannose chain (1-4) and lateral galactose on 6.

Carob seed gum is obtained from *Ceratonia siliqua*. Its sugary pods have provided human food since time immemorial. The "husks" spoken of in the New

Testament as eaten by the prodigal son and the "locust" that St John the Baptist lived upon in the wilderness are considered to have been the pods of the carob. The gum is present in large amount in the seeds and is a cheap substitute for gum tragacanth (used as size in paper-making, emulsifier in salad creams and ice cream, for thickening sauces, for pharmaceutical purposes, etc.).

Its structure is a main chain of 1-4 mannose and side branches of galactose 1-6.

*Caesalpinia praecox*, a small tree in the NW provinces of Argentina and in Chile, yeilds gum brea.

#### Glucomannans

Mucilaginous polysaccharides composed of glucose and mannose are found in the tubers of various species of *Amorphophallus*, such as *A. oncophyllus*, yielding "Iles mannan," in Indonesia, which has a D-mannose:D-glucose ratio of 1:2, with a linear structure 1-4.

Konjal mannan, (also known as "konjaku flour" or "conjac") comes from a closely related species. The mannan is present in the leaves and stalk as well as the root of *Amorphophallus rivieri* [or *A. konjac* – the taxonomy is disputed]. The flour is prepared by cutting the bulbs of the three-year-old plants into thin slices, followed by drying and grinding. It is not soluble in water and can be cast into films. In structure it is a linear chain of 29 hexoses: 16 mannose + 10 glucose, with one mannose and two glucose side branches.

#### C. CELLULOSE DERIVATIVES

Cellulose is the principal constituent of plant cells. Since the second half of the 19th century, it has been used as the base material in the preparation of many film-forming materials. In chronological order these are: cellulose nitrates and the esters and ethers of cellulose.

Cellulose is composed of units of anhydroglucose bound in the 1-4 position in the  $\beta$  configuration [143] (fig. 34). Each unit has three hydroxyl units that can be replaced by nitro- groups, ester groups or that can form ether compounds. These hydroxyl units are distributed at intervals along the cellulose chains. In this way it is

Fig. 34



possible to obtain materials that are very different (notably in regard to their solubility), depending upon the length of the chain and the nature and number of the substitutive groups.

# **Cellulose nitrate**

The cellulose nitrates used as film-forming materials have a molecular weight of about 50 000, and a degree of polymerization of between 50 and 500. There are one to two nitrated groups per anhydroglucose unit.

The cellulose nitrates are very seldom used by themselves in picture varnishes or in paints. Solutions, called *collodions*, are normally obtained by dissolving cellulose nitrate in a mixture of alcohols (ethyl, butyl) and esters (ethyl acetate, butylacetate). Emulsions obtained by adding a surface-active agent and a plasticizer are also available.

The products that can be added to the cellulose nitrates are very diverse (melamine and urea formaldehyde resins, the glycerol phthalates, isocyanates, polyesters, polyurethanes, epoxies, styrene-butadines, acrylics, vinyls, silicones, etc.).

Resins based on cellulose nitrates are used on metals, wood, paper and leather. The films formed are sensitive to ultraviolet light, which is a poor recommendation for use in conservation. An example of their use is as a protective coating for metals [144].

### **Cellulose acetate**

The cellulose acetates used as varnishes and in paints have a molecular weight of about 18 000, and a degree of polymerization of less than 200. The acetyl groups that replace the OH groups in the cellulose molecule are larger and less polar, and therefore reduce the attraction between the cellulose chains.

A distinction must be drawn between the diacetates which are partially acetylated, and the triacetates in which all the OH groups have been substituted. The former are soluble in ketones and esters, whereas the latter are soluble in chlorinated solvents.

Varnishes based on cellulose acetates are stable to heat and light. They are used on glass, paper and metal.

### **Cellulose ethers**

The cellulose ethers are formed by replacing the hydrogen atoms in the hydroxyl groups by alkyl radicals, hydroxy alkyl radicals and carboxy alkyl radicals. Unsubstituted cellulose is insoluble in water despite the presence of large numbers of hydrophilic OH groups, because of hydrogen bonds which impede the dispersion of the chains. The ether groups are more or less hydrophobic, and it is possible to prepare resins of varying solubility. The methyl groups give a material that is completely soluble in water, when at least two out of the three hydroxyl groups have been substituted. The sodium salt of the carboxymethyl cellulose remains soluble in water even when the degree of substitution is very low.

The cellulose ethers are used for a variety of purposes: as thickening agents, protective colloids, glues and varnishes for paper, varnishes that can be peeled, varnishes for leather, rubber, etc.

In many studios these compounds are tending to replace starches, particularly in the conservation of paper. It would, however, be prudent to await the outcome of ageing tests which are still (1994) far from complete. The large variety of materials sold on the open market, as a result of the many substitution possibilities, complicates this research.

Wilt and Feller have recently studied the stability of some cellulose ethers. The methylcelluloses resist the best during ageing. Isopropylcellulose (*Klucel*) fairly yellows [156].

### **III. PROTEINS OR ALBUMINOUS MATERIALS**

Proteins are amongst the most important components of living cells. They are essential for life, and are to be found in almost all animal tissues, mucous membranes, skin, hair and nails, as well as in hormones, enzymes, antibodies, etc.

They are composed of chains of amino acids having the general formula:



They contain both the acid functional group (–COOH) and the basic functional group NH<sub>2</sub> (amine), and are known as *amphoteric* compounds. What is known as the *isoelectric pH* point is the pH at which there are an equal number of positively charged groups (NH<sub>3</sub>+) and negatively charged groups (COO<sup>-</sup>), so the net charge on the molecule is zero.

There are 22 naturally occurring amino acids. The number present in a protein molecule, and their positions, are determined genetically and the properties of the protein depend on these factors [95].

The CO-NH group is known as the *peptide linkage*. It is rigid, in contrast to the C-NH and C-CO bonds which can rotate. Because of this rotation the protein molecules can assume different configurations in space, but each protein occurs in nature in its own special configuration; this is *the native state*. This native conformation is easily changed by various factors, such as light, heat, adsorption on surfaces and by

the action of strong acids and bases, etc., and this loss of the natural form is called denaturation.

Denaturation is associated with a decrease in solubility and very often leads to coagulation of the protein. Loss of solubility on ageing guarantees the toughness of paintings done using a protein binding medium.

The stability of proteins has been the subject of an extensive review [145]. The author shows that those proteins that contain sulphur (egg, casein) are more sensitive to denaturation. Animal glue is very stable. The author also draws attention to possible interactions with other materials such as oils, carbohydrates and natural and synthetic resins. Humidity is undoubtedly one of the most important factors involved in these alterations.

Analysis of proteins has made tremendous improvement in recent years. Staining tests were developed [110, 113, 114, 151, 152], as well as (TLC) [109, 171], Fourier-transform-infrared (FT-IR) spectroscopy [157], gas chromatography [108, 153] and high-pressure liquid chromatography (HPLC) [111, 112, 170].

# Gelatin and animal glue

### Composition

Collagen is the chief protein in the skin, bone and tendons of mammals, and is the sole source of the substances known as gelatin and animal glue. In the old days, skin glue made from parchment clippings was used, and, more recently, rabbit-skin glue, but this is very rare today.

Depending upon the way in which the hydrolysis is carried out, gelatins can be obtained with high molecular weights, such as photographic gelatin (150 000 to 50 000) and food gelatin (100 000 to 20 000), or products that are much more broken down and impure, such as animal glue (40 000 to 10 000).

The distinction between the gelatins is thus related to the difference in size of the molecules and to their purity. Analysis shows, however, the presence of exactly the same amino acids in each case.

The composition of gelatin is characterized by a high proportion of *glycine*, *proline* and *hydroxyproline*.

Properties

The molecules of gelatin are long and flexible. In solution they have a helicoidal form. This molecular configuration is responsible for one of the most interesting properties of gelatin, namely its ability to pass easily and reversibly from a viscous solution (the *sol*) to a firm state (the *gel*) by simple cooling.

A gel state is attained by virtue of the attractions of a limited number of unencumbered sites in the molecule which permit the chains to draw closely together.

A molecular weight of at least 20 000 is necessary to ensure that there is a sufficient number of such sites for this to occur.

Gelatin swells in cold water, and above 30°C it goes into solution. To prepare a solution, it is recommended that the solid gelatin be allowed to swell in cold water (for 15 to 30 minutes if powdered, or for two hours if in beads). Then it is heated, preferably in a double boiler, taking care that the temperature does not exceed 60°C. Any surface that can be wetted with water can be glued with animal glue.

After the hot glue is applied to a surface, it changes from a sol into a gel upon cooling, passing through an intermediate tacky phase. The two surfaces should be brought together, if possible before the tacky phase is reached, so that a continuous film can be formed. The join hardens quickly because of two phenomena: formation of a gel and the diffusion of water into the substrate. Drying goes on after gelling and finally the gelatin returns to its original dry state.

The *contraction* of the glue on drying is, therefore, proportional to the amount of water used to make up the solution.

The *adhesive quality* of gelatin is only partly due to mechanical anchorage. The specific physico-chemical interactions (see page 29) are very important, and this applies even in the case of a material as porous as wood. It has been shown [97], in fact, that animal glue creeps along the cell walls and on drying forms hollow tubes, having taken on the internal shapes of the pores.

It is possible to prepare layers of animal glue that become sticky when they are re-wetted; this is what is used in the case of gummed brown paper tape. It is only necessary to dry the solution while it is warm. It has been noted that the glue, if dried in a cold state, passes through a sticky phase and then forms a gel. On re-wetting with cold water, the gel is then re-formed without passing through the sticky phase, because the bonds responsible for the structure of the gel are already present in the dry film.

On the other hand, if the solution is dried from a warm state, it forms a glossy film before the molecules have time to arrange themselves into a gel form. On re-wetting, a viscous solution is formed and normal gelling ensues, this time passing through the sticky phase.

The viscosity of gelatin solutions varies greatly with pH, for a given concentration. This phenomenon is undoubtedly related to the ionic repulsions that can provoke a rolling or unrolling of the actual molecules. In fact, minimum viscosity is observed at the isoelectric pH point, pH 4.5-5 (see page 56). Advantage is taken of this property in fixing flaking paint, when it is necessary for the glue to penetrate easily beneath the paint flakes. The pH is adjusted by adding acetic acid.

In certain applications where gelatin is used, it may be necessary to add plasticizers (glycerol, sorbitol, honey), preservatives (boric acid,  $\beta$ -naphthol, zinc sulphate) or chemical agents that promote insolubility (formaldehyde, potassium dichromate in the presence of light, etc.).

#### Fish glues [99]

Fish glues are extracted, using slightly acid hot water, from the skins and other waste products of fish, including bones.

Famous glues were in the past made up from sturgeon swim-bladders. They are said to be more flexible and better penetrating than animal glue.

# • Composition

The gelatin obtained differs somewhat from that obtained from mammals. Some slight differences are observed in the proportions of serine, threonine, methionine and hydroxyproline [100].

• Properties

Because of its low molecular weight, the gelatin obtained from fish does not form a gel. The films are sensitive to moisture and are not very tough.

Luybavskaya [169] compares the kinetics of growing and relaxing tension appearing in calf glue and in sturgeon glue when water evaporates and the glue layer hardens. Sturgeon glue shows higher inner tensions (20 MPa) than hide glue (10 MPa).

The viscosity of calf glue is half that of sturgeon glue. It can be explained by the high molecular masses of the molecules in high-quality sturgeon glue. In the more usual fish glues, this is not true, as they are usually less viscous than animal glue.

# Casein [101]

Casein is precipitated from skimmed milk by adding an acid (sulphuric, hydrochloric or lactic acids). The commercially produced caseins are often contaminated by a number of impurities such as butter (0.1 to 3%), acids (0-3%) or lactose (0 to 4%). These impurities have an adverse effect on adhesive quality.

Composition

Casein contains a mixture of proteins ( $\alpha$ ,  $\beta$  and  $\gamma$  caseins) that are characterized by containing phosphorous (0.8%). The molecular weight varies from 75 000 to 375 000.

• Properties

Casein is almost insoluble in water at its isoelectric point, pH 4.6. In order to dissolve casein, its pH must be adjusted to the range of 9-13 by adding a base, so as to form a caseinate salt.

If ammonia or sodium hydroxide are used for this, the solution remains stable for several hours, but the dried product is moisture-sensitive.

If chalk is used there is an improved resistance to water, but the glue has to be used within one or two hours.

The addition of formaldehyde or cupric chloride also makes the film less sensitive to water.

The sequence of film formation could be shown as follows:

Solid casein + water (250%)  $\rightarrow$  swollen casein  $\rightarrow$  caseinate of calcium  $\rightarrow$  gel

or: caseinate of sodium or of ammonium  $\stackrel{\rightarrow}{\leftarrow}$  gel

When the water is removed by evaporation and diffusion into the substrate, the gel dries into a film that is hard and brittle [102]. The flexibility can be improved by adding some glycerol, glucose, agar-agar or dimethylglycol phthalate. The usual preservatives are sodium phenylphenate or chlorinated phenols.

Casein is often used as a protective colloid (see page 6) in emulsions. A current formulation is a mixture of calcium resinate + drying oil + casein which has been rendered soluble by the addition of an alkali. Such paints are matt and porous, and they allow free movement of humidity. Casein is also used as a carpenter's glue and for completing frescoes when the mortar is too dry for normal work. Yarosch and Zakharova have found casein in a mural painting of a Turkmenian tomb dating from the 11th-12th century [175].

#### Eggwhite

#### Composition

White of egg contains nearly 87% water, a small amount of polysaccharides (about 2%) and 12% of proteins.

The protein component is a mixture of which about 65% is *ovalbumin*, a protein having a molecular weight of 44 000, and the molecules of which are almost spherical (22 Å in diameter). Among the other proteins are *mucin* (2%), which is rich in carbohydrates, *globulins* (6%), *lysosyme* (3%), *conalbumin* (9 to 17%) and *ovomucoid* (9 to 14%).



In order to extract these proteins, the eggwhite is first beaten to rupture the membranes. The resultant liquid is used as a film-forming material after the residual solids have been removed.

#### • Properties

The film obtained from eggwhite is very brittle, and for this reason it is necessary to add a plasticizer such as glycerol. Eggwhite contains all the standard amino acids in proportions that give it the highest nutritional value of all protein foodstuffs. Only *lactalbumin*, obtained from milk, can equal it in this respect.

In spite of its numerous shortcomings, brittleness and insolubility after ageing, eggwhite has been used as a binding medium [188, 190], as a retouching medium [191] and as a varnish [172].

# Egg-yolk

### Composition

Egg-yolk is an emulsion containing more than 51% water, 17 to 38% lipids, 15% proteins (*livetine* and *phosvitine*) and a phospholipid, *lecithin* (2.2% phosphorous), which has remarkable surfactant properties.

The yellow colour is due to the presence of carotene pigments (*lutein* and *zeaxanthin*).

The amino acid composition of egg-yolk is very similar to that of eggwhite, so it is difficult to distinguish between the two on the basis of an analysis of the protein fraction.

• Properties

The lipids present in the yolk are non-drying. They can, therefore, act as plasticizers, but they should be used with care because they have an adverse effect on the solidification of oils.

The presence of the surfactant lecithin gives egg-yolk its ability to stabilize emulsions (mayonnaise).

Yolk is a very old painting medium and is still highly appreciated nowadays. It solidifies quickly and presents a pleasant flexibility but it remains soft for long time and does not resist mechanical abrasion [173].

#### **Temperas - Distempers**

The terms tempera and distemper have often been used interchangeably, and there is still some confusion about their respective definitions.

Havel [103] along with Doerner [106] used the term *tempera* to designate any emulsion or suspension of pigments regardless of the composition of the emulsion; the external phase or dispersing medium (see page 1) may be egg, polysaccharide gums, etc., and the internal or dispersed phase may be drying oils, resins, waxes ... and vice versa. It should be remembered that it is the external phase or the dispersing medium that gives the emulsion its characteristics.

Laurie [104] gives the following definition: "When I write of a tempera medium, I mean a medium in which the binding material is mixed or dissolved in water, such as gum size, and white and yolk of egg."

Thompson [105] prepares his "tempera" by mixing an egg-yolk with one or two soup spoons of water.

Some people reserve the word *distemper* (*détrempe* in French) for paintings done in a proteinaceous medium such as animal glue or egg, but this rule is far from receiving general acceptance.

Extreme caution, therefore, is necessary in the interpretation of these terms, as they often mean very different materials to different authors [117].

Numerous analytical studies have been carried out at IRPA [107, 108, 109, 110] and elsewhere [111, 112, 91, 113, 114, 115, 79, 89] and these, over many years, have brought about a precise understanding of the materials used by the Old Masters.

Innumerable recipes for emulsions are reported in the literature (see Introduction, page vii), and some examples are given in the following table.

External or internal phase	Surfactant, protective colloids	Internal or external phase	Remarks	Ref.
water + eggwhite 1 litre 20 g		oil	optional: alum 2.5%	106
		dammar-mastic resin	not handy	106
water + egg-yolk ( <sup>1</sup> ⁄2 shell) 1		oil (1⁄2 shell)		116
water + egg-yolk 2 vol 1 vol		oil or mastic varnish: 1 vol		105
vinegar + egg-yolk 2 vol 1 vol		linseed oil: 1 vol	vinegar: dangerous for some pigments	117
water + egg-yolk 2 vol 1 vol		Venice turpentine	mediocre	105
water + egg-yolk 2 vol 1 vol		wax + turpentine	flower paintings	105
water + whole egg 2 vol 1 vol		oil (1 vol)	first add oil, then water	106
		linseed oil + dammar $(\frac{1}{3} + \frac{2}{3})$ or $(\frac{3}{4} + \frac{1}{4})$		106
vinegar + egg 2 vol 1 vol		linseed or poppy oil: 1 vol		117
water + egg ½ lb ¼ lb		fatty varnish: 1/4 lb	+ small amount of wax	116

#### **EMULSION RECIPES**
External or internal phase	Surfactant, protective colloids	Internal or external phase	Remarks	Ref.
vinegar + eggs ½ litre 50	black soap: 1 shell + 1/2 litre tepid water	3/8 litre oil + 1/8 litre oil of turpentine		116
water + egg 350 ml 200 ml		drying oil 100 ml + spirit varnish 100 ml	+ 10 ml vinegar; add water last	117
water + egg 2 parts 2 parts		linseed oil: 1 part + copal or mastic: 1 part	add water before using	117
water + animal glue		boiled oil (with lead) + oil of turpentine		118
water + animal glue	egg-yolk	oil		117
water + casein 1⁄4 250 ml + 10 g ammonium carbonate		oil, resins, stand oil, poppy oil, aspic [spike oil], wax soap	turns yellow	106
water + casein 100 g 20 g + 10 ml ammonia		oily varnish	very easy to handle	119
water + gum arabic 2 parts 1 part		oil up to 6 parts	matt appearance	106
water + gum tragacanth 2 parts 1 part		oil up to 6 parts	matt appearance	106
water + rye paste		fatty varnish		118
water + cherry tree gum or gum arabic		oil boiled for 1 hour at approx. 240°C + 5% litharge (a small amount of	glossy but moisture-sensitive	118

It is often difficult to identify from the recipes which is the external phase and which the internal. A simple test is to add one of the two phases to the emulsion, knowing that addition of the internal phase will thicken it, whereas the addition of the external phase will make it more liquid. Moreover, since it is the external phase that gives an emulsion its characteristic properties, it will be fatty or lean depending upon whether the external phase is oily or aqueous.

Emulsions seem to have excited the interest of painters throughout the ages. Indeed, it is tempting to try to combine the qualities of the two types of binding media, aqueous and oil. Many people believe, moreover, that this is the principle of the famous binding media used by the Flemish Primitives.

#### IV. TERPENES OR RESINOUS MATERIALS [120, 121, 122]

The terpene resins constitute one of the most widespread classes of substances in the vegetable kingdom.

Although formed into highly varied substances that include resins, balsams and essences, terpenes are all built up from the same single unit, *isoprene*:

$$CH_{2} = CH - C = CH_{2}$$

According to the number of isoprene units in the molecule, the terpenes are classified as follows:

- Monoterpenes: 2 isoprene units (oil of turpentine, lavender oil, rose oil, aspic [spike oil], etc.)
- Sesquiterpenes: 3 isoprene units (oil of turpentine, vetiver, bergamot, patchouli, citronella, shellac, etc.)
- Diterpenes: 4 isoprene units (rosin, sandarac, copals, etc.)
- Triterpenes: 6 isoprene units (mastic, dammar, elemi, etc.)
- **Rubber**: *n* isoprene units.

Terpene resins, like polysaccharide gums (see page 48) appear to have as their main purpose the function of sealing injuries in certain species of trees. Mono- and sesquiterpenes are liquids, and often serve as solvents for the di- and triterpenes found in the viscous exudations from wounds. They are found worldwide (see Map 2 opposite).

The composition of the resinous substances is always very complex. The nature of the soil and climate can produce differences even in the same species. Ageing also brings about profound changes. However, as reported by Mills and White [123], there are certain permanent components that enable particular resins to be characterized.

Thus the two types of materials in solid resins, the di- and the triterpenes, have up to now never been found together. The main producers of the diterpenes are the conifers and a family in the huge order of leguminous plants, the Caesalpiniaceae.

The triterpenes are mainly derived from the Angiosperms.

The following table showing the composition of resins is taken from Mills and White.



Map 2: Origin of the most important terpenoid resins [202]

1. Rosin or Colophony 2. Congo copal 3. Zanzibar copal 4. Copaiba balsam 5. Manila copal 6. Brazil copal 7. Damar 8. Kauri copal 9. Shellac 10. Accroides 11. Sandarac 12. Mastic 13. Peru balsam 14. Elemi.

### CHARACTERISTICS OF RESINS ACCORDING TO MILLS AND WHITE [123]

Order & class	Family	Genus & species	Composition
Coniferales	Pinaceae	Pinus haploxylon (pine)	abietadiene acids (abietic, dehydroabietic and 7-oxodehydroabietic acids) pimaradiene acids (little) thunbergene
		Pinus diploxylon	abietadiene and pimaradiene acids (less)
		Picea abies (spruce)	undoubtedly similar to pines
		Abies spp. (firs)	abietadiene acids pimaradiene acids abienol: drier
		Larix spp. (larches)	abietadiene acids pimaradiene acids, manool, larixyl acetate 30% in Venice turpentine
		<i>Pseudotsuga</i> spp. (Douglas fir; Oregon pine)	abietadiene acids pimaradiene acids, thunbergene, thunbergol (unstable)
	Cupressaceae	(cypresses, junipers)	≈ no abietadiene acids pimaradiene acids, (sandaracopimaric acid)
			totarol – ferruginol = phenols
	Araucariaceae	Agathis dammara (Manila copal)	sandaracopimaric acid polymerized communic acid agathic acid
		<i>Agathis</i> spp. (Kauri copal)	sandaracopimaric acid polymerized communic acid copolymerized communic acid + communol, abietic acid
		<b>A</b> gathis australis Kauri	sandaracopimaric acid polymerized communic acid agathic acid, abietic acid, neoabietic acid
		Araucaria sp.	labdane
Leguminosae (Angiosperms)	Cesalpiniaceae	<i>Copaifera</i> spp. (copaibas)	labdanes neither abietane nor pimarane ozic acid
		<i>Hymenaea</i> spp. (courbarils)	
Guttiferales (Angiosperms)	Diperocarpaceae	<i>Dipterocarpus</i> spp. (dammar)	damm <b>arane (som</b> etimes oleanane <b>and</b> ursane)

Order & class	Family	Genus & species	Composition
Terebinthales	Anacardiaceae	Pistacia lentiscus (mastic)	euphane oleanic acid
	Burseraceae	<i>Commiphora</i> spp. (myrrh)	
		<i>Boswellia</i> sp. (olibanum)	
		<i>Canarium luzonicum</i> (elemi)	$\alpha$ and $\beta$ amyrine and uphane

Natural resins have been used since ancient times, mainly as varnishes but also as painting media and adhesives. They are often mixed with oils or waxes in order to improve their toughness or adhesivity, and to increase the melting point.

Numerous publications report the use of different di- and triterpenoid resins since pre-history for caulking vessels and ships [192, 193, 194]. Resinous substances were found in 15th and 17th-century shipwreck sites excavated in waters off Thailand and Saipan. Styrax benzoin was identified in several samples taken from large storage jars: it was an important incense and medicinal resin which was traded north to China from at least the 13th century. Samples from two southeast Asian ships are triterpenoid resins, probably dammar. They were used as sealants to attach lids of storage jars and as caulking between ship timbers [195].

Myrrh and mastic resin were identified by HPLC, UV and IR spectroscopy in Egyptian objects from tombs of the XIIth Dynasty [197].

Natural resins have been found in patinas of Italian Renaissance bronzes [176] and in tracing paper from the 19th and 20th centuries [174].

### A. and B. MONO- AND SESQUITERPENES

#### **Oil of turpentine**

This is obtained by steam extraction from secretions of Pine species. Its specific gravity lies between 0.860 and 0.875, and its refractive index between 1.465 and 1.483. Its boiling point is in the range of 150°C to 180°C. It will act as a solvent for most of the terpene resins, even polymerized oils and the metallic soaps used as driers [124].

### Oil of spike or aspic [125]

This is extracted from the flowers of the great, broad-leaved or spike lavender (*Lavandula latifolia* or *L. spica*). Like turpentine, it acts as a solvent for terpene resins and oils.

### A. B. and C. MONO-, SESQUI- AND DITERPENES

#### Venice turpentine

This comes from the larch (*Larix decidua*), which grows in the mountains of Central Europe.

The resin occurs in the core of the tree-trunk and not on the outside. In order to extract the resin, therefore, a deep hole must be bored. The opening to this hole must then be sealed and the resin allowed to accumulate, in the absence of air, throughout the summer months.

This resin was widely used in the 18th and 19th centuries.

#### Strasbourg turpentine [Alsatian; Strasburg]

This is obtained from a fir (*Abies excelsa* or *A. pectinata*). The resin ducts are located on the surface of the trunk so that the resin can be recovered directly.

Also included in this group are Bordeaux turpentine, extracted from *Pinus* maritima, and from which Burgundy pitch is obtained as a solid residue after pyrolysis; Jura turpentine which comes from *Picea vulgaris* or red pine; and Canada balsam, obtained from the Canadian or balsam fir, *Abies balsamea* Mill. The trunk is covered with blisters wherein the resin is found.

Properties

All of these essential oils and oleoresins contain not only volatile components that dissipate rapidly during film formation, but also a series of more or less viscous components that harden by oxidation and polymerization reactions, similar to those that take place in the drying of linseed oil (see page 16). The process is slow, which explains why the film remains sticky for a long time.

Moreover, the oxidation reaction leads to the formation of coloured products, so that there is a pronounced darkening of the film with age.

#### C. DITERPENES

#### Rosin (colophony)

Rosin generally comes from the secretions of pine trees. It is also produced by other species: firs, spruces and larches – in other words the majority of the Pinaceae (see Table).

Depending on the method of extraction, three sorts of rosin are produced: gem rosin, wood rosin and tall oil rosin.

#### Gem rosin

Gem is secreted by pine trees to help in healing wounds. The compounds produced stick the wood fibres together and also have antimicrobial properties (ferruginol, podocarpic acid, ...) [126].

Gem is a mixture of rosin (68 to 72%), turpentine (22 to 24%) and water (5 to 12%). After successive decanting and filtering to remove mineral and vegetable impurities, steam or vacuum distillation is carried out in stainless steel vessels, in order to separate the turpentine from the rosin. Any overheating must be avoided, as these products readily oxidize and polymerize and this leads to highly coloured resins.

# Wood rosin

It was in North America, particularly, that the technique for producing wood rosin was developed. Pine stumps are subjected to an aromatic solvent extraction process. Since this process is carried out on a large scale, the net price is much lower than that of gem rosin.

# • Tall oil rosin

Tall oil is a by-product in the manufacture of cellulose from pine wood. It contains about 54% of resin acids, but also some unsaturated fatty acids (50%) which must be separated off.

# Composition

Reference should be made to the table on page 66. A few comments only will be given below.

Fresh rosin contains up to 95% of resin acids, which can be classified into three categories according to their ease of oxidation:

- a) Acids that contain conjugated double bonds and are very prone to oxidation. These are the abietadienic acids (abietic acid, neoabietic acid, levopimaric acid and palustric acid), 60%.
- b) Acids that contain non-conjugated double bonds and are less prone to oxidation. These are the pimaradienic acids (dextropimaric and isodextropimaric acids), 20 to 25%.
- c) Acids that are much less prone to oxidation, namely dehydrobietic acid, dihydroabietic acid and tetrahydroabietic acid), 5 to 10%.

The positions of the conjugated double bonds are interchangeable. Under the action of heat, a mixture is formed in which the more stable abietic acid predominates and levopimaric acid is almost absent.

Dehydroabietic acid tends to increase with ageing, because of dehydrogenation reactions that occur during oxidation. This acid is in turn oxidized to form 7-oxodehydroabietic acid. These two components are thus major constituents of aged resins.

# • Properties

Rosin has a number of defects that limit its use to the manufacture of cheap, temporary varnish:

- It has a low melting point, so that it becomes tacky simply by exposure to the sun.
- Its extreme susceptibility to oxidation leads to rapid darkening and chalking.

- Its high acid value makes it dangerous for use with basic pigments and in contact with cellulose fibres.
- Its high solvent-retention characteristic makes for slow-drying films, which remain sticky for a long time.

It seems, however, that this resin, despite its poor qualities, has been used the most in the past, at least in western Europe. It has, in fact, been identified several times in old varnishes and resins [147]. White [148] has also found a Pinus resin in the varnish of several Italian musical instruments of the 18th century.

#### Sandarac

Sandarac resin comes from small conifers of the family Cupressaceae (see Table, p. 66), which grow in North Africa (*Tetraclinis articulata*), on the Mediterranean coasts (*Juniperus communis, J. phoenicea, J. thurifera*), and in Australia (*Callitris quadrivalvis, C. columellaris, C. endlicheri*), and commonly known as cypresses and junipers.

The resin exudes from the trunk in small transparent drops. The flow of resin is increased by making grooves in the trunk. The material collected in this way is in the form of shiny, elongated teardrops, very pale yellow in colour.

An inferior-quality sandarac is made from blocks of resin that accumulate where the resin falls to the base of the tree. This material is contaminated with impurities and has a darker colour.

Composition

See Table, p. 66. The absence of abietadienic acids should be noted. Among the pimaradiene acids, sandarocopimaric acid remains the most abundant after ageing.

• Properties

The resin has almost the same defects as rosin, but has a lesser tendency to darken.

It is often mixed with Venice turpentine to prevent chalking. Films made from sandarac are hard and lustrous. In former times it was often used for coating metals.

An old varnish made of linseed oil and a resin of cupressaceous origin was found on an early Italian tempera painting (1371), the *San Pier Maggiore* altarpiece attributed to Jacopo di Cione and which is now displayed as a group in the National Gallery of London [180]. Many ancient recipes – from Theophilus in the 12th century to the Strasbourg manuscript in the 15th century – report the use of linseed oil and sandarac [181].

### Copals

This term covers a number of resins of very different origin; of these the fossil resins are the hardest, sometimes derived from vegetable species that are now extinct. The most important sources of production are the Araucariaceae (conifers) and the Caesalpinaceae (legumes).

The term copal seems to be of Mexican origin, but it is harvested in many regions of the world: in South America (Demerara and Para copals, locust gum, Brazilian copal), in eastern Africa (Zanzibar, Lindi, Tanganyika, Madagascar and Inhambane copals), in West Africa (Congo copal, Sierra Leone, Benin, Accra, Angola, Loango, Benguela, Gabon and Cameroon), in New Zealand (kauri copal), in the East Indies (Malaya copals, Pontianak, Philippines, Sumatra and Borneo) and in Manila (Manila copal).

• Composition

See Table, p. 66.

• Properties

Most of the copals have high melting points. They are insoluble in most solvents and in oils. They have to undergo pyrolysis (melting at about 320°C) to make them soluble. The resins then lose about 20% of their weight and undergo decarboxylation. This has the effect of making them less acid but also more highly coloured. The resins are then soluble in oils and turpentine.

Some oils and varnishes used in the past had the following formulations [127]:

### a) Lean varnish, (oil : resin = 0.75-2 : 1)

Congo copal	•	•	•	•	33.00
Stand oil					24.00
Lead resinate					0.75
Cobalt resinate.					0.25
Oil of turpentine					42.00

This was used as a stopping-up varnish, drying in three hours and hardening in five.

### b) Fatty varnish, (oil : resin = 1.5-3 : 1)

Madagascar copal				25.0
Linseed oil	•	•		27.0
Lead linoleate				0.5
Cobalt linoleate .				0.2
Oil of turpentine .		•	•	39.5

This was used as a finishing varnish, drying in four hours and hardening in eight.

Copals from Zanzibar and Madagascar give films that are very tough, very glossy and durable, and in which large amounts of oil can be incorporated. They are frequently used for exterior varnishes and for boats.

The very hard variety of Congo copal has often replaced the above copals because it is cheaper, while still guaranteeing a varnish of good quality. Its high acidity, however, causes an undesirable thickening when it is mixed with basic pigments.

The semi-hard variety of Congo copal was used as an indoor varnish for floors, furniture, toys, etc.

*Manila gum*, after pyrolysis, becomes soluble in alcohol, unlike the varnishes mentioned above. However, it is only possible to add small amounts of oil to it, and this limits its usefulness to making spirit varnishes for interior use.

The *Manila* and *Pontianak* copals give rise to products that are very soluble in alcohol. They are especially appreciated for the flexibility of the films they form.

#### **D. TRITERPENES**

#### Dammars

These resins come from trees belonging to the family of Dipterocarpaceae (Angiosperms), (see Table, p. 66), that are found from New Zealand to the Philippines, but especially in the islands of Indonesia.

Some of the resins are of fossil origin and are very hard. The varieties that are most used are obtained by making incisions in the trunks of trees, but the harvesting of the resin is often very difficult. In fact, it is necessary to wait 50 years before the trees produce well. As the trees age, they become more and more susceptible to insect attack, and furthermore the original trees have to be found amongst all the others in the virgin forest.

The resin is found as rounded masses, very pale yellow in colour. The pieces are graded according to size into quality categories of A, B, C, D, E and F. "A" grade is for pieces as big as pigeons' eggs, "E" for pieces the size of small seeds, and "F" for powder.

Composition

(See Table, p. 66)

• Properties

As in the case of most of the triterpene resins, the dammars make good varnishes; they are used as picture varnishes because of their good solubility in organic solvents and because they yellow to a lesser extent than varnishes made from diterpene resins.

Dammar resins are soluble in white spirit, aromatic solvents and turpentine. It is recommended that they be dissolved in lukewarm solvents, since the resultant varnishes are more transparent than those prepared cold. These are the famous *crystal varnishes*.

The addition of alcohol to the dammar solution precipitates a waxy residue in the amount of 15-20%.

Dammar is of particular interest because of its excellent adhesive properties. For this reason it is often added to wax to increase its stickiness or adhesive quality.

Compared to the other natural resins, dammar has the advantage of being only slightly acidic. Thus there is no danger when it is used with basic pigments or with linen canvas. This is an added reason for preferring it in the formulations of wax-resin mixtures used in relining. Unfortunately, the films obtained from dammar are soft, have low resistance, and tend to become slightly tacky. On ageing the film yellows and becomes less soluble.

To overcome these drawbacks, La Fontaine [149, 150] proposes that 1% by weight of an antioxidant (Ciba *Irganox 565*) be added to the dammar solution.

De la Rie has also studied how to avoid yellowing of mastic and dammar [159]. These resins are indeed still of frequent use because of their interesting optical properties. Thanks to their refractive index which is almost the same as that of aged oil, these varnishes give a nice transparency to oil paintings even in the dark areas. He proposes adding 3% of a stabilizing amine, *Tinuvin 292* (Ciba-Geigy). This guarantees a projected 136 years of transparency and solubility for a dammar varnish exposed to light at 1000 lux without UV; 4% of the amine is needed for the same performance in the case of mastic varnish. The additive causes a lowering of the glass-transition temperature which is beneficial for flexibility but makes the surface sticky at room temperature [186].

Dammar varnish can also be protected by a layer of *Acryloid B72* resin blended with UV absorbants [187].

#### Mastic

Mastic resin is produced by another family of Angiosperms, the Anacardiaceae, principally the pistachio tree, *Pistacia lentiscus*, which is widespread along the Mediterranean coasts. Mastic is harvested especially on the island of Chios, where it has been used since ancient times.

Composition

Still very little known (see Table, p. 66).

• Properties

Mastic is very soluble in aromatic hydrocarbons. Like dammar, the addition of alcohol causes precipitation of waxes, about 15 to 20%.

Mastic films are lustrous and flexible, but they lack toughness.

Percival-Prescott compares the formulation of some 17th- and 18th-century paints. At the end of the 18th century, several new vehicular components were commercially offered to artists and brought increased risk of degradation. "Megilp" was a mixture of mastic resin and turpentine. On drying, the paint layer becomes very matt. Because of that defect, many dangerous additives were used, such as Venice turpentine and Copaiba balsam. They strongly accelerate the degradation of the paint layer [182].

Thixotropic gels were very fashionable in the 19th century. Carlyle reports the use of "Gumtion" which was a mixture of lead acetate, raw linseed oil and mastic resin. Like megilp, this medium causes darkening and cracking in the final painting [183].

#### Elemi

A third family of angiosperms, the Burseraceae, produces a range of balsams and soft, sweet-smelling resins, in particular elemi, which comes from different species of *Canarium (C. commune, C. luzonicum*, etc.), widely distributed in many regions of Africa and in Mexico, Brazil, the Philippines, etc.

#### Composition

In addition to the triterpene derivatives (see Table, p. 66), elemi also contains some more volatile derivatives that are responsible for its smell: sesquiterpenes such as elemol or elemecin.

Properties

Elemi is soluble in aromatic hydrocarbons and in alcohol. It is used as a plasticizer and also gives good adhesion and lustre.

### V. RESINOUS MATERIALS NOT (exclusively) TERPENES

In this category there are a number of different soft and hard resins that do not always contain terpenes.

#### Benzoin

This is a balsam extract - also known as gum benjamin - from *Styrax benzoin* or *S. Tonkinense*. These species are found in the Indonesian islands, Cambodia and Thailand.

Composition

This balsam contains derivatives of benzoic and cinnamic acids, and up to 39% of vanillin – which gives the balsam its characteristic smell – and resins, etc.

Properties

Good-quality benzoins are soluble in alcohol. They are used as plasticizers in spirit varnishes, and as skin ointments in the pharmaceutical industry.

#### **Balsam of Peru**

This is extracted from *Myroxylon balsamum* var. *pareirae* (syn. *Toluifera pereirae*), a leguminous plant growing in the Pacific coast forests of Central America.

Composition

It contains derivatives of cinnamic and benzoic acids, vanillin and some unidentified resins.

Properties

This viscous liquid is insoluble in water, but soluble in alcohol, chlorinated solvents and acetic acid. It is used as a plasticizer in spirit varnishes, and in the pharmaceutical and perfume industries. It appears to have been used by the Incas for embalming, like the balsam of Tolu, obtained from a closely related species (see next section).

### **Balsam of Tolu**

This is extracted from *Myroxylon balsamum* (syn. *Toluifera balsamum*), a leguminous plant of South America, growing chiefly in the mountains.

It composition and properties are similar to those of balsam of Peru.

### Copaiba balsam

This comes from a leguminous plant, *Copaifera officinalis* (syn. *C. landsdorfii*), native to South America.

Composition

Copaiba balsam is a mixture of resins and oils that are more or less volatile.

Properties

It is insoluble in water, but soluble in chlorinated, aromatic and saturated solvents, and partially soluble in 96% alcohol.

Von Pettenhofer [128] used it in Germany for softening old picture varnishes, and even for impregnating paint layers in order to fix them, which would seem to be a risky procedure in view of the prolonged softening effect of this balsam.

A recent study [184] shows that this treatment provokes disaster: in some paintings, the paint layers were so strongly softened that there was a migration of detached fragments of the ground layer towards the surface.

### **Dragon's blood**

This is a general name applied to several reddish resins used in varnishes, etc., originally obtained from *Dracaena cinnabari* (on the island of Sokotra), and later from *D. draco* (in the Canary Isles). More recently it has been obtained from *Daemonorops* spp., palms growing in south-east Asia. The product from Indonesia has been called Sumatran dragon's blood in the trade.

It is sometimes confused with the gum *kino*, an astringent red resin coming particularly from *Pterocarpus erinaceus*, a leguminous plant that grows in West Africa, the Indies, Guinea and Australia.

Composition

The secretions contain about 55% of a red resin, from which there has been separated 15% of an amorphous yellow compound, dracoresene, and 8% of a whitish compound, dracoalban. The nature of these compounds has still not been determined.

#### Properties

The resin is soluble in alcohol, and has been used to colour varnishes used on musical instruments, and as a protective varnish for zinc in the preparation of aqua fortis (nitric acid).

#### Amber

Amber is a fossil resin that is found in deposits dating from the Cretaceous period to the Pleistocene (60-70 million years before present). One possible source could be the extinct pine, *Pinus succinifera* Goepp., which once grew along the Baltic Sea and in what was then Burma [129].

#### Composition

Mills and White [89] have reported on the current state of knowledge concerning the composition of amber. Depending on its origin, it appears to contain two types of constituents: one of these consists of derivatives of a dimer of abietic acid, and the other of co-polymers of comunol and communic acid, somewhat similar to those found in kauri copal.

Properties

To judge by the De Mayerne manuscript, it would appear that amber was frequently used in the formulation of varnishes. It should, however, be noted that a certain confusion exists regarding the precise meaning of the terms ambre *succinum*, *carabé* and *glossa* used in the past to describe the resin. It is indeed quite possible that these terms were sometimes used to describe another hard resin, for example a copal.

Like some of the previously mentioned resins, amber must be subjected to pyrolysis to enable it to be mixed with oils. De Mayerne describes an interesting procedure in which a solution of the amber is made by adding amber oil, i.e., the terpene fraction obtained by destructive distillation. This method would not produce such a dark solution as the pyrolysis method.

#### Lacquer of the Far East or true lacquer

True lacquer is a gummy, resinous latex obtained by making incisions in the lacquer trees, the best known of which is the Japanese lacquer tree, *Rhus verniciflua* (syn. *R. vernicifera*). Lacquer can also be obtained from other species in China, Indonesia, Cambodia, etc. [130].

The fresh lacquer is filtered and collected in non-metallic receptacles carefully covered over with impermeable black paper. The lacquer can be kept for a long time if humidity is avoided. It is usually left in darkness and completely still for three or four years. It is then decanted, the upper levels being the best. For the lacquer to polymerize, the presence of both an enzyme and a humid environment is required (see page 16). It then hardens in five to eight hours at 15°C to 20°C with 75 to 90% RH.

The application of the lacquer is very laborious, because each object requires a large number of coats (up to 60).

Known in China since the Chou dynasty (1000 B.C.), lacquer has been used in Japan since around the 6th century, and later in other countries of the Far East.

In 1760, a priest, Father d'Incarville, revealed to Europeans the secret of its manufacture. *Coromandel lacquer* was very popular in the 18th century in European high society. The name Coromandel comes from the old name for the east coast of India, frequented by the cargo ships of the East India Company. These lacquered objects were usually large screens made of of twelve panels, corresponding to the months of the year.

In the 18th century, the *Martin brothers* invented a varnish that was an imitation of Chinese lacquer and used it for decorating furniture. This Martin's varnish appears to correspond to the following recipe [132]:

On an open fire melt 3 kg hard copal, homogeneous and of the best quality. While stirring well to ensure a thorough mix, add 1.5 kg of boiled linseed oil to the molten mass. Dilute with 4.5 kg of oil of turpentine.

Composition

The main constituent is a phenolic acid, urushiol:

 $(2,3(OH)_2 C_6 H_3 - C_{15} H_{31})$  [131]

• Properties

Once it has polymerized, Chinese lacquer becomes completely insoluble and very resistant to chemical agents such as acids, alkalis and ozone.

### Lac, gum lac or shellac

Gum lac or shellac, like cochineal, is an insect product, usually from *Laccifer lacca*, *Coccus lacca* or *Tacchardia lacca*, of the family Coccidae. These insects, like the cochineal beetle, also produce a red dyestuff, known in Europe since the 10th century [133].

The insects live mainly as parasites on an Indian tree, *Butea frondosa*. The female insect secretes most of the resin (up to 150 mg per insect) during the gestation period.

Although the insect's life cycle only lasts six months, the lac is collected just once a year. The raw "*sticklac*" is washed and sorted ("*seedlac*"), then melted, filtered and solidified into drops, "*button lac*" or sheets, "*shellac*." According to Heaton [134], the use of gum lac in Europe began towards the end of the 16th century. It would have been used to varnish the famous Stradivarius and Guarnerius violins.

### Composition

Gum lac consists of a complex mixture of esters of hydroxy fatty acids and sesquiterpene acids on a cedrene skeleton [135]. There is also between 3 and 5% of a wax with a melting point between 78°C and 82°C. It was used in the past as a substitute for carnauba wax.

Gum lac is often mixed with rosin (up to 10%).

### • Properties

Shellac shows some anomalies when in solution. Judging by its behaviour, the solution is midway between a colloidal dispersion and a molecular dispersoid. When preparing a solution of shellac, it is recommended that the resin first be left to swell in a small amount of solvent; the rest of the solvent should be added gradually at a later stage. In this way there is an unlimited swelling of the dry lac which facilitates the dissolving process.

Shellac is soluble in alcohol, alkalis such as borax, aqueous solutions of sodium carbonate or ammonia, and also in formic, acetic and lactic acids, and in pyridine.

Shellac forms films that are sensitive to water and that bloom in a humid environment. The films are shiny and adhesive, but become insoluble and darken with age.

Shellac has been used for a long time as a polish for wood (French polishing) and for finishing leather [136].

#### VI. EMPYREUMATIC MATERIALS: TARS, BITUMENS

In this section two classes of compounds with different origins have been grouped together: these are tars obtained by dry distillation of various combustible materials (wood, peat, lignite, coal, bituminous shales, etc.) and bitumens that are derived from petroleum [137]. Their physical and chemical properties nevertheless show some similarities.

#### A. TARS

#### Vegetable tar - Wood tar

Dry distillation of wood, carried out in a closed vessel at approximately 350°C separates out the volatile products and the pyroligneous liquor, leaving behind a solid residue, the tar. This is a brown substance, more or less viscous and sticky and having an acrid, burnt odour.

Composition

The composition of tars depends upon the species of woods from which they are derived.

The term pitch is usually confined to tars obtained from resinous woods. It contains some terpene compounds derived from the resin, and in addition a very complex mixture of pyrolysis products, in particular aromatic hydrocarbons, notably the poly-condensed hydrocarbons. There are also phenolic compounds (phenol, creosol, methycreosol, phlorol, etc.).

#### Properties

These materials are only slightly soluble in water, but readily soluble in alcohols, chlorinated solvents, ether, acetone, acetic acid and oils. They have been found to be

very useful because of their notably durable adhesive power [138], and also because of their ability to make certain materials (wood, flax, hemp, leather) watertight and rot-proof: e.g., caulking for boats, shoemakers' pitch.

Some tars such as Norwegian tar, derived from *Pinus sylvestris*, or cade oil from the juniper, *Juniperus oxycedrus*, are used in dermatology because of their antiseptic properties. The tar obtained form birch bark was used in the dressing of Russian leather. Paraffin and waxes are often added to tars.

### Animal tar

This is obtained principally by the distillation of bone. It contains pyridine and quinoline compounds.

Grease tar: residue left after the distillation of lanolin.

### Coal tar

This is a product obtained by the destructive distillation of coal.

• Composition

This material contains aromatic compounds: benzene, toluene, xylene; phenolic compounds: phenol, cresols, xylenols; pyridine bases, derivatives of naphthalene, anthracene, etc.

• Properties

Coal tar is a dark, hard substance that softens with heat. It is mainly used for the surfacing of roads.

# **B. BITUMENS**

This is a general term applied to a number of natural combustible materials that are rich in carbon and hydrogen. They burn easily with a flame and give off a heavy smoke.

Many surface deposits have been known of from antiquity, and Forbes [139] gives a very detailed account of these.

Composition

Bitumens are composed mainly of hydrocarbons of high molecular weight (about 1 000), in particular the saturated and olefinic hydrocarbons.

• Properties

Bitumens are black solids, many of which soften at 50°C. They are readily soluble in most organic solvents. Their density is about 1.

Bitumens have been used since antiquity for many different purposes, as described by Forbes [139]: as waterproofing, as cement, for lighting, heating, in magic, medicine, agriculture, mummification and as pigments. Its use as a pigment has had disastrous results when some painters like Géricault used it in oil painting. In fact, an overall darkening of the pictures has been observed due to the bitumen's starting to

liquify when even slightly heated [140], and penetrating all the paint layers. It may be the result of particular surface-active properties.

Various types of bitumens have been used in western Europe, notably Judea bitumen extracted from Lake Asphattite.

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