Window and Glazing Topics – Pinking of PVC-U

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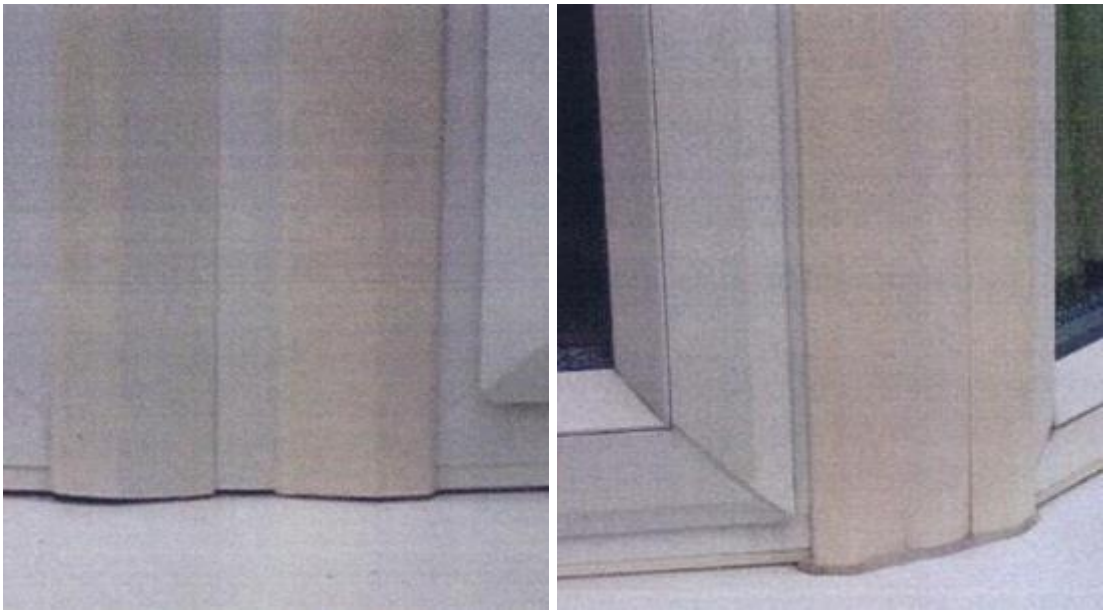
1. Introduction

The ‘pinking’ of PVC-U products continues to affect consumers, suppliers and products long after the first discoveries of the effect. For purchasers of PVC-U windows, the appearance of pinking is considerably worrying and in some cases the response from the industry has been less than helpful. In some cases, it has bordered on being aggressive and consumers have little information to work with. For installers, fabricators and some systems suppliers the support from their suppliers has been equally

Pinking, when first found, represented a new type of aging/discolouration mechanism in PVC-U and was poorly understood. At the time of writing, 30 years after the first sighting of pinking, the process is still poorly understood in terms of the primary causes and there is no current reliable predictive test method for the process. Despite this, there are certain common aspects that can be defined for pinking. This document attempts to clarify some of these common aspects, define some of the issues regarding pinking and the likely possible causes.

Pinking is a surface process only. The pink discolouration extends only to around 5 $x10^{-6}$m into the bulk of the material. Despite the obvious cosmetic failure of the produce, there are no substantial deleterious effects on the mechanical properties of the bulk polymer and pinking does not indicate failure of the product in physical terms.



Examples of Pinking

2. Basic chemistry

Introduction

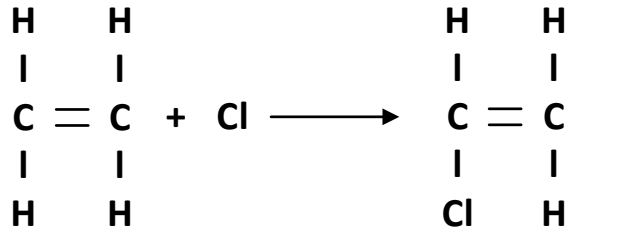
The material used for almost all PVC-U window products is an unplasticised impact modified PVC. This material is termed ‘PVC-U’ to distinguish it from other types of PVC such as plasticised or soft PVC.

Polymer production

All polymers are long chain molecules made up of many repeated units of a basic building block or monomer. The basic building block for PVC is called ‘vinyl chloride’ and this is manufactured from chlorine (obtained from the electrolysis of salt) and ethylene (obtained from the catalytic cracking of oil). The use of a commodity material, such as salt, both reduces the energy used in the production of PVC and helps to keep the price more stable than that of materials based on petrochemicals alone.

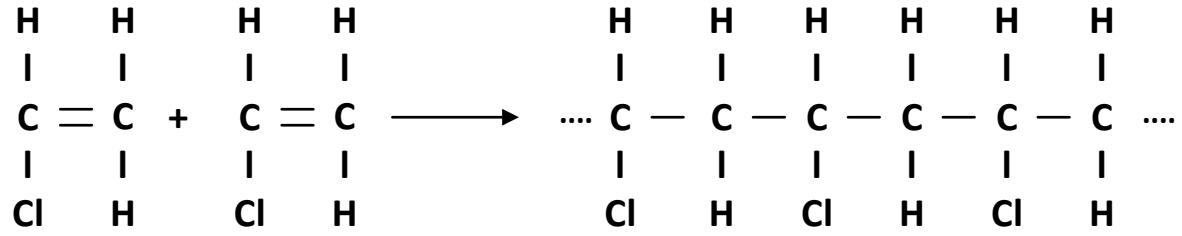
The ethylene and chlorine are then used to produce the basic vinyl chloride monomer (VCM).

Monomer Production



The VCM is then reacted by one of several methods so that it polymerises (or joins together) in long chains of about 1000 repeated units to form PVC.

Polymer Production



The resulting white powder is 'stripped' so that no unreacted VCM is left and is ready for compounding into a usable material.

Polymer compounding

The PVC resulting from the polymerisation process is not suitable for processing and must first be compounded to form a useful material. The PVC before compounding can be thought of as similar to flour, by adding various ingredients flour can be used to make for bread, cakes or many other items but on its own the flour is useless. PVC at the raw stage is useless and the compounding is essential for further processing.

At this stage the PVC is combined with a range of additives to tune the properties to the particular application. The versatility of PVC is due to this ability to tune the properties. Typical additives are:

Impact Modifiers - These are generally acrylic compounds added to PVC to increase the impact strength of the material at low temperatures. The base PVC is a tough material but the resistance to impact is increased even more by the addition of these materials.

Stabilisers - These are added to the PVC to improve the resistance to heat, UV light, general weathering and oxidation. In some cases a blend of stabilisers is used to give the optimum for all conditions. Stabilisers are generally tin, lead or mixed metal based soaps but significant changes are taking place as the industry tries to meet increased environmental requirements for stabiliser usage. The changes in stabiliser package used has been significantly implicated in the occurrence of pinking.

Lubricants - These are added to prevent the PVC sticking to the hot metal surfaces during processing and to improve the flow properties of the PVC. A variety of waxes or fatty acids are used depending on the stabiliser system used.

Colours - These are added for obvious reasons and must be heat and light stable to give the best product life. It is often necessary to consider the climate for the best mix; a stable colour in Britain may not be suitable for use in the Arabian Desert. The colourant and UV stabiliser titanium dioxide (TiO_2) has also been significantly implicated in the occurrence of pinking.

Processing Aids - These are added to improve general processing.

Fillers - These are added to improve the mechanical properties by acting as a reinforcing agent in the compound, typical fillers are minerals such as clay and calcium carbonate.

These additives are all blended together to form the compounded PVC. In the case of PVC-U there is no plasticiser added and the material is therefore termed PVC-U. The compounded material can then be extruded to form the basic profiles for window manufacture.

Properties

The properties of PVC-U used for window production must generally comply with or exceed the requirements of: BS 7413 (the British Standard for White PVC-U Extruded Window Profiles) or MOAT 17 (the materials specification of the BBA). The properties and the specifications are given in the relevant standard.

Weathering Effects and Colour Fastness

PVC-U used for window profiles is specifically designed for outdoor usage and the mechanical properties are largely unaffected by long-term exposure to weathering in normal environments. The material should meet the artificial ageing requirements of both BS 7413 and MOAT 17 for retention of impact strength. In highly polluted/acidic climates any change in properties are magnified but still does not provide a cause for concern. The colour fastness of PVC-U should meet the requirements of BS 7413 for colour changes in temperate climates. This current colour fastness testing is concerned mainly with what is later termed the ‘conventional aging mechanism’.

3. Pinking

Introduction

Pinking is a phenomenon that occurs with PVC-U under a specific set of circumstances and is now regarded as being entirely different to the conventional ageing and weathering performance of PVC-U.

A variety of causes have been postulated for the ‘pinking’and the causes may indeed be varied but there is no current suggestion that the effect is caused by processing. All the postulated mechanisms are related to the material used and the interactions between the raw materials or the quality of the raw materials.

The history of pinking

The phenomenon of pinking in plastics is not a recent one. It has been experienced in the UK since the late 1970’s in various PVC products. PVC researchers at ICI during this time were well aware of the phenomenon.

Pinking became more widely known at the end of the 1980’s when it was widely seen in foamed PVC-U profiles used for external cladding of houses. Papers published in the early 1990’s as a result of research work in the late 1980’s claimed to understand and be able to prevent this mechanism of discolouration in PVC (‘The Pinking of PVC oriented North, an atypical behaviour but not unavoidable’ - Walreavens, Bandol Conference,1993).

The occurrence of pinking in UK window profiles became a major issue in the very early 1990’s and there were also occurrences with guttering and injection mouldings. The British Plastics Federation Window Group set up a Working Party in 1992 to investigate the mechanisms involved in the concern, to quantify the extent of the concern and to try to identify methods of predicting the onset of pinking.The Working Party meetings were strongly attended by most of the major manufacturers (raw materials and processors) in the UK window industry.

The role of titanium dioxide (TiO_2)

Titanium Dioxide (TiO2) is the most commonly used white pigment for PVC-U. Titanium gives high opacity and brightness, a neutral undertone and high brilliance in use. TiO_2 is a pigment or colourant and is not a paint.

TiO_2 has two different forms of crystal: rutile and anatase, and these have significantly different physical and chemical properties. With particular reference to outdoor weathering, anatase type

pigments are considerably more photochemically active than rutile pigments. Anatase pigments are not generally recommended for outdoor use.

The dosage of TiO_2 used is dependent on the application area intended. This is due to variations in the amount of incident UV radiation and the amount of weathering protection required. For standard Northern European exposures (including the UK and Eire) the dosage would be approximately 4 PHR and for higher UV areas (Southern Europe / Mediterranean the dosage would be approximately 6 PHR.

The role of stabilisers

Stabilisers are included in PVC-U to prevent thermal degradation at the temperatures needed for processing of the polymer. At the processing temperatures used in practice (150˚C to 235˚C) PVC will degrade sufficiently to make it impossible to produce a serviceable product. Stabilisers are incorporated to retard or reduce the thermal degradation so that useful products are available. Stabilisers are usually inorganic or organometallic compounds and there are four main groups used in PVC processing. These are:

- Lead stabilisers
- Tin stabilisers
- Mixed metal soaps
    - Cadmium containing
    - Cadmium free
- Organics

The choice of stabiliser system is related to not only the efficiency of the stabiliser but also to legislative and other pressures. The traditional stabiliser system for many years for PVC-U for window applications was Barium-Cadmium-Zinc (Ba-Cd-Zn) but environmental pressures on cadmium usage lead to a migration from this system in the late 1980's towards Lead (Pb) based systems. In the mid 1990's there has been a further migration towards Tin (Sn) based systems and the future systems will probably be Calcium-Zinc (Ca-Zn) based. These changes in the stabilisation systems used for extrusion came about mainly via environmental pressures on the use of heavy metals in any process.

The essential point is that during the early 1990's there were considerable pressures to modify the stabiliser systems used in PVC-U blends.

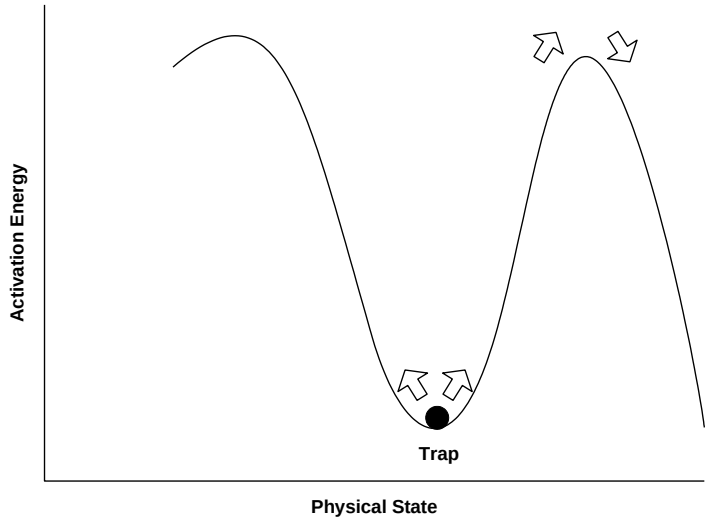
Conventional weathering of PVC-U

The conventional weathering of PVC leads to progressive yellowing and degradation of the PVC and is not strictly related to the mechanism of 'pinking' but the concepts involved can be used to describe the pinking phenomenon.

An activation energy model of conventional ageing.

The activation energy for any chemical reaction is the minimum energy that the particles of the reactants must have for them to react when they collide. The rate of reaction depends on how many particles have this minimum energy. In many reactions, the particles already have this energy and react straight away. In others, energy has to be supplied for the particles to reach the activation energy. This energy can be supplied by heating or by other means - in weathering phenomena the energy is normally supplied by the absorbed radiation from incident light.

Activation energy can be considered by reference to the diagram below. The black ball is stable in the 'well' of the reaction and small amounts of applied energy will simply move the ball 'to and fro' up the sides of the well but there will be no reaction or change in state until the applied energy is sufficient to move the ball over the top of the energy hill. At this stage the reaction will take place and the ball will move to another stable state. This oscillation takes place for every reactant and a 'fast' reaction is one where the applied energy easily moves the ball out of the energy well and on to a new state.



The detailed chemistry of PVC-U weathering and degradation is not at issue in this report and the mechanisms, whilst not fully understood are at least agreed upon in principle.

4. The common factors in pinking

The current concern appears to be quite different in causes to the conventional ageing mechanism. The concern is not universal and is restricted to certain blends of PVC. Not all compound suppliers and processors have experienced the concern despite the range of skills in each processor. In fact, certain processors have never experienced the concern whereas other more technically able processors appear to have suffered badly. There are, however, some common factors in the occurrence of pinking. These are:

North facing

The affected products are almost always north facing and do not receive the full incident UV radiation but are affected only by reflected and ambient radiation. Products from the same batch of material that receive normal sunlight are totally unaffected by the concern. This indicates that a specific energy input is required to activate the reaction.

Moisture

There is some evidence to show that the wetter the climate then the worse the pinking will be. This might indicate that water is a factor in the reaction. The concern has been seen in other parts of Europe but appears to be concentrated in the more coastal areas under relatively high relative humidity conditions.

Conventional ageing tests can be carried out in an ‘Arizona type’ climate (hot and dry) or in a ‘Florida type’ climate (hot and wet). The Florida type of climate is far preferred for accelerated replication of the UK climate but this does identify the susceptibility of a compound to pinking.

Lead stabilisation systems

There is some evidence that lead-based stabilisation systems can accentuate the pinking phenomenon and whilst it is not easy to obtain impartial information and detailed recipes the presence of a lead based stabilisation system does appear to be necessary for the formation of pinking. This is not to say that the use of all lead-based stabilisation systems will result in pinking and some lead systems do not appear to cause pinking as rapidly or as intensely as others.

Titanium dioxide photoactivity

When lead stabilisers are used, the occurrence and the intensity of pinking appears to be directly related to the photoactivity of the TiO_2. It appears that the higher the photoactivity of the TiO_2, the sooner and the more intense the pinking colouration is seen.

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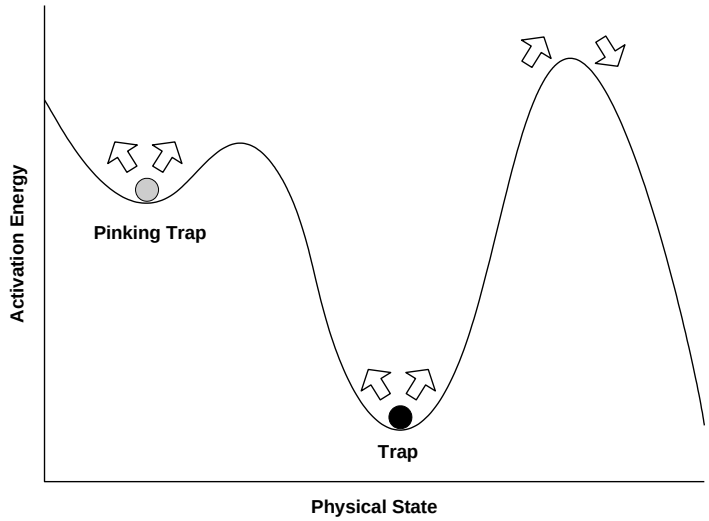
Exposure to normal light

There is considerable evidence that exposure of affected products to normal incident light reverses the concern and experiments carried out by Tangram indicate that this is the case. The pinking goes away if a product is removed from the shade and placed in full sunlight. This can be explained in terms of a modified activation energy concept where the colour-creating compound is a meta-stable or reversible state (as shown by the diagram below). The conventional curve is modified by the inclusion of an intermediate energy hill at a lower energy than that necessary for conventional ageing. The incident energy of reflected sunlight is sufficient to move the reaction to the meta-stable state but is not sufficient to move the reaction to the full reaction.

Exposure to normal incident light provides more energy to the system and the reaction moves out of the 'pinking' trap and in to the normal state or begins to degrade as per normal.



Surface thickness

Work has been carried out by various companies to try to identify the active compounds but the effect is located in the surface layer and no experiments have successfully isolated these yet. These surface layers are less than 1 micron deep and the effect is concentrated in the surface layer.

Processing conditions

On the basis of the current mechanisms proposed, the concerns that have been experienced with other processors throughout Europe and other evidence available there is nothing to indicate that faulty processing has a significant role in the susceptibility of a material to pinking.

It is therefore not thought that pinking is due to a fault in the manufacturing process itself but rather a concern that is generated by the formulation of the PVC used in the process.

For materials that are inherently susceptible to pinking then over-processing appears to accelerate the pinking process but processing does not appear to create pinking in materials that are not inherently susceptible to pinking.

Summary

- Itis not possible to be definitive regarding the absolute cause of pinking but it appears that the cause is most likely an undesirable reaction between lead-based stabilisation systems and the type or quality of TiO_2 used.
- It is not thought that pinking is due to a fault in the manufacturing process itself but rather a concern that is generated by the formulation of the PVC used in the process.