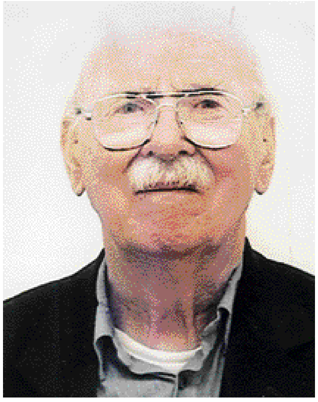
The disintegration of thermally toughened glass by nickel sulphide inclusions



By John Bowler-Reed PhD DIC, FICorrST, ARICS, BSc

The Centre for Window and Cladding Technology at Bath University (CWCT) has assembled a committee, of which I have been a member, for the writing of a report with the provisional title of "Nickel Sulphide in Toughened Glass a Guide to Good Practice", but although good progress has been made it is not yet ready for publication.

It seemed appropriate, on my recent retirement from active consultancy work, to set down my considered personal views on the role of nickel sulphide inclusions in the disintegration of thermally toughened glass.

My introduction to this subject occurred in December 1974 when I had the good fortune to be present at a site meeting when the late independent consultant, Dr S M Cox, acting for Pilkington Glass, gave an account of his conclusion that the presence of nickel sulphide in the body of the glass had contributed significantly to the disintegrations of toughened enamelled glass panels at a large office block and forecast the frequency of future disintegrations.

At that time neither Dr Cox nor any glass manufacturer had published any information on this subject, and I was unaware of the seminal investigation of E R Ballantyne, published by the Australian CSIRO Division of Building Research in 1961.

His report on "Fracture of Toughened Glass Wall Cladding, ICI House, Melbourne" showed that nickel sulphide alone amongst the inclusions of impurities (stones) in the body of the glass was responsible for the disintegrations that occurred on the building.

As is now well known, one of the impurities known to occur as an inclusion in all window glass is nickel sulphide (millerite). It is insoluble in glass, and occurs as discrete particles.

This substance has a far more disruptive effect than other impurities, because it expands by approximately 4% on slowly changing its crystalline structure from that which was stable at the high temperature (approximately 650°C) of the toughening process, the a form, to the ß form which is stable at temperatures below 380°C, and its expansion puts the surrounding glass into tension.

Where a nickel sulphide inclusion of critical size (NSICS) occurs in the inner portion of toughened glass, which is already in tension, the resulting increased tensile stress can exceed the strength of the glass.

Once a crack starts, it propagates throughout the pane almost instantaneously, reducing the pane to dice.

The high internal tensile stress (associated with a surface compressive stress of 100-150 MPa, responsible for the safety characteristics of fully toughened glass) is necessary for the disintegrating effect of nickel sulphide inclusions; breakages found to be due to nickel sulphide are unknown in ordinary annealed glass or in glass that has been heat strengthened to a surface compressive stress of 25-60 Mpa.

Since the publication of Ballantyne's report there have been a number of papers in scientific journals, mostly concerned with varying stoichiometric* ratios between nickel and sulphur that have been found as inclusions in glass, the majority of these inclusions having been found after artificially incorporating nickel in the glass composition.

In my opinion, the most important of these papers is that by M V Swain (Journal of Materials Science 16 (1981) 151 158), who had been seconded to St Gobain Research from CSIRO; the glass that had been investigated by E R Ballantyne had been manufactured by St Gobain.

Swain's paper has great practical importance, in spite of the artificiality of the studied glass composition, whereas consideration of the stoichiometric ratios of nickel and sulphur in nickel sulphide inclusions has been a dead end.

To my knowledge, the first statement by a glass manufacturer on this subject was a presentation on Heat Strengthened Glass given by L A Spoek of Luxguard S.A. at the FAECF congress in London on February 15, 1990.

Pilkington Glass had not given out any information on this subject and had taken the legal and commercial attitude that their products were free of defects, which only arose when they were thermally toughened (usually by a third party).

During the early 1990s and subsequently, breakages of overhead toughened glass have been widely blamed in the technical press on nickel sulphide inclusions.

By now it had become generally realised that disintegration by nickel sulphide could be characterised, when the glass had not yet fallen out of its frame, by tracing the fracture pattern back along the radial cracks to the origin where a characteristic butterfly or double D was to be found, at the centre of which an inclusion could generally be found and identified by X ray diffraction scanning electron microscopy or by laser microprobe mass spectrometry.

Investigations for the British Council of Shopping Centres by Messrs Sandberg into reported breakages in the glass roofs of new shopping malls were not published, but I understood that the major causes of breakages were found to be edge damage of the glass, damage by impact and weld spatter, poor glazing techniques and glass/ metal contact at fixings; nickel sulphide inclusions were responsible only for a minority of breakages.

Exactly the same conclusions were drafted by Pilkington in October 1992 for a proposed presentation to an invited audience at the RIBA (but this was not given because there was insufficient interest by surveyors/ architects at the time). I have no reason to doubt these conclusions, although my own differ markedly from them.

My investigations, and those that have kindly been reported in confidence to me, have found a preponderance of breakages of toughened panes that originated far from the edges in the absence of evidence of impact damage, and these occurred in high quality sophisticated framing systems where glazing had been carried out by skilled personnel.

Until the Glazing Forum organised by CWCT at the Institute of Civil Engineers on June 17,1993, when Brian Waldron and John Colvin gave a presentation on the state of knowledge concerning the disintegration of thermally toughened glass by nickel sulphide, the progress made by Pilkington Glass in minimising the occurrence and effects of nickel sulphide in its float glass had not been made public.

It was reported that the rate of occurrence of NSICS (nickel sulphide inclusions of critical size) in float glass had been reduced from one in approximately 500 kg in 1965 to less than one in 1,300 kg by 1988.

This reduction in rate of occurrence was due to control of the nickel content of raw materials, fuels and processing plant (control of sulphur content had been found to be impossible).

I suppose that Pilkington would not have published these figures if they thought that they compared unfavourably with

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those achieved by other glass manufacturers.

Maintaining toughened glass at a temperature that is high enough to accelerate the transition from the high temperature to the low temperature forms without relaxing the toughening stress is known as heat soak testing.

Unpublished work by Pilkington, St Gobain and St Roch led to a patented process, details of which have remained confidential to licensed users, although the patent ran out in 1960.

The critical size of such inclusions is generally accepted as 0.03mm diameter, far too small to be detected by normal means before disintegration has occurred.

The rate of change of crystalline form, conversion, increases at higher temperatures, and the heat soak process is designed to accelerate this rate in order to disintegrate the glass before it is put into service.

If the patented process is carried out correctly, a conversion rate of more than 90% is achieved and the incidence of nickel sulphide inclusions larger than the critical size is reduced to less than a tenth of the original content.

Heat Soak testing to the German DIN 18516 Teil A specification is generally offered by continental glass manufacturers and tougheners and is now also carried out by some UK tougheners.

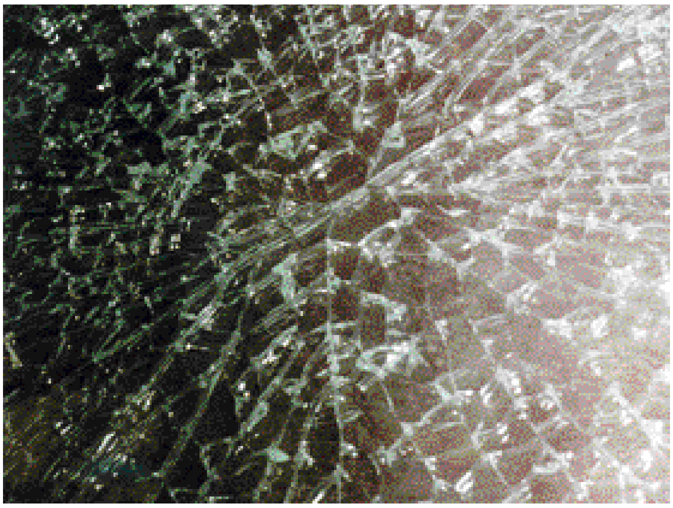
It is reputed to have a conversion rate of 99% or more.

No practical and cost effective non-destructive method for detecting the occurrence of NSICS (nickel sulphide inclusions of critical size) has yet been reported.

A photographic detection method has been used on a large building in Brisbane, Australia. Of the 4,194 panes of toughened glass (vision and spandrel) on the building, 291 inclusions of nickel sulphide were detected, but this result has to be viewed in relation to the 140 breakages that had occurred previously and had been replaced and the further ten breakages (all of which occurred where indicated) during the following seven months.

In my opinion, which I know to be shared by two other experts in this field, this method of detection is not cost effective now that current production control methods have reduced the rate of occurrence in float glass.

Pilkington's confidence in its claimed rate of occurrence since 1988 stems from subjecting,



since 1965, much of the glass it has toughened to the routine use of the online heat soak process. The company's claimed conversion rate is presumably derived from repeated heat soak testing on the same panes of toughened glass.

In practice, the wide variation in the number of breakages due to inclusions on the façades of buildings having similar if not identical glasses, climatic conditions and compass aspects have led me to conclude that on these lucky and unlucky buildings the glass for the latter was manufactured when a clump of relatively impure raw material was passing through the float tank.

A rate of occurrence of one NSICS (nickel sulphide inclusion of critical size) in the tensile region of 13,000 kg of glass is roughly equivalent to a nickel content of 1.2 x 10^{-14} parts by weight.

Controlling the purity by sampling and analysis of the raw materials used in glass manufacture to this standard is almost inconceivable.

It seems, likely that the quality control measures used by Pilkington include the diversion of product surrounding whatever has a higher than normal breakage rate on its routine

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online heat soak test after toughening, to serve as cullet in the manufacture of glass which will not be used for toughening.

It is generally believed in the flat glass trade, though this belief is unlikely to have been based on truly reliable data, that breakages due to NSICS start about two to three years after glazing, rise to a maximum at about five to seven years and then decrease.

Some believe that such breakages cease absolutely after about ten years, but there are established instances of breakages shown to be due to NSI that have occurred after 30 years.

With so much confusion it is quite understandable that when breakages start to increase, building owners and their insurers are anxious to have a reliable forecast of future breakages.

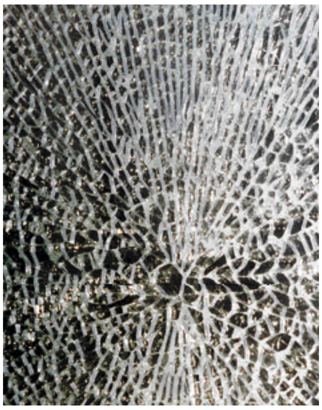
I prepared the following extract for discussion at the Glazing Forum held on June 17, 1993: "My investigations into the possibility of forecasting future breakages have been seriously limited by the lack of data.

They have also been difficult to pursue because everyone tells me that many eminent specialists have tried in the past, and been proved wrong.

But as I get older, the odds of being proved wrong in my lifetime are lengthening. In the few, four, cases where data have come my way, one by the kindness of Steve Green of Cladtech Associates, I've concluded that there is an initial chaotic period of relatively numerous breakages, after which the cumulative number of inclusion fractures settles down to being linearly proportional to the logarithm of the time since glazing. A plot of this relationship can be extrapolated to forecast future inclusion fractures.

"This theory needs testing against more actual data for more confidence in it, but it is all I have at present for quantitatively justifying the extra cost of heat soak testing of toughened glass.The initial chaotic period seems to be two to four years, which also covers many breakages which are not truly due to NSICS. Before one can hope to make a decent forecast, one must have reliable records extending over several years; at least the normal warranty period of five years for insulating glass units."

Since that opinion was drafted, a few more instances of similar breakages have been reported to me.



Because of the crippling expense and chancy nature of actions in court, disputes concerning the responsibility for the costs of replacing glass broken by NSICS have all been settled out of court in the UK, and the terms of settlement have all been confidential.

In the few cases where reliable data have been reported to me, the logarithmic plot has changed from the original straight line found for the first approximately seven years to a less frequent plot which is also straight and of lower (about 30%) slope.

It is interesting to note that a straight line logarithmic plot is equivalent to a rate of breakage which is inversely proportional to the time since installation.

Statistical analyses (linear regression) of these data give correlation coefficients of over 99%, lending support to the straight line logarithmic plots, without, of course, providing any explanation why these relationships should be obeyed.

Thus the latest data available to me indicate that although breakages never cease absolutely, it is comforting that the rate of breakage decreases sharply after about seven years, becoming so infrequent as to be comparable with accidental breakages such as impact by cleaning cradles, vandalism, etc.

As mentioned above, no legal precedent has yet been established in this country for apportioning financial responsibility for the cost of replacing toughened glass that has disintegrated because of nickel sulphide inclusions of critical size.

Now that so much information on its likelihood of occurrence and its control by heat soak testing has become available in the public domain, in my opinion specifiers can no longer reasonably plead ignorance of the risks involved in current specifications of fully toughened glass.

Stoichiometric: Pertaining to the branch of chemistry treating of chemical combinations in definite proportions, the mathematics of chemistry.