STUDIES OF THE AGEING BEHAVIOUR OF GUN-GRADE BUILDING JOINT SEALANTS –THE STATE OF THE ART

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Abstract
In the mid-1970s the first studies, in the form of inspections of building joints, were conducted in England and Germany into the failure rate of sealants. As a consequence of these studies, the ageing behaviour of sealants was investigated with the aid of artificial accelerated ageing methods and by storing sealants outdoors for several years in moderate or tropical climates. The results acquired with these ageing methods can only be interpreted on the basis of a comprehensive understanding of the environmental factors responsible for ageing and the synergy of such factors. In this context, particular attention must be paid to the cyclic mechanical strain upon sealants which occurs in a building joint due to expansion, compression and shearing. By comparing the results acquired using different ageing methods, it is possible to demonstrate the short-comings of the accelerated ageing methods currently in use and to submit recommendations for the future development of standardised methods.

1 Preface
This paper was prepared as part of the programme of RILEM Technical Committee 66-BJS (Building Joint Seals) under the chairmanship of Dr Per-Gunnar Burstroem of Lund University, Sweden. Similar state-of-the-art papers will in due course be produced to cover other aspects of the work programme of the technical committee. These include movement capability, performance in service, sealant classification systems, performance-related sealant properties, and changes in properties with time. As the first report in this series, a paper on test methods for the movement capability of building sealants has been published [1].

The members of RILEM 66-BJS include representatives from Australia, New Zealand, France, the United States, Canada, West Germany, Israel, Sweden and the United Kingdom. There are also corresponding members in the Netherlands and Singapore. The first meeting of the committee was held in Brno, Czechoslovakia, in August 1983.

2 Introduction
The purpose of a building joint sealant is to seal a joint between various components or construction materials. Here, the “seal” is a barrier against certain environmental factors, which differ according to application, e.g. moisture, driving rain, standing or pressurised water, draughts, sand or dust.

The materials discussed below are gunable (extrudable) sealants which are processed in a paste-like state and which subsequently become plastic or elastic due to
physical drying or chemical reactions. In contrast to preformed gaskets, gunable sealants - because of the processing in the paste-like state - are capable of compensating for even relatively large dimensional tolerances; hence they can be employed practically universally. Care must be taken, however, not to fall below a certain minimum joint width even locally, as otherwise the sealant will be stressed beyond its movement capability.

Owing to the trend towards modular construction, gunable sealants have rapidly evolved into a major element in the building trade over the last 30 years. They are used, for example, to seal expansion joints and connection joints in façades, for the edge seal of insulating glass units, and or seals in interior finishing - especially in sanitary engineering. Sealants are used to seal joints in roads and runways as well as joints below ground level or under water.

Like any other construction material, sealants are subject to natural ageing. In contrast to other construction materials, however, they are used in a multitude of disparate areas of application and are therefore subject to greatly varying individual environmental factors of combinations thereof. This fact complicates any comparison between the ageing properties of sealants on different construction projects and the attempt to develop a method based on accelerated ageing which might provide representative results for utilisation in the field.

3 Studies of the ageing properties of sealants in building joints

In the mid 1970s the British and German governments sponsored a series of studies [2-5] with the aim of obtaining statistics on the failure rate with respect to gunable sealants and on the basic causes of such failure by inspecting the largest possible number of building joints. The advantage of the visual inspection of building joints rests in the simplicity of the method, since it permits direct observation of the end result of joint design, quality of workmanship, joint movements and environmental factors. A great deal of experience is required, however, to attribute the specific sealant failure to individual causes or combinations of a number of possible causes. Clearly, the disadvantage of this method is that comparisons are made of sealants stemming from different eras of technological development and that the results of such comparisons can be correctly interpreted only if the inspectors know the formulations for the particular sealants. Unfortunately, this is generally not the case.

Undoubtedly the most sophisticated study of this type was conducted in Germany by Grunau [4,5] for the Federal Minister for Regional Planning, Building and Urban Planning. Over 2 600 000 m of façade and window joints on more than 600 buildings were examined with respect to surface changes and cohesion or adhesion cracks of the sealant. The buildings selected for the study had been erected and the joints sealed between 1956 and 1975. In the statistical evaluation of the sealant failure noted, Grunau took into consideration the fact that the formulations of the sealants had undergone substantial change during this period; the tough sealants used at the outset were increasingly abandoned in favour of low-modulus sealants at about the mid or late 1960s. Grunau consequently ascertained the rates of specific types of failure

The most important result of Grunau’s study may be viewed as his classification of the types of sealant failure in accordance with the different causes - planning errors, material faults, processing errors and errors in workmanship during carcase work. As is apparent by comparing the periods 1958 to 1965 with 1970 to 1975 in Tables 1 and 2, both the overall rate of damage and the loss of seal due to material failure decrease sharply. The latter aspect assuredly reflects the progress achieved in the realm of sealant formulations between 1958 and 1970. Unfortunately, the report does not specify the criterion of failure; in particular, no distinction in drawn between an adhesive and adhesive and a cohesive failure. Grunau estimates the maximum movement capability of the sealants examined to be 20% of the joint width. No specific details of the exposure of the joints to weathering, such as differences between the north side and the south side of a building, are mentioned. However, he does expressly point out that it was not possible to detect any effect of aggressive contaminants in air - either in the form of dust or gas.

Table 1. Failure rates of inspected joints by area of application according to Grunau [5]

<table>
<thead>
<tr>
<th>Area of application</th>
<th>Failure rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exterior wall</td>
<td>31</td>
</tr>
<tr>
<td>Window seal</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 2. Distribution of failure rates on inspected joints by causes according to Grunau [5]

<table>
<thead>
<tr>
<th>Cause of failure</th>
<th>Failure rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exterior wall</td>
</tr>
<tr>
<td>Planning errors</td>
<td>31</td>
</tr>
<tr>
<td>Material faults</td>
<td>24</td>
</tr>
<tr>
<td>Processing errors</td>
<td>32</td>
</tr>
<tr>
<td>Workmanship errors in carcase work</td>
<td>13</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

The comparative studies on joints of existing buildings made it possible to draw concrete conclusions for the first time as to the incidence of failure. In so far as damage due to material failure is concerned, however, they provided no information whatsoever as to which variable was ultimately responsible for the failure.

The influence of the various ageing factors on organic plastics had already been studied in the 1950s and 1960s; hence it was possible to employ these results as a starting point for more detailed studies of sealants.
4 Determining the environmental factors causing ageing

Environmental factors known to cause ageing [6-8] are:

1. Sunlight (ultraviolet light, heat)
2. Cold
3. Moisture or precipitation
4. Oxygen or ozone
5. Corrosive gases (sulphur dioxide, nitrogen oxides)
6. Cyclic mechanical strain and
7. Microbiological and macrobiological agents.

4.1 Influence of the ultraviolet component of sunlight
The ultraviolet component of the solar spectrum (<400 nm) is capable of triggering photochemical reactions on the surface of a sealant. According to Ashton [9], ultraviolet light can evoke the following reactions in organic construction materials:

1. Chain scission,
2. Crosslinking,
3. Formation of low-molecular compounds and
4. Modification of existing or formation of new functional groups.

Of these, chain scission and crosslinking are by far the most important reactions. As a rule, both processes occur simultaneously in response to light, but one of them usually predominates for a given elastomer. If this is chain scission, the surface of the material softens over the course of time. If crosslinking predominates, the surface becomes brittle.

The effects of ultraviolet light may considerably accelerate the oxidation of the elastomer’s outer layer by atmospheric oxygen, causing a hard, brittle and inelastic skin to form on the sealant’s originally elastic surface. The increasing formation of oxidised compounds in the surface of the sealant inhibits further oxidation, however [10], hence the layer of skin is usually only 1 to 2 mm thick. Even without being subjected to stress due to movement, the brittle skin breaks in irregular Craquele cracks, a phenomenon referred to as “crazing”.

According to Alsleben et al. [11], polyurethane sealants exhibit a high degree of crazing in response to ultraviolet light, whereas the surface of polysulphide sealants becomes brittle due to increasing crosslinking of the polymer chains, developing an “orange peel” with wrinkles and cracks 0.5 to 2 mm deep. On the other hand, UV light has practically no effect on the surface of silicone and polyacrylate sealants.

The above changes caused by UV light involve only the surface of the sealant. However, in the case of sealants used for glazing or insulation glass units, the effects of ultraviolet light on the adhesion of these materials to glass is of decisive importance. For regular glazed insulation glass units, approximately 3 to 5% of the sunlight incident on the pane as a whole is transferred to the edge sealant owing to internal reflection within the pane.

The glazing sealant is, in addition, affected by the sunlight passing through the two glass panes and striking it directly. It must be taken into consideration that the expo-
sure is always to rays passing through the pane and that the wavelengths shorter than 280 nm are therefore eliminated due to absorption in the glass. Gjelsvik [12] already pointed out in 1975, however, that the photon energies of ultraviolet light with wavelengths above 280 nm are quite sufficient to split a number of organic chemical bonds such as C-N, C-Cl, C-O, C-C or C-H.

If the total number of the chemical bonds formed in a sealant is compared with the number of chemical bonds between sealant and substrate surface, it is apparent that the adhesion of the sealant to the substrate stems from a relatively small number of bonds. It is therefore obvious that the irreversible destruction of a comparable small number of chemical bonds in the boundary area between sealant and substrate is sufficient to evoke a permanent loss of the sealant’s adhesion. Moreover, the bonds to the substrate exist only in a boundary layer of the sealant approximately 0.5 to 2.0 nm thick. Hence the additives normally called upon to protect organic elastomers against ageing by rendering them more stable to ultraviolet rays can exert little effect on the UV stability of the glass adhesion of organic sealants, since their concentration within this boundary layer is too low.

Studies on insulating glass sealants [13] have succeeded in demonstrating that the adhesion of organic sealants to glass is destroyed by ultraviolet light at different rates but is eventually completely lost, sooner or later. On the other hand, ultraviolet light has practically no effect on the adhesion of silicone sealants to glass [13,14].

4.2 Influence of radiated heat
The infrared component of sunlight (>780 nm) constitutes approximately 53% of the total solar spectrum striking the earth’s surface. The infrared rays warm the surface of a material. The temperature achieved at the surface depends on the intensity of the sun’s rays and the colour of the building material’s surface. According to Kuenzel [15], the surface of a dark or black wall reaches between 60 and 70°C on a summer day with intensive solar radiation. However, since the surface of these building joint sealants with a synthetic polymeric base is smooth, they absorb far less radiation than porous masonry. The maximum surface temperature ascertained by Burstroem [6] in measurements involving matt black sealants was 45°C, whereas the average surface temperature of a white sealant with a glossy surface was about 4°C lower.

In sealants, heat can trigger physical as well as chemical effects. Thermoplastic sealants such as the solvent acrylates soften when heated. This is the result of the loss of weak physical bonds between the polymer chains. If the heating period is brief, most of the effects on the thermoplastic sealant are reversible, assuming that the temperatures in question were not so high as to initiate polymer degradation [7]. Elastic sealants contain plasticisers, which can be released in response to high temperatures, causing the sealants to stiffen.

This evaporation of plasticisers usually does not occur until the temperatures achieved exceed 70 to 80°C. For certain applications in the construction sector, such as solar collectors or dark-tinted insulation glass units, where the sealants used are subjected to extremely high temperatures, particular attention must be paid to the evaporation of plasticisers or other constituents of the formulation. Not only is stiffening of the sealant possible here, but also the low-molecular weight plasticiser vapours may condense on cold locations and thus detrimentally affect the efficacy of the solar collector or the insulation glass unit [16].
After the temperature exceeds a certain threshold, which is primarily a function of the type of polymer used in a sealant formulation, a chemical “post-cure” occurs between the polymer chains. This additional increase in the degree of crosslinking can be detected on the basis of an increase of the moduli and a decrease in elongation in a tensile test.

The tensile strength of the sealant remains almost constant, since the increase in cohesion is approximately compensated by the reduction in elongation. Furthermore, the post-cure is apparent from an increase in the Shore A indentation hardness. If the temperature is elevated even more, increasing polymer degradation reactions occur upon reaching a second temperature threshold, once again primarily a function of the polymer type. The sealant becomes increasingly softer; the modulus and Shore A hardness of the material then decline [17].

According to Burstroem [6,7], temperature-related ageing exhibits the greatest influence upon sealants. Sealants with a polysulphide or polyurethane base incline towards a readily apparent post-cure after only brief storage at 70°C. The extent of this post-cure is however, highly dependent upon the sealant’s formulation. For silicone sealants, an interrelationship exists between the maximum resistance to high temperature and the cure system [17]. Generally speaking, silicone sealants with an acetoxy cure exhibit hardly any response to temperatures until they reach 140 to 150°C, whereas silicone sealants with a benzamide cure display readily apparent changes even at 80 to 90°C. A frequently noted phenomenon is that the build-up of full adhesion of a sealant to a substrate can be accelerated by briefly storing the sample at elevated temperatures, for 2 to 3 days at 70°C for example. This effect was described by Karpati [18] in connection with both heat and outdoor storage.

4.3 Influence of cold
Cold results in the stiffening of all sealants, with the extent of this stiffening being highly dependent on the specific polymeric components of the sealant. This dependency is greatest for the solvent acrylate sealants, whose glass transition temperatures are in the -18 to -25°C range. On the other hand, temperature has very little effect on the flexibility of polyurethane and silicone sealants. The influence of cold on sealants is reversible; the original flexibility is recovered on returning to room temperature. Nevertheless, an adhesive or cohesive failure of the seal may result from the stiffening of a sealant due to cold as the joint expands at the same time.

4.4 Influence of moisture/water
Water and moisture can exert chemical and physical influences on sealants. The physical influences include swelling and leaching of sealants. As the result of diffusion, water molecules penetrate into the sealant and are deposited in the free volume of the polymer matrix. Due to the filling of the matrix cavities, a macroscopic swelling of the sealant occurs. The stored water has the function of a plasticiser, hence the Shore A hardness, modulus and tensile strength decrease, while the elongation increases [10].

The swelling of the sealant due to water is reversible. However, the water can also leach formulation constituents such as plasticisers or active and passive fillers out of the sealant, which results in a lower sealant weight upon drying.
Once again, the degree of swelling is very highly dependent upon the polymeric components of the sealant, but also varies in relation to its formulation; the type and the surface treatment of the fillers used play an important role. Polysulphide, polyacrylate and polyurethane sealants usually exhibit very extreme swelling; in the course of water immersion for 80 days at room temperature they absorb 8 to 20% water by weight. In comparison, silicone sealants swell very little; their water absorption is approximately 3 to 6% under the same storage conditions [13, 19-22]. The tendency towards leaching is very highly dependent on the formulation of the sealant; however, polysulphide and polyacrylate sealants show a higher propensity to leaching than do sealants with a polyurethane or silicone base.

In studying polyurethane sealants for insulating glass units, Massoth [22] discovered a certain residual water content following drying, which apparently stems from the formation of hydrogen bonds between the water molecules and the polar urethane groups.

The water diffused into the sealant also attacks it chemically by the hydrolysis of bonds. Worthy of particular note are the effects of moisture and/or water on the adhesive strength of sealants. All sealant-substrate bonds can be hydrolysed; the extent and speed with which adhesion is lost depend on the number of such bonds, their binding energy and the possible reversibility of the hydrolysis.

The hydrolysis of chemical bonds can be accelerated by alkalis, which stem, for example, from the substrate. Hence a primer must be applied to highly alkaline substrates, relatively fresh concrete for example. This forms a film, creating a barrier adequate to prevent the rapid hydrolysis of bonds to the substrate.

### 4.5 Influence of oxygen/ozone

Atmospheric oxygen is capable of oxidising organic sealants. This reaction occurs very slowly at room temperature but is greatly accelerated under the influence of short-wave light or elevated temperatures. Generally, noticeable oxidation occurs only in the outer layer of the sealant, causing the formation of a brittle skin on its surface. The literature currently available does not document any results of studies on the influence of oxygen as the sole ageing factor.

Although the average concentration of ozone is very low at the earth’s surface, the influence of ozone on the properties of sealants cannot be ignored, since ozone exhibits a chemical aggressivity about 200 to 500 times greater than atmospheric oxygen. Burstroem [7] discovered that polysulphide sealants are highly affected by ozone even at concentrations of only 2 ppm. The effect is greater, the higher the polymer content of the sealant. On the other hand, sealants with a polyurethane or polyacrylate base exhibit no effects from ozone. The damage caused by ozone is not apparent, however, until the sealant expands and is exhibited by cracks forming in the surface.

### 4.6 Influence of corrosive gases

Nitrogen oxides result in oxidation of organic polymers with simultaneous nitrification. Sulphur dioxide and trioxide and the sulphuric acid resulting therefrom in the presence of moist air split hydrolysable groups.

Although it can be assumed that these corrosive atmospheric influences, which are the main components of acid rain, markedly affect the service life of building joint
sealants, no detailed studies on the ageing patterns of sealants in acidic atmospheres have as yet been published.

4.7 Influence of cyclic mechanical strain
Owing to changes in temperature and/or moisture, cyclic movements occur in every joint of a building, subjecting the sealant to mechanical strain in the form of expansion, compression or shearing. Such strain, which recurs daily and varies as a function of the season, brings about ageing of the sealant. Karpati [23] regards the mechanical strain as the greatest ageing factor.

If a sealant is permanently subjected to cyclic movements, cracks may gradually form at the surface perpendicular to the direction of the stress. The number and amplitude of the imposed movements, the speed (frequency) with which they occur, and the temperature in the sealant during the movements cycle are decisive factors in terms of the scope of mechanical ageing [7]. These parameters are interrelated to the extent that an increase in the speed of deformation increases the stress in the sealant, whereas an increase in the temperatures results in a reduction of the stress. If the sealant is subjected to movements greater in amplitude than its capacity to absorb movement, the cracks in the sealant surface grow and may finally culminate in a cohesion failure.

4.8 Influence of microbiological stresses
Mould fungi constitute the most frequent cause of microbiological damage to sealants [24-26]. Mould detrimentally affects the service value of sealants from an aesthetic and a hygienic perspective. The dyes created by the mould frequently discolour the sealant surface, and spots of various colours remain on the material after the mould has been removed.

Divergent conclusions are to be found in the literature on the resistance of sealants to mould fungus cultures; however, it is certain that the inorganic/organic polymer backbone of silicone sealants cannot be broken down by mould fungi. Mould fungus cultures are therefore unable to settle on silicone sealants unless additional organic nutrients, such as traces of shampoo, soap residue, flakes of skin, etc., are available. On the other hand, polyurethane sealants and some polysulphide sealants, depending upon their formulae, can apparently be broken down by mould fungi.

For certain areas of application, such as below grade joints or joints in sewage treatment plants, the bacterial resistance of the sealants used is of decisive importance. No systematic studies are as yet available, but two-component polyurethane sealants containing special bactericides or biocides have been classified for these areas of application [27].

5 Synergism of the ageing factors
In the case of natural ageing, a number of the ageing factors described above normally occur at one and the same time, e.g. light, oxygen, ozone and heat or water and light can exert their influences on a sealant simultaneously. The effect of these combinations does not equal simply the sum of the individual effects; it may instead be considerably greater or lower. The experimental studies conducted to date demonstrate
that the individual effects are generally reinforced, a phenomenon referred to as syn-
ergism.

One example of a combination in which the effect is reduced is the simultaneous influence of sunlight and airborne dust. The dirt deposit on the surface protects the seal from short-wave UV light. This accounts for the lower ageing of sealants in industrial areas compared to rural areas with clean air [4,5].

All ageing processes described up to this point exhibit a marked dependence on temperature. This is because the speed of chemical reactions approximately doubles when the temperature increases by 10 K. This is not to infer, however, that any chemical reaction can be accelerated as desired by sufficiently elevating the temperature - once a certain temperature threshold has been reached, a reaction other than the one being studied suddenly may occur, because its activation energy has been reached. Hence great care must be exercised in selecting the temperature for heat storage in order to accelerate ageing.

To date, very few studies have been conducted on the synergetic effect of different combinations of ageing factors on sealants. For the discussion of the various results achieved through accelerated (artificial) ageing processes, however, a knowledge of the interaction of the individual ageing mechanisms and their synergy is of decisive importance. Let us therefore mention a few of the combinations with synergetic effect.

5.1 Water and sunlight
The hydrolysis of chemical bonds, which is activated by water, can be greatly accelerated by simultaneous exposure to sunlight, especially to the short-wave segment of the spectrum. This phenomenon is to be kept in mind particularly when studying the adhesion of sealants to glass; under some circumstances, sealants which have successfully resisted any loss of adhesion to glass during dry storage in conjunction with UV light, as well as protracted storage immersed in water, may lose their adhesion relatively quickly, if both ageing factors are effective simultaneously. Aware of this synergism, a number of national test standards dealing with sealants for glazing and insulation glass units have incorporated specifications with respect to the simultaneous effect of water or moisture and ultraviolet light.

5.2 Oxygen and sunlight
By enhancing the formation of reactive radicals photo-chemically, the short-wave segment of sunlight can drastically accelerate oxidation. The crazing effect due to oxidation on the surface of the sealant was described earlier. In the case of polyurethane sealants it is often so pronounced that practically the entire polymer component in the outer oxidised surface layer is degraded, causing the surface of the sealant to chalk. If such a sealant is subjected to heavy winds on site, possibly in conjunction with swirling dust and sand, the outer heavily oxidised layer is continuously eroded. Thus the oxidation does not cease as described above; instead, the cross-section of the sealant decreases in the course of time due to the permanent erosion of oxidised mate-
rial. In the case, what is involved is an additional synergism of oxygen, sunlight, wind and dust/sand.

5.3 Atmospheric influences and mechanical strain
Undoubtedly, this must be regarded as the most important synergism of all. The effect of all atmospheric ageing factors is enhanced by simultaneous mechanical strain upon the sealant. Cracks, which have formed in an embrittled sealant surface, are deepened due to the cyclic movements of the sealants. Sealants, which stiffen under the effect of the heat, may tear away from their substrate if the joint expands again during cold weather. Sealants, which have swollen due to the absorption of moisture, are mechanically eroded due to movement strain. Sealants lose their adhesion to glass when exposed to UV light much more quickly when they are subject to mechanical pre-stress.

6 Experimental studies on the ageing behaviour of sealants
After a perusal of the literature to date with its multiplicity of various test set-ups and testing methods, it appears practical to arrange them according to the following three criteria:

- Type of ageing (natural or artificial),
- Consideration or neglect of mechanical strain, and
- Determination of characteristic material properties.

6.1 The tests with artificial ageing
The initial studies on the effect of various ageing factors on sealants were conducted in laboratories around the mid 1970s. The objectives of the various research projects deviated greatly, however. The projects initiated by industry were primarily concerned with finding accelerated ageing processes, which would yield information as to the service life of a newly developed sealant as quickly as possible. On the other hand, the projects of government research institutes were directed towards gaining more information on the effects of certain ageing processes on sealants.

Although the respective objectives would appear to render the other indispensable, the starting points were nevertheless totally different. In order to arrive at an ageing effect as quickly as possible, industry most frequently applied combinations of various ageing factors such as water, ultraviolet light and heat. The public research institutes on the other hand, conducted primarily studies of individual ageing factors such as heat or water and the specific ageing factor often appeared to have been selected arbitrarily. Only in the studies of Poschet [28] and Burstroem [6,7] were the individual influences of three or four ageing factors systematically examined. Up to the present, no systematic study has been conducted on the synergetic effects exerted by the various combinations of ageing factors. The testing methods and results of the various studies will be compared below.

6.1.1 Influence of moisture/water
Table 3 provides a comparison of the various tests. A basic distinction must be drawn between tests in which the influence of water or moisture on the sealant itself was ex-
amined and tests whose primary purpose was to acquire information on the breakdown of the adhesive properties to a given substrate. The latter has been the subject of a great deal of application-related literature, which will not be discussed here, since the conclusions reached refer only to certain sealant-substrate combinations and the adhesive properties were decisively affected by the formulation of the particular sealant. However, two publications by Gan et al. [29,30] should be mentioned, which did deal with the influence of water immersion on the adhesion of elastic sealants in lap joints from a more general viewpoint.
Table 3. Influence of moisture/water

<table>
<thead>
<tr>
<th>Authors</th>
<th>Sealant investigated</th>
<th>types</th>
<th>Test pieces</th>
<th>Conditioning</th>
<th>Storage</th>
<th>Test methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poschet [28]</td>
<td>PU (1p), Si (1p),</td>
<td>ASTM</td>
<td>test rods, Sheets: 2 months, joints 15mm X 15mm; substrates: concrete, aluminium</td>
<td>standard climate (23/50); joints: T = 20°C; tensile test, relaxation, months, duration: 2, 4, 8, 16 weeks</td>
<td>shear test, DTA</td>
<td></td>
</tr>
<tr>
<td>Burstroem [6,7]</td>
<td>2 X PS (2p), PU (1p),</td>
<td>Joints 12mm X 12mm; substrates: asbestos, concrete,</td>
<td>On saturated sponge: (a) distilled water, (b) saturated Ca (OH)₂ solutions; duration: 14, 18, 56 days</td>
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<td></td>
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<tr>
<td>Hanheia et al. [19]</td>
<td>3 X PS (2p)</td>
<td>Sealant beads</td>
<td>“Completion of cure”</td>
<td>Water immersion, Swelling T = 25, 50, 70, 90°C; duration: 200 days</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aubrey and Beech [20,21]</td>
<td>PS (1p), Si (1p), PU (1p), PU (2p), PS (2p)</td>
<td>Joints 12mm X 50mm; substrates: one-part: completion of cure at 35°C/95% rel. humidity; two-part: 3 weeks at 35°C/normal humidity</td>
<td>Water immersion, T = 20 or 25°C; weight, hysteresis, relaxation duration: 14 or 46 days</td>
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<td></td>
</tr>
<tr>
<td>Gan et al. [31]</td>
<td>Si (1p)</td>
<td>Sheets 15mm X 1mm; 15mm28 days, room climate</td>
<td>Water immersion, Change of weight, T = 50, 70, 90°C; expansion duration: 1, 2, 6, 12 months</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Massoth [22]</td>
<td>3 X Si (1p), Joints 12mm X 12mm2</td>
<td>standard climate (23/50); months, Water immersion, Change of weight, T = 20, 40, 50, 60°C; tensile test duration: 900 h</td>
<td></td>
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<tr>
<td></td>
<td>3 X Si (2p), X 50mm</td>
<td>standard climate (23/50); months, Water immersion, Change of weight, T = 20, 40, 50, 60°C; tensile test duration: 900 h</td>
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<tr>
<td></td>
<td>3 X PS (2p), PU (2p)</td>
<td>standard climate (23/50); months, Water immersion, Change of weight, T = 20, 40, 50, 60°C; tensile test duration: 900 h</td>
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All the authors [6, 7, 19-22, 28, 31] discovered an increase in weight and volume as a result of the water immersion, which can be related to the diffusion of water molecules into the polymer matrix. The degree of swelling is determined by the polarity of the polymeric and plasticiser components, the hydrophilicity of the fillers used and the degree of elastomeric crosslinking. Aubrey and Beech [20,21] specify the degree of water absorption in the following descending order: polysulphide (1p) >> polyurethane (2p) > polysulphide (2p) > polysulphide (2p) > polyurethane (1p) > silicone (1p) (p = parts).

The results of Poschet’s study [28] concur, to the degree that this author also noted a markedly higher rate of water absorption on the part of the one-component formulations compared to the two-component formulations. This may be due to the use of highly hydrophilic fillers, as Aubrey and Beech [20,21] indicated, but it is also possible to attribute it to a lower degree of crosslinking of the one-component, moisture-curing formulations. In his study, Massoth [22] discovered very high water absorption for polyurethane and polysulphide sealants, but only very low values for the silicone sealants. Both Poschet [28] and Burstroem [6,7] note a very high rate of water absorption among water-based polyacrylate sealants, where water continued to be absorbed until re-dispersion of the sealant components occurred.

At low to moderate water temperatures, the water absorption as the result of Fick’s diffusion is initially proportional to the square root of time. After a protracted period (about 4 to 12 months) most sealants approach a saturation value, which is determined by the solubility of the water in the sealant formulation and the degree to which it is absorbed at hydrophilic fillers. Arrhenius’ law applies for the temperature dependence of the rate of diffusion at the water-bath temperatures.

The maximum water absorption arising in saturation equilibrium is also temperature dependent. At elevated water-bath temperatures water nevertheless continues to be absorbed; no saturation equilibrium is achieved. This phenomenon is the result of the hydrolytic breakdown of the polymer; hence it is only initiated upon reaching a temperature threshold, which varies as a function of the polymer type. For polysulphide and silicone sealants the hydrolytic polymeric degradation was not noted until the temperature reached 90°C, with no degradation reactions being noted at up to 70°C [19,29]. No results are available with respect to the hydrolytic stability of other types of sealant.

In the studies of several authors [20-22, 31], the water immersion was followed by a drying period during which they noted a weight loss of various sealants compared with the original weight prior to the water immersion. This phenomenon can be attributed to a leaching of plasticisers or fillers from the polymer matrix. It was also noted [22], however, that ~5% water remained in a polyurethane insulation glass sealant after drying, having evidently been bound to the polar urethane groups by hydrogen bonds.

The influence of stored water on the mechanical properties of the seals was studied by most of the authors quoted. The absorbed water functions as a plasticiser, causing a decline in the Shore hardness and modulus and an increase in the elongation of the sealant.

6.1.2 Influence of heat
Table 4 furnishes a comparison of the various tests. Both Poschet [28] and Burstroem [6,7] report the occurrence of a post-cure in the initial phase of heat storage in the case of certain sealant types. Evidently, this was because the curing of these sealants had not been completed during the conditioning phase. Consequently, the increase in temperature during the heat storage initially resulted in the crosslinking being completed. Although the conditioning phase selected in Poschet’s study [28] was very long - over 3 months - the modulus and tensile strength of a two-component polysulphide sealant as well as those of the water-dispersed polyacrylate sealant increased considerably during the first five weeks of heat storage.

From actual practice we know that various two-component polysulphide sealant formulations require eight months or longer at room temperature before the curing is virtually completed. Even a three-month pre-storage period does not suffice for such slowly reacting sealants. Heat storage or alternating storage for one or two weeks, for example in accordance with the UEATC cycle [32], is required before they achieve a testable reference state. From this perspective, the UEATC cycle incorporated into various national standards is to be viewed not as ageing, but rather as conditioning of the sealants.

The same applies for the water or solvent-dispersion polyacrylates. Even after protracted storage at room climate, these sealants still contain small amounts of water or solvents, which function as plasticisers. These evaporate during the initial phase of the heat storage, causing stiffening of these sealants. In an on-site joint, however, the dispersion acrylates again absorb considerable quantities of water during periods when the climate is moist (see Section 6.1.1).

Apart from the post-cure reactions and the evaporation of dispersing agents in the case of polyacrylate sealants, additional reactions occur during heat storage, for example the evaporation of plasticisers [7] or reactions with the fillers [28], which may give rise to a stiffening of the sealants.

6.1.3 Influence of ozone
So far, the influence of ozone on elastic and plastic sealants has been systematically studied only by Burstroem [6,7]. As for all elastomers, the damage evoked by ozone is most severe when the sealants are subject to a pre-stress. The damage, which occurs in this case, is proportional to the tension present in the sealant and to the ozone concentration. Sealants in which tensions are more quickly relieved because of their plastic behaviour consequently sustain less damage. Burstroem subjected the sealant joints to an ozone concentration of 0.5 to 2 ppm for 96 h at pre-stresses of 25 and 50%. Only the polysulphide sealants suffered damage.
Table 4. Influence of heat

<table>
<thead>
<tr>
<th>Authors</th>
<th>Sealant types investigated*</th>
<th>Test pieces</th>
<th>Conditioning</th>
<th>Storage</th>
<th>Test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poschet [28]</td>
<td>Pu (1p), Si (1p), ASTM test rods, Sheets:</td>
<td>2 months, Water immersion, Change of weight, tensile test,</td>
<td>15mm × 15mm standard climate (23/50); T = 20°C; relaxation, shear test, DTA</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 × PS (2p), joints 15mm × 50mm; substrates: concrete, aluminium</td>
<td>3 months, duration: 2, 4, 8, 16 weeks</td>
<td>standard climate (23/50)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PAc (W), Bu (S)</td>
<td>7 or 21 days, on saturated sponge: a) distilled water of weight, Shore A hardness</td>
<td>2 × PAc (S), concrete, aluminium</td>
<td>b) saturated Ca (OH)_2 solution; duration: 14, 18, 56, days</td>
<td></td>
</tr>
<tr>
<td>Burstroem [6,7]</td>
<td>2 × PS (2p), joints 12mm × 12mm</td>
<td>14, 18, 56 days, on saturated sponge: a) distilled water of weight, Shore A hardness</td>
<td>2 × PS (1p), × 50 mm; standard climate (20/50)</td>
<td>b) saturated Ca (OH)_2 solution; duration: 14, 18, 56, days</td>
<td></td>
</tr>
</tbody>
</table>

*Refer to Table 3 for key to abbreviations.
6.1.4 Influence of ultraviolet light

Table 5 furnishes a comparison of the various tests. Only two of the studies, Burstroem [6,7] and Alsleben et al. [11], deal with the independent effect of UV light on the appearance and the mechanical properties of the sealants. The other studies [14, 28, 33] are devoted to combinations with other ageing factors, water or humidity in particular, but heat and cold as well. Furthermore, the tests described differ decisively with respect to the type of radiation source and the surface temperature of the sealants during the test. Hence it is not surprising that the test results cannot be directly compared.

Whereas concurrence exists as to the effects of ultraviolet radiation on the sealant surfaces, e.g. the crazing effect with polyurethane sealants, or orange peel formation in the case of polysulphide sealants, absolute disagreement prevails with respect to the observed changes in the mechanical properties. This discrepancy is an outgrowth of the different action mechanisms of the ageing methods described; the effects stemming from the UV light itself can only affect the surface of the pigmented sealants, since the UV light cannot penetrate into the interior of the material. Furthermore, if the surface temperature of the test pieces is kept constantly low by means of ventilation in the test chamber, the simultaneous manifestation of heat ageing can be excluded.

Under such circumstances the changes due to UV light are in fact primarily at the surface and exert only a slight influence on the sealant’s mechanical values. However, if the sealant is subjected to UV storage without ventilation, the mechanical properties are altered chiefly as the result of the heat ageing which occurs. Under alternating storage, the cracks forming in the surface of the sealant due to thermal contraction and expansion can progress into the interior of the material, permitting the UV light to penetrate deeper as well.

The simultaneous effects of UV light, water or moisture, heat, etc. due to alternating storage or storage in a commercial weatherometer have been described by various authors. Synergetic effects radically accelerated the ageing of the sealants. Nevertheless, the ageing results obtained in particular studies were highly dependent on the specific contribution of the individual ageing factors in the action combination.

Commercial weatherometers permit the free selection of the intervals during which the various ageing factors are applied. These devices usually allow the following possibilities:

- Dry ultraviolet exposure;
- Exposure to water, e.g. by flooding the test chamber (Suntest tester [34]), by spraying water (Xenotest equipment [35]) or by condensation of moisture on the surface of the sealant (Q-UV tester [36]);
- Combination of ultraviolet light and the effects of water; and
- Combination of ultraviolet light with heat, e.g. by switching off the test chamber ventilation.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Sealant types investigated*</th>
<th>Test pieces</th>
<th>Conditioning</th>
<th>Storage</th>
<th>Test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poschet [28]</td>
<td>PU (1p), Si (1p), ASTM test rods</td>
<td>2 months, standard climate Xeno tester 150; cycle: visual inspection, 29 min dry, 1 min rain; elongation, relaxation, total irradiation: 0.2 or 0.4 MW s cm⁻²</td>
<td>Visual inspection, elongation, relaxation, change of weight, DTA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Burstrom [6,7]</td>
<td>2 × PS (2p), PU (1p), Joints 12 mm × 12 mm × 7 days, standard climate Osram HNS 15W; duration: 14, 28, 56 days</td>
<td>Visual inspection, elongation, relaxation, change of weight</td>
<td>Visual inspection, elongation, relaxation, Shore A hardness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cahill [14]</td>
<td>2 × Si (1p) ASTM test rods, Unknown test samples for peel test</td>
<td>Atlas XW carbon arc lamp; visual inspection, spray, elongation, peel test, Shore A hardness</td>
<td>Visual inspection, elongation, Shore A hardness</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alsleben et al.</td>
<td>Si (1p), PS (1p), Joints 15 mm × 15 mm × 4 weeks, room climate Suntest 150 Xenon radiation Visual inspection, source; duration: 2000 h</td>
<td>Visual inspection, elongation</td>
<td>Suntest 150 Xenon radiation Visual inspection, Source; duration: 2000 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Welsh et al. [33]</td>
<td>PS (2p?), Si (1p), U-profiles, dimensions: 19 mm × 25 mm × 175 mm</td>
<td>Innera) Marr-weatherometer Visual inspection, mm carbon arc lamp with penetration test at constant rate mm water spray; b) IR/UV/heat/cold ageing cycle with 1 week 250 W + 1 week 1200 W UV mercury lamp; c) Xenotest 150; 150 h irradiation, 41 h of which with spraying</td>
<td>Marr-weatherometer Visual inspection, mm carbon arc lamp with penetration test at constant rate mm water spray; b) IR/UV/heat/cold ageing cycle with 1 week 250 W + 1 week 1200 W UV mercury lamp; c) Xenotest 150; 150 h irradiation, 41 h of which with spraying</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Refer to Table 3 for key to abbreviations.
The weatherometers differ greatly in the manner in which the ultraviolet light is generated: tubular lamps with a high UV component, carbon arc lamps, mercury discharge lamps or xenon arc lamps. By employing various optical filters, the spectral distribution of the light generated is largely brought into conformance with the sunlight striking the earth’s surface. The various devices are, however, not all equally successful in achieving this correction. Under no circumstances should unfiltered UV light sources be employed for artificial UV ageing tests if strong emission lines superimpose their continuous spectral distribution.

The effects of UV light on the adhesion of sealants to glass have already been described in Section 4.1. To date, however, very few systematic studies on this topic have been published [13,14].

To date, no author has published any study on the effects of artificial ageing with simultaneous movement strain of the sealants. On the other hand, the initial studies on natural ageing have already disclosed the importance of mechanical strain as an ageing factor and it has therefore been included in outdoor exposure tests.

6.2 Test with natural ageing

Only a few tests have been conducted on the natural ageing of sealants without simultaneous movement strain; Table 6 lists the pertinent tests. In addition, comparisons between samples stored outdoors for two years and reference samples stored outdoors for two years and reference samples stored at room temperature disclosed no changes. With respect to outdoor storage, Kuenzel [37] distinguishes between samples with and those without shade; however, no significant difference can be perceived between the two types of storage after samples were stored outdoors for 22 months.

Welch et al. [33] discovered interesting differences related to the various storage sites. Samples stored in jungle lighting developed dirt deposits, chalking and microbiological growth. Samples stored in the deep jungle exhibited heavy dirt deposits and microbiological and macrobiological growth, but little chalking. No microbiological growth was apparent on the samples stored in the desert but a high degree of chalking did occur. On the other hand, samples stored in England exhibited slight dirt deposits, but no chalking or microbiological growth. However, the results obtained with the constant-rate penetration method did not permit any unambiguous correlation with the storage site.

The results obtained in the three studies suggest that outdoor storage without movement strain on the sealants, while permitting conclusions in terms of the natural ageing of the sealant surface, provides only limited information pertinent to the influences on the material properties of a sealant in an on-site joint.
<table>
<thead>
<tr>
<th>Author</th>
<th>Sealant investigated</th>
<th>Test pieces</th>
<th>Conditioning</th>
<th>Outdoor storage</th>
<th>Test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cahill [14]</td>
<td>2xSi(1p)</td>
<td>ASTM test rods; test samples for peel tests; substrates: various materials</td>
<td>Unknown</td>
<td>Midland and Florida (USA); Visual inspection, elongation, duration: 2 years</td>
<td>peel test, Shore hardness</td>
</tr>
<tr>
<td>Kuenzel [37]</td>
<td>Si (1p), PS (2p?), PU (2p?)</td>
<td>Joints 15 mm × 15 mm × 50 mm; Unknown substrate: concrete</td>
<td>Unknown</td>
<td>Southern Germany; Visual inspection, elongation duration: 22 months</td>
<td></td>
</tr>
<tr>
<td>Welch et al. [33]</td>
<td>PS (2p?), Si (1p), U-profiles, inner dimensions: Unknown 19 mm × 25 mm × 175 mm</td>
<td>Unknown</td>
<td>Unknown</td>
<td>Unknown</td>
<td>Visual inspection, penetration cleared jungle, jungle, desert; at constant rate duration: 6, 12 months, 7 years</td>
</tr>
</tbody>
</table>

*Refer to Table 3 for key to abbreviations.
Table 7 show the test parameters of experiments with natural ageing, which incorporated mechanical strain. Until a short time ago, all authors utilised the same basic principle to generate the joint movements. Weathering racks were set up from components with radically differing coefficients of thermal expansion. For example, PVC strips 2 m long were flexibly attached to the top crossbar of a solid steel frame, appropriate holders were attached to the bottom crossbar of the steel frame and the sealant joints clamped between them. It was possible to tilt the entire set-up at any desired angle to the earth’s surface so as to ensure optimal incidence of sunlight. Under incident solar radiation, the PVC strips expand more than the steel frame and the joints are compressed; upon cooling, the movement process is repeated in reverse and the joints expand. The first prototypes of such weathering devices in which the test joints pass through movement cycles as a function of the outdoor climate were constructed as early as the mid to late 1960s in Australia [38,39] and Switzerland [40].

The movement cycle which these weathering devices caused in the test joints proved exaggerated, however, when compared with normal building joints. The reason was the relatively low heat capacity of the materials used in the weathering equipment, which, because of the very different disparate coefficients of expansion, evoked overly rapid joint movements.

The speed with which an actual joint, e.g. between pre-cast concrete components, moves, is comparatively low. The movements due to the annual temperature fluctuations are of the magnitude of 0.0002 mm min\(^{-1}\); in addition, the movements resulting from the daily temperature fluctuation are modulated on to the annual joint movement at \(\approx 0.001 \text{ mm min}^{-1}\) [23]. In order to ensure a better correlation between the results obtained in the weathering racks and those in actual practice, the movement speed of the test joints had to be reduced to about 0.01 to 0.001 mm min\(^{-1}\). This was achieved by increasing the heat capacity of the components used in constructing the weathering devices; the PVC plates were replaced by water-filled PVC pipes [37]. Other devices were based on a solid concrete beam with a high heat capacity [6,7]. A further disadvantage of the early devices was that they subjected all of the test joints to the same movement strain. Thus, in the later devices, which were based on the differing thermal expansions of two different device components, the joint holders were attached to the tester’s flexibly suspended member at regular intervals from its single-sided fastening point [6,7,41]. The degree of movement induced in the various test joints is then greater the further the joints are away from the single-sided fastening points.

The test method by Karpati et al. [42] can be regarded as the latest development. Here the cyclic mechanical strain on the test joints is no longer caused by the environmental climate as a function of differing thermal expansion on the part of the tester’s components, but is instead preset manually with adjustable vice clamps. To this end, the clamps are mounted on a weathering rack out of doors and the joint width is altered on a quarterly basis, in accordance with the sequence of movements over the course of the year. Although the manual adjustment of the joint width is performed very quickly, Karpati states that the results exhibited an excellent correlation with those on conventional weathering testers.
Table 7. Influence of natural ageing under cyclic movement strain

<table>
<thead>
<tr>
<th>Authors</th>
<th>Sealant types investigated*</th>
<th>Test pieces</th>
<th>Conditioning</th>
<th>Type of assembly</th>
<th>Outdoor storage</th>
<th>Test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burstroem [6,7]</td>
<td>2xPS(2p), PU (1p), x 50 mm; standard climate (20/50)</td>
<td>Joints 12 mm x 12 mm</td>
<td>days, Coefficient of thermal expansion; concrete/aluminium movement: max; ±30%</td>
<td>Southern Sweden; Visual inspection, elongation, relaxation, change of weight, Shore A hardness</td>
<td>39 months</td>
<td></td>
</tr>
<tr>
<td>Kuenzel [37]</td>
<td>Si (1p), PS (2p), x 50 mm; substrate: concrete</td>
<td>Joints 15 mm x 15 mm</td>
<td>Unknown</td>
<td>Coefficient of thermal expansion; steel/PVC</td>
<td>Southern Germany; Visual inspection, elongation</td>
<td>22 months</td>
</tr>
<tr>
<td>Sharman et al. [44], Fry and Whitney [45]</td>
<td>5xPAc(W), 2xPAc(S), 3xPS(2p), 2xPU(2p), 7xSi(1p)</td>
<td>Butt joints: 12.5 mm, 3 to 14 days, Coefficient of thermal expansion; wood/aluminium</td>
<td>New Zealand; Visual inspection, elongation</td>
<td>2.6 years</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Karpati [18]</td>
<td>Si(1p)</td>
<td>Joints 12.7 mm x 50.8 mm; 2 months, Coefficient of thermal expansion; steel/aluminium</td>
<td>Canada; Visual inspection, elongation</td>
<td>3 years</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Karpati et al. [42]</td>
<td>PS(2p)</td>
<td>Joints 12.7 mm x 12.7 mm “A few days”; substrates: aluminium</td>
<td>Mechanical movement to ±80%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Refer to Table 3 for key to abbreviations.
All studies conducted on the weathering testers clearly demonstrated that the movement strain constitutes a significant element in the ageing of sealants [6,7,18,37-45]. The changes in sealant properties resulting from such ageing factors as UV light, water, heat etc. arise much more quickly when the sealants are subjected to cyclic mechanical strain. Sharman et al. [44], for examples, discovered that the results they obtained in a six-year weathering test using the CSIRO tester [39] correlated well with statistical studies on on-site joints [2,3].

6.3 Determining the characteristic material properties

Most of the authors characterised the degree of sealant ageing on the basis of the visually detectable surface changes and on the basis of changes in the mechanical properties. A method, which demonstrated particularly good results, was the recording of stress-strain diagrams for standardised joints. Changes in indentation hardness can only be used for the characterisation of the ageing behaviour, if sufficiently large changes are involved (>10 points Shore A). By determining the change in weight, additional data are provided on plasticiser or solvent evaporation, swelling, etc.

According to Poschet [28], differential thermal analysis (DTA) measurement of changes in glass transition temperature can be successfully employed to determine a change in the degree of crosslinking resulting from sealant ageing. In the process, it is possible to study the sealant one layer at a time. In the case of polysulphide sealants aged through UV light, for example, this method disclosed great differences in the glass transition temperature of samples taken from the sealant surface compared to others taken from the centre of the sealant. Recently published sealant studies [46] based on thermo-mechanical analysis (TMA) indicate that this method can be employed to characterise the mechanical properties of sealant samples before and after ageing very rapidly and as a function of temperature.

7 Correlation of artificial and natural ageing tests with studies of on-site joints

Various authors [6,7,14,33] have repeatedly attempted to compare the results obtained through artificial ageing with those from natural ageing. However, these attempts were generally unsuccessful because of the current lack of knowledge as to the synergistic effect of various combinations of ageing factors such as occur in natural weathering.

While it was possible, in the case of certain sealants, to establish correlation factors between artificial ageing such as heat-ageing in the laboratory and outdoor storage over several years, these factors could not even be applied for other sealants of the same type of raw material because these sealants, although they exhibited embrittlement when aged at elevated temperatures, also absorbed great quantities of water during outdoor storage and therefore softened [6,7]. The comparison became particularly difficult if the natural ageing was always carried out with no mechanical strain placed on the sealant, the comparison had to take into account not only the different ageing but the influence of the mechanical strain as well, and this has only recently been subjected to detailed examination.

Burstroem [6,7] succeeded in demonstrating that test pieces of sealants, which had been stored in the outdoor climate just after being manufactured, always achieved
higher surface hardesses than others, which had been conditioned in a standard climate for a protracted period before being placed in outdoor storage. Consequently, to be able subsequently to compare the results of laboratory and outdoor storage results, it is of decisive importance that the same type of conditioning be used during both ageing methods. On the other hand, the ageing effects achieved with natural weathering exposure methods demonstrated a good correlation with the behaviour of sealants in on-site joints if the sealants was subjected to a cyclic movement strain during the ageing process [6,7,18,38,42,44,45].

Sealants, which were subjected to natural weathering exposure without mechanical strain, aged much less with respect to the observable surface changes and the viscoelastic properties of the elastomer itself. Hence it can now be regarded as proved, especially after the studies by Karpati (see e.g. [40]), that the mechanical strain in the form of cyclic movements decisively affects the natural ageing of sealants in movement joints, since it develops a synergy with many other ageing factors.

8 Development of standards for testing the ageing behaviour of sealants

Since weather varies radically from one time or place to another, natural weathering exposure is not a suitable basis for developing standardised methods to evaluate the ageing behaviour of sealants. On the other hand, there is no denying the limited correlation of the results of artificial ageing methods with on-site experience and the difficulty, which the interpretation of these results entails. This dilemma has prevented the creation of more than just a few national standards for evaluating the ageing behaviour of sealant. Table 8 shows typical standardised ageing tests. It does not include alternating storage methods such as the UEATC cycle mentioned earlier.

From the studies cited, it is apparent that the greatest progress has been made in the standardisation of ultraviolet ageing, alone or in combination with water sprinkling. A fundamental distinction must be drawn between two methods: those, which give rise to an ageing of the sealant itself, and those, which examine the influence of ageing on the adhesion of the sealant to glass. Round-robin tests performed in the last two years within the scope of various national standards associations and in the ISO TC 59/SC 8 committee have demonstrated that the type of UV light source plays a decisive role in determining the ageing result. Basically, the best correlation with natural sunlight ageing is achieved with light sources, whose spectral distribution is as close as possible to that of the sunlight striking the earth’s surface, the “D 65 global spectrum”. Maximum light efficiency is desirable in conjunction with a device, which is low-priced and inexpensive to maintain. A high light intensity guarantees a high time-acceleration effect for rapid ageing, since increasing the intensity only affects the kinetics of the ageing process.
Table 8. Standardised test methods for determining the ageing behaviour of sealants

<table>
<thead>
<tr>
<th>Test standard</th>
<th>Area of application</th>
<th>Test samples</th>
<th>Conditioning</th>
<th>Test method</th>
<th>Evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Change of sealant due to ultraviolet light</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>ASTM C718 Elastomeric, solvent-based, one-component sealants</td>
<td></td>
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</tr>
<tr>
<td>[47]</td>
<td>U-profiles, inner dimensions: 152 mm × (23/50)</td>
<td>48 h, standard climate</td>
<td>Alternating storage: 10 cycles, loss of adhesion storage: 8 h ultraviolet light + 16 h - 23°C</td>
<td>Surface cracking,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>19 mm × 9 mm</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>ASTM C793 Elastomeric sealants</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>[48]</td>
<td>Joint sealant layer, × 40 mm × 3 mm on (23/50)</td>
<td>72 h, standard climate</td>
<td>250 h in Weatherometer type D-G23; cycle: 102 min light, 18 min water spray + 24 h - 25°C; 180° bend of samples</td>
<td>Surface cracking, chalking</td>
<td></td>
</tr>
<tr>
<td>NT-Build 20 Joint sealants</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[49]</td>
<td>Sealant layer, × 40 mm × 3 mm on (23/50)</td>
<td>7 days' standard climate</td>
<td>Xenotest device; Colour change, duration: until discoloration of bleeding, surface cracking</td>
<td>Colour change, bleeding, surface cracking</td>
<td></td>
</tr>
<tr>
<td><strong>2. Change in glass adhesion of sealants due to ultraviolet light</strong></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>DIN 52455, T3 Glazing seals</td>
<td></td>
<td></td>
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<tr>
<td>[50]</td>
<td>Joints, × 50 mm; standard climate (23/50)</td>
<td>14 days or 3 months, 7 days’ immersion in distilled water + UV irradiation through top pane of glass</td>
<td>Peel test</td>
<td>Elongation</td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td>ASTM C794 Elastomeric sealants</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[51]</td>
<td>Peel test samples, × 76 mm; climate (23/50); one-part: 21 days UV storage + 7 days of immersion in distilled water</td>
<td>Peel test</td>
<td></td>
<td>Elongation</td>
<td></td>
</tr>
<tr>
<td>NT-Build 021 Plastic or elastomeric glazing seals</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[52]</td>
<td>Joints, × 80 mm; (23/50) + 7 or 14 days of water with UV irradiation through top glass pane</td>
<td>Peel test</td>
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<td>NT-Build 022 Elastic sealants</td>
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<tr>
<td>[53]</td>
<td>Peel test samples, None</td>
<td>28 days’ immersion in distilled water with UV irradiation through glass pane</td>
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<td><strong>3. Change in sealants due to heat</strong></td>
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<tr>
<td>ASTM C792 Elastomeric sealants</td>
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<tr>
<td>[54]</td>
<td>Sealant layer, × 40 mm × 3 mm on (23/50)</td>
<td>7 days, standard climate</td>
<td>21 days of heat storage at 70°C</td>
<td>Weight loss</td>
<td></td>
</tr>
</tbody>
</table>

*Refer to Table 3 for key to abbreviations.*
The following light sources can be classified as basically suitable for accelerated UV ageing [55]:

- Various types of high-pressure xenon and mercury vapour lamps, whose short-wave light component requires that the filtration of radiation be particularly good;
- Medium-pressure mercury arc lamps; and
- Fluorescent lamps with an emission maximum of ~310 nm.

Unsuitable for accelerated ageing are low-pressure mercury vapour lamps, which radiate a primarily monochromatic light, as well as all unfiltered ultraviolet lamps, whose continuous spectra are superimposed by heavy emission lines.

The radically divergent results of the round-robin tests on accelerated ultraviolet ageing have motivated various standards associations to postpone new editions of the affected standards until a certain degree of uniformity has been achieved in the UV light sources used within the framework of international standardisation.

9 Summary

Over the past 20 years a number of papers have been published on the ageing behaviour of sealants in which various methods of artificial and natural ageing are described. The divergence in the selection of test parameters makes it extremely difficult, however, directly to compare the results. The results achieved in artificial ageing, in particular under ultraviolet light (dry or in combination with water), demonstrated a satisfactory correlation with on-site experience in terms of surface changes and the loss of the adhesive strength of sealants. None of the artificial ageing processes, however, permits a reliable prediction of the changes in the sealants’ viscoelastic properties, which occur in an actual on-site joint. This deficiency arises, firstly, because of our continued lack of knowledge as to the synergetic effect of various combinations of ageing factors and, secondly, because of the fact that none of the papers on artificial ageing involved cyclic mechanical strain on the sealants.

It can now be regarded as having been established that the cyclic movements arising in an on-site joint due to changes in the temperature and moisture level of the neighbouring components exhibit a decisive influence on sealant ageing behaviour. Like artificial ageing, simple outdoor storage without forced mechanical strain on the sealants furnishes an unsatisfactory correlation with field conditions, since the ageing processes are considerably slower in sealants not under strain. Consequently, the objectives of future studies should be:

- More detailed investigation of the synergetic effects of various combinations of ageing factors,
- Conducting artificial ageing tests which incorporate cyclic mechanical strain on the test pieces, and
- Documenting the influence of various sources of UV radiation on the results acquired and attempting to standardise the procedures with respect to the radiation sources employed.
10 References

17. Dejun Ji, University of Harbin, People’s Republic of China, unpublished study.


32. UEATC Directive for the Assessment of Building Sealants, Union Européenne pour l’Agrément Technique dans la Construction.


36. Operating manual for the Q-UV Accelerated Weathering Tester (The Q-Panel Co., 26200 First St, Cleveland, Ohio, USA).


