8. GLASSES

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FORTUNA VITREA EST: TUM CUM SPLENDET, FRANGITUR

Abstract

In architecture, glass established itself as an element that provided cohesion between the inside and the outside. Glass is a transparent structural material and one of the few building materials that combines tradition with technological innovation. Glass is a product that harmonizes colour, reflectance, transparency or opacity, texture and thickness, flatness or curvature with, for example, some control over opacity or selfcleaning properties, whilst at the same time being low-emissive, heat and/or sound insulator, offers protection and security, as well as resistance to thermal shock and impact from projectiles. Moreover glass is the only material that is 100% recyclable, what we should bear in mind, as sustainable development is only possible by careful use of resources and technology. Glass is, definitively, a hard product to beat.

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1. GLASS IN CONSTRUCTION AND ARCHITECTURE: BRIEF HISTORY

Glass is a material that was manufactured 5000 years ago (*hollow glass*) and first used in houses at least 2000 years ago (*flat glass*). Today it has a significant role in building construction, particularly in lightweight *façades*, where increasingly light structures are constantly being developed and applied. The choice of thickness and type of glass to use is up to the architect and materials engineer.

But glass was used even before it was manufactured. Some of the natural phenomena that produced glass include the melting of magma and meteorite impacts, followed by rapid cooling. Natural glass is structurally disorder; it is very tough, with *shell-like* fracture, very shiny, translucent or transparent, with many different colours, from grey to dark brown, red to green, and irisation due to colloidal dispersion of metallic impurities. Natural glass was used for millennia as a raw material to produce works of art along with functional objects, such as the point of a lance or as arrow tips, where it competes with silex (**Figure 1**). Of all natural glass, obsidian was the most used due to its relative abundance.



Figure 1 – Obsidian chips and arrow tips, sécs. IV e VI, Mexico (courtesy of Museu Arqueológico do Carmo, Lisboa, Portugal)

Associated with high temperature manufacturies - such as ceramics and metallurgy glass production would have emerged accidentally; melting copper minerals can cause opaque and blue tinted vitreous slag to form and heating the ceramic pieces can cause them to vitrify. The first manufactured glass would have been used as a *coating* (*glaze*) for ceramic or metal pieces, and natural rock. The oldest known glass *glaze* (dating from 12000 BC) comes from Ancient Egypt. The fired ceramic pieces were dipped in a slurry made of sand (rich in quartz) and sodium salts (carbonates, bicarbonates, sulphates, chlorides or plant ash) and submitted to a second fired, forming a glaze.

Over time, various types of glaze were developed. Opaque and coloured glazes in many shades were developed using tin; the Ishtar Gate (Babylon, 7th century BC) is one stunning example. Lead rich glaze, with a low melting point, emerged in China (during the Han dynasty, 206-200 BC).

But the *democratization* of glass pieces developed much later. The temperature needed to melt the raw materials would definitely have been one of the main obstacles. The oldest known hollow glass object (a dark blue Egyptian amulet dating from 7000 BC) has a high level of copper oxide, supporting the hypothesis that metalbased slag was remelted. The Egyptians developed a new moulding glass concept which replaced the earlier methods and improved the quality of the glassware. New glass products reasonably transparent, although usually still filled with bubbles and other flaws, were produced. The bottles and pots were formed by winding glass ribbons around a mould of compacted sand. After cooling the glass, the sand was scraped from inside the bottle, leaving a hollow container with rough, translucent walls and usually lopsided shapes [1] (**Figure 2**).



Figure 2 – Oriental Mediterraneo glasses produced with Egiptian technique (internal sand mould): (a) amphoriskos, séc. II-I AC and (b) alabastron, séc. V AC (courtesy of Museu da Farmácia, Lisboa, Portugal)

In Mesopotamia (3000 BC), along with the large-scale production of (hollow) glass pieces, a glass protocol was written. From 2000 BC to 1000 BC, the glass-producing centre spread to Syria, Greece and Italy. In 200 BC, in the city of Babylon, the first industrial revolution in glass manufacturing takes place – glass-blowing, where glass is blown using a blow tube. The quality of glass-blowing improved dramatically and glass drinking vessels became popular. Coloured glasses came into common use, with techniques for production of many colours regarded as family secrets, to be passed on from generation to generation of artisans [1] (**Figure 3**).



Figure 3 - Oriental Mediterraneo blown-glasses: (a) sprinkler-bottle, séc. V and (b) fish bottle, séc. III-IV (courtesy of Museu da Farmácia, Lisboa, Portugal)

The Syrian glass-blowing technique and the Alexandrian art of *mille-fiori* were quickly adopted by the Romans. But the splendour of the arts in Rome also included flat glass (**Figure 4**). Flat glass was used to build *high standard* buildings, for floors and wall decorations, but it was its use for windows (where it replaced mica and shells) where it contributed most to Architecture. In the ruined cities of *Pompeii* and *Herculanium* there are numerous traces of sheets of glass probably used in the windows of the public baths. The fall of Imperial Rome and the instability caused by the Huns in medieval Europe caused the glass-producing centres to decline.



Figure 4 – Roman flat glass in Conímbriga: (a) pieces of window glass and (b) window frame, where a piece of glass can still be seen (courtesy of Museu de Conímbriga, Portugal)

During the European Middle Ages small glass-making centres were established hidden in forests (**Figure 5**). The combination of the discovery of many new colourants with the invention of glass-blowing eventually led to the magnificent stained glass windows of so many of the great cathedrals of Europe and the Near East [1] (**Figure 6**).



Figure 5 – During the European Middle Ages small glass-making centres were established hidden in forests (British Library, Londres)



Figure 6 – Our Lady Rosário, sixteenth century *vitral* from chancel of Mosteiro da Batalha, Portugal (courtesy of Dr. Pedro Redol, Director of Mosteiro da Batalha, Portugal)

In the 8th Century, the revival of trade with the Byzantine Empire led to renewed glass production in Europe. Venice became the most prestigious glass-producing centre, which kept various manufacturing methods and techniques secret for centuries. Under the pretext of protecting Venice from fire, Venetian artisans were forced to reinstall their kilns in Murano, where they would remain, prisoners of their art and ingenuity.

For five millennia various glass objects were manufactured, initially as containers and mainly for holding food, oils, perfumes, or simply for decorative purposes. Initially Roman architecture and then the monumentality of medieval and Gothic religious art had a great artistic influence on flat glass. However the manufacturing process for producing flat glass constantly faced big problems. It was only with the dawn of the Industrial Revolution that sheets of glass could be produced that were large enough to allow more extensive use in architecture and throughout society in general. With glass, more than with any other material, art and technology have been merged in an exceptional way for millennia.

2. GLASS COMPOSITION AND STRUCTURE

2.1 WHAT IS GLASS?

Although most solid materials are crystalline (or partly crystalline), some materials do not organized their atoms within a 3D periodic network. Thermoplastics, transparent polymers, rubbers, oxide glass, fluoride, chalcogenides and also metallic glass are some examples.

A glass can be defined as an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behaviour. Any material, inorganic, organic, or metallic, formed by any technique, which exhibits glass transformation behaviour is a glass.

Most commercially available glasses are prepared by traditional melting and quenching processes, while preventing crystallisation, with the melt structure becoming '*frozen*' below Tg. Crystallisation and glass formation are commonly discussed on the basis of either enthalpy or volume *versus* temperature diagrams, such as that shown in **Figure 7**. Since enthalpy and volume behave in a similar fashion, the choice of one of them is quite similar. As we cool the liquid, its atomic structure continuously changes depending on the temperature of the liquid. Cooling to any temperature below the melting temperature (T_M) of the system would commonly result in the formation of a crystalline solid, where the atoms, molecules or ions arrange themselves to create a solid with long range, periodic arrangement. When this occurs, the enthalpy/volume shows a discontinuous decrease relative to the enthalpy of the liquid. Continued cooling of the crystal. All the materials tend to crystallise at T_M . However, crystal formation is not instantaneous but occurs over time as molecular and/or ionic restructuring takes place, through diffusion.

When the liquid is cooled below T_M of the system without crystallisation, a supercooled liquid is obtained. (Figure 7). As the temperature decreases the structure of the liquid continues to rearrange, but no discontinuity in the enthalpy curve is observed. While the liquid cools, the viscosity increases, atomic and molecular movements slow down, and a point may be reached where the liquid structure becomes 'frozen' and no longer depends on temperature. Meanwhile, the enthalpy line deviates from the equilibrium enthalpy curve, by decreasing its slope. The

temperature range limited by the temperature of the last liquid in equilibrium and that of the first 'frozen' solid is known as the glass transformation region. Since the temperature where the enthalpy starts diverging from the equilibrium curve is controlled by the liquid viscosity, a lower cooling rate will shift the glass transformation region to a lower temperature range.



Figure 7 – Volume versus temperature diagram

GLASS FORMATION

When a liquid cools its specific volume decreases (**Figure 7**). When it cools slowly, the liquid crystallises at melting temperature, T_M . At this temperature there is a drastic reduction in volume, due to the smaller average spacing between the chemical bonds and the restructuring.

All materials tend to crystallise at T_M as this is the lowest free energy state of the system.

The crystallisation process is not instant but occurs over a period of time in which atomic/ionic/molecular diffusion takes place forming a crystal network.

For many materials it is possible to suppress crystallisation by rapidly cooling the melt.

Any amorphous (or glassy) material is defined by a key temperature - the temperature of glass transition (T_g). T_g marks the limit between which the amorphous material is in a rigid state ($T < T_g$) and where it demonstrates plastic behaviour.

GLASS TRANSITION TEMPERATURE

The temperature of glass transition (T_g) is a set temperature which separates the point at which an amorphous material has a rigid state and when it demonstrates plastic behaviour.

At temperatures below T_g , where it is in a brittle state, the amorphous materials are called glass. In this temperature range the glass is structurally rigid and thus unable to absorb mechanical energy.

Between the glass and liquid state, amorphous materials are essentially supercooled liquids. In this temperature range the molecules can move around, causing the amorphous material to become plastic.

If glass is left around a glass transition temperature for a long enough time period, the likelihood of devitrification increases. Although this is not a problem in the modern glass-making process.

Modern theories of glass formation no longer address the question of why a specific material will form a glass, but rather how fast it needs to be cooled from melting to allow glass formation. In theory, any material can be turned into glass, provided that the cooling down of its molten state is fast enough to enable the atomic/ionic diffusion required to form crystals. The term crystallisation actually refers to a combination of two processes – nucleation and crystal growth. Crystallisation requires the presence of a nucleus on which the crystal will subsequently grow to a detectable size. The nucleus may be either homogeneously formed, through a driving force for solidification when a liquid is cooled below T_M ; or heterogeneously formed at a pre-existing surface, such as the surface of an impurity, a nucleating agent (a deliberately added nano/micro-crystal), crucible walls, etc. Homogeneous nucleating systems are uncommon, and the majority of crystallisation is heterogeneous.

If no nuclei are present, crystal growth cannot occur and the material will form a glass. When some nuclei are present but no growth has occurred, the extremely small size and low volume fraction of the nuclei prevents their detection, so the solid is, for all practical purposes, still a glass. Even if long-range order is lacking, some crystalline clusters or *ordered domains* extending beyond nearest neighbours to the subnanometer scale may be present. These small *clusters* can act as seeds for crystallisation and, therefore, affect the final structure and final properties of the glassy material.

PROPERTIES OF GLASS MADE FROM OXIDES

- transparency
- smooth and shiny surface
- less dense than glass with an identical chemical composition
- temperature of glass transition (T_g)
- high chemical stability (except for fused silica or silica that has been modified using hydrofluoric acid)

Glasses made using silica (SiO_2) are non-crystalline ceramic materials. They share the same raw materials, structural characteristics and even physical properties as crystalline ceramics. For example, the fact that the chemical bonds are strong and directional means that they are poor conductors of heat and electricity and have a low dilatation coefficient. As there are no grain growth limits they are more chemically stable and more resistant to corrosion.

In terms of mechanical performance glass behaves in a unique way. A piece of window glass, for example, is brittle at room temperature but quite plastic when heated up for artisans to work with, or heated up by automated machines. With the same behaviour as rubber, as amorphous material, it can be shaped by hitting it with a hammer (because it is able to absorb mechanical energy) but it becomes brittle after being immersed in liquid nitrogen (77 K).

2.2.1.1 ZACHARIASEN RULES OR CRYSTALLOCHEMICAL THEORY

Structural models can be used to understand glass formation. Amongst them Zachariasen rules, or *random network theory*, were the first to have a significant impact in glass science. Based on the outstanding glass-forming ability of silica Zachariasen postulated that the ultimate condition for glass formation is the ability to form extended three-dimensional (3D) networks lacking periodicity, with energy content comparable (only slightly higher) with that of the corresponding crystal network. Its basic postulates are the similarity of interatomic forces, interatomic bonds and type of first coordination polyhedra between the glass and the corresponding crystal. Based on these postulates, Zachariasen stated four rules that make it possible to predict glass-forming ability:

- each oxygen atom in a glass is bonded only to one or two glass-forming cations (e.g. Si⁴⁺, Ge⁴⁺, B³⁺, P⁵⁺)
- the coordination number of the glass forming cation is small (and small means 3 or 4)
- 3. the oxygen polyhedra share corners, but not edges or faces
- 4. polyhedron structural units form a 3D aperiodic network in which every polyhedral shares at least 3 corners with its neighbors.

In crystalline or amorphous silica, short range order is represented by the $[SiO_4]^4$ tetrahedron, as a base with triangular edges, with an oxygen one each side and a silicon atom in the centre (**Figure 8**). This basic building block has a cationic coordination number of 4 (rule 2), all the O-Si-O angles have the tetrahedral value of 109° 28' and all Si-O bonds have the same length ~0.162 nm. In silica glasses all $[SiO_4]^4$ are linked to all four corners, Q₄, (rules 3 and 4) to form a continuous 3D network, where each oxygen is shared between two silicons (which are bridging-oxygens, BO) (rule 1). The Si-O-Si bridging angles exhibited a relatively broad (but not random) distribution, from 120°-180°, which is an intermediate range order feature of *v*-SiO₂, rather than a short range order. Lack of long range order is achieved by allowing a broad bridging angle distribution of siloxane (Si-O-Si) bonds, believed to range from ~120° - 180°. Rotation of adjacent tetrahedrons around each bridging-oxygens to a silicon atom also contributes to disorder (**Figure 9**).



Figure 8 – Silica tetrahedron, $(SiO_4)^{4-}$, the unit structure of quartz and amorphous silica. (Blue sphere represents the Si atom, and the red spheres the O atoms)



Figure 9 – 2D diagram showing: (a) quartz, (b) silica glass and (c) modified sodium-silicate glass. The fourth oxygen atom of each tetrahedron, $(SiO_4)^{4-}$, is located either in front or behind the silicon atom, in relation to the diagram on paper

Zachariasen's rules exclude non-oxide glasses (e.g. in fluoride, chalcogenide and metallic glasses), chain-like oxide glass structures (e.g. metaphosphate glasses) and high coordination number oxide glasses. Although Zachariasen's rules predicted the existence of the main oxide glass formers (B₂O₃, SiO₂, GeO₂, P₂O₅, As₂O₅, P₂O₃, As₂O₃, Sb₂O₃, V₂O₅, Sb₂O₅, Nb₂O₅ and Ta₂O₅), although at his time, only B₂O₃, SiO₂, GeO₂, P₂O₅, As₂O₅ and As₂O₃ were made into glass.

Zachariasen also predicted the existence of glass modifiers (Na₂O, CaO,...). Although it is possible to produce glass using 100% quartz (silica glass, SiO₂- ν) the more common glass compositions contain alkali metal oxides (Na₂O, K₂O, Li₂O,...) and/or alkaline earth metals (CaO, BaO,...). These oxides have the important role of lowering the melting temperature of the mixture (and are known as *fluxes* in factory production) and in doing so they reduce hugely the production costs (**Figure 10**).



Figure 10 – Binary phase diagram of SiO₂-Na₂O

The structure of modified-silica glasses can be viewed as a network of silica tetrahedra with occasional breaks in connectivity (Figure 9(c)). Glass modifiers reduce the glass melting temperatures and melt viscosity by decreasing the connectivity and dimensionality of the glass former network. The breakage of siloxane (Si-O-Si) bonds originates non-bridging oxygen (NBO) species, where Si-O⁻ provides charge compensation for the modifying cations- ions are mobile and allow ion diffusion, while alkaline-earth ions are relatively immobile and hinder the diffusion of other ions, in particularly alkali ions, enhancing the chemical (and also the mechanical) resistance of the glass. These alkali ions occupy the interstices in the network, reducing the unoccupied free volume of the structure.

There is some evidence that the alkali ions are not randomly distributed throughout the network, but rather exhibit some degree of *clustering*, probably occurring in pairs near some non-bridging-oxygens. The concentration of non-bridging oxygens increases with a decrease in the concentration of bridging-oxygens, proportionally to the alkali (or alkali-earth) content, until a glass network can no longer be maintained and devitrification occurs.

GLASS FORMERS

Elements S, Se, P

Oxides: B2O3, SiO2, GeO2, P2O5, As2O5, Sb2O3, In2O3, SnO2, PbO, SeO2

Halides BeF₂, AlF₃, ZnCl₂, Ag(Cl, Br, I), Pb(Cl₂, Br₂, I₂)

Sulphurides: As₂S₃, Sb₂S₃, CS₂

Selenides: various components of Se, Sn, Pb, As, Sb

Tellurides: TeO₂, PbO e As₂O₅

Nitrates: KNO₃, Ca(NO₃)₂

Sulphates: KHSO₄

Carbonates: K₂CO₃, MgCO₃

Metals: Au₄Si, Pd₄Si, (Fe-Si-B)

Polymers: polystyrene, polymethyl methacrylate, polycarbonate, polyethylene, nylon[®]

Silica is an excellent glass former, and silica glass formed more easily than silica crystal. Like silica, other good glass former compositions have high viscosity melts, where the atomic rearrangements occur slowly.

NOTE: A common nomenclature system known as Q_n notation expresses the concentration of bridging oxygens per tetrahedron by varying the value of the subscript n. A tetrahedron fully linked into the network *via* four bridging oxygens is designated as a Q_4 unit (like *v*-SiO₂), while an isolated tetrahedron with non-bridging oxygens is designated as a Q_0 unit. The value of *n* is thus equal to the number of bridging oxygens on a given tetrahedron. Determination of the five possible Q_n units (Q_0 , Q_1 , Q_2 , Q_3 and Q_4 in silica-based glasses) therefore characterises the connectivity of the structure.

2.2 RAW MATERIALS

Silicon is the predominant element in the Earth's crust (\sim 75% in total); it combines with oxygen to form silica (SiO₂), and with oxygen and other metals (alkalis and/or

alkaline earth metals) to form silicates. Most rocks contain silicates. Thus, as glass is a transparent structural material, the use of raw materials that contain contaminants that may opacify the glass is not appropriate. Only silica, with its high level of purity - as grains of rock or sand - enables the production of transparent glass.

Crystalline silica is a polymorphic substance, able to exist in different crystalline forms with the same chemical composition. Quartz, tridymite and cristobalite are some examples. In crystalline silica, the structural units $((SiO_4)^{4-}$ tetrahedron, <u>Figure</u> <u>8</u>) interconnect by joining vertices (Si-O-Si), where the 3D organisational diversity of these tetrahedron units leads to the different allotropic forms of silica.

Silica is a brittle, hard crystalline material; the chemical bonds that bind the tetrahedrons together are so strong that a temperature of over 1723 °C (T_M) is needed to break them down. At these temperatures, the tetrahedrons constantly break down and are renewed, separating the tetrahedrons and allowing them to move around - the silica melts. This process of breakdown and renewal of the chemical bonds continues making the molten substance very viscous (μ =1013Pa). If the molten silica is slowly cooled, the tetrahedrons are rearranged three-dimensionally, re-establishing covalent bonds and crystal is made. When silica cools quickly the tetrahedrons are randomly immobilised and glass is made. This is why the density of an amorphous or vitreous structure (d_{VITREOUS SILICA}, 20 °C = 2.20 g/cm³) is always lower than the corresponding crystalline structure (d_{QUARTZ}, 20 °C = 2.65 g/cm³, d_{TRIDYMITE}, 20 °C = 2.27 g/cm³ e d_{CRISTOBALITE}, 20 °C = 2.33 g/cm³). In vitreous silica, although the silica tetrahedrons share all their vertices with other tetrahedrons, they don't do this in a regular manner, so the structure does not have long range order (**Figure 9 (b)**) (although it retains short range order, (SiO₄)⁴⁻).

Although it is possible to produce glass with 100 % quartz (vitreous silica, $SiO_2-\nu$), the high melting point makes it so expensive, that its use is limited to very specific technical applications, such as, for example, glass for use in laboratories and for optics and optoelectronics.

By adding fluxes to the molten glass (Na⁺, Ca²⁺, etc., which cannot form covalent bonds) it becomes less viscous and lowers the melting point, as well as reducing the T_g and the working temperature of the base-glass (**Figure 10**). For example, whilst the

 T_M of pure silica is 1723 °C, simply adding 33% (mol) of Na₂O, or 20% (mol) of K₂O or even, 66% (mol) of PbO, reduces the T_M to 789 °C, 769 °C or 714 °C, respectively.

SOME COMMON GLASS COMPOSITIONS (% mol)

Fused silica	99.5 % SiO ₂
Window glass	73 SiO ₂ 17 Na ₂ O 5 CaO 4 MgO 1 Al ₂ O ₃
Aluminium-silicate	62 SiO ₂ 17 Al ₂ O ₃ 8 CaO 7 MgO 5 B ₂ O ₃ 1 Na ₂ O
Fibreglass	55 SiO ₂ 16 CaO 15 Al ₂ O ₃ 10 B ₂ O ₃ 4 MgO
Borosilicate (Pyrex 7740)	81SiO ₂ 13B ₂ O ₃ 10 ZnO 4 Na ₂ O 2 Al ₂ O ₃

The most common glass compositions contain oxides from alkali metals (for example, Na₂O, K₂O, Li₂O) and/or alkaline earth metals (CaO, BaO). These oxides are added through soda (Na₂O), potassium (K₂O) and lime (CaO). Soda is the most efficient flux but if too much is added it can compromise the chemical inertia of the glass. Potassium speeds up the process of glass corrosion through leaching, in acid medium (see *Glass Corrosion*). The fluxes are added in carbonate form, as they break down they form oxides and release CO₂. The lime is added as limestone or dolomite (which also contains magnesium carbonate), and the soda as sodium carbonate. Currently sodium carbonate is produced using the Solvay method, but previously it was added in the form of plant or animal ash.

Today a raw material that should not be overlooked is *cullet* (pieces of waste glass). *Cullet* is used on an *industrial* level when it is a waste by-product of the manufacturing process and on a *domestic* level when it is taken from waste left from pieces used for domestic or restoration purposes. In the manufacture of *float* (see *Float*) glass up to ~ 20% (wt) of industrial *cullet* can be used; in the production of container glass, the use of *cullet* is not restricted to just industrial *cullet*, and up to 90% wt can be used. In addition to *cullet* (or instead of it), some float glass production uses blast furnace slag (metallurgy) as a raw material.

The granular distribution of each raw material is dependent on its molten viscosity. For example, quartz should have larger grain size than all other raw materials, as it should be the last raw material to be melted then the last to be incorporated into the molten bath. As SiO_2 is an excellent glass former, its melt it is very viscous. By retarding the SiO_2 incorporation into the molten bath, it will keep the viscosity of the molten material low for longer, thus helping the *homogenisation* and *refining* processes (see *Glass Flow Chart*). The *cullet* is added with coarser grains than all other raw materials.

Now it is clear why the composition of window glass, container glass and glass for vehicles is made using modified silica, whilst glass for crucibles is made of pure silica (100 % SiO₂). The high operating temperature of the crucibles (e.g. T~1700°C) means there are no modifiers, so a glass with a high T_g is produced. For other purposes the relatively low working temperature means modified silicate glass to be used, with low T_g levels as well as low processing temperatures, which reduce the cost of production.

In spite of its excellent physical properties the use of silica glass is limited due to its high cost. As a result of applications that required high operating temperatures, such as for example on doors or plates of domestic ovens, it is common to use glass-ceramics². For fire-resistant purposes LAMINATED GLASS is used².

Pyrex[®] glass (a registered *Corning* brand), which is made using two components, SiO_2 and B_2O_3 , and two modifiers, Na_2O and CaO, has physical properties between those of silica and silica-based glasses. With Pyrex[®] glass the low coefficient of thermal expansion creates a glass with three times as much resistance to heat shock than modified silica. Pyrex[®] glass is used for test tubes and household glass objects (for use over hobs and in the oven), as it can tolerate temperatures ranging from melting ice or flames.

Nowadays, besides traditional silica-based glass it is possible to produce glass using practically any material. Metallic glasses can be produced using metal bonds or vitreous polymers, covalently bound where secondary chemical bonds play a key role.

Metals used to produce glass are metal alloys, typically 80% (mol) of one metal and 20% (mol) of a semimetal, with a relatively low melting point. $Cu_{80}Zr_{20}$, $Au_{80}Si_{20}$, $Fe_{78}Si_9B_{13}$ or $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ (Metglas[®], an *Allied Chemical* registered brand) are some examples.

Metals are perhaps the hardest materials to vitrify. As they are not very viscous in their molten state, they enable high atomic mobility, with fewer elements in the chemical composition and with simple crystalline networks (preferably *cfc*, *ccc*, *hc*) the crystallisation process is easier. A very high cooling speed is needed to obtain vitreous metals around 10^{8} °C/s.

The operating temperature limit for metallic glasses is low, around just a few hundred degrees, so the atoms crystallise as they acquire some mobility. As there are no grain growth limits metallic glasses are more resistant to corrosion.

METALLIC GLASS WITH A SEMIMETAL

- The introduction of a semi-metal in the alloy composition reduces its T_M , lowering the temperature interval that the material needs for rapid cooling from T_M to room temperature.
- The size of the single unit increases so the atoms have to travel further to find their equilibrium positions in the network, taking longer to crystallise.
- The crystal energy increases as the crystalline network distorts to accommodate the differently sized semimetal.

3. GLASS TECHNOLOGY

3.1 MELTING, HOMOGENIZATION AND FINING

The furnace batch is formulated according to the chemical composition of the glass to be produced (**<u>Table 1</u>**). The raw materials are weigth, mixed and pre-heated. After introducing them in the furnace they are heated until a liquid, viscous paste is obtained. In glass process a batch methodology was common. Today the glass production process is continuous, the raw materials are added continuously to the furnace entrance, and the glass is extracted just from the opposite side of the furnace.

Tabela I – Typical glass batch

BATCH COMPOSITION	MOLTEN GLASS COMPOSITION

			(wt%)							
			66,51	9,04	19,82	1,86	10,82	11,55		
			SAND	Feldspat	SODIUM	POTASSIUM	DOLOMIT	E LIME		
			(99,2%	(65,6% SiO ₂ ,	CARBONATE	CARBONATE	(21,9 %	(CaCO ₃)		
			SiO ₂)	17,8 % Al ₂ O ₃	(Na_2CO_3)	(K ₂ CO ₃)	MgO			
				10,3 % Na ₂ O,			30,3%			
				6,3% K ₂ O)			CaO)			
OXIDE	% Mol	% WT	% OXIDES INCORPORATED BY RAW MATERIAL							
SiO ₂	71,81	71,91	65,98	5,93						
Al ₂ O ₃	0,95	1,61		1,61						
Na ₂ O	12,12	12,52		0,93	11,59					
K ₂ O	1,17	1,84		0,57		1,27				
MgO	3,52	2,37					2,37			
CaO	10,43	9,75					3,28	6,47		
			Weight of each raw material (as reference 100 proportions of sand)							
<u> </u>	100,00	100,00	100	13,59	29,80	2,80	16,27	17,37		

Of all the raw materials, *cullet* is what re-melts at the lowest temperature, which speeds up the melting process. Re-melting *cullet* saves energy as sand, sodium and lime do not need to be melted down. That is why the amount of energy needed in the glass process decreases with the amount of *cullet* added. The energy needed to melt (q) in kJ/kg of glass can be estimated using the following equation (where the parameters of the equation are based on the furnace capacity for isolation and melting):

$$q = \pm 4800 - (1200 * b)/100$$
[1]

where b is the percentage of *cullet* in the furnace. From equation [1] fuel reduced by ~ 2.5 % for every 10% of cullet added. In practice the melting is speeded up by adding more *cullet*.

Fluxes, besides reducing the typical temperatures of glass (T_M , T_g and ΔT for work), also reduce the surface tension of the melted glass (σ) (helping gas bubbles formation,

as shown in [2]), increase heat conduction in the molten glass and enable melting to take place at lower temperatures.

The pressure *p* required for a sperical gas bubble to form with a radius of *r*, in a liquid with surface tension σ , is calculated using the equation:

$$p = \frac{2\sigma}{r}$$
[2]

whereby it is difficult to form bubbles with a small radius.

During the melting process different chemical reactions take place, one of which is breaking down/dissolving (as carbonates and sulphates), as well as dehydration (of hydrate salts) and other solid states, involving reactions/changes between other components. The breaking down of carbonates produces small bubbles of carbon dioxide (CO₂), as the glass melts. As the molten vitreous material is quite viscous, these bubbles are hard to remove (as they rise to the surface of the bath where they escape into the atmosphere). In small-scale production furnaces (100 to 200 kg) it is not hard to remove these bubbles; however, in modern factory equipment (with 200 to 600 ton furnaces) it can become a problem. To speed up the process of releasing gas bubbles CO_2 (refinement) sodium sulphate is added. The sodium sulphate rapidly releases sulphur dioxide as shown in eq. [3] (for T > 900 °C):

$$2Na_2SO_{4(s)} \Leftrightarrow 2Na_2O_{(s)} + 2SO_{2(g)} + O_{2(g)}$$
[3]

Although at first glance adding more gas bubbles to the molten vitreous material may not appear to make sense, the fact is that the bubbles formed (with sulphur dioxide composition) are larger in volume (and chemically different from the gas dissolved in the molten bath), thus absorbing the carbon dioxide dissolved in the molten bath. The bigger bubbles rise more quickly, speeding up the refinement process as shown in [4]. The hydrostatic rising of gas bubbles in the molten material is quantified using the Stokes equation:

$$v = \frac{2}{9}r^2g\frac{\rho_1 - \rho}{\eta}$$
^[4]

Where v is the ascending speed of the gas bubble, r is its radius, g the increased gravitational speed, ρ_1 - ρ is the difference in density between the glass and the gas in the bubble, and η is the viscosity of the glass.

The maximum temperature reached in the furnace is around 1600 °C (*hot spot*). After the homogenization and fining processes (where the glass is chemically homogenized and bubbles are removed), the molten batch rested for a while and then undergoes thermal conditioning (where it is thermally homogenized). After decreasing its temperature to around 1100 °C, the glass can be moulded.

The glass melting process consumes a lot of energy. The energy consumption for continuous glass production is normally 5-10 MJ / kg of glass, which means that in order to produce 1 kg of glass 5-10 MJ of natural gas, fuel or electricity are needed. Over the last few decades there has been a drop in energy costs for glass production, which is mostly due to improved heat insulation in the furnaces and more efficient combustion, the pre-heating of raw materials and the use of *cullet*. As well as providing energy this has environmental benefits, such as reducing the use of natural resources, municipal solid waste (MSW), gas emissions, etc. Using 100 kg of *cullet* can save 120 kg of primary raw materials. This 20% difference corresponds to a loss of gas as carbonates or sulphates are broken down as it melts.

3.2 FLAT GLASS FORMING TECHNIQUES

3.2.1 ROMAN GLASS

The molten glass is poured out onto a flat slab, where it is stretched into the desired shape. The glass panels produced are relatively thick but allow light through without distorting the image. This technique, which was developed by the Romans, was used to produce flat glass until the Industrial Revolution (19th century).

3.2.2 MEDIEVAL GLASS

A hollow piece of glass is cut with tongs, and then immediately blown using a blow tube and flattened out over a table. Various pieces of glass are then cut into smaller pieces which are mounted in a metal tin structure, creating a stained glass window. Colouring the glass is done on *bulk* (during the melting process) or by manually painting onto the glass surface. This technique, which developed during medieval times in Europe, was used until the Industrial Revolution (19th century).

3.2.3 CROWN GLASS

Today the English term *crown* is used generically for soda-lime glass. The term *crown* comes from a manual method used for producing flat glass - a piece of glass is supported in a blow tube and quickly rotated to create glass pieces in disc or *crown*-shaped pieces.

Manual methods for producing flat glass are still used today, for example when glass is required for restoration purposes.

3.2.4 COLBURN-LIBBEY-OWENS GLASS

Continuous flat glass production was patented in 1902 by Colburn. The method consists of vertically stretching a sheet of glass using a shallow tank of molten glass. Two sprockets, cooled with water, secured the edges of the glass sheet and stretched it vertically. After stretching it 60 to 70 cm, during which time it cooled down, it was folded over and laid our horizontally over a flattening table. After being flattened the sheet of glass was polished on both sides (**Figure 11**).

3.2.5 FOURCAULT-PITTSBURGH GLASS

During the same period Fourcault developed a vertical draw method for continuous glass production. The main differences compared to the Colburn process are: i) the part used to stretch the glass piece, as Fourcault's process uses a die immersed in the molten vitreous material; ii) in the fact that the whole process takes place vertically, including the annealing and cutting of the glass sheet. After annealing, the glass sheet is polished from both sides (**Figure 11**).



Figure 11 – Continuous flat glass production: (a) Fourcoult, (b) Pittsburgh and (c) Libbey-Owens

3.2.6 FLOAT GLASS

In 1952 Alastair Pilkington, the technical director of the family business Pilkington Brothers (UK), developed a float glass process, a technique which would revolutionize the flat glass process from the 60s onwards. The float technique represented the biggest advance since the invention of *blown-glass*, in 200 BC. Alastair Pilkington was knighted in 1970 in recognition of the benefits he had brought to technology and the British economy.

Until then, flat glass had been produced using a process where sheets of glass were mechanically stretched; the sheets of glass produced were left with marks where the rollers had been in contact with them (the Colburn-Libbey-Owens system) or were distorted (using the vertical stretching methods introduced by Fourcault or Pittsburgh). Production costs were high, mostly due to the final polishing of the sheets of glass. The float method produced flat glass with an excellent surface finish on both sides (avoiding any latter polishing process), reducing both the time and costs required to produce it.

Besides the more traditional applications of glass in the building and vehicle industries, float glass is used in the aeronautical industry, for windows for commercial planes to the most sophisticated military jets, heat shields on guided missiles, submarine periscopes and in the Challenger project.

Float glass is formed by pouring the molten glass (~ 1150 °C) over a metallic tin bath (Sn^0) , about 30 cm deep (**Figure 12**), forming a (*floating*) thin glassy layer. In order to avoid tin oxidation (formation of S²⁺ and S⁴⁺ species), the *floating chamber* is kept under a strong reductive atmosphere (nitrogen (N₂) with 0.5 % hydrogen (H₂)). Both the glass, which is very viscous at this temperature ($\eta \sim 10^3$ Pa.s), and the molten tin, which is quite fluid, are immiscible and have a flat interface. A sheet of glass forms over the top of the molten metallic tin, and spreads over it *floating*; then cools and solidifies. After leaving the float unit the glass is immediately annealed and cut.



Figure 12 – Float unit – (a) photography of the float chamber; b) photography of the *top roller*, inside the *float* chamber (courtesy of Saint-Gobain Portugal)

The important and original element of the float process in the manufacturing of flat glass is the chance to obtain flat pieces of glass that are polished on both sides without need to polish them afterwards. On the surface that is exposed to the air, the sheet of glass is heat polished and on the surface in contact with the molten tin - it ends up with a specular polish.

3.3 ANNEALING

The glass takes shape during the rapid cooling process, turning from a viscous and easily malleable state to a vitreous state over a short period of time (**Figure 13**). As the temperature drops and the viscosity increases the ionic movements become slower, preventing the diffusion needed to form crystal. The glass then retains a state with high inner tension, which makes it susceptible to brittle fracture, for example.

From an industrial perspective, the melting point is defined as the temperature at which the viscosity has a value of 10 Pa.s. The work area, where the vitreous substance can be shaped, is limited by the viscosity values 10^3 Pa.s and $10^{6.5}$ Pa.s.



Figure 13 - Viscosity-temperature graphs for sílica and sodium-calcium glasses

During the rapid cooling process, due to the poor heat conduction in glass, the release of heat does not occur at the same rate throughout the glass sheet, establishing a temperature gradient from the centre (of the glass pane) to the surface. The outer layers, which cool faster, become rigid and contract, whilst the internal layers remain hotter and more viscous. As the temperature gradient drops (through a homogenising heat treatment), the inner layers contract, but they do not do this freely as there is opposition from the rigid surface layers (that push them outwards, preventing them from reaching the required dimensional stability driven by the expansion coefficient). In thermal equilibrium, the inner layers remain under tensile stress and the outer layers under compressive stress (**Figure 14**).



Figure – 14 Stress gradient from the centre of the glass sheet to the surface

In industrial practice, after forming, the glass is cooled slowly to reduce internal tension. This cooling process is known as *annealing*.

Annealing is the single operation used to lower the internal free energy of the glass. After annealing, the structure is relaxed in the most uniformly way possible and acquires the same specific volume at all points.

3.4 FLOW CHART OF FLOAT GLASS PRODUCTION PROCESS

RAW MATERIALS

MAIN:

Sedimentary rocks, sands, sandstones, quartz and quartzites, dolomite, lime, felspar, sodium sulfate, carbon and cullet.

Raw materials, with suitable particle size distribution, are weighed and mixed with the cullet. The mixture is then introduced into the furnace.

✓ MELTING AND FINING FURNACE

Raw materials will mix with the molten batch and melt, at a temperature ~ 1550 °C. During the initial stay at the furnace the temperature is around ~ 1100 °C, and homogenization and finning take place.

```
      MELTING
      T \sim 1550 \,^{\circ}C
      \eta = 10 \,^{2} Pa.s

      FINNING
      T \sim 1100 \,^{\circ}C
      \eta = 10^{2} \,^{2} Pa.s

      WAY OUT
      T \sim 1050 \,^{\circ}C
      \eta = 10^{3} \,^{3} Pa.s

      \downarrow
      FLOAT
```

The molten glass leaves the melting furnace and enters the float chamber, where it floats over tin bath (Sn^0). From the *float chamber* entrance to the exit the temperature will decrease from 1050 °C to 600°C.

The glass sheet thickness (between 3 and 25 mm, *standard*) and the glass sheet width (maximum 3210 mm) are controlled by the lateral *top rollers* speed pull.



Coatings grant glass particular optical or termal performance (ex., *ANTI-REFLECTION GLASS, MIRROR GLASS, LOW E* GLASS). Chemical vapor deposition (CVD) occurs *on-line* inside the *float chamber*.

↓ PATTERNING*

ROLLED PLATE GLASS is produced by stretching and rolling the glass after it is produced (*offline*). When it is rolled a motif is pressed on using one of the rollers.



In the *annealing chamber*, the glass is slowly cooled down from 600 °C to ambient temperature, in order to minimize internal stresses.

After annealing, the glass sheet can be cutted and stored.

↓ CUTTING AND STORAGE

After annealing, the glass is optically checked by laser, classified and ordered, accordlingly to the level of quality.

Then the glass sheets are automatically cutted (6 m \times 3,21 m, *standard*) and stored in the factory warehouse.

* - MARKED OPERATIONS ARE NOT MANDATORY, BEING PRESENT ONLY FOR PARTICULAR GLASS TYPES NOTE: COLOR IS AN OPTION. IN FLAT GLASS DYES ARE INTRODUCED INSIDE FURNACE.

> COLOR: GREEN: IRON, CHROMIUM OXIDE BLUE: COBALT AND COPPER OXIDE VIOLET: MAGNESIUM OXIDE AMBAR: IRON AND AND SULFUR RED: SELENIUM AND CADMIUM SULFATE

4. GLASS PROPERTIES

Unlike cement, wood and heterogeneous composite materials, glass is homogeneous even on a molecular scale. Although metals are macroscopically homogeneous, they are formed of micro crystals with a different bond composition.

Glass is isotropic so its properties do not depend on directionality. Cement and metals are also isotropics, unlike composite materials, whose properties depend on the direction in which the fibres are positioned.

4.1 OPTICAL PROPERTIES

Glass is traditionally the transparent material used in architecture. The choice of glass for architectural projects is, in most cases, made for its optical performance.

Light interaction with transparent materials occurs through different processes as illustrated in <u>Figure 15</u>. The **incident ray** can be **reflected** (R) off any surface. The light that passes through it can be **scattered** (S) or **absorbed** (A). Part of the light absorbed can be re-emitted in a phenomenon known as **fluorescence** (F). And, finally, the light that passes through the material is **transmitted** (T).



Figure 15 – Light interaction with transparent materials

Excluding fluorescence, light interaction with a transparent material can be classified in the following way:

$$l = R + S + A + T$$
^[5]

In materials with good optical quality, the light fractions scattered (S) and absorbed (A) can be disregarded:

$$1 = R + T \tag{6}$$

4.1.1 REFLECTION

4.1.1.1 SPECULAR REFLECTION

When light hits a smooth surface, the light is reflected specularly (an incidental fraction of light is reflected off the surface at an angle that is equal to or greater than the angle of incidence, so that the incidental ray, the reflected ray and the normal ray reflected from the surface at the point of incidence along the same plane). This is the phenomenon found in mirrors and polished surfaces. It is the regularity of specular reflection that allows images to be displayed in mirrors.

The fraction of light that is specularly reflected off a surface depends on the refractive index of the material according to the Fresnel formula (valid for normal incidence with transparent materials):

$$R \approx \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2$$
[7]

where R –specular reflection

 n_1 –refactive index of medium 1

 n_2 - refactive index of medium 2

When the light is transmitted for example through a vacuum or from the air to inside glass in a window then:

$$R \approx \left(\frac{n_s - 1}{n_s + 1}\right)^2$$
[8]

the refractive index of the air is approximately one.

The bigger the refractive index of a solid, the bigger the specular refraction. For example, the high refractive index of diamond ($n_D = 2,43$) means that when it is multifaceted it shines brightly due to multiple reflections (R = 17.4 %). The same is true of lead crystal (R = 18,4 %), which has a refractive index ($n_D \sim 2,50$) significantly higher than normal window glass ($n_D \sim 1.5$) with a surface reflection of 4 %; so whenever a ray of light passes through a glass/air surface its intensity is reduced

by 4% (**Figure 16**). With window glass, after the reflection on the first surface the luminous intensity is reduced to 96%. After passing though the second surface, it is reduced by 4% again (now 0.04 of 96%), so the fraction of light transmitted will only be 92.16% of the incident ray.



Figure 16 – Specular reflection

If instead of glass a gap with *DOUBLE GLAZING*, there are four reflective surfaces, so the radiation transmitted will only be 84.90% of the incident ray.

Some architectural and civil engineering projects try to minimise the reflective component; for example, in commercial displays or museum exhibits ANTI-REFLECTION GLASS IS USED. To reduce the loss in reflection, it is common to coat the glass with a material which refractive index is lower than the glass underneath, and with a thickness around 1/4 thickness of radiation waves in order to allow destructive interference between the glass reflection and the film reflection (**Figure 17**).



Figure 17. ANTI-REFLECTION GLASS. Light reflected by the glass surface is 180° or $\lambda/2$ antiphase relatively to the light reflected by the glass coating, as its passes over twice the coating thickness $\lambda/4$

In other architectural solutions the opposite is intented, i.e., to minimise the transmission component at the cost of the reflection component. This is often the solution used for outer surfaces of services buildings, with MIRROR GLASS. The effect of MIRROR GLASS is created by a special surface coating on the glass with a refractive index higher than the glass underneath.

Another type of glass in architecture is high solar control glass. This category includes glass with a silver, nickel or gold film coating on the surface that is very efficient for reflecting infra-red (IV) and ultraviolet (UV) rays.

4.1.1.2 DIFFUSE REFLECTION

When a beam of light hits a bumpy surface, the reflected component is diffused more the rougher the surface is (**Figure 18**). The diffuse reflection increases as the specular reflection decreases. A surface made out of fine grains only provides the diffuse reflection component unlike a mirror surface, which only has the specular reflection component.

$$R = R_{DIFUSE} + R_{SPECULAR}$$
^[9]



Figure 18 – Diffuse reflection in bumpy surface. The diffuse reflection increases as the specular reflection decreases

4.1.1.3 MIXED REFLECTION

Mixed reflection combines specular and diffuse reflection, which is more realistic. This is why the diffuse reflection component associated with the specular reflection component determines the appearance of a solid. The shininess of a surface is caused by this.

Architectural projects can use glass with a high diffuse reflection component, as is the case with *open spaces*, where it is common to use ROLLED PLATE GLASS or SILKSCREEN PRINTED GLASS.

4.1.2 REFRACTION

When light passes through transparent interfaces (between mediums with different densities), such as for example air/water or air/glass, not only is the direction of the beam of light changed but also its phase velocity and the wavelength of the light change abruptly between them. This phenomenon, which is known as light refraction, is responsible for distorting the image of objects immersed in cups of water, inside swimming pools, aquariums or even objects near to the ground on really hot days (near to the ground the refractive index will be higher, decreasing as we move away from it).

The easiest way to describe the refractive index is through the relationship between the speed light in a vacuum and the speed of light in air:

$$n = \frac{\mathcal{V}_{v\acute{a}cuo}}{\mathcal{V}_{mat}}$$
[10]

If *i* represents the angle of incidence, and *r* the angle of refraction, these are related to the speed of light in a vacuum, v_{vac} , based on the refractive index, *n*, according to Snell's law:

$$n = \frac{V_{vac}}{V_{mat}} = \frac{\lambda_{vac}}{\lambda_{mat}} = \frac{\sin i}{\sin r}$$
[11]

In glass, the index refraction is independent of direction, but is a function of radiation wavelength. In general, the refraction index decreases when the wavelength increases and for the same material the infra-red refractive index is lower than the ultraviolet refractive index. This is the phenomenon that causes rainbows.

4.1.3 SCATTERING

Scattering occurs whenever small crystals or other heterogeneities are present in the glass. Current float glass production enables the production of flat glass free from these types of defects (mass defects). Generally scattering is undesirable, but sometimes the phenomenon can be exploited. *Opal* and *ruby* glass are examples of this, deliberately manufactured with scatter centres. Scattering is maximised whenever the diameter of the particles is around the length of the radiation wavelength (around 400-700 nm for visible scattering).

4.1.4 ABSORPTION

When light hits glass and the glass transmit it at all frequencies, the glass is colourless. However, if the glass absorbs light differently depending on frequency, the glass appears coloured.

When scattering is absent and the centers of absorption are evenly spread across the material, we may calculate the light absorbed using the Lambert-Beer law:

$$I = I_0 \exp(-\alpha_a l) \tag{12}$$
where *I* is light intensity on transmission, I_0 incidental transmission, *l* optical thickness and α_a the linear absorption coefficient. The coefficient of absorption varies significantly with the frequency, within visible light range. Glass with excellent optical performance has α_a values as low as 0.002 cm⁻¹, with values of 0.04 cm⁻¹ common.

The main components of glass are colourless, so colouring agents need to be added (usually by adding frits) to produce coloured glass. The use of metal oxides creates a purer colour, compared to coloured glass produced using paint or surface coatings.

For LAMINATED GLASS, for example, the colour can be easily incorporated in the synthetic PVB coating. However, the use of colour in the glass adds greater durability and a better aesthetic effect.

4.1.5 TRANSLUCENCE, OPACITY

Transparency is an optical property that enables clear image transmission. A material that is not transparent but which still allows light through is translucent. In this case, the light transmitted has a specular component and a diffuse component (Figure 15).

$$T = T_{difuse} + T_{specular}$$
[13]

When there is a total loss of transmitted light, the material is defined as opaque.

Many types of glass and glazing contain opaquifying components that form a second refractive index phase over the base glass ($n_D \cong 1.5$). The level of opaqueness caused by the existence of a second phase, such as pores or (micro- or nano) particles, depends on the average size and concentration, as well as the difference between the refractive indexes.

4.2 MECAHNICAL PROPERTIES

4.2.1 STRESS AND STRAIN

All materials change shape and/or size when subjected to tensile forces. This phenomenon is called strain and results from a combination of many deformations occurring in the material's chemical bonds. The extent of deformation will depend on the arrangement of the atoms and the type of chemical forces present.

For low levels of tensile stress, stress and strain are related linearly exibiting a proportionality constant – Young's modulus, E (*i.e.*, resistance to deformation). In this regime a material under tensile stress resumes its initial size and form when the tensile stress is removed. A material with a low E value has a high level of deformation even for low tensile levels (e.g. metals). High E values are associated with very rigid materials (*i.e.*, with high resistance to deformation such as glass and ceramics).

The tensile stress where deformation cannot be reverted is known as yield strength and corresponds to the elastic limit. This stress value is sometimes hard to identify, and so the test stress is used, which corresponds to the point where the strain is 0.2 % higher than the elastic limit (strain is 1.002 times higher than elastic deformation, calculated by linear extrapolation). For stress values over the yield point, some materials are permanently deformed - this is known as plastic deformation (**Figure 19**). This is where chemical bonds are broken down, and glasses and ceramic structures collapse. (Metals have mechanisms that allow the absorption of mechanical energy – the linear defects *dislocations*).



Figure 19 - Stress and strain curves for glass, metal and polimeric materials

Glass does not deform plastically, but breaks as soon as it is out of its elastic domain (**Figure 19**). The stress-strain curve of glass reflects its mechanical behaviour:

i) The linearity of elastic range allows that:

- when stress is applied and removed, the piece of glass recovers its shape and initial size exactly.

ii) The lack of plastic deformity leads to:

– brittle fracture. Materials with a large amount of plastic deformation before breaking are known as ductile; those that break without any plastic deformation are brittle. The lack of grain boundaries and dislocations (linear defects present in crystalline metals) causes a lack of resistance to crack propagation, so a crack can develop even at low levels of stress. Catastrophic fracture is therefore typical in glass;

- toughness. A material's impact strength is greater the more elastic energy is absorbed before breaking. This depends on the area within the stress-strain curve. In the absence of plastic deformation, the area within the stress-strain curve is small, so the glass is very susceptible to breaking under an impact;

 absence of fatigue. As structural rearrangement cannot take place on a structural level, glass cannot suffer fatigue (unlike metals);

- susceptibility to too much tension applied to one area, due to the inability to absorb energy and plastically deform. Metals have a natural mechanism of energy absorption - moving in many slip rate systems. Glass cannot undergo structural rearrangements on an atomic level, so the glass has catastrophic (brittle, explosive) fractures. This issue is particularly important at glass fixture points. Any load to be applied should be distributed as evenly as possible (*i.e.*, spread over the biggest area) and preferably over a material that is able to absord the load and deform The main objective of glazing materials is to avoid contact between the glass and other surrounding hard (and brittle) materials and be able to absorb the applied load;

– fragility, due to an inability to absorb energy, and plastically undeforming make the glass more susceptible to cracks. A steel structure can take local stress and redistribute it in small plastic deformations. Glass cannot do this; it deforms elastically until the point where the chemical bonds break and create a crack.

4.2.2 BRITLE FRACTURE

Rupture strength, calculated based on the strengths of the chemical bonds, is around 20 000 N/mm^2 for silica glass. In practice, the stress needed to break glass is much lower than in theory. A glass windowpane, for example, has a rupture strength around 100 N/mm^2 , with the break usually occurring on the surface of the glass.

The microcracks on the glass surface can explain this phenomenon. The development of a crack creates two new surfaces, which demands a certain amount of energy; when elastic deformation energy accumulates around the crack, it exceeds the energy value needed to create two new surfaces, thus providing the conditions needed to create the crack. The energy of elastic deformation can be turned into surface energy, creating new surfaces. According to A. A. Griffith (1893-1963), for a break to happen, energy released in deformation should at least be equal to the energy spent in creating new surfaces, according to Griffith's criterion:

$$\sigma = \sqrt{\frac{2E\gamma}{\pi a}}$$
[14]

which relates the fraction tension σ needed to create a crack with the modulus of elasticity, E, the surface energy of the crack, γ , and the behaviour, *a*, of the crack.

For cracks that are smaller than the critical figure, the energy from the formation of new surfaces exceeds the energy gained from releasing the stress, thus a crack does not spread and the glass does not break. On the other hand, if the cracks are equal in length or longer than the critical figure, the energy from the release in tension exceeds the energy cost of the increase in surface energy, so the crack grows significantly and gives rise of a catastrophic fracture.

Griffith's criterion only applies to brittle materials, unable to undergo plastic deformation, *i.e.*, where the work on the material creates new surfaces.

4.2.2.1 FRACTURE PATTERN (ANNEALED GLASS)

In glass, the crack normally starts from a microcrack on the surface and has a fixed origin point (**Figure 20**). Originally elastic stress (of a higher intensity than a given critical value) and the presence of a crack (also longer than a critical value) combine to create a catastrophic fracture.

The crack starts relatively slowly but increases the more stress is applied. Around the source, the crack spreads relatively slowly. As the speed at which it spreads increases, the surface of the fracture becomes unstable (mixed area). The speed at which it spreads is higher and the crack is compounded (rough area). At each new ramification the speed of the crack is reduced. If the stress is higher a new ramification occurs. The number of ramifications gives us an idea (even if its qualitative) of the energy or intensity of the stress that caused the crack. A simple crack suggests low energy stres; multiple ramifications suggest high stress or high energy.



Figure 20 - Padrao de fractura em vidro: espelho, zona mista e zona encrespada

4.2.2.2 FRACTURE PATTERN (TEMPERED GLASS)

As Griffith cracks are only created when subjected to a tensile force (over a given critical value), glass under compression exhibited higher mechanical strength. Any (external) applied tensile stress will have to exceed compression (internal and surface) before being used for the crack growth.

In TEMPERED GLASS there is an outer layer under compression (~ 20% of the thickness of the glass on each surface), and an inner layer under tensile forces (corresponding to the remaining 60% of the thickness). The stress under compression is aditive; thus if a piece of glass were to fracture at a tensile force of 30 N/mm², once tempered (with an outer layer in compression of, for example, 70 N/mm²) the new fracture stress will be 100 N/mm².

In TEMPERED GLASS, if a crack reaches the inner area under tensile force, the fracture becomes explosive. The high elastic stress available (since the gap beat the compressive strength) allows the fracture to propagate violently, which will lead to a very high number of ramifications, forming the fractures that are characteristic of TEMPERED GLASS (Figure 21). Another advantage of TEMPERED GLASS is that the pieces do not have sharp edges.



Figure 21 – Fracture pattern in TEMPERED GLASS

Tensile stress (inside) of 45 N/mm^2 (related to a compressive stress of 90 N/mm^2) causes ramifications in the fracture every 6 mm, and creates a larg number of fragments.

When, in TEMPERED GLASS, the fracture does not originate from the edge, it is called a *butterfly pattern fracture*. In this case, the fracture starts from opposite sides, creating two pieces, twice the size of the remaining pieces, which contain the source of the fracture.

4.3 THERMAL PROPERTIES: HEAT TRANSMISSION

In glass, heat is essentially transmitted through conduction and thermal radiation. Both its conduction and thermal radiation are measured by coefficients that are characteristic for the material - thermal conductivity λ_C , and conductivity for radiation, λ_r , respectively. The sum of both coefficients provides the effective thermal conductivity.

When a heat flow passes through a sheet of glass with a thickness of d, through a surface S, the amount of heat that passes through the glass (Q), in the time period t, for a temperature gradient T_1 - T_2 between both surfaces of the glass, is shown by the equation:

$$Q = -\lambda_c S \frac{T_1 - T_2}{d} t$$
[15]

The minus sign shows that the direction of the heat flow is against the temperature increase. The thermal conductivity of glass depends on the composition and is found in the interval 2.90 to $3.60 \text{ kWm}^{-1}\text{K}^{-1}$.

At temperatures below 200 °C, heat transmission in glass is almost exclusively through conduction. The conduction coefficient increases with temperature, although it does so in progressively smaller increments, becoming practically constant for temperatures over 900 °C.

Over 550 °C, the mechanism of transmission is replaced with thermal radiation, which predominates above 1000 °C.

For a given wavelength (or for an interval of wavelengths where the wavelength absorption coefficient, ε , is constant), the heat transfer coefficient is calculated by:

$$\lambda_r = \frac{16\sigma n^2 T^3}{3\varepsilon}$$
[16]

where *n* is the refractive index for the glass, and σ , the radiation constant equal to 5,746.10⁻¹² Js⁻¹cm⁻²K⁻⁴.

DOUBLE GLAZING improves heat insulation with a gap (usually filled with air) between the glass panels. Thermal insulation is quantified by U, a calculation of the rate of heat loss through a material. A piece of ORDINARY GLASS has U ~ $5.7 \text{ W/m}^2\text{K}$ and DOUBLE GLAZING (with panels of ordinary glass) has U ~ 2.5 to $3.5 \text{ W/m}^2\text{K}$.

In DOUBLE GLAZING, the heat passes through the gap between the glass through conduction, convection and radiation. For DOUBLE GLAZING, formed out of two panels of ordinary glass with a 12 mm air box, the speed of heat transfer is approximately the same for the three mechanisms.

The amount of heat transferred through conduction can be reduced by increasing the thickness of the air box in the *DOUBLE GLAZING*. In contrast, the amount of heat transmitted through convection is reduced by reducing the thickness. Thermal insulation in DOUBLE GLAZING is thus optimised by the space in between the two panes of glass ~16 mm thick.

In DOUBLE GLAZING, the balance between conduction and convection can also be affected by the choice of gas used to fill the gap. Replacing the air with argon reduces U by between 0.15 and 0.4 W/m^2K . A vacuum is better than any gas. In this case, the difficulty is in choosing a sealant that is effective at atmospheric pressure.

Heat transfer by radiation does not depend on the gas in between the glass panels. The amount of heat transferred by radiation does not depend on what is filling the gap or the thickness of the box - it only depends on the emissivity of the glass surfaces. Emissivity is a property of the material's surface that measures its capacity for absorbing or emitting electromagnetic radiation (light, colour), on a scale of 0 to 1. For any material, emissivity can change depending on radiation wavelength. Materials with low emissivity within the visible wavelengths create good mirrors - the light reflects the whole surface. Metals have low emissivities (emissivity ≤ 0.02). The vast majority of materials present high emissivity, around 0.9. COATED GLASS with an emissivity below 0.2 is defined as a LOW EMISSION GLASS or LOW E GLASS.

A coating that contains silver nanoparticles can provide emissivity of between 0.02 and 0.12. Using glass with this sort of coating, in DOUBLE GLAZING, can effectively reduce the radioactive component of heat transfer from the gap in the DOUBLE GLAZING, reducing U by ~ 40 %.

5. CORROSION

The high resistance of glass to corrosion is due to the high chemical stability of the structure combined with a lack of grain limits. Because of this, glass is considered to be a (chemically) inert material.

But in practice, no material is chemically inert. In glass, although the mechanisms of chemical degradation are sometimes hard to establish, knowledge of the chemical composition of glass and the environmental conditions it will be subjected to are essential. In architecture, situations where it is exposed to highly reactive chemical solutions, as is the case in pipelines, containers with chemical products or even the packaging of some food products are excluded. However, in acid rain, warm salt-water environments, for example in aquariums, contact with chemical products used for sealants or in the assembly of the windows or other building materials, or also, the use of unsuitable cleaning products are relatively common situations.

Chemical attack on glass occurs with two different mechanisms that can occur simultaneously: etching and leaching.

5.1 ETCHING

Etching is characteristic of an alkaline attack. In the initial stage, a gel forms on the surface of the glass, due to physical water adsorption. The absorbed water starts to chemically attack the silicate by breaking up the hydrolytic balance of the hydrogen as shown:

$$\equiv Si - O - Si \equiv +H^+ + OH^- \longrightarrow \equiv Si - OH + HO - Si \equiv$$
[17]

The silica is gradually destroyed and silicic acid is produced, Si(OH)₄.

Along side with the attack on the protons, groups of hydroxyls attack according to:

$$\equiv Si - O - Si \equiv +OH^{-} \longrightarrow \equiv Si - OH + \equiv Si - O$$
[18]

The non-saturated $\equiv Si - O^{-}$ groups, can react with water molecules and form new silanol groups OH^{-} , as shown in:

$$\equiv Si - O^- + H_2 O \longrightarrow \equiv Si - OH + OH^-$$
[19]

As the silica network is destroyed, the remaining components in the glass are released while the glass is partially dissolved.

Assuming that a deposit of reaction products doesn't form on the surface and that the concentration of the solution remains the same, the corrosion continues at a constant speed. The temperature and speed of corrosion is measured using the Arrhenius equation:

$$\log Q = C/T \tag{20}$$

where Q is the speed of corrosion, T is absolute temperature and C is a constant of the process. For every 10°C increase, the speed of the corrosion reaction in an alkaline medium will double.

In most *etching* situations, deposits are not formed on the surface as it is kept clean. However, if the chemical attack was selective or if a deposit formed, the surface will remain uneven and rough to the touch. The accumulation (adhesion) of reactive produces on the surface, like silica or reactive insoluble products, makes it hard to monitor the corrosion process.

Alkaline chemical attack is sensitive to pH levels, increasing the reaction speed for every pH unit. The surface of glass is hydrophilic and water is an aggressive agent. But water attack is minimal compared to alkaline attack. When water wets the surface of a crack the energy in the surface of the glass decreases so the energy needed to spread the crack is reduced. The amount of water can be an important variable when it comes to the speed at which cracks spread.

5.2 LEACHING

Predominantly in acid, the leaching is a process of ionic exchange, with selective removal of the soluble components of glass (Figure 22). Here the process is controlled by diffusion, involving the permutation of hydrogen ions, in the solution, with alkaline ions in the glass. The attack is generally selective, with the network cation modifiers:

$$\equiv Si - O^{-}Na^{+} + H^{+} + OH^{-} \longrightarrow \equiv Si - OH + NaOH$$
[21]

The silica network remains intact however, whilst the ion modifiers are leached. As in the basic attack, the speed of corrosion follows the Arrhenius equation, doubling for every increase by 10°C.



Figure 22 – Secundary corrosion: risks and stings in a medieval glass from Mosteiro da Batalha (courtesy of Dr. Pedro Redol, Director of Mosteiro da Batalha, Portugal)

Corrosion by leaching leads to the formation of a surface deposit enriched with silica (**Figure 23**). When the deposit reaches 0.1 μ m, there is interference with reflected light. Deposits that are over 0.1 μ m thick create iridescence, micro-cracks or break down the glass. However the formation of these deposits can even improve the chemical resistance of the glass to corrosion as they act as a protective barrier and make diffusion more difficult - one of these examples is that of ancient Roman glass (**Figure 24**).



Figure 23 – Leaching of a silica-modified glass



Figure 24 – Iridiscence in Roman glasses

With an acid attack, the pH effect is not relevant as in basic attack. pH of 1 is only a little more corrosive than a pH of 6. The speed of acid corrosion is still much slower than the speed of basic corrosion.

A process of corrosion, beside changes in chemical compositions, can lead to surface microporosity of around 1–10 μ m or the formation of microcracks. In extreme cases a leached glass surface can break or damage the surface structure. In these cases the glass will take on a smoky appearance and a surface deposit or microcracks may become visible.

Glass that has been strengthened with *HEAT TREATMENTS* or *TEMPERING* develops greater resistance to chemical corrosion; those that have been excessively annealed become thick and susceptible to corrosion.

For glass with surface coatings, these coatings should be viewed as potential contaminating agents after chemical attack.

The chemical composition of glass determines its resistance to corrosion. Depending on the acid attack, the greatest resistance to corrosion is found in pure silica glass, where there are no modifiers. As the level of modifiers increases and the network becomes more open, vulnerability to corrosion increases. The presence of alkaline earth oxides or the presence of large cations restricts mobility within the glass network, and improves resistance to corrosion.

6. CONSERVATION, DURABILITY, CLEANING

6.1 CONDENSATION

Condensation often occurs on glass and mirror surfaces. When water vapour inside a room remains in contact with a window surface, and dew point temperature is reached, then the vapour condenses into droplets. This is what can be found for example on a mirror or on bathroom walls after a hot shower. Condensation can also occur inside windows if temperatures of the inner surface are much higher than the outer surface.

The variables that affect condensation inside the windows of a room are: i) temperature of the outer surface of the glass; ii) temperature of the inner surface of the glass; iii) relative indoor humidity and iv) natural ventilation of the house.

6.2 REMOVING CONDENSATION FROM INSIDE WINDOWS

Using *DOUBLE GLAZING*, in frames with a thermal break, is mandatory for avoiding condensation. In *DOUBLE GLAZING* if possible use *LOW E GLASS* to reduce the temperature gradient between the inner and outer glass.

Keep the level of relative humidity inside the room at around 30-50 %.

Keep the level of ventilation in the house high (check extraction units, get the level of forced ventilation right, open windows on a daily basis, even if its just for short periods, air out basements and attics each year).

6.3 HANDLING AND STORAGE

There are specific recommendations for different types of glass for *STORAGE* and *HANDLING*.

6.4 CLEANING

Cleaning products used on glass should be chosen carefully (see CORROSION). It should be highlighted that the chemical composition of the surface of glass can be very different to its inner composition, due, for example, to the presence of surface

coatings (see *ANTI-REFLECTION GLASS*, *LOW EMISSION GLASS*) or by the fact that chemical degradation may have started (see CORROSION).

There are specific recommendations for different types of glass for CLEANING AND MAINTENANCE

7. RECYCLING. LIFE CICLE

Glass is the only material that is 100% recyclable! We should bear that in mind when facing a project, as sustainable development is only possible by careful use of resources and technology.

Implementing recycling management systems depends largely on government directives. For container glass, EU directive 94/62/EC harmonises legal, regulatory and administrative legislation for the member states on packaging and packaging waste. The transposition into the Portuguese legal system is through Executive Law no. 322/95 and Ministerial Order no. 313/96. European directive 94/63/EC proposes the principles of **prevention** (by reducing the amount of packaging waste produced), **reduction** (by encouraging reuse or recovery of waste) **responsibility** (making economic operators responsible for dealing with packaging waste) and **elimination** of trade barriers and free circulation of packaging within the European Union. The management of flat glass recycling, whether it is destined for use in residential building construction and architecture or the vehicle industry, is not regulated.

Glass made using cullet results in lower energy costs. From an environmental point of view, the extraction of raw materials is reduced, gas emissions during glass melting is minimised and the creation of municipal solid waste (MSW) is managed. For every tonne of glass recycled, the amount of raw materials needed is reduced by 120 kg, the fuel needed is reduced to 130 kg and MSW is reduced by 1000 kg.

In flat glass production, due to the high quality raw materials needed, recycling is limited to rejects from the factory production line (industrial cullet). Although glass is always recyclable, the recycled artifact produced is gradually contaminated, turning a brownish green, making it unsuitable for use in architecture and the building industry. This is the reason why domestic cullet is forbidden in float glass factories. Processed float *glass* is also problematic when it comes to recycling With LAMINATED GLASS, for example, the layers of polymers contaminate the production process; in COATED GLASS (MIRROR GLASS, LOW EMISSION GLASS, etc.), the films on the surface contaminate the glass. Glass with defects (stones, devitrification, etc.) cannot be used in the glass production process.

Glass that cannot be reused in the productive process can be used in other products as an inert material.

ENVIRONMENTAL FACTORS

Raw materials	Silicon oxide (SiO_2) is one of the main components of the Earth's
	crust (75 % of its mass).
Extraction	Changing the landscape
Energy	Intensive energy use
Safety	Low chance of toxic metals
Recycling	100 % Recyclable

8. GLASSES USED IN CONSTRUCTION AND ARCHITECTURE

In projects, thickness should be calculated, whether for simple glass (ORDINARY GLASS, SILKSCREEN PRINTED GLASS, ROLLED PLATE GLASS, ANTI-REFLECTION GLASS, MIRROR GLASS, LOW E GLASS, SELF-CLEANING GLASS, TEMPERED GLASS) or composite glass (LAMINATED GLASS, DOUBLE GLAZING), using software provided by the manufacturer. These programmes optimise the optical and heat performance.

8.1 Ordinary Glass (clear float glass)

Simply annealed glass is the easiest flat glass to manufacture. It can be coloured or colourless. The majority of *float glass* is just annealed glass – referred to here as *ORDINARY GLASS*.

HOW IT IS PRODUCED

To produce ORDINARY GLASS a float process is used.

WHERE IT SHOULD BE USED

ORDINARY GLASS was traditionally used in windows and openings in rural and urban dwellings. Nowadays more efficient solutions are sought to tackle the problems of heat and sound insulation, as well as optimising lighting conditions in buildings and housing.

ORDINARY GLASS is often damaged and weakened by *CORROSION*. When carrying out renovation work *DOUBLE GLAZING* is often recommended.

THICKNESS	WIDTH	LENGTH
(mm)	(mm)	(mm)
2,1	2520	
2,3	2700	
2,6	2900	
2,85	2920	
2,90	2960	until
3,15	2980	6000
3,50	3000	
3,85	3020	
3,90	3030	
4,85	3050	
4,90	3060	
5,85	3100	
5,90	3120	
8	3150	
10	3180	
	3200	
	3210	
	3300	

STANDARD SIZES OF *FLOAT* **GLASS**

DIMENSIONAL TOLERANCE FOR FLOAT GLASS (ASTM C1036)

TH	ICKNESS	RANGE OF TOLERANCE			
DENC	MINATION	MIN.	MAX.		
((mm)	(mm)	(mm)		
1,0	MICRO-SLIDE	0,79	1,24		

1,5	РНОТО	1,27	1,78
2,0	SQUARE	1,80	2,13
2,5	SIMPLE	2,16	2,57
2,7	LAMINATED	2,59	2,90
3,0	DOUBLE - 1/8"	2,92	3,40
4,0	5/32"	3,78	4,19
5,0	3/16"	4,57	5,05
5,5	7.32"	5,08	5,54
6,0	1/4"	5,56	6,20
8,0	5/16"	7,42	8,43
10,0	3/8"	9,02	10,31
12,0	1/2"	11,91	13,49
16,0	5/8"	15,09	16,66
19,0	3/4"	18,26	19,84
22,0	7/8"	21,44	23,01
25,0	1"	24,61	26,19
32,0	1-1/4"	28,58	34,93

Recommendations for all glass types

► STORAGE

In the storage facility, always avoid contact between two glass pannels. There is a possibility of chemical and/or mechanical damage due to acid attack (see *CORROSION*). All types of glass should have sheets of paper or flexible spacers between them to keep them separate.

► HANDLING

Glass is a fragile material so it should be handled with care.

► CLEANING

Hydrofluoric acid solutions or other flouride compounds should not be used around any glass surface.

► NOTE

Standard sizes can vary a little from one manufacturer to another. Float glass can also be produced to a size that is not considered standard. Check with the manufacturer before approving the project.

8.2 DECORATED GLASS

DECORATED GLASS – *SILKSCREEN PRINTED GLASS* or *ROLLED PLATE GLASS* – enables light transmission to be controlled, reduces the absorption of solar energy and can create different environments, with or without visibility, defining levels of privacy.

8.2.1 SCREEN PRINTED GLASS

SILKSCREEN PRINTED GLASS is float glass decorated by screen printing.

HOW IT IS PRODUCED

SILKSCREEN PRINTED GLASS is decorated using a screen printing technique. The frit is applied using screen printing in three distinct patterns - dots, lines, empty gaps or across the whole surface. Depending on the pattern, the end product can be transparent, translucent or opaque. The combination of a large range of basic glass and a huge range of frit colours offers designers great creative flexibility.

SCREEN PRINTED GLASS is longer lasting than glass decorated using chemicals or sand baths. *SCREEN PRINTED GLASS* is heat treated to reduce the risks of cracking when exposed to the sun for long periods of time.

WHERE IT SHOULD BE USED

SCREEN PRINTED GLASS is designed to be used indoors, for example in doors, screens, decorative ceilings, bathrooms, shower cabinets, lift walls and in hotel awnings. Designed for enclosed or open spaces, *SILKSCREEN PRINTED GLASS* is easy to clean and *graffiti* resistant.

When COATED, SILKSCREEN PRINTED GLASS can be used outdoors.

SPECIFIC RECOMMENDATIONS FOR SCREEN PRINTED GLASS

► STORAGE

The screen printed surface should be coated.

8.2.2 ROLLED PLATE GLASS

ROLLED PLATE GLASS is a clear, colourless or coloured glass with a design printed on one side.

HOW IT IS PRODUCED

ROLLED PLATE GLASS is produced by stretching and rolling the glass after it is produced (*offline*). When it is rolled a motif is pressed on using one of the rollers.

WHERE IT SHOULD BE USED

ROLLED PLATE GLASS is designed for indoor such, such as in doors, screens and urban furniture.

ROLLED PLATE GLASS can be WIRED, *i.e.*, during the rolling process a metal netting is applied to the glass which makes it more resistant and retains the glass pieces if it breaks whilst stopping people from breaking through it.

SPECIFIC RECOMMENDATIONS FOR ROLLED PLATE GLASS USE IN CONSTRUCTION

ROLLED PLATE GLASS features a pattern. This has an aesthetic effect, so when it is assembled the cut pieces need to be placed so they are aligned and facing in the same direction.

► NOTE

Rolled plate glass cannot be laminated.

8.3 COATED GLASS

The term *COATED GLASS* coves any type of glass (*ORDINARY* or *TEMPERED*) to which a coating has been applied. The coatings most common in float glass are metallic films and metal oxide films. The term *COATED GLASS* does not include varnish.

COATED GLASS can be divided into two main categories – *COATING* during the production process (*online coating*) and *COATING* after the production process (*offline coating*).

In *OFFLINE* coated glass, the coating is applied by chemically polishing the surface using acids or pyrolysis. All these methods were developed in the 1960s and can be applied to glass that has been previously treated with heat or temper.

The coatings applied during the float process emerged in the 1970s - the coating occurs inside the bath used in the float glass process. Placing *sputtering* units (thermal evaporation) at the end of the *float chamber* allows the glass to be coated with different materials, before annealing. Deposition takes place at high temperatures (~ 600 °C) and creates tough and durable coatings, whilst in use, at room temperature. After coating, the glass can be tempered.

The colour of coated glass is not due to the colour of the film coating but due to the constructive interference caused by the layers of film deposited (**Figure 17**).

Glass with different levels of solar control can be produced by controlling the composition and thickness of the film deposited.

8.3.1 ANTI-REFLECTION GLASS

ANTI-REFLECTION GLASS is glass with a special surface coating that has specific optical properties. *ANTI-REFLECTION GLASS* allows the light reflective components to be minimised and the transmission component to be maximised so that transparency and visibility in transmission are optimised.

Through the chemical composition of the coating it is possible to control the levels of glass transmission, tunning visibility along with IV and UV reflectivity.

WHERE IT SHOULD BE USED

High transmission makes *ANTI-REFLECTION GLASS* suitable for use in displays and show windows, in commercial and museum settings.

ANTI-REFLECTION GLASS is also used to produce DOUBLE GLAZING, outdoors, with the coated surface placed on the outside of the DOUBLE GLAZING.

8.3.2 MIRROR GLASS

MIRROR GLASS is glass with a special coating that has specific optical and thermal properties. *MIRROR GLASS* maximised the light reflection and minimises light transmission.

WHERE MIRRORS SHOULD BE USED

MIRROR GLASS is also used in *DOUBLE GLAZING*, outdoors, with the coated surface placed on the outside of the *DOUBLE GLAZING*. *MIRROR GLASS* is used for the outdoor surfaces of buildings.

8.3.3 LOW EMISSION GLASS

LOW EMISSION GLASS is glass where one of the surfaces is coated with an invisible metallic film that reflects UV radiation. The film coating can be applied using pyrolysis or vacuum deposition. Cobalt oxide and chrome oxide are used for coating *LOW EMISSION GLASS*. Indian oxide and titanium oxide reflect UV radiation whilst remaining transparent for visibility, so they are also used in *LOW EMISSION GLASS*.

Copper, aluminium and nickel oxides are used for indoor coatings, as the coatings are less durable.

LOW EMISSION GLASS is glass that increases energy efficiency in a building as it reduces the transfer of heat from inside to outside (it is usually used in *DOUBLE GLAZING* or *COATED GLASS*).

STANDARD OPTICAL PERFORMANCE*

						U		U (european)	SOLAR COEF.				
THICKNESS	VISIBLE		VISIBLE		VISIBLE		Е. то	OTAL	UV	SUMMER	WINTER		
(mm)	%T	%R	%T	%R	%T	ar	ar	ar					
2.5	64	10	48	13	51	0.69	0.75	3.7	0.55				
3	65	10	48	12	49	0.69	0.75	3.7	0.55				
4	64	10	47	12	46	0.69	0.75	3.6	0.54				
5	62	10	46	12	45	0.69	0.75	3.6	0.53				
6	61	10	44	11	43	0.69	0.75	3.6	0.52				

*Characteristic values may depend on the manufacturer.

WHERE IT SHOULD BE USED

LOW EMISSION GLASS is also used in *DOUBLE GLAZING*, with the coated surface placed on the inside of the *DOUBLE GLAZING*.

LOW EMISSION GLASS, when used in *DOUBLE GLAZING* or *COATED GLASS*, easily brings high thermal confort levels. It is recommended for use in public buildings, such as hospitals, schools, offices, shops or homes.

► BEWARE!

There may be legal restrictions for using *MIRROR GLASS* on the outside of buildings. In some places where there is high solar radiation, councils place a maximum limit on reflective coatings on buildings. In urban environments, a highly reflective coating can significantly increase the energy costs of air conditioning in surrounding buildings.

Designers can always use high absorption glass to achieve the right energy balance.

RECOMMENDATIONS FOR COATED GLASS

► STORAGE

There are limits to how long you can store glass with special coating. Check with the manufacturer!

► HANDLING

Manual or other types of handling should be carried out using lint-free soft cotton gloves that are low friction. Do not use paper gloves.

For machine handling, place a thin, smooth sheet of paper between the glass coating and the mount.

► CUTTING

The glass should be placed on the cutting table with the coated surface face up.

Cutting should be carried out on the coated surface when dry. Never use water as a lubricant, as it can chemically react with the film coating or the freshly cut surface (see CORROSION). If necessary, use oil based lubricant, but never too much.

The glass shards should be cleaned up using dry compressed air.

► WASHING

The glass should be regularly cleaned after it has been fitted.

An automatic washing machine should be used for washing *COATED GLASS* (rotating brush and fast drying).

8.4 SELF-CLEANING GLASS

SELF-CLEANING GLASS is a self-sufficient glass when it comes to cleaning, and reduces the cost of building maintenance.

SELF-CLEANING GLASS is glass with a surface coating with hydrophilic or photocatalytic properties.

► HYDROPHILIC SURFACE COATING

SELF-CLEANING GLASS is coated with a hydrophilic film. The hydrophilic nature changes the angle between the drop of water and the glass from $30^{\circ} - 40^{\circ}$ to $4^{\circ} - 7^{\circ}$, so a thiner water film forms on the glass. Raindrops spread out easily and evenly on the glass surface without leaving marks from the run off. The reduced thickness of the water film allows it to dry faster. Both effects reduce the level of residual minerals left on the glass.

► PHOTOCATALYTIC SURFACE COATING

SELF-CLEANING GLASS is coated with a photocatalytic film. The film is generally made of titanium oxide; it is activated with UV radiation and oxygen released in a photocatalytic reaction, which gradually but continually breaks down the bonds in the organic compounds left on the glass. *SELF-CLEANING GLASS* is thus able to process the organic waste at the same time as it breaks away from the glass, making it easier to remove. The presence of a photocatalytic and hydrophilic film keeps the glass clean for longer (provided that it is exposed to both solar radiation and rainwater).

The photo-catalytic film is stable and resistant to oxidation, ensuring good performance over time.

WHERE IT SHOULD BE USED

SELF-CLEANING GLASS should be used on outer surfaces that are well exposed to the sun and in rainy climates (when it doesn't rain water should be used to clean it to remove organic waste).

SELF CLEANING GLASS can be used in DOUBLE GLAZING, as the outer glass with the option of the second glass being LOW EMISSION GLASS.

SELF CLEANING GLASS should always be used on the outside especially with *LAMINATED GLASS* and *DOUBLE GLAZING*.

SPECIFIC RECOMMENDATIONS FOR SELF-CLEANING GLASS ► WASHING

Each year, THE SURFACE OF THE *SELF CLEANING GLASS* SHOULD BE CLEANED. The frequency of this cleaning depends on the outdoor conditions (i.e position in relation to the sun, intensity of UV radiation, annual rainfall).

An automatic washing machine specifically for washing coated glass (rotating brush and fast drying) should be used.

For automatic washing machines, polypropylene is recommended and nylon® brushes are not advised (polypropylene has a lower friction coefficient and is softer and more flexible than nylon®).

It is recommended that brushes are used for cleaning to avoid using abrasive materials on the glass.

Dry air should be filtered (to avoid leaving water marks on the surface of the glass).

For manual washing, a liquid soap or other washing fluid should be used. It should be dried using soft paper to prevent leaving marks on the photocatalytic coating. The drying process should stop when there is still a thin film of water still on the surface.

Check with the manufacturer to find out what temperature water should be used to wash it.

Check with the manufacturer to find out if purified water should be used for the final rinse.

► NOTE

The inner surface of *SELF CLEANING GLASS*, which is not coated in photocatalytic film, should be washed regularly.

It is possible that the photocatalytic effect can be impaired by an unusually high build up of organic or non-organic materials on the glass, deposited for example by rain water.

► USE IN BUILDING

Check with the manufacturer whether the photocatalytic coating needs to be activated. If it does, expose the glass to solar radiation for 48 hours (in the northern hemisphere it should be facing south to optimise UV exposure). Check that the coated surface is facing the sun. If the weather is not suitable, increase the length of time for which it is exposed to the sun. To check that the photo-catalytic film has been activated, pour water over the surface and check to see if it spreads out forming an even and unbroken film (not forming drops). If it does, the film has been activated.

The glass should be set in place immediately after the photocatalytic film has been activated. If it is not then it may be necessary to repeat the activation process.

After activating the photocatalytic coating, do not wash the glass.

The surface of *SELF-CLEANING GLASS* should be protected from sealants. Sealants that are based on polyurethane, polysulphate etc. may temporarily affect the hydrophilic nature of the coating. Silicon-based sealants may effect the photocatalytic nature of the coating several centimetres from the point of contact.

Neoprene or butyl based glazing tape contains a high level of oils that are hard to remove from the glass surface.

BEWARE!

Sharp objects, steel wool and acid, basic or abrasive detergents are not allowed on the coated surface of the glass.

8.5 SAFETY GLASS

SAFETY GLASS is understood to be glass with safety performance that protects goods, spaces or people. This category includes *LAMINATED GLASS* and *TEMPERED GLASS*.

8.5.1 LAMINATED GLASS

LAMINATED GLASS was first sold commercially in 1910. A sheet of polymeric material is placed between two glass plates and they are heated until the polymeric material binds to the inner surface of the glass panels. The polymeric sheet first used was based on biodegradable celluloid and makes the *LAMINATED GLASS* quite susceptible to hydrolytic attack. The use of *LAMINATED GLASS* in vehicle windscreens was then replaced by *TEMPERED GLASS*, in the 1930s, which is chemically inert when in contact with water. It was only in the 1950s that polyvinyl butyral (PVB) started to be used, and *LAMINATED GLASS* remained in use in the industrial vehicle industry. In the 60s, LAMINATED GLASS became the preferred choice for vehicle windows and in the 70s it started to be used in buildings. PVB can be replaced by polyurethane, EVA or CIP (SentryGlasPlus[®]), polymer materials that give *LAMINATED GLASS* better mechanical performance although with higher production costs.

HOW IT IS PRODUCED

LAMINATED GLASS has two (or more) sheets of glass that joined by one (or more) synthetic film coating(s) of polyvinyl butyral (PVB). After the polymeric film is placed between two sheets of glass, the composite is introduced in an autoclave, where the heat treatment under pressure helps it to stick. Once sealed, the resulting material (a sandwich of glass and PVB) behaves as one complete unit and looks like a single piece of glass.

ORDINARY or *TEMPERED GLASS*, as well as *COLOURED GLASS* or *WHITE GLASS*, *LOW E*, or *ANTI-REFLECTION GLASS* can be used to produce LAMINATED GLASS. The sheet (or sheets) of PVB can be colourless, opaque or coloured. The number and thickness of each one of the parts can vary. The combination of a wide range of glass and PVB films offer a large flexibility in projects with *LAMINATED GLASS*. An assemblage of *LAMINATED GLASS* with multiple sheets of glass joined with various PVB films offers increased safety and protection.

Beware - mechanical performance of the PVB synthetic film is only stable between the temperature range of 10°C and 45°C!

WHERE IT SHOULD BE USED

Nowadays, *LAMINATED GLASS* is considered to be the best choice for external cladding on buildings. It is difficult to harmonize in a single material a high quality finish, transparency, light and solar control, thermal and/or sound insulation, protection against cyclones, wind or even explosions, bullets or missiles. *LAMINATED GLASS* is no more resistant to breakage than *ANNEALED GLASS*. Although, in the case of an impact, the PVB film is able to absorb the mechanical energy, so the material resistance of *LAMINATED GLASS* is increased a lot. And, if broken, the PVB film retain glass fragments, preventing them from dropping out and potentially causing an accident, whilst they continue to act as a barrier against people or objects.

After breaking, *LAMINATED GLASS* continues to prevent people or objects from getting in, with the pieces of glass held in the support or frame.

It is also hard to beat its resistance to corrosion in urban environments (except in some industrial environments).

Apart from high performance and multi-functionality, *LAMINATED GLASS* is very durable, preserving the aesthetic side of the glass. *LAMINATED GLASS* offers a combination of solutions to many of the problems in architectural projects, whilst offering protection.

LAMINATED GLASS can be designed to satisfy the most demanding project requirements. Some typical thicknesses of laminated glass are 6.4 mm (3|0.46|3), 8.8 mm (4|0.76|4), 10.8 mm (5|0.76|5) and 11.5 mm (5|1.52||5).

PROPERTIES OF LAMINATED GLASS

► NOTE

All glass can be LAMINATED with the exception of ROLLED PLATE GLASS.

► SAFETY

LAMINATED GLASS meets all the safety requirements for glass, for vertical or oblique use or as roofing. If it breaks, the glass pieces stick to the PVB preventing accidents involving people or property, continuing to provide a barrier against penetration, thus *LAMINATED GLASS* offers a series of advantages compared to *TEMPERED GLASS*. *LAMINATED GLASS* is often used in halls and skylights in hotels and public galleries.

LAMINATED GLASS, although it breaks more easily than *TEMPERED GLASS*, continues to act as a barrier to prevent people or objects getting through. However, *LAMINATED GLASS* breaks in a star pattern and in sharp pieces unlike *TEMPERED GLASS*, which breaks into small pieces with no sharp edges.

► PROTECTION

LAMINATED GLASS offers more protection for people and property than other types of glass. *Standard LAMINATED GLASS* (two glass sheets) is enough to protect against forced entry. In multi-layered pieces or where the thickness of the PVB film is double or triple than *standard* one, *LAMINATED GLASS* can even resist projectiles, heavy objects or small explosions. Normally various projectiles hitting in the same pattern are needed to break through it. The thickness of LAMINATED GLASS offers between 2.5 cm and 7.62 cm in protection, depending on the calibre of what it is trying to resist.

LAMINATED GLASS is recommended in police or army barracks, courts, high security courtrooms, banks, insurance companies and pharmacies.

SOUND CONTROL

LAMINATED GLASS is efficient for providing sound insulation in commercial and residential properties and particularly in television sound studios. The acoustics of *LAMINATED GLASS* are due to high sound absorption by the PVB. Where even higher performance is needed, *LAMINATED GLASS* can be produced with several sheets of glass composed with multiple PVB film coatings.

LAMINATED GLASS is currently used in airports, museums, sound studios and schools with the aim of insulating against unwanted noise from planes, heavy machinery, traffic or other factors.

The ASTM standards define a sound transmission classification (STC). STC is a number calculated from individual transmission loss at specific test frequencies (ASTM E 90 and ASTM E 413). The higher the STC rating the greater the reduction in sound.

Sound and UV FILTER CONTROL

Solar energy is turned into heat energy when it is absorbed. In many buildings, the primary goal is energy control. This objective requires coating surfaces with a material that can reflect and absorb and re-emit solar energy.

Transmission, reflection and light and energy absorption are factors that depend on the colour of the PVB. *LAMINATED GLASS* is an efficient filter of UV radiation (~95 %). That is why it protects against de-colouration and deterioration of materials caused by UV radiation, and is especially useful in shop windows.

ENERGY CONTROL

The heat transfer coefficient of *LAMINATED GLASS* is similar to *SIMPLE GLASS* of the same thickness.

For greater heat performance, a combination of *LOW-EMISSION GLASS* with *LAMINATED GLASS IS RECOMMENDED*.

► NATURAL HAZARDS AND EXPLOSION

LAMINATED GLASS has a key role in protecting against accidents. Adhesion between the glass and the PVB helps prevent accidents caused by falling pieces of glass.

► GLASS FITTED VERTICALLY, OBLIQUELY OR AS ROOFING

Glass fitted at more than a 15° angle is considered oblique glass. *LAMINATED GLASS* is recommended for oblique or roof fitting, as after breaking the glass remains in the PVB.

SPECIFIC RECOMMENDATIONS FOR LAMINATED GLASS

► HANDLING

The edges of *LAMINATED GLASS* should be handled with care, avoiding contact with water or organic solvents. Exposure to water can cause the glass to become opaque or even wear away the laminate, so it is essential that the edges are well protected whilst it is stored and fitted.

► COMPATIBILITY

All *LAMINATED GLASS* contains polymers. That is why solvents, acids or alcohol solutions that are present in insulation tape and sealants can chemically react with the organic components of the *LAMINATED GLASS*. Most sealants used on glass react chemically with the polymeric materials. Compatibility should not be assumed.

Sealant manufacturers should produce reports showing the test results for compatibility between *LAMINATED GLASS* and insulating materials with silicon, painted or anodised aluminium, insulation tape, masonry, etc. Silicon, which is commonly

used as a sealant, in contact with PVB can wear away the laminate up to 50mm in depth.

► ASSEMBLAGE/USE IN BUILDING

LAMINATED GLASS can be produced to suit the project requirements, in terms of the size, type of glass or PVB. *LAMINATED GLASS* can also be used as a monolith or in double glazing. *LAMINATED GLASS* can be cut or drilled during the building process unlike *TEMPERED GLASS*.

LAMINATED GLASS should be sealed to avoid any potential condensation or humidity inside. Inside the frame of the *LAMINATED GLASS* there should be at least three holes (each 5mm) that allow rainwater or condensation to drain quickly.

Prolonged exposure of the laminated surface to humidity can lead to nebulosity or wear off the laminate from the surface. When fitting, more elastic sealants are recommended, such as silicon, polyethylene foam or chloroprene rubber.

LAMINATED GLASS can be cut during building work.

► NOTE

LAMINATED GLASS performs well, particularly in terms of SAFETY and PROTECTION, provided that a suitable frame is used (frame standards: prEN 1627-1, EN 1522 and EN 1523).

European and North American standards for safety glass and protection: ASTM C1036, C1172, C1048, PR EN 356 (European Standard), CTK 4 Union Professionelle des Entreprises d'Assurance (UPEA or BVVO), CPSC 16CFR 1201ANSI Z-971 – 1984.

STANDARD DIMENSIONS OF LAWINATED GLASS							
Τιρο	Standard	MAXIMUM					
(GLASS	THICKNESS	DIMENSIONS					
COMPOSITION)	(mm)	(mm)					
ORDINARY GLASS							
+							
ORDINARY GLASS							
3 + 3	6,0	1.800 × 1200					
5 + 5	10,0						
6+6	12,0	2.800×2000					
8 + 8	16,0						
10 + 10	20,0	3.500×2500					
12 + 12	24,0						
15 + 15	30,0						
5 + 6.8	11,8						
6 + 6.8	12,8	2.400×1800					
		2.100 × 1000					

STANDARD DIMENSIONS OF LAMINATED GLASS

8 + 6.8	14,8	
8 + 10	18,0	
10 + 10	20,0	3.500×2400
12 + 10	22,0	
ANTI-REFLECTION		
+		
ORDINARY GLASS		
6 + 6	12,0	2.400×1800
8 + 8	16,0	
10 + 10	20,0	
12 + 12	24,0	3.500×2400
TEMPERED		
+		
ORDINARY GLASS		
5 + 5	10,0	2400×1800
6 + 6	12,0	2.100 × 1000
8 + 8	16,0	
10 + 10	20,0	
12 + 12	24,0	3500 × 2400
15 + 15	30,0	5500 × 2400

* Standard dimentions may depend on the manufacturer

SECURITY GLASS / PROTECTION CLASSES EN356

(EN 356 «classes in construction –	Performance	Class	Level
security glass - tests and rating for			
resistance to manual attack »)			
*TESTS			
Fall of 3 bols, height 1.5 m	uncrossed	P1A	1°
Fall of 3 bols, height 3 m	uncrossed	P2A	1°
Fall of 3 bols, height 6 m	uncrossed	P3A	1°
Fall of 3 bols, height 9 m	uncrossed	P4A	1°
Fall of 9 bols, height 9 m	uncrossed	P5A	2°
Mass + Ax 30 blow	manway not held	P6B	2°
Mass + Ax 51 blow		P7B	2°
Mass + Ax 71 blow		P8B	2°

NOTE: Test sample, glass plate 110 cm×90 cm, horizontally positioned. Bols of 4,1 kg. The third impact the glass must not fracture. Machetes perform an opening of 40 cm×40 cm, designated by «manway».

TYPE OF GUN	CALIBER	ТҮРЕ	MASS (g)	GUNSHOT (m)	SPEED (m/s) * gunshot	CLASS EN 1063
shotgun/ carbine	0,22 LR	L/RN	$2,6\pm0,1$	$10 \pm 0,5$	360 ± 10	BR1-S
shotgun / carbine	0,22 LR	L/RN	$2,6\pm0,1$	$10 \pm 0,5$	360 ± 10	BR1-NS
pistol	9 mm automatic	FJ/ RN/SC	8 ± 0.1	5 ± 0,5	400 ± 10	BR2-S
pistol	9 mm automatic	FJ/ RN/SC	8 ± 0,1	$5\pm0,5$	400 ± 10	BR2-NS
pistol	0,357 Magno	FJ/ CB/SC	$10,2 \pm 0,1$	$5\pm0,5$	430 ± 10	BR3-S
pistol	0,357 Magno	FJ/ CB/SC	$10,\!2\pm0,\!1$	$5\pm0,5$	430 ± 10	BR3-NS
pistol	0,44 R.Mag.	FJ/ RN/SC	$15{,}6\pm0{,}1$	$5\pm0,5$	440 ± 10	BR4-S
pistol	0,44 R.Mag	FJ/ RN/SC	$15{,}6\pm0{,}1$	$5\pm0,5$	440 ± 10	BR4-NS
pistol	0,44 R. Mag	FJ/ RN/SC	$15{,}6\pm0{,}1$	$5\pm0,5$	440 ± 10	BR4-NS
shotgun /carbine	5,56×45	FJ/PB/SCP1	$4 \pm 0,1$	$10 \pm 0,5$	950 ± 10	BR5-S
shotgun / carbine	5,56×45	FJ/PB/SCP1	4± 0,1	$10 \pm 0,5$	950 ± 10	BR5-NS
shotgun /carbine	7,62×51	FJ/PB/SC	$9,5\pm0,1$	$10 \pm 0,5$	830 ± 10	BR6-S
shotgun /carbine	7,62×51	FJ/PB/SC	$9,5 \pm 0,1$	$10 \pm 0,5$	830 ± 10	BR6-NS
shotgun /carbine	7,62×51	FJ/PB/HC1	$9,8 \pm 0,1$	$10 \pm 0,5$	820 ± 10	BR7-S
shotgun /carbine	7,62×51	FJ/PB/HC1	$9,8 \pm 0,1$	$10 \pm 0,5$	820 ± 10	BR7-NS
shotgun	12/70	Brenneke	$31 \pm 0,5$	$10\pm0,5$	420 ± 20	SG1-S
shotgun	12/70	Brenneke	31 ± 0,5	$10 \pm 0,5$	420 ± 20	SG1-NS
shotgun	12/70	Brenneke	31 ± 0,5	$10 \pm 0,5$	420 ± 20	SG2-S
shotgun	12/70	Brenneke	$31 \pm 0,5$	$10 \pm 0,5$	420 ± 20	SG2-NS

SECURITY GLASS / PROTECTION CLASSES EN 1063

NOTE: Specimen, 110 cm×90 cm piece of glass positioned horizontally. 4.1kg test balls. On the third impact the glass should not break. It can be struck with an axe to create a 40 cm×40 cm opening for a person to get through.

• Three impacts with the exception of SG1-S and SG1-NS, which involves just one impact.

• Key: L – lead, CB – cannon ball, FJ – metal coated bullet, FN – cylindrical/conical truncated bullet, HC1 – steel centre (m = 3.7 ± 0.1 g), PB – cylindrical/conical bullet RN – cylindrical bullet/warhead, SC – lead centre, SCP1 – steel coated lead centre.

8.5.2 TEMPERED GLASS

Although medieval manuscripts make reference to extremely mechanically durable glass, there is no proof that it existed. In 1870, in France, TEMPERED GLASS was produced for the first time using vertical tempering in water. This glass was used in low-pressure viewfinders. In the 1930s the first registered brand of tempered glass, Securit®, was marketed. The sheet of glass is supported by clamps on one of the edges and put into the furnace until it reaches a temperature of 600-640 °C. At this point, the glass is removed from the furnace and placed between two high-pressure air jets for thermal tempering. Over 500 °C the glass becomes much less viscous so the marks from the clamps are left in the glass. TEMPERED GLASS is more mechanically resistant than annealed glass and if it breaks it does so in small pieces with smooth edges. This glass was an immediate success, and it has been used in the vehicle and construction industries, and used in high standing buildings. In the 1970s, a horizontal tempering process was developed that did not leave clamp marks. Once this aesthetic issue was overcome TEMPERED GLASS became one of the first choices for public buildings and, in particular, for the restoration and conservation of historical or prestigious buildings, as long as frames weren't required.

TEMPERED GLASS is glass that has been chemically or thermally treated to improve its mechanical performance*. TEMPERED GLASS is two to five times more resistant than ANNEALED GLASS. TEMPERED GLASS breaks into small harmless pieces, with edges that are not sharp, preventing people from getting injured.

HOW IT IS PRODUCED

Tempering can be thermal or chemical.

► THERMAL TEMPERING

ORDINARY GLASS is given a thermal treatment where it is reheated until it is soft (~ 680 °C for soda-lime-silicate glass) and rapidly cooled.

If rapidly cooled, the glass becomes four times more resistant than annealed glass (*ORDINARY GLASS*) and if it breaks it does do in multiple pieces (with smooth surfaces). Minimum surface compression is 69 MPa. For the temper to be effective after breaking, the area of the ten biggest pieces of glass should be no more than 6.5 cm^2 .

If after the thermal treatment the cooling process is slow, the glass is only twice as strong as *ORDINARY GLASS*, and if it breaks it does so in linear pieces, in a bigger area than *TEMPERED GLASS*, but will still hold well in the support (thermally toughened glass). Surface compression is between 21 MPa and 69 MPa.

► CHEMICAL TEMPERING

The cation exchange between lithium ions (Li⁺), on the glass surface, and potassium ions (K⁺) on the outside (immersion liquid), takes place by immersing the glass in a potassium nitrate solution for ~ 16 hours at 400 °C. The exchange of lithium ions for potassium ions changes the chemical composition of the glass surface and, as the potassium ions are bigger than the lithium ions, it compresses the glass surface structure. The mechanical resistance of *TEMPERED GLASS* chemically increases by five times compared to *ORDINARY GLASS*.

Chemical tempering gives *ORDINARY GLASS* properties identical to those of glass that has been thermally tempered. Chemically *TEMPERED GLASS* presents a surface compression of between 45 MPa and 69 MPa.

WHERE IT SHOULD BE USED

THERMALLY TEMPERED GLASS is used for building fronts, sliding doors, entrance doors, museum exhibit cases, shower cubicles, stair gates, balconies or other uses where more resistance is needed. It can be used in the furniture industry and the electrical appliance industry or in fireguards. TEMPERED GLASS should be used whenever there is a chance of physical contact with the glass.

CHEMICALLY TEMPERED GLASS is used for factory fittings where a finer strong glass is needed. Chemically tempered glass is mostly used in ophthalmic glass.

TEMPERED GLASS should not be used in situations where an explosion may occur (e.g. an explosion at a firewall).

TEMPERED GLASS should not be used to prevent forced entries or as a bullet shield. However, a combination of *TEMPERED GLASS* and annealed glass (see *LAMINATED GLASS* and *DOUBLE GLAZING*) can be used.

For fireguards, the project should consider heat expansion as well as the thermal insulation of the sealants.

► Beware!

Tempering creates permanent stress that can sometimes distort images reflected from certain angles. This is considered an intrinsic feature of *TEMPERED GLASS* and not a defect.

The reflection or transmission of polarised light can create stress or iridescence. Again, this is considered an intrinsic feature of *TEMPERED GLASS* and not a defect.

TEMPERED GLASS can also show signs of where it has been held by support grips (in vertical tempering) or a slight wave in the sheet from the rollers when produced using horizontal tempering.

TEMPERED GLASS is associated with a risk of serious breakage**. The project designer is responsible for the project specification for specific use.

TEMPERED GLASS used in DOUBLE GLAZING and used above ground level should only be used as the inner layer of composite glass.

*Glass breaks whenever the surface or edges are placed under a certain amount of tension. In these conditions any slight crack on the surface or edges can spread to form visible damage.

The main principle behind tempering lies in creating a situation with initial compression of the surface or edges. This is achieved when the glass is reheated and rapidly cooled. In this way, the centre of the glass will remain warm compared to the surface, which will cool quickly. When the centre area of the glass cools it compresses the surfaces and edges.

Wind pressure, the impact of a stone, heat tension or other applied forced can overcome this permanent surface tension and break it.

**A spontaneous catastrophic fracture, often referred to in TEMPERED GLASS, is rare. Some of the causes of this fracture can include the presence of impurities such as nickel sulphate crystals,

incomplete tempering, forces on the glass frame, accumulation of surface risks (microcracks) or excessive exposure to the sun.

SPECIFIC RECOMMENDATIONS FOR TEMPERED GLASS

► HANDLING

The increased mechanical resistance of *TEMPERED GLASS* leads to less care being taken when handling it, which could lead to damage to the edges. In this case, even low heat or mechanical stress can lead to a catastrophic fracture.

► ASSEMBLY / USE IN BUILDING

TEMPERED GLASS cannot be cut or modified in any way after the thermal treatment. Perforation of the compressed surface layer causes the whole TEMPERED GLASS TO BREAK.

8.5.2.1 CURVED TEMPERED GLASS

CURVED TEMPERED GLASS is *TEMPERED GLASS* that is not geometrically flat and can satisfy the project needs.

HOW IT IS PRODUCED

CURVED TEMPERED GLASS is glass treated with a heat cycle *TEMPERED GLASS*) where the maximum temperature (~ 600 °C in soda-lime-silicates) is slightly lower than the softening temperature (~ 680 °C in sodium-calcium-silicates). The shape is created in a mould designed using CAD.

WHERE IT SHOULD BE USED

CURVED TEMPERED GLASS can be used in a monolith or set in *LAMINATED GLASS* or *DOUBLE GLAZING*, ensuring the performance of each of the properties of this type of glass.

Whether its *DOUBLE GLAZING*, or *LAMINATED GLASS*, both of them or other monoliths must have the same curvature.
8.6 FIRE-RETARDING GLASS

The first *FIRE-RETARDING GLASS* was *WIRED GLASS*, which was first retail in 1895. *WIRED GLASS* remains in place after breaking so it was chosen at the time to prevent the spread of fire and smoke inside and between buildings. Even nowadays *WIRED GLASS* has retained an important share of the market for *FIREPROOF GLASS*.

8.7 DOUBLE GLAZING

DOUBLE GLAZING uses two (or more) panes of glass, separated by a spacer bar that seals the cavity width (usually filled with dehydrated air) between the two glass panes. The glass-air-glass system is hermetically sealed by a frame especially designed for this purpose. In addition to the frame, the presence of a desiccant is recommended to absorb humidity inside the glass and ensure good performance long term.

Glass that is simply ANNEALED OR TEMPERED GLASS, TRANSPARENT OR COLOURED GLASS, SILKSCREEN PRINTED GLASS OR TEMPERED GLASS, as well as LOW EMISSION GLASS, ANTI-REFLECTION GLASS OR SELF-CLEANING GLASS, can be used in DOUBLE GLAZING. The thickness of the glass used can vary, as well as the thickness of the air cavity between the glass.

DOUBLE GLAZING improves thermal performance, keeping the inside of the buildings more comfortable and reducing running costs. The thermal barrier that the air cavity creates between the two panes of glass means that the inner sheet of glass does not cool down below the dew point, minimising condensation on the inner layer of glass, as well as other problems associated with humidity.

HOW IT IS PRODUCED

DOUBLE GLAZING is generally made by companies involved with the production of float glass. The glass used in *DOUBLE GLAZING* is fitted in frames, in whose quality the performance of the *DOUBLE GLAZING* will largely depend.

WHERE IT SHOULD BE USED

The combination of *LOW EMISSION* or *ANTI-REFLECTION COATINGS*, *COLOURED GLASS*, *ROLLED PLATE GLASS* or *LAMINATED GLASS*, offers a range of configurations, able to respond to the most demanding of projects.

DOUBLE GLAZING is for outdoor use.

COLOUR

Glass that is *COLOURED* can be better integrated into the building to suit the surrounding architectural elements, as well as improving solar control. *COLOURED GLASS* often requires a thermal treatment.

ARGON

Using argon in the air cavity instead of dehydrated air (in the *DOUBLE GLAZING*) increases the thermal performance.

DOUBLE GLAZING WITH A BUILT-IN BLIND

By incorporating a built-in blind to the *DOUBLE GLAZING* the project has new possibilities.

DOUBLE GLAZING can be produced to suit the project requirements, in terms of the size or type of glass.

SPECIFIC RECOMMENDATIONS FOR DOUBLE GLAZING

► ASSEMBLY

Although insulation increases with the thickness of the air pocket in *DOUBLE GLAZING* for the transfer of heat through conduction, for convection the opposite it true. Insulation is optimised for air cavities that are 16 mm thick.

Humidity has more heat potential than other forms of air, so drier air significantly reduces the flow of heat through the window. A desiccant (drying agent), molecular sieves or silica gel, can affect the long-term performance, as the desiccant absorbs humidity that may pass through the sealant.

The quality of the frames is critical in *DOUBLE GLAZING*. The stress caused by strong winds can be enough to misplace the outer glass and cause it to touch the inner glass,

reducing or removing the air cavity. This situation can be avoided by pressurising the air cavity or fitting a spacer to prevent the two pieces of glass from moving.

► COMPATIBILITY

The edges of the *DOUBLE GLAZING* should be clean and free from defects. The frame surrounding the insulation should ensure that it is impermeable to prevent water from getting in between the glass. Pliable frames are recommended.

► GUARANTEE

DOUBLE GLAZING generally has a 10-year guarantee, provided by the manufacturer, against low visibility caused by dust, humidity or films on the inner surface of the *DOUBLE GLAZING*, or by the lack of insulation at the edges, caused by a defect in the materials.

The edges can crack due to vibrations or high temperature rises, and this leads to a crack in the *DOUBLE GLAZING*.

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united glass corporation - usa

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RUBIS[©], DTU (Saint-Gobain)

SciGlass

Square One

Figures Caption

Figure 1 – Obsidian chips and arrow tips, sécs. IV e VI, Mexico (courtesy of Museu Arqueológico do Carmo, Lisboa, Portugal)

Figure 2 – Oriental Mediterraneo glasses produced with Egiptian technique (internal sand mould): (a) amphoriskos, séc. II-I AC and (b) alabastron, séc. V AC (courtesy of Museu da Farmácia, Lisboa, Portugal)

Figure 3 - Oriental Mediterraneo blown-glasses: (a) sprinkler-bottle, séc. V and (b) fish bottle, séc. III-IV (courtesy of Museu da Farmácia, Lisboa, Portugal)

Figure 4 – Roman flat glass in Conímbriga: (a) pieces of window glass and (b) window frame, where a piece of glass can still be seen (courtesy of Museu de Conímbriga, Portugal)

Figure 5 – During the European Middle Ages small glass-making centres were established hidden in forests (British Library, Londres)

Figure 6 – Our Lady Rosário, sixteenth century *vitral* from chancel of Mosteiro da Batalha, Portugal (courtesy of Dr. Pedro Redol, Director of Mosteiro da Batalha, Portugal)

Figure 7 – Volume versus temperature diagram

Figure 8 – Silica tetrahedron, $(SiO_4)^{4-}$, the unit structure of quartz and amorphous silica. (Blue sphere represents the Si atom, and the red spheres the O atoms)

Figure 9 – 2D diagram showing: (a) quartz, (b) silica glass and (c) modified sodiumsilicate glass. The fourth oxygen atom of each tetrahedron, $(SiO_4)^{4-}$, is located either in front or behind the silicon atom, in relation to the diagram on paper

Figure 10 – Binary phase diagram of SiO₂-Na₂O

Figure 11 – Continuous flat glass production: (a) Fourcoult, (b) Pittsburgh and (c) Libbey-Owens

Figure 12 – Float unit – (a) photography of the float chamber; b) photography of the *top roller*, inside the *float* chamber (courtesy of Saint-Gobain Portugal)
Figure 13 – Viscosity-temperature graphs for sílica and sodium-calcium glasses

Figure – 14 Stress gradient from the centre of the glass sheet to the surface

Figure 15 – Light interaction with transparent materials

Figure 16 – Specular reflection

Figure 17. ANTI-REFLECTION GLASS. Light reflected by the glass surface is 180° or $\lambda/2$ antiphase relatively to the light reflected by the glass coating, as its passes over twice the coating thickness $\lambda/4$

Figure 18 – Diffuse reflection in bumpy surface. The diffuse reflection increases as the specular reflection decreases

Figure 19 – Stress and strain curves for glass, metal and polimeric materials

Figure 20 - Padrao de fractura em vidro: espelho, zona mista e zona encrespada

Figure 21 – Fracture pattern in TEMPERED GLASS

Figure 22 – Secundary corrosion: risks and stings in a medieval glass from Mosteiro da Batalha (courtesy of Dr. Pedro Redol, Director of Mosteiro da Batalha, Portugal)

Figure 23 – Leaching of a silica-modified glass

Figure 24 – Iridiscence in Roman glasses