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Ageing and deformation properties of building joint sealants

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1979

Link to publication

Citation for published version (APA):
Burström, P. G. (1979). *Ageing and deformation properties of building joint sealants*. [Doctoral Thesis (monograph), Division of Building Materials]. Division of Building Materials, LTH, Lund University.

Total number of authors:
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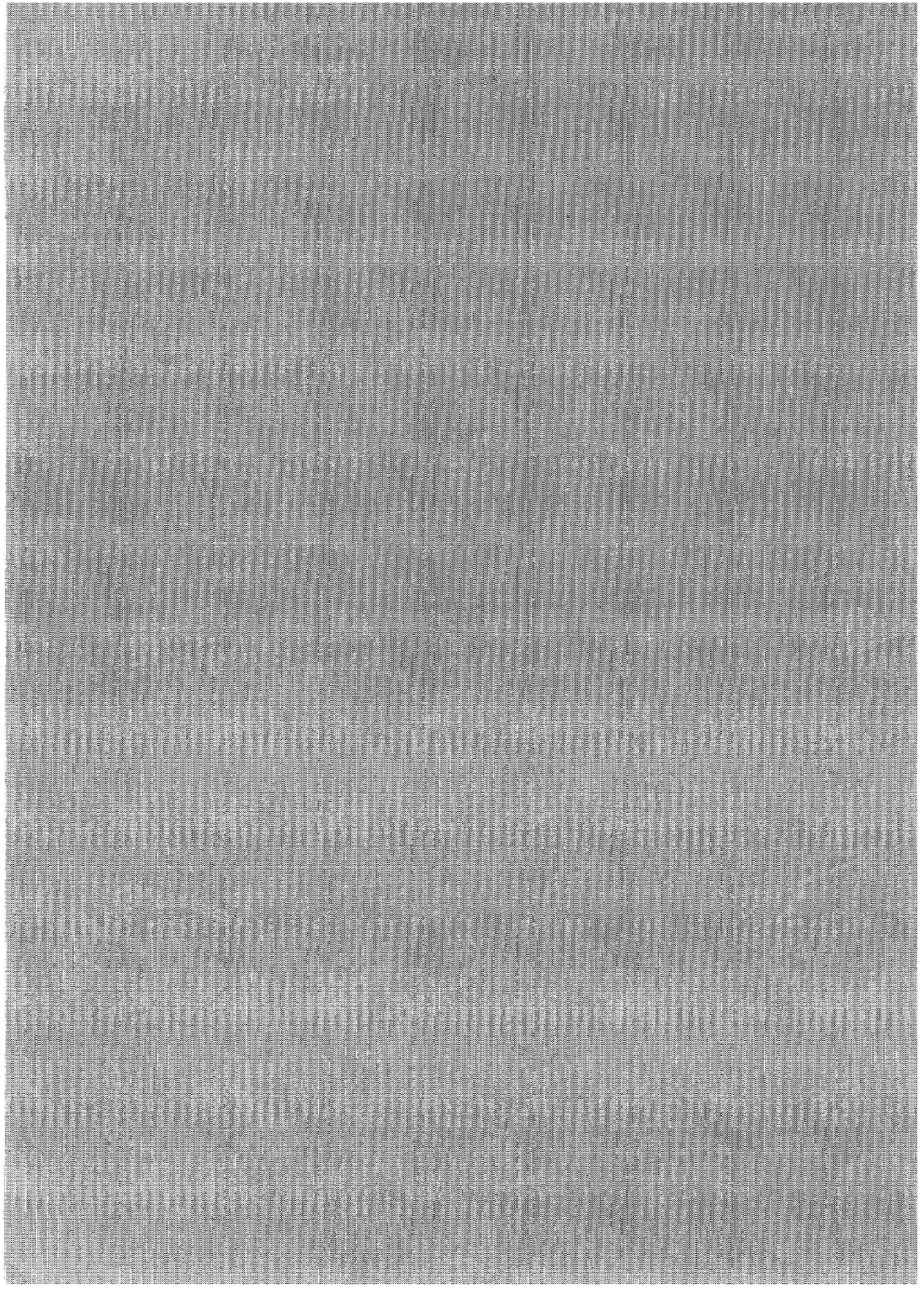
AGEING AND DEFORMATION PROPERTIES OF BUILDING JOINT SEALANTS

PER GUNNAR BURSTRÖM

REPORT TVBM-1002
LUND SWEDEN 1979



CODEN LUTVDG/(TVBM-1002)/1-150/(1979)

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PREFACE

In spite of, or maybe partly because of, all the failures which have occured, sealants have found an increasing use in building constructions. It has to some extent been a kind of trial-and-error usage. Knowledge concerning some of the fundamental properties of sealants has been defective.

This thesis is an attempt to clear the horizon to a certain extent regarding ageing and deformation properties of the sealants. It is my hope, that some of the results will be useful when choosing a sealant for example, when needing material data, when working out appropriate accelerated ageing methods, and when manufacturing new products.

The first desideratums in the investigation came from the industries which manufactured sealants in Sweden. The work was then carried out in two different projects at the Division of Building Materials, Lund Institute of Technology. The projects have in the majority been financed by grants from the Swedish Board for Technical Development and the Swedish Council for Building Research.

The author would like to express his appreciation to the head of the Division of Building Materials, Professor Arne Hillerborg, for his valuable opinion and views.

Leif Erlandsson and Sture Sahlén have been of invaluable help during the development of new equipment, the laboratory experiments and solving of other problems.

Britt Andersson, Birgitta Hellström, Mona Hammar and Birgit Olsson have been involved with the production of this report and have all shown a never failing enthusiasm.

To all the above mentioned and to all others who have taken part in the projects I would like to extend my sincere gratitude.

Lund, April 1979

Per Gunnar Burström

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SUMMARY

This report deals with the ageing and deformation properties of building joint sealants. In spite of the fact that they are two different processes they are interrelated, but mainly treated separately. The first major part is concentrated upon the ageing and durability characteristics of sealants. The second part deals with some important deformation properties of sealants.

In the first part of the report a short review is given of the literature concerned with the ageing and durability of organic building materials, and the main factor causing durability problems are described. These factors are heat, moisture, alkaline, UV radiation, ozone and some other gases. The action and the effects of these factors on organic building materials are described without any more explicit chemical explanations.

A brief survey is also given of the limited literature regarding the ageing of sealants.

In the experimental part of this thesis the aim has been to try and clarify how the factors causing ageing affect sealant properties, and particularly the deformation ones. The purpose has also been to draw up a line of directions for accelerated laboratory ageing methods and designing rules for sealing joints.

The effects of thermal, moisture, alkaline, UV radiation and ozone action have been studied on eight different types of sealants. These were two polysulfide based, two polyurethane based, two acrylic based (type solvent release), one acrylic based (water dispersed), and one oleo-resinous based sealant.

In view of the changes in the stress-strain curves, determined during well controlled conditions, the effects of the ageing factors were evaluated for the different sealants. Determinations of the changes in hardness in ^{o}Shore A were carried out as a matter of routine. Measurements of changes in weight and volume were made after storage in different environments. Photographing and Scanning Electron Microscopy have also been used as evaluation methods.

The results of the laboratory investigations have been correlated to the results obtained from specially built equipments, where the sealants were simultaneously exposed to climatic forces and varying joint movements. Comparisons have also been made to practical experiences.

The temperature was the ageing influencing factor which was found to have the greatest effect on the deformation properties of the sealants. Heat ageing at +40 - +70 ^{o}C usually increased the deformation resistance to a high extent. However, a polysulfide based sealant turned softer after heat ageing at +70 ^{o}C!

In sealants where the effect of heat ageing clearly dominated the effects of other factors, some connections were found between heat ageing and outdoor exposure.

In the concluding chapter of the investigations regarding the ageing of sealants some ways of estimating the durability of different groups of sealants are discussed.

The second part of the thesis deals with the deformation properties of sealants. A short review of the literature regarding joint movements is given. Factors affecting the deformation properties of sealants are discussed and examples are given for some sealants.

The last chapter discusses how the joint movements at a joint opening, resting and closing affect the sealants. A probable destruction mechanism for sealants is suggested in this discussion, and some methods of estimating the movement capability of sealants are also proposed. These methods are exemplified for three different types of sealants.

CONVERSION FACTORS

To convert	To	Divide by
millimeter (mm)	inch (in.)	25.40
centimeter (cm)	inch (in.)	2.540
meter (m)	inch (in.)	0.0254
meter (m)	foot (ft)	0.305
meter (m)	yard (yd)	0.91
square centimeter (cm^2)	square inch (sq in.)	6.45
square meter (m^2)	square foot (sq ft)	0.093
square meter (m^2)	square yard (sq yd)	0.0836
cubic centimeter (cm^3)	cubic inch (cu in.)	16.4
cubic meter (m^3)	cubic foot (cu ft)	0.028
cubic meter (m^3)	cubic yard (cu yd)	0.765
kilogram (kg)	pound (lb)	0.453
kilogram (kg)	ton (ton)	907.2
newton (N)	one pound force (lbf)	4.45
newton (N)	one kilogram force (kgf)	9.81
density (kg/m^3)	pounds per cubic inch ($lb/in.^3$)	$2.77 \cdot 10^4$
density (kg/m^3)	pounds per cubic foot (lb/ft^3)	16.018
newton per square meter (N/m^2)	pounds per square foot (psf)	47.9
kilonewton per square meter (kN/m^2)	pounds per square inch (psi)	6.9
pascal (Pa)	newton per square meter (N/m^2)	1.00
megapascal (MPa)	pounds per square inch (psi)	0.0069

1 degree Fahrenheit (deg F) = $\frac{9}{5}$ degree Celsius + 32

1. INTRODUCTION

Most sealants are used in external walls e.g. between concrete elements, between the frame and the wall, in expansion joints, when glazing etc. This means that the sealants are exposed to great climatic and mechanical stresses. First and foremost the efficiency of the one-step joint, which is very common in Scandinavia, is completely dependent on the properties of the sealant, its ability to follow the joint movement without any crackings or other faults occurring and also to be able to maintain these properties in the surrounding environment.

The environment differs considerably from joint to joint even in the same building. The amount and rate of joint movement depend on the orientation of the facade, the material in the outer wall, the design and the fixation of the different wall components etc.

The environment and the weather also differ a lot. The well-known elements of weather are thermal conditions, moisture, radiation and gases. These elements also vary a great deal within the same building. E.g. the thermal conditions and radiation have a much more severe effect on a joint facing southwards than on one facing northwards.

Because of the organic nature of the sealants, some changes in the material do occur with time, in other words the sealant ages. The extent of the ageing depends on the above mentioned circumstances but the type of sealant is also important as some polymers are more resistant than others.

There is a wide range of sealants available on the market. The chief variable of the different products is the binder in the sealant. The binder, which is always a type of polymer, determines the main properties of the sealant. However, where the same class of binder is concerned, great variations can occur in the final product.

In Scandinavia one normally differs between "elastic" and "plastic" sealants. However, this basis of division causes large variations of properties within each respective class. Furthermore, the limit between these two groups is not defined clearly. In spite of this, these terms

will be used here in some cases. But, when referring to elastic and plastic sealants, definitions according to a proposal from a committee of the International Organization for Standardization will be referred to. These definitions are:

- "Elastic sealant: A sealant which after application exhibits predominantly elastic behaviour, i.e. remaining stresses induced in the sealant as a result of joint movement are almost proportional to the strain".

- "Plastic sealant: A sealant which after application retains predominantly plastic properties, i.e. the remaining stresses induced in the sealant as a result of the joint movement are rapidly relieved".

At present, knowledge regarding sealant ageing and deformation properties is very limited. This means that the material choice and the design of the joint are often made at random. Therefore, after a relatively short time, one may be faced with difficult and expensive resealings.

The aim of this work has been to try and clarify how certain factors which cause ageing affect sealant properties, and then mainly the deformation properties. Furthermore the purpose has been to clarify those variables which are most essential when characterizing the sealants from a mechanical point of view. Finally the purpose has been to draw up a line of directions for accelerating laboratory ageing methods and designing rules for sealing joints.

2. AGEING AND DURABILITY OF ORGANIC BUILDING MATERIALS

2.1 Introduction

Naturally the ageing and durability of organic materials used in buildings are of great interest to the architect, the builder, and the customer.

Organic materials used in buildings can be classified according to their use. They include e.g. paints, plastics, sealants, and roofing materials. Normally organic materials contain inorganic compounds such as pigments, but the basic properties of the mixture are derived from the organic matrix.

Recently, a very comprehensive book is published regarding durability of rubber and plastics, Dolezel (1978). In this chapter a short summary is given of the literature concerned with how the weathering factors affect organic building materials. As previously mentioned these factors are thermal conditions, moisture, radiation and gases.

Very often these factors combine in the degradation of an organic material. In many cases the total effect of these combinations may be highly enlarged (synergism).

The influence of the weathering factors on the polymeric materials can be divided into physical and chemical actions. Physical action means a process which does not break the primary (covalent) bonds in the polymer. Consequently, chemical action means a process which breaks the primary bonds. Of course, both these actions lead to effects of a physical nature. e.g. discolouring and increased brittleness.

2.2 The effect of thermal action on organic building materials

The temperature may have both a physical and chemical action on organic materials.

Physically, heating of polymeric materials first results in a softening of the material. This is due to the breaking of the weak secondary bonds. During heating for a short time the changes are mostly of a

reversible nature but are of course depending on the temperature reached. This is the case where thermoplastics are concerned. Materials which are highly cross-linked, i.e. the thermoset materials, usually decompose before a great deal of softening has occurred.

Another physical action is that the plasticizer (softener) may vaporize when there is an increase in temperature. Many organic building materials contain plasticizers. These are included in the composition of the product in order to regulate the hardness of the material. These plasticizers are chemically stable up to a certain temperature. If these limits are exceeded vaporization may occur with several physical effects as a result.

A decrease in temperature increases the hardness of organic building materials, consequently making them more brittle. The material regains its properties when the temperature returns to normal again. However, increasing brittleness at low temperatures could be fatal if a material in this condition is exposed to great deformation. E.g. sealants are required to elongate most when they are least able to, due to hardening or stiffening.

When heated sufficiently there is a chemical action on rubber materials. This normally leads to an increase in the hardness at the same time as the tensile strength decreases (Friberg (1970a)). According to Schröderheim (1971) this may be due to a transformation within the molecules. Fig. 1.1 shows how a few, long cross-links are transformed into several short ones with an increased hardness as a result.

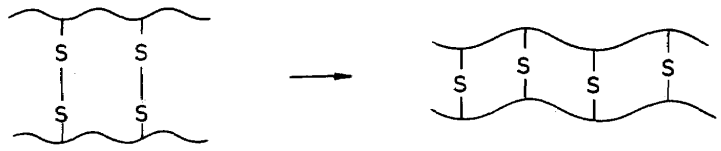


FIG. 1.1 Molecular transformations in rubber due to thermal action (Schröderheim (1971)).

Temperature changes the rate of chemical reactions. According to the general rule of thumb the reaction rate is roughly doubled when the temperature rises $10^{o}C$. All chemical ageing processes depend on the temperature. The durability under hot conditions depends on the strength of the chemical bonds, this means the dissociation energy necessary to break up the chemical bonds. When the temperature has reached a certain level the thermal decomposition starts.

Solar radiant energy is converted into heat when it impinges upon and is absorbed by a material. On reaching the earth, the infrared part (wavelengths longer than 0.78 μm) comprises about 53% of the total radiation. The temperatures of the outside surfaces of a building (roofs and walls) depend to a great extent on the colour of the surface in question. An example of this is shown in Fig. 1.2 according to Künzel (1969).

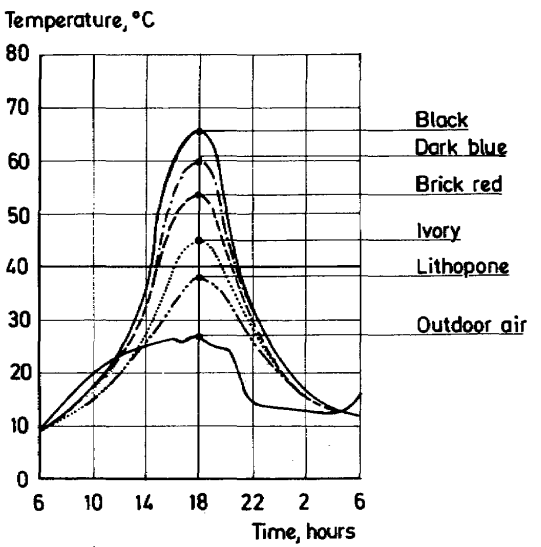


FIG. 1.2 Temperature curves, as a function of time, of differently coloured outer surfaces (west walls), measured on a highly radiating summer day (June). The walls are of identical structural design, they differ only in outer-surface colour (Künzel (1969)).

The design and form of the outer surfaces also affect the temperature levels. Usually one can calculate with +70°C for a dark surface, but in some cases the levels are considerably higher, e.g. in solar collectors. Höglund (1974) describes a method of calculating extreme surface temperatures.

2.3. The effect of moisture action on organic building materials

Humidity and moisture can also have a physical and chemical action on organic materials. Very often moisture combines with other weathering factors, e.g. heat and radiation, cf. below.

Among the physical processes swelling and leaching are essential. Water swells the hygroscopic substances in rubber and plastics. Urethane-rubber of the ester-type may show a reversible increased degree of plasticity due to water absorption. This means that the water acts as a plasticizer upon the rubber. After drying the rubber regains its original properties (Friberg (1970a)).

The leaching of water-soluble substances may be both an advantage and a disadvantage. The advantage being the leaching of formed oxidation catalysers. The leaching of anti-oxidants and light stabilizers is naturally a disadvantage (Saare (1960)).

The chemical action of moisture on organic materials is very complicated. Most degradation reactions are greatly accelerated in the presence of water. This is e.g. due to an increased mobility of the reaction products and an increased dissociation.

All organic materials which contain hydrolysable groups (hydrolysis could be defined as a chemical reaction, where a molecule or an ion is transformed into two or more molecules or ions by reacting to water) are affected by water. If these groups are in the side chains the molecular weight is barely affected and consequently neither is the strength. But, if the hydrolysable groups are in the main chain, this results in a chain-scission and a consequent loss of strength.

2.4 The effect of alkaline action on organic building materials

In many building materials there are free calcium compounds. Where water is concerned these compounds (mainly $Ca(OH)_2$) form an alkaline

environment for other building materials, e.g. sealants between facade panels of concrete, glues on concrete floors.

Some binders in organic building materials are sensitive to this alkaline environment. The alkaline action is of chemical nature. In most cases a water sensitive or a water soluble calcium-salt and an alcohol are formed. The effect of this chemical reaction is analogous to the hydrolysis previously described.

2.5 Radiation action on organic building materials

Solar radiation is an electromagnetic radiation. It can be described as the wavelength or the frequency of vibration. As the wavelength decreases the frequency increases. The radiation consists of multiples of a quantum, which is the smallest quantity of energy. The energy of a quantum is proportional to the frequency of the radiation, i.e. the shorter the wavelength, the higher the energy content. Sometimes a quantum is also called a photon.

One of the most important weathering elements is the part of the solar radiation which lies in the ultraviolet range. Ultraviolet (UV) is normally defined as the electromagnetic radiation of wavelengths between 4 and 400 nm (Rosato and Schwarz (1968)). According to Ashton (1970a) the range is 10-400 nm. From practical point of view the actual range is about 190-400 nm as the shorter waves are absorbed by ozone in the atmosphere.

The energy of any radiation is equally as important, or more so, as its total quantity. Many reactions are unable to take place unless a minimum energy, often called the activation energy, is reached. Consequently, ultraviolet with its short wavelength has the energy to initiate reactions which would either not occur or which would occur at a very low rate. Although it amounts to only 4% of the total radiation received by the earth's surface, it is responsible for many of the changes which occur when polymeric materials are exposed outdoors (Rosato and Schwartz (1968)).

Organic building materials are composed of long-chained molecules. These may be bound to each other by secondary forces or, depending on the type of polymer, by chemical bonds as well. Because the primary

bonds are chemical and their strength depends upon the elements involved, they can be broken by sources of energy that exceed the attractive forces between the atoms, thus disrupting the molecules. In Fig. 1.3 the energy per photon in sunlight is shown as a function of the wavelength (Gjelsvik (1975)). The dissociation energy per bond for some of the most common bonds in organic materials is also shown. As can be seen there are several types of bonds which can be broken by the UV light.

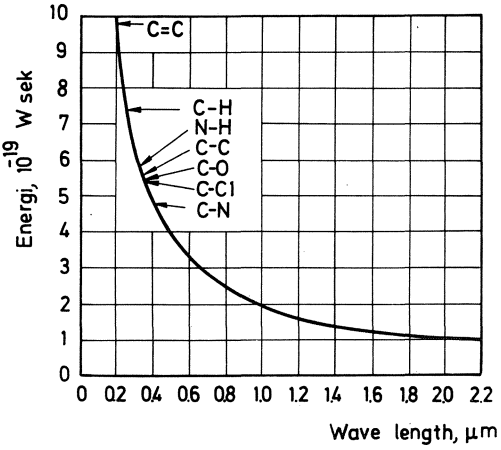


FIG. 1.3 Energy per photon and examples of dissociation energy per bond (Gjelsvik (1975)).

When a molecule absorbs radiation it is raised to an excited state, usually at one particular atom. It may return to its ground state by dissipating the energy by reradiation of fluorescence, phosphorescence or heat. (The fluorescence finishes at the same time as the irradiation ceases, while phosphorescence may last for a measurable time interval after the exciting radiation is turned off). In such a case the molecule is unaffected. This is what happens with longer-wave radiation which is converted into heat. However, if the radiation contains sufficient energy, it may cause a chemical reaction at the excited atom and this frequently leads to degradation of the material.

According to Ashton (1969a), the degradation of organic building materials attributable to UV can take two paths:

1. In some materials the energy starts a process which is the reverse of the polymerization reaction that produced the large molecules ("unzipping"). It is a chain reaction and it leads to catastrophic failure.

2. In the other degradation mechanism, the smaller molecules produced by chain scission frequently react across the chains. This results in more cross-linking than was present originally.

The physical effects of these degradation mechanisms are, in the first case, a loss of strength and, in the second case, an increased hardness and brittleness.

In rubber materials sunlight causes oxidation in the outer layer, which leads to an inelastic skin forming. The skin cracks in an irregular pattern, so-called crazing. When the amount of oxidation products increases, a further attack is prohibited and the oxidation decreases (Friberg (1970a)). The crazing is a surface phenomenon and should not be confused with ozone cracks, cf. Chapter 2.6.

Even though the polymer itself in an organic material may be resistant, it is possible for UV light to cause undesirable changes if the material is coloured and the colorant, many of which are organic, is not resistant. The previously mentioned photo chemical reaction can be catalysed by such colorants.

The resistance to UV light by polymeric materials can be greatly improved. The most common procedure is to prevent the polymer from absorbing the UV light. If it is not necessary for the material to be transparent this can readily be accomplished by the incorporation of pigments that reflect radiation or absorb it preferentially. The few compounds that do perform satisfactorily are referred to as UV absorbers or stabilizers. These act by absorbing energy and then transforming it mainly into heat. However, these absorbers are rather specific in their action; even compounds that are closely related chemically may show large differences in effectiveness with different resins. It must also be taken into consideration that the absorbers do not last indefinitely, but are slowly degraded, and consequently the absorption they are supposed to prevent will ultimately occur (Ashton (1970b)).

2.6 The effect of ozone action on organic building materials

Ozone is a highly reactive gas. The formation of ozone takes place in the upper atmosphere. The UV radiation from the sun forms free oxygen atoms due to photochemical reactions. These atoms react with oxygen molecules in the air forming ozone (O_3) (Friberg (1970b)).

This gas diffuses slowly on its way down to the earth where a fairly rapid scattering takes place. As the concentration of ozone is very low on the earth, the content is given in pphm = parts of ozone per hundred million parts of air.

Usually the ozone content on the earth is below 10 pphm, normally about 1-3 pphm. The average ozone concentration is usually at its lowest in the winter, increases in the spring and reaches its maximum in the early summer only to decrease again. However, in some areas, circumstances may combine resulting in very high ozone concentrations. E.g. in the Los Angeles-area very high ozone-concentrations have been measured (115 pphm). These are due to the smog, emanating from the combustion of petroleum products, and a special topography (Friberg (1970b)).

In spite of the normally low ozone content on the earth, this concentration is still sufficient to cause cracks in some rubber qualities. The ozone attacks the double bonds in the unsaturated rubber molecules consequently causing a crack formation at right angles to the tensile direction. However, these cracks only arise if the rubber is tensioned. If the rubber is under compression the ozone resistance is considerably greater.

Amongst other things, the crack formation rate depends on the amount of deformation, the ozone content, the temperature, and the intensity of the sun light (Friberg (1970a)).

In order to protect rubber mixtures from ozone attack some means of protection can be added. The chemical compounds which protect against ozone attack are called anti-ozonants. Many of these are also anti-oxidants, i.e. protect against oxidation.

Another type of protection against ozone is a wax-film on the surface of the rubber. Soluble wax is added to the rubber mixture and a film is consequently formed on the surface which protects the rubber against ozone.

2.7 The effect of oxygen action on organic building materials

The atmospheric gas that causes the most damage to organic materials, because of its high concentration and reactivity, is oxygen. Chemical linkages that are not completely saturated (chemically called double bonds) are particularly susceptible to oxidation (Ashton (1969)).

At normal temperatures plastics are usually oxidized very slowly. This oxidation does not lead to any measurable changes. However, natural rubber and many synthetic rubbers contain double bonds. These susceptible links allow oxygen to enter the molecule, thus leading to an increase in weight and eventually to a chain scission at the place of the double bonds.

According to Ashton (1969a) unsaturation is not essential in order for oxidation to occur. Polymers that contain reactive hydrogen atoms are also attacked. Polystyrene and polyethylene are examples of such polymers. Because oxygen has to diffuse into the material in order to continue the reaction, oxidation often occurs only at the surface unless the material is in a thin film.

The effects of oxidation are e.g. discolouration, hardening, crazing and finally cracking.

In order to protect polymeric materials against oxidation, chemical compounds called antioxidants are added to the mixture. Some types of antioxidants only protect against one particular kind of degradation, while others are also effective against other types of degradation. Mixtures of antioxidants are frequently used. However, it is important to remember that the antioxidants do not prevent oxidation, they only delay it.

2.8 The effect of action of other gases on organic building materials

Due to the burning of sulphur-containing fuels we obtain an increased content of sulphur dioxide in the atmosphere. This is especially pronounced in industrial atmospheres. The action of SO_2 is to form sulphuric acid. This may e.g. diffuse through organic coatings and attack the underlying metal (Ashton (1969a)).

The action upon the polymeric materials themselves has only been dealt with briefly in literature. This could imply that this type of pollution has not caused any problems yet.

2.9 The effect of synergistic action on organic building materials

The process of weathering is a combination of the factors mentioned previously. The combination of the factors produces an effect greater than the sum of the individual effects. This synergism, or reinforcing action, has been demonstrated many times in studies regarding durability. Consequently, the combined actions as well as the individual processes must be estimated. The latter is of course a necessary first step and must be studied before the former can even be attempted.

In Ashton (1970b) there is a survey about radiation and its combination with other weather factors. Radiation tends to be one of the most important factors among the weather factors. In this case, some examples regarding synergistic effects will be given.

2.9.1 Radiation and water

Most organic building materials are resistant to attacks by water at normal temperatures. But, it is possible for radiation to raise the temperature to a point where solution or hydrolysis occurs. Thus, some plasticizers may be removed if they are sufficiently soluble in water at elevated temperatures.

The low-molecular fragments from scission after irradiation by UV light could act as plasticizers, but they are removed if water is present. The result is an increased brittleness, added to the brittleness caused by cross-linking.

2.9.2 Radiation and heat

Degradation reactions that only proceed at temperatures higher than those reached when normally exposed may occur at much lower temperatures due to the influence of UV light.

2.9.3 Radiation and oxygen

A natural weathering combination that has a great effect is radiation and oxygen, referred to technically as photo-oxidation. Polymeric

materials subjected to oxygen are degraded much faster in the presence of radiation than in its absence and vice versa. Because of the synergistic action of radiation and oxygen, UV absorbers as well as antioxidants are generally added to polymeric materials designed for external use.

Apart from the above mentioned examples of synergism there are many other possible combinations, e.g. heat, UV light and oxygen. All the possible combinations of weathering factors contribute to making the picture of degradation of organic building materials very complex.

2.10 Evaluation methods

It is difficult to choose a good method of evaluating changes in polymeric materials, especially as demands on these methods are known to be great. E.g. such a method should be

- easy to carry out
- sensitive
- preferably non-destructive
- adaptable to all types of materials

As yet the method which can fulfil all these demands does not exist. In literature one can find many methods used in different investigations some of which are presented here.

Different types of evaluation methods are frequently used in the same investigation. Naturally the reason for this is, as mentioned above, the lack of one unique, and outstanding method. Frequently, the method used also depends on the type of polymeric material. E.g. coatings, thin films or plastics in bulk.

Many of the tests have been qualitative and not readily evaluated numerically. Many attempts have been made to convert them into instrumental versions so that some kind of readings could be obtained. E.g. the use of Differential Thermal Analysis (DTA) in evaluating changes in glass transition temperature (cf. below).

Coatings, the oldest of the organic building materials, have long had their physical properties described simply as flexibility, hardness, and resistance to impact, scratching and abrasion. It was natural, therefore, to try to predict durability by following up changes in these properties (Ashton (1969b)).

Mechanical properties such as tensile strength, permanent strain after rupture, work to break (toughness), yield strength, flexural strength, creep, stress relaxation, and elastic modulus govern the ways a material responds to physical forces.

A bibliography regarding the long-term weather resistance of polymeric materials of different kinds was published by Rilem Committee 8-SR (1975). The bibliography covers the years from about 1968 up to 1974, and comprises more than one hundred works. In this, the most common methods of evaluation are the determination of impact strength and changes in colour. Other fairly common methods of evaluation in the reviewed works are: Determination of elongation at rupture, tensile or compressive strength, flexural strength, gloss, tensile stress-strain behaviour, variations in dimension and weight.

In other works, e.g. Wright (1972), determination of a "modulus" is carried out. The modulus may then be defined as the stress at different elongations, 100, 200, and 300 per cent.

Apart from all these determinations which mainly concern mechanical properties there are also methods for determining changes in the chemical structure. In Binder/Sultan (1973) some methods of molecular weight determinations of polyethylene are mentioned. These methods are Gel Permeation Chromatography (GPC) and melt flow index.

During the last few years many works dealing with glass transition temperatures of aged polymeric materials have also been published. E.g. in Künzel et al (1975) Differential Thermal Analysis is used as a method of determining the glass transition temperature of sealants which were aged in different ways. They found that the method was so important that they stated that "the displacement of the glass transition temperature should be measured in all ageing experiments, for example by means of DTA. The measuring of the glass transition temperature and its changing give an exact value about the ageing properties of the sealant".

During recent years many research workers have also reported the use of Scanning Electron Microscopy (SEM) as a means of determining different ageing phenomena in polymeric materials. For example compare Blaga and Yamasaki (1977), Bendel (1974).

In literature some attempts have also been made to obtain models for ageing and for the correlation between natural and accelerated ageing. However, the difficulty in using mathematical models in this field is that one model is often only valid for a certain property in a particular material.

3. LITERATURE SURVEY REGARDING AGEING OF SEALANTS

There is a great insufficiency of information in literature regarding durability properties of sealants. The investigations reported chiefly follow two directions. One deals with the examination of sealants in joints in actual buildings, the other one deals with accelerated ageing of sealants in the laboratory. Combinations of both these types of investigations are rare.

The oldest investigation found in literature which deals with long-time properties of sealants was carried out by Nylund (1964). This was in the form of two field experiments comprising 25 sealants of various kinds. The sealants were used in joints between concrete panels. The joints and the sealants were inspected after about 12 and 28 months respectively. Changes regarding adhesive and cohesive failure, wrinkling, cracking, and colour were noted.

At that time most of the sealants used had a polysulfide or an oleo-resinous binder. The indications of the results of these investigations were not surprising bearing in mind today's experiences. This means that most of the polysulfides worked satisfactorily while problems arose regarding some of the oleo-resinous sealants. Another indication was that if there were any problems with a sealant, these usually appeared during the first observation period, i.e. 12 months.

Grunau (1968) treats sealants and problems connected to sealing of joints in buildings in a very ambitious way. Amongst other things he shows many pictures of sealants of various kinds and in various conditions. However, it is difficult to draw any general conclusions from this work regarding long-time properties of different kinds of sealants. The conditions vary too much in the different cases for that.

McCarty (1972) gives results from a 4 1/2 year field test which dealt with sealers for longitudinal joints in pavements. The investigation comprised both preformed sealers and liquid ones. Among the sealants, a polyurethane sealant proved to have the best overall serviceable life.

Andersson and Hasselblad (1972) summarize the experiences gained regarding joints in a special prefabricated concrete panel system. About a hundred buildings were examined regarding the function of the joints. The sealants used were mainly oleo-resinous-, acrylic- or polysulfide-based.

The oleo-resinous sealants were found to produce a great scatter in properties. In some cases this type performed well even after 12 years in the joint, while in other joints the sealants had hardened and failed cohesively.

The acrylic-based sealants indicated a plastic behaviour during the various deformations. They were also sensitive to alkali influence, for example from wet concrete.

An examination of the local deformations in a cross-section of the polysulfide sealants showed a high degree of deformation at the edges, especially at compression. In some cases these deformations caused cohesive failure along the edges, Fig. 3.1. Some surface effects were also reported and were probably due to UV- and/or ozone-attack.

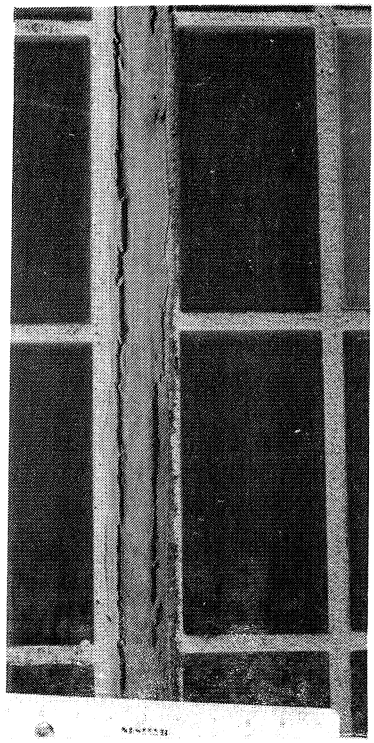


FIG. 3.1 Cohesive failure in a polysulfide sealant in a joint between concrete panels with pebble-dashed surface. This type of failures are due to large local deformations along the edges at a compression (Andersson et al (1972)).

Grunau (1976) examined joints and sealants of various ages (from 1956 to 1975). A total of more than 2 600 000 meters of joints were examined! The type of joints examined were outer wall joints and window joints (top sealing and joints between the wall and frame). The frequency of damage in outer wall joints was 31% during 1958-1965 and 11% during 1970-1975. The sealants used in the various cases were polysulfides, butyls, silicones, polyurethanes and acrylics.

The results of the findings from this investigation are summarized in Table 3.1.

TABLE 3.1 The probable lifetime of different sealants (Grunau (1976)).

Type of sealant	Documented use (years)	Expected lifetime (years)	Allowable deformation (% of joint width)
Polysulfide	16	22	20
Silicone	8	15	20
Polyurethane	7	10	5-10
Butyl	13	15	3
Acrylic plastic	13	15	5
Acrylicterpolymer	7	15	10

Some figures in the Table may be a slightly surprising, e.g. the maximum allowable deformation. In Scandinavia we calculate with ± 25% allowable deformation for polysulfides, silicones and polyurethanes. However, recent experience indicates lower values, but not as low as Table 3.1 indicates.

Karpati (1968) includes some literature concerning weathering of sealants. Among others the polysulfides are said to be resistant to light, oxygen and ozone. Furthermore the polysulfides are sensitive to heat and urethanes are sensitive to water. Silicones are resistant to both water and heat. These data are mainly from laboratory experiments.

Another reference dealing with laboratory investigations regarding the ageing properties of sealants is by Jagfeld (1968). Specimens of eight different sealants were exposed to three different types of environments: Normal climate +20°C/65% RH, Weather-Ometer, and an alternating climate comprising heat, UV light, low temperature and alkaline water. Stress-strain curves were determined for the different specimens. All the elastic sealants showed a decreased adhesion if they were exposed to accelerated ageing. However, the sealant shape was very unsuitable for tensile tests: The cross-section was 20 x 20 mm and the width 10 mm! It was difficult to make any general conclusions.

Lerchenthal and Rosenthal (1972) also reported results from accelerated ageing tests. They worked with five brands of polysulfide-based sealants exposed to various kinds of accelerated tests. Comparison of the physical characteristics of the sealants before and after ageing showed that the changes observed were dissimilar and sometimes also went in divergent directions.

In Künzel et al (1975) results from both outdoor exposure and accelerated ageing tests in laboratory were reported.

Three different sealants were investigated outdoors. One polysulfide-, one polyurethane- and one silicone-sealant. They were either protected against sunlight, exposed to sunlight and at the same time either exposed to deformations or not deformed. It was decided that when testing these sealants the most essential parameter is exposure to the sun. Consequently it is not necessary to expose the sealants to varying joint movements at the same time.

From the accelerated ageing tests in the laboratory it was found that heat had a great effect on most of the sealants investigated.

More weathering tests of sealants are taking place in other places. E.g. Karpati et al (1977) describe a special weathering rack for sealants, where the sealant specimens are exposed both to normal climate and to varying dimension changes.

4. LABORATORY INVESTIGATIONS REGARDING AGEING OF SEALANTS

4.1 Evaluation methods

The determination of the shape of the stress-strain curve according to different forms of ageing has been used as the main method of evaluation. The specimens have been elongated at a rate of 1.5 mm/min and at a temperature of $+2^{o}C$. At this temperature the elongation resistance of the plastic sealants increases especially after certain forms of ageing.

The elongation rate 1.5 mm/min is much too high compared to those rates which occur in most joints in the actual buildings (cf. Chapter 8.2). The rate greatly affects the form and level of the stress-strain curves. The rate dependence is greatest where plastic sealants are concerned. A completely elastic material is independent of the rate. However, these matters are dealt with more thoroughly in Chapter 8.3.3.

Consequently, the effects of the rate 1.5 mm/min on the results obtained are that the measured stresses are too high compared to cases in reality. Furthermore, a mainly plastic sealant may show too much of an "elastic stress-strain curve", i.e. a curve without the characteristic maximum point typical for plastic sealants.

As the method has mostly been used for comparative determinations these negative effects may be neglected. The positive effects are for example more rapid tests and also a possibility of testing rather soft sealants.

When evaluated, all the specimens were extended 100%, which is less than the permanent strain after rupture where the majority of the materials are concerned. There are several reasons why deformation of up to only 100% was chosen:

- the length of the specimen has a greater effect on the test result the greater the elongation
- generally, the adhesive stresses increase with increased elongation. As the sealant is primarily examined this can mean that adhesive failure may occur and interfere with the comparisons

- 100% elongation is very much on the safe side compared to the deformation the materials are usually designed for.

When 100% elongation was reached the stress relaxation was registered for about 10 minutes. One can suppose that a sealant which is mainly plastic can show stress-strain curves up to 100% which are similar to those of an elastic sealant, cf. above. However, the determination of the time dependence of the stress relaxation shows the difference between an elastic and a plastic sealant.

The appearance and shape of the stress-strain curve supplies information regarding softening or hardening, brittleness, increased temperature dependence etc. The test equipment used for this purpose is shown in Fig. 4.1a and b.

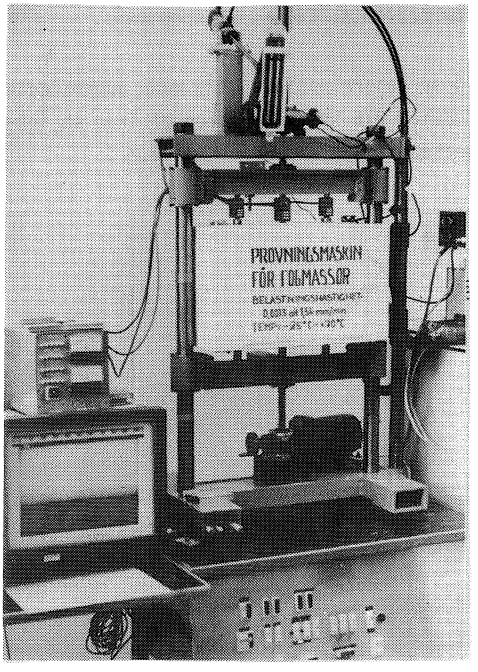


FIG. 4.1a Testing equipment for sealants. Climate chamber closed. Deformation rate 0.001--1.5 mm/min tension/compression. Testing temperature -25 - +70 °C.

Another way to evaluate changes in the sealants is to determine the loss in volume and weight after different periods of time and kinds of ageing. This determination of the loss in volume and weight supplies information regarding the amount of volatile components, the thermostability of the plasticizer, continued polymerization, de-polymerization,

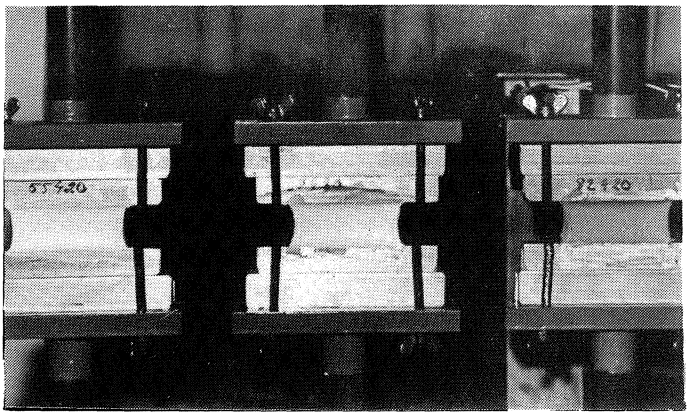


FIG. 4.1b Testing equipment for sealants. Fixing of specimens.

and the changes in density. These determinations were made approximately according to the method NT Build 015 "Determination of free shrinkage" (Gjelsvik (1976)). The methodics are shown in Fig. 4.2.

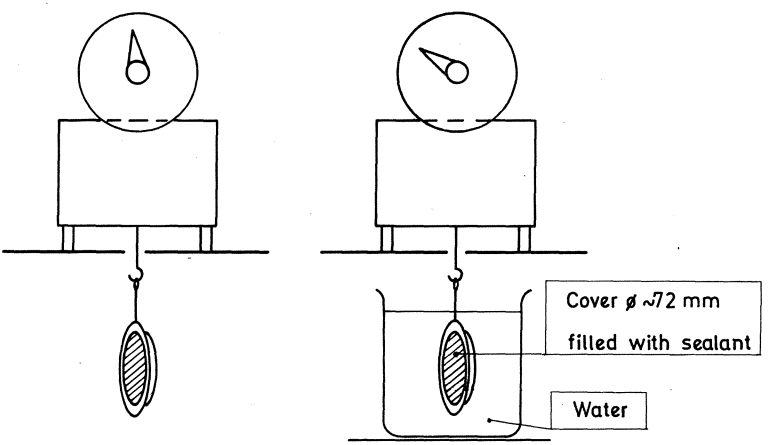


FIG. 4.2 Measuring of weight loss and shrinkage.

One method, which is very simple to carry out, is the determination of hardness by means of a Durometer. This method can be used for the mainly elastic sealants. The more plastic ones are either too soft or show

too high a degree of stress relaxation for the measurements to be important. Thus the instantaneous values in degrees Shore A have been determined for all the mainly elastic sealants after different kinds of ageing.

On data sheets from the different manufacturers of sealants the hardness values are very often given in terms of degree Shore A. As can be seen below, the values found in this investigation frequently differ a great deal from the values given by the manufacturers.

This may be due to at least three reasons. Firstly, there are many different ways of determining this value. One can e.g. make the readings instantaneously, after 15 seconds, after 1 minute etc. Because of the stress relaxation and creep phenomenon in the sealants, these values are completely different.

An example of how the Shore A-value depends upon the time factor is shown in Fig.4.3 when testing a couple of sealants (Andersson (1972)). The time-dependence is naturally least for the most elastic sealant, the silicone-based one.

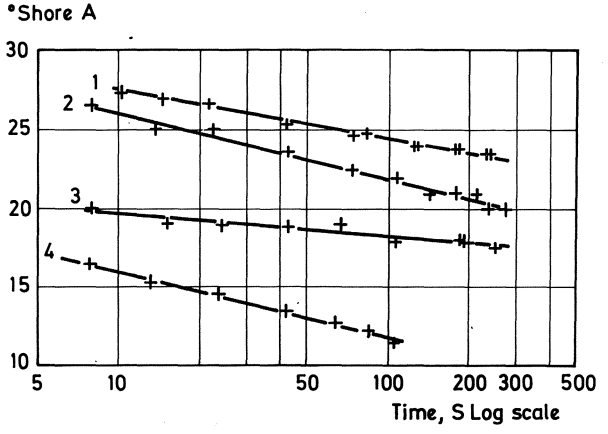


FIG. 4.3 Durometer characteristics for sealants at room temperature after storing for six months at room temperature. The level at which the curve is situated is a measure of the deformation resistance for loading times of different lengths. The inclination of the curve is a measure of the rate of creep of the compound. The curves are practically straight lines in this type of diagram.

1= Polysulfide-based sealant type 1, 2= Polysulfide-based sealant type 2, 3= Silicone-based sealant, 4= Polyurethane-based sealant (Andersson et al (1972)).

In Fig.4.4 the same relationship is shown for four other sealants in a linear scale and with instantaneous readings. The curves are very similar to the creep or stress-relaxation curves.

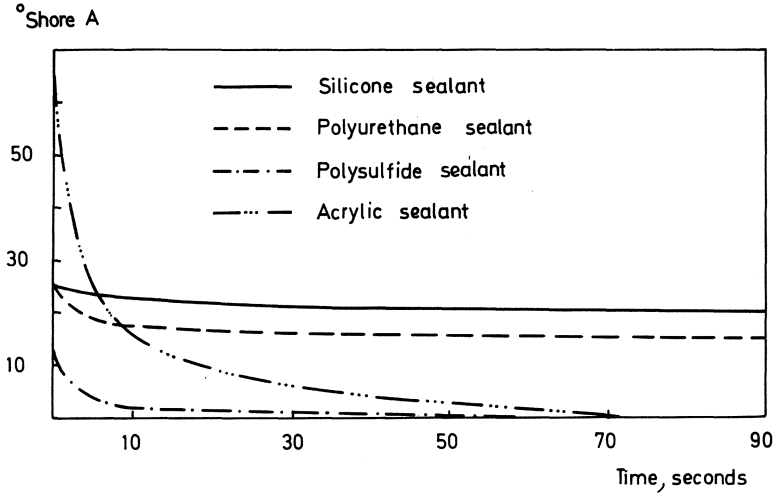


FIG. 4.4 Examples of Shore A-hardness as a function of time for four different sealants. The sealants have been stored at +20°C/ /50% RH five years before testing.

Secondly, the rate when setting the needle on the sealant gives different values. Higher rates give higher values and vice versa, cf. above. Thirdly, there is a trend among most of the manufacturers to give values which are too low. These are looked upon as being better from a functional point of view. However, one cannot accuse the manufacturers of not telling the truth, because sometimes the stated values are true!

However, if a Shore A-value is to be of any interest, the stated value should be given according to a known test method, e.g. NT Build 005 (Gjelsvik (1976)).

Only an approximation of the changes can be obtained by photographing the specimens before and after different periods of ageing. But, in spite of this, this method has also been used to a certain extent.

Scanning Electron Microscopy (SEM) photography has been used in some experiments. These investigations were made at the Zoological Institution at Lund University.

4.2 Specimen size and shape

When examining the elongation resistance of sealants, discussions regarding the appropriate shape of the specimens often occur. Where the shape of the cross-section is concerned the width/depth relationship should be as large as possible, in order to minimize the tensile stresses that occur and thereby the adhesion stresses. This is particularly true where mainly elastic sealants are concerned. These matters have been dealt with in a work by Tons (1962).

Where the length of the joint specimen is concerned, great strains on a short joint will result in stresses, which are too small compared with those they are exposed to in buildings.

Cook (1965) has dealt with these questions. Assuming the sealant is a perfectly elastic material and with a square cross-section (1 x 1 in.) he found theoretically that, at an extension of 100%, a specimen with a length of 2 inches showed a principal stress 21.5% lower than the infinite length specimen. The corresponding value for a specimen with a length of 6 inches was about 10.5%.

In some experimental work he also determined the ultimate strain and modulus of elasticity. This work was carried out with 2-, 4-, and 6-in. long specimens. Cross-section dimensions of the specimens were 1 1/2 by 3/4 in. (probably width to depth). Exactly how the modulus of elasticity was defined is not clear. In a book by Damusis (1967) Cook says "A tensile modulus should be clearly defined. Classically, the modulus of elasticity is the value of stress at 100% strain. However, in elastomeric work, a 300% modulus is often used ...".

Judging the results, the modulus of elasticity might have been defined as the stress at 100% strain. Anyway, there was practically no difference at all in the values of modulus for the different length specimens tested.

At the time of the investigations by Tons and Cook, other demands upon

the ideal sealant were made as compared to nowadays. The sealants were more rubber-like, showed a high degree of recovery and high stresses when extended. Many adhesion problems influenced the trend towards softer sealants and a rather high degree of stress relaxation. For example Tons (1962) made the assumption that the strain in the sealant along the parabolic curve-in line is uniformly distributed. However, today this assumption is probably not valid for many types of sealants. E.g. the acrylics do not fulfil this assumption and probably the soft polysulfides do not either.

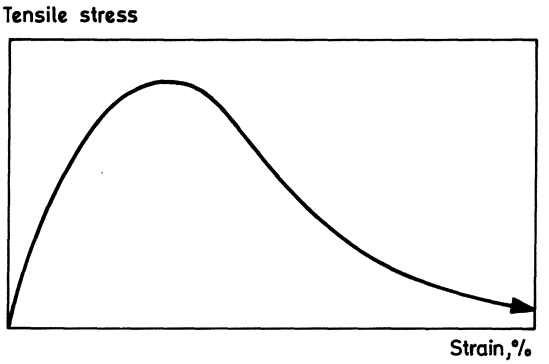


FIG. 4.5 Principle stress-strain curve of a plastic sealant.

When the stress-strain curve is determined for a more plastic sealant one obtains a principal curve as shown in Fig. 4.5. Here the stress is calculated in the usual way, i.e. by dividing the load by the original cross-section. Where the more plastic sealant is concerned the elongation is distributed unevenly along the joint width (in the direction of force). This means that most of the deformation takes place in the weakest part of the cross-section. Consequently this part gradually diminishes and thereby also the recorded load. That is the reason why the stress-strain curve produces a maximum point.

Because of the above mentioned change in philosophy when developing new sealants it was decided to establish the size effect on three common sealants of different kinds. The estimation of the extent to which the specimen size affects occuring stresses was made on the following

types of sealants:

1. One-component silicone sealant, 25-30° Shore A
2. Two-component polysulfide sealant, approx 15° Shore A
3. One-component acrylic sealant, solvent release

The cross-section was nominally 12 x 8 or 12 x 12 mm (width x depth). The length was 50, 80 or 150 mm. The specimens were stored at +20°C/ /50% RH for 14 months before testing.

Before starting the testing, the true dimensions were measured. The specimens were elongated at least 50% at +20 ±2 °C and at a rate of 1.5 mm/min. The elongation 50% instead of 100% was chosen in order to reduce the adhesion problems and also the total forces occuring especially in the longer specimens. The results are shown in Figs. 4.6-4.9. For the silicone sealant, which can be characterized as being elastic, the relative positions of the different specimens correspond well with the positions expected, Fig. 4.6. For example, in a case of 25% defor-

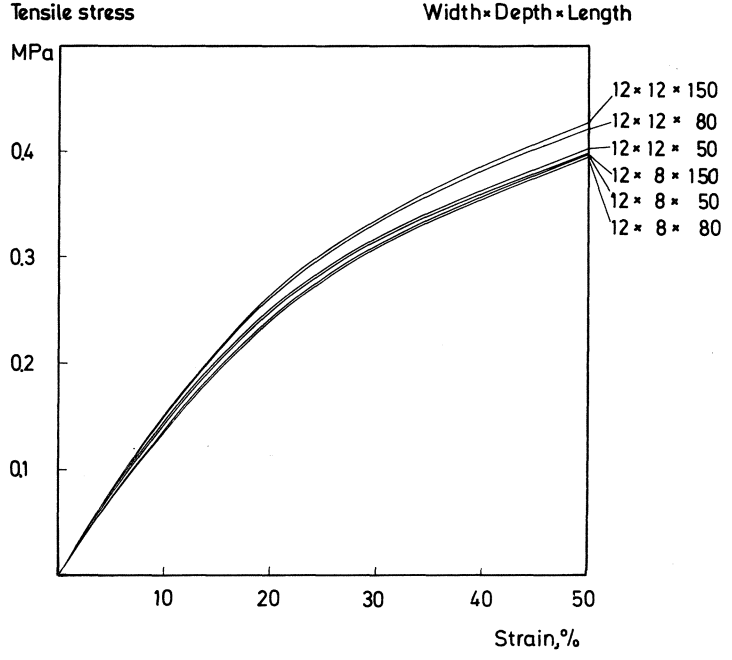


FIG. 4.6 The influence of the specimen dimension on the stress-strain curve for a silicone-based sealant of 14 months age.

mation a specimen with a length of 50 mm shows about 7% less tensile stress than one with a length of 150 mm. The difference will be somewhat larger at 50% elongation.

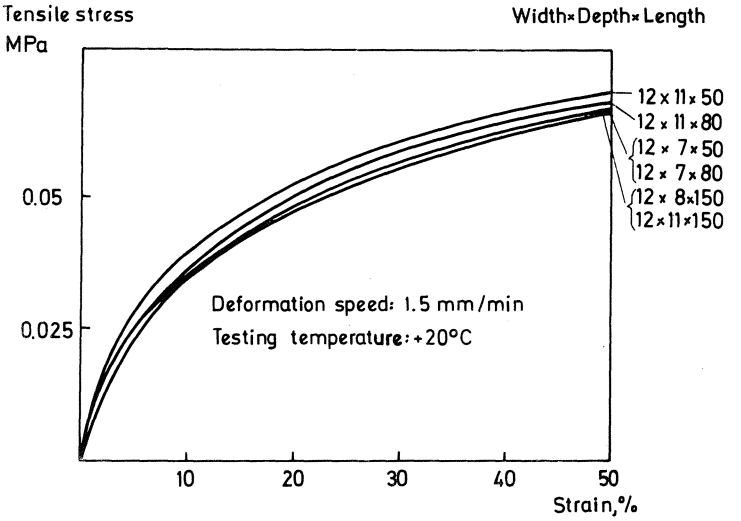


FIG. 4.7 The influence of the specimen dimension on the stress-strain curve for a polysulfide-based sealant of 14 months age.

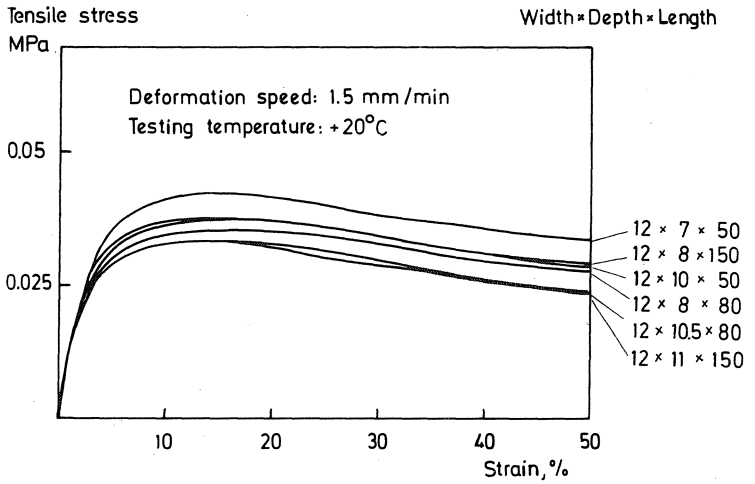


FIG. 4.8 The influence of the specimen dimension on the stress-strain curve for an acrylic-based (solvent release) sealant of 14 months age.

Where the more plastic polysulfide and acrylic sealants are concerned the distribution of the results has produced a somewhat unexpected order in the curves, Figs.4.7-4.8. The distribution of the results dominates the effect of the specimen shape. E.g., for the acrylic sealant the curve which was expected to be the highest was the lowest.

The results of this study were that the variation in specimen size was of no significance for the measured stresses at deformations below approximately 50% and for materials of a certain plasticity, i.e. for most sealants.

For these reasons, the specimen size 12 x 12 x 50 mm was chosen. These dimensions correspond well with the American, English, and German standards. Asbestos cement, alternatively aluminium (grade SIS 41 04-6) were used as block materials.

4.3 Sealants used in the investigation

When choosing between the different types of sealants to be included, the purpose was to get as many types as possible represented, of those which were used frequently when the investigations started. It was also intended that these materials which were comparatively unknown on the market, but were expected to become increasingly used, should be included. For example, two different types of polyurethane based sealants and one water dispersed acrylic sealant were included.

Furthermore, the purpose was also to make comparisons possible between sealants of the same type (approximately the same polymer) but of different formulations.

The final choice of materials was made together with the largest Swedish manufacturers of sealants. The choice is presented in Table 4.1.

Eight different materials of five different makes were used. The values of the Shore A hardness have been taken from the information given by the manufacturers. As can be seen no silicone sealant was included. At that time (Autumn 1973) there were very few silicone sealants on the market and the low-modulus ones had not yet been introduced.

TABLE 4.1 Different types of sealants in the investigation

Material No.	Kind of binder	Number of components	Note
1	Polysulfide	2	Hardness ~13° Shore A
2	Polysulfide	2	Hardness ~40° Shore A
3	Polyurethane	1	Hardness ~25° Shore A
4	~ Polyurethane	2	Hardness ~18° Shore A
5	Acrylic	1	Solvent release
6	Acrylic	1	Solvent release
7	Acrylic	1	Water dispersed Hardness ~15° Shore A
8	Oleo-resinous	1	

4.4 The effect of thermal action on sealants

4.4.1 Introduction

For several reasons a comparatively thorough study was carried out concerning the temperature influence on the ageing and deformation properties of the sealants; storing in heat, frequently at +70°C, is used fairly often in laboratories in order to accelerate the ageing of the sealants. This method is also very easy to carry out.

Three of the sealants were studied more thoroughly than the others. These were materials Nos. 1, 3, and 6. From a hardening or curing point of view these materials represent three different types of sealants: 2-component chemically curing, 1-component chemically curing, and 1-component chemically curing/drying sealant respectively.

+20°C/50% RH was used as the standard climate. Heat ageing was carried out at +40°C and +70°C. Heat storage normally started after 7 days in the standard climate. However, in some cases the heat ageing also started after 21 days. Some undesirable effects can occur if the heat storage is started too early. For example, blisters may form in sealants containing solvents (Burström (1977)).

Heat can affect sealants in many different ways, depending e.g. upon the type of binder. Such effects are continued polymerization, de-poly-

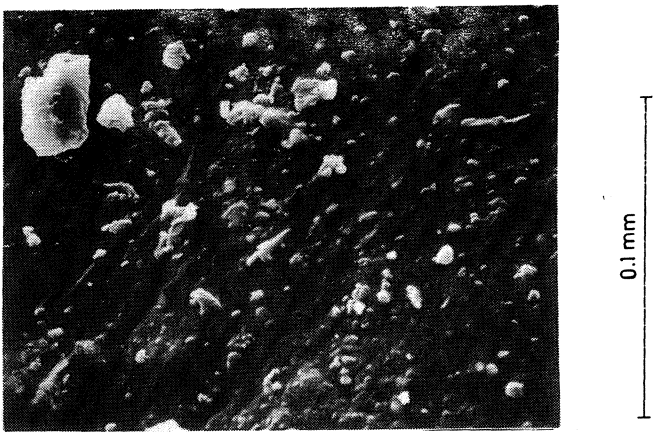


FIG. 4.9 SEM-photograph of the surface of a polysulfide-based sealant stored at +20 °C/50% RH. Enlargement 600x. Photo: The Zoological Institution of Lund University.

merization, oxidation. Fig. 4.9 shows the surface of a polysulfide sealant stored at +20°C/50% RH. If the same sealant is heat-aged at +70°C for 21 days the material changes. The surface can be seen on Figure 4.10. Obviously a chemical change has taken place in the sealant. In spite of there not being any movements there are a lot of cracks on the surface. These cracks will induce stress-concentrations, where cohesive failure may start when the sealant is elongated.

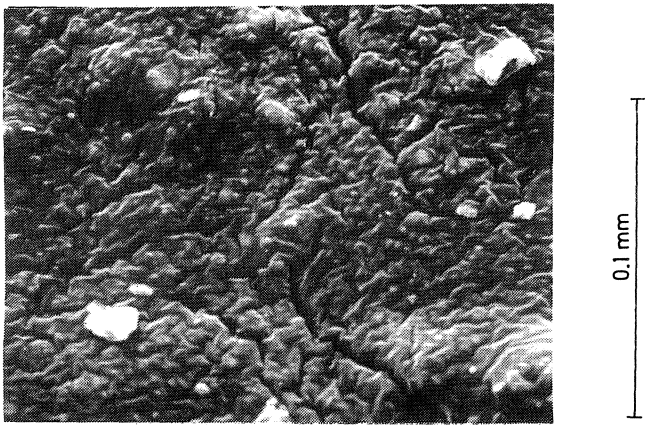


FIG. 4.10 SEM-photograph of the surface of a heat-aged (21 days at +70 °C) polysulfide-based sealant. Enlargement 600x. Photo: The Zoological Institution of Lund University.

4.4.2 Results

The results for Material No. 1, a two-component polysulfide sealant, are summarized in Fig. 4.11. σ_{50} is the tensile stress at 50% elongation. As can be seen there is a slight increase in the hardness of material stored for an increasing length of time in a normal climate +20°C/50% RH. The sealant is unaffected by the heat-ageing at +40°C. However, heat-ageing at +70°C made the material softer! This is very surprising as so far, experience has shown that polysulfide sealants usually become harder when heat aged.

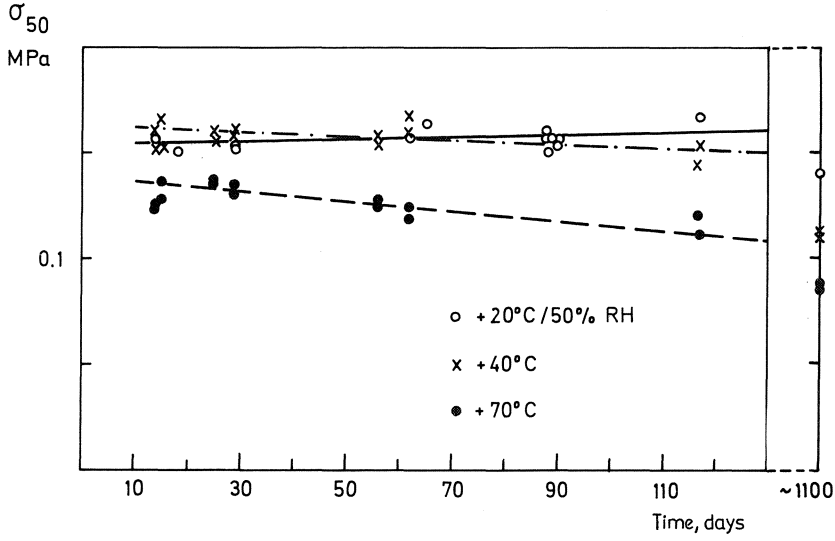


FIG. 4.11 Tensile stress at 50% elongation (= σ_{50}) for Material No. 1 as a function of storing time at different temperatures. Initial storing: 7 days at +20 °C/50% RH.

Fig. 4.12 shows the stress-strain curves after 7+56 days. The softening after heat-ageing at +70°C is fairly evident. In Fig. 4.13, showing the stress-strain curves after almost three years at different temperatures, the softening after heat-ageing at +40°C is also evident.

The same pattern was repeated when heat-ageing was started after 21 days initial storage in the normal climate, i.e. the result is independent of when the accelerated ageing was started.

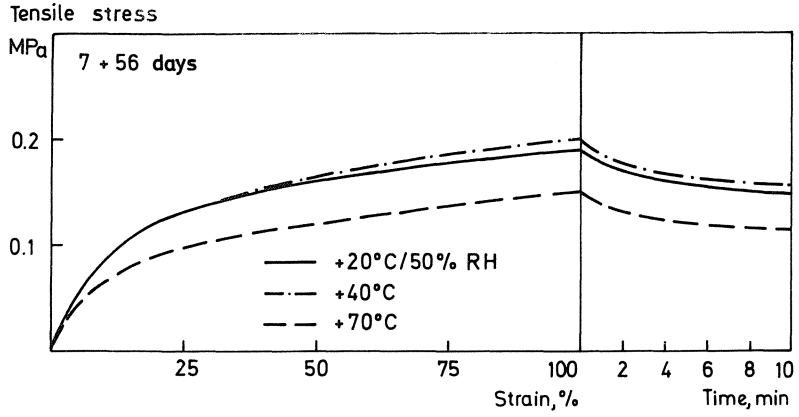


FIG. 4.12 Stress-strain curves for Material No. 1 after heat-ageing at different temperatures. Deformation speed: 1.5 mm/min. Testing temperature: +2 ^{o}C.

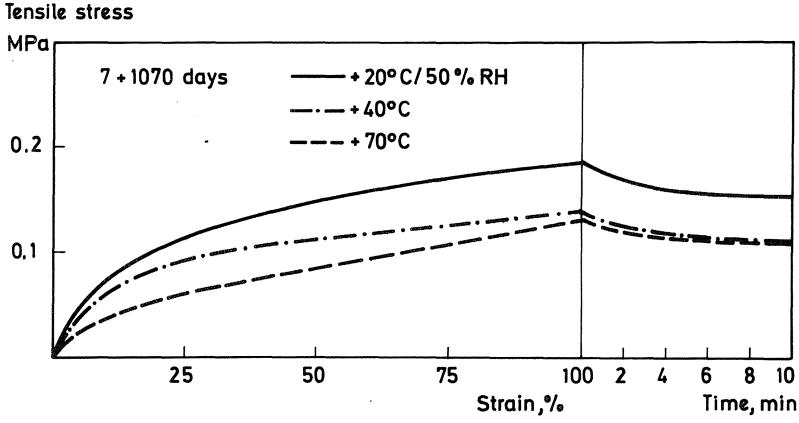


FIG. 4.13 Stress-strain curves for Material No. 1 after about three years at different temperatures. Compare Fig. 4.12! Deformation speed: 1.5 mm/min. Testing temperature: +2 ^{o}C.

By means of determining the hardness in ^{o}Shore A it was almost impossible to detect the softening, Fig. 4.14. The distribution among the readings when using this method was too great. Note also that the value of 13^{o} Shore A as stated by the manufacturer does not correspond satisfactorily with the measured values. A more accurate value is approximately 25^{o} Shore A.

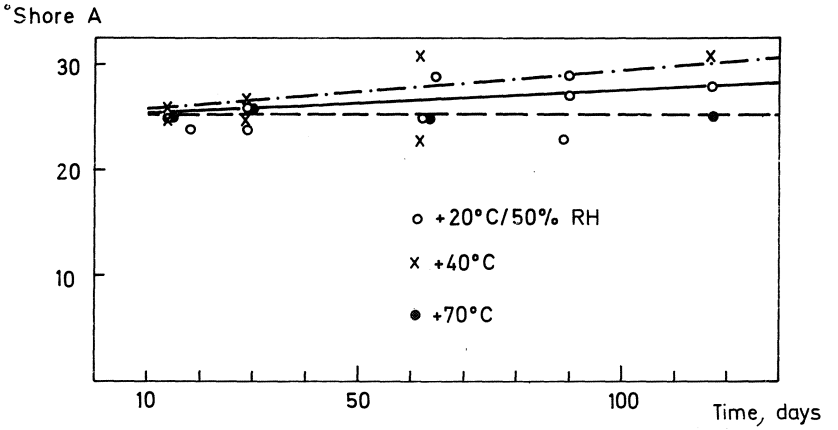


FIG. 4.14 Instantaneous Shore A-values for Material No. 1 as a function of storing time at different temperatures. Initial storing: 7 days at +20 °C/50% RH.

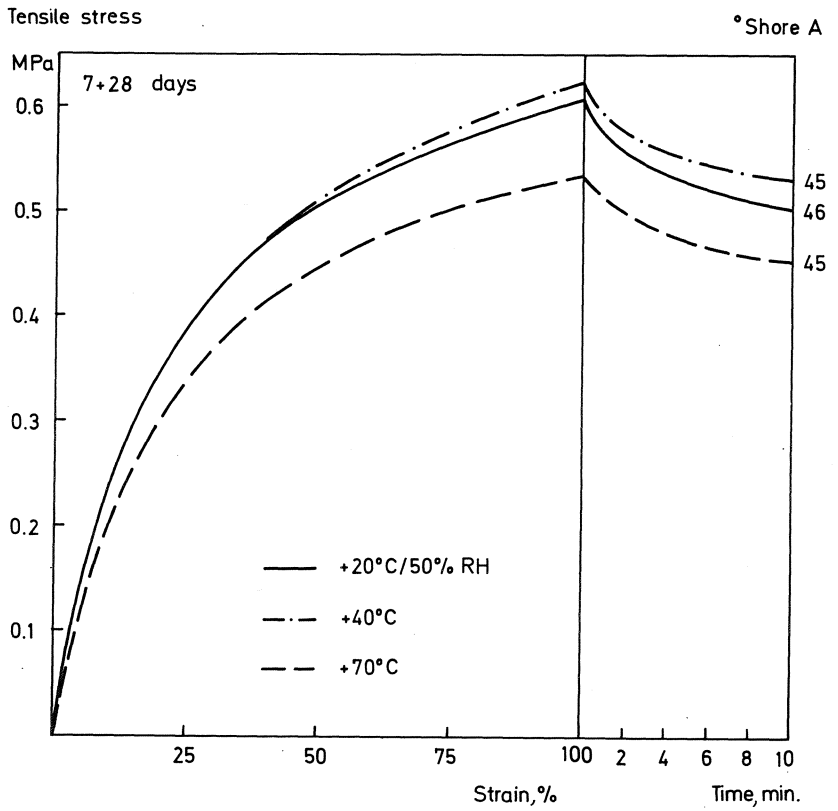


FIG. 4.15 Stress-strain curves for Material No. 2 after heat-ageing at different temperatures. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

However, if by his statement the manufacturer refers to the value e.g. after 15 seconds, his value might be reasonable. Anyhow, if a value is to be of any use, the method should also be given.

The other polysulfide-sealant, Material No. 2, is formulated in another way. The polymer content is higher compared to Material No. 1 and the hardness is approximately 40^{0} Shore A. The adhesion properties were found to be very poor sometimes. This interfered with the comparisons.

Fig. 4.15 shows the effect of heat ageing. In this case there is also a definite tendency to a decrease in the elongation resistance after storage at $+70^{o}$C. With the aid of the Durometer this tendency was not evident.

When tests were carried out after longer periods of heat ageing, there were different results. Fig. 4.16 shows the stress at 50% elongation as a function of time at different temperatures. The pattern is very irregular. There is a tendency to increased hardness due to continued curing at $+20^{o}$C/50% RH. There is also a tendency to increased hardness due to heat ageing, but the values after about 1000 days at $+40^{o}$C derange the conclusion.

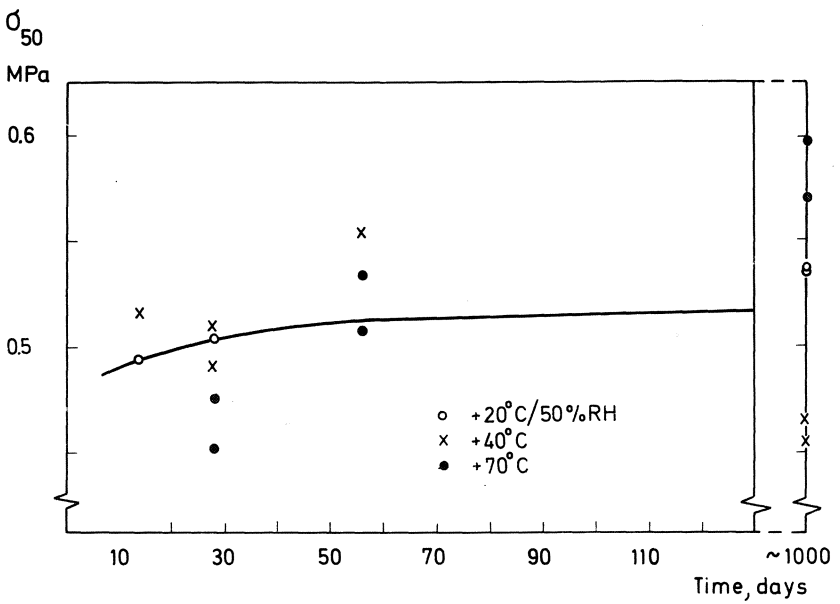


FIG. 4.16 Tensile stress at 50% elongation (= σ_{50}) for Material No. 2 as a function of storing time at different temperatures. Initial storing: 7 days at $+20$ ^{o}C/50% RH.

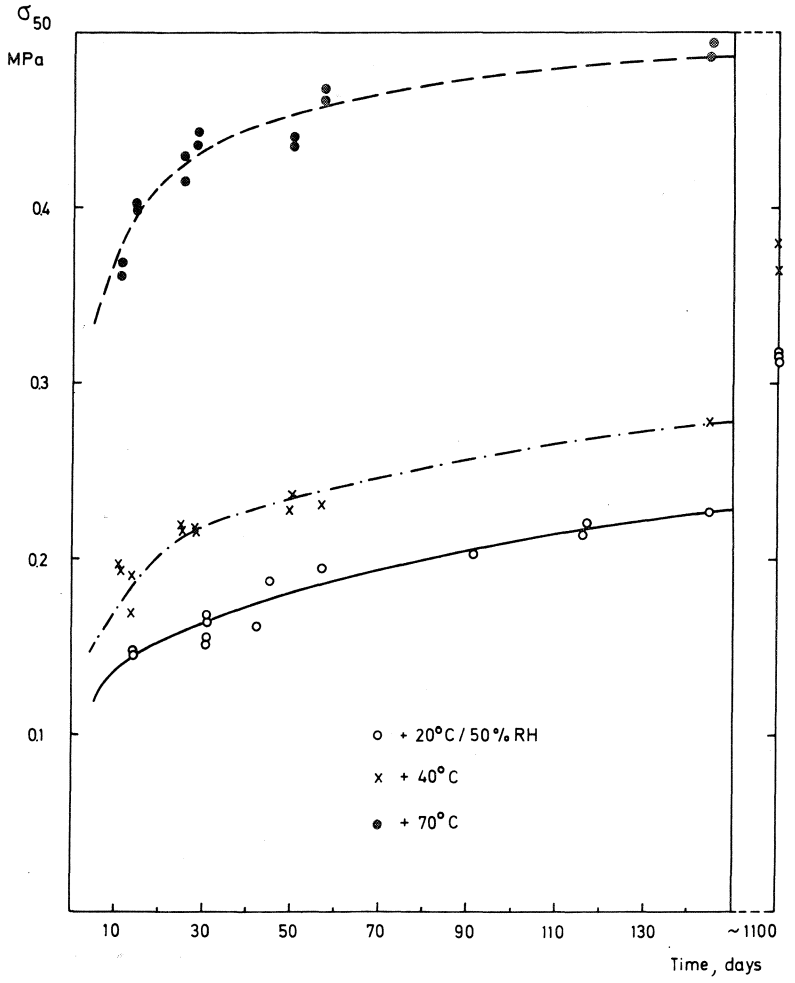


FIG. 4.17 Tensile stress at 50% elongation (= σ_{50}) for Material No. 3 as a function of storing time at different temperatures. Initial storing: 7 days at +20 °C/50% RH.

Fig. 4.17 summarizes the results of the heat ageing of Material No. 3, the one-component polyurethane sealant. The sealant cures with the aid of moisture in the air. (The curing mechanism is e.g. described by Evans and Greene (1976)).

The curing rate is very slow and it still continues after three years in a climate of +20°C/50% RH. If the temperature is increased there is

a remarkable increase in the hardness in spite of the relative humidity being very low at the higher temperatures. The relative humidity is about 10-15% at +40°C and about 3% at +70°C. The increase in hardness is not linearly dependent upon the rise in temperature. But it is possible to compare the increase in hardness after heat ageing at +40°C to the hardness after storing in a climate of +20°C/50% RH. E.g., take the value of 0.2 MPa. This value is reached after about 20 days at +40°C, and after about 80 days at +20°C (besides the initial 7 days in a climate of +20°C/50% RH). This relationship is valid almost throughout the entire range of time studied. The factor 4 ($= \frac{80}{20}$) agrees very well with the one expected when using the rule of thumb: A temperature increase of 10°C doubles the rate of a chemical reaction.

The results are the same whether the heat ageing is started after 7 or 21 days at +20°C/50% RH.

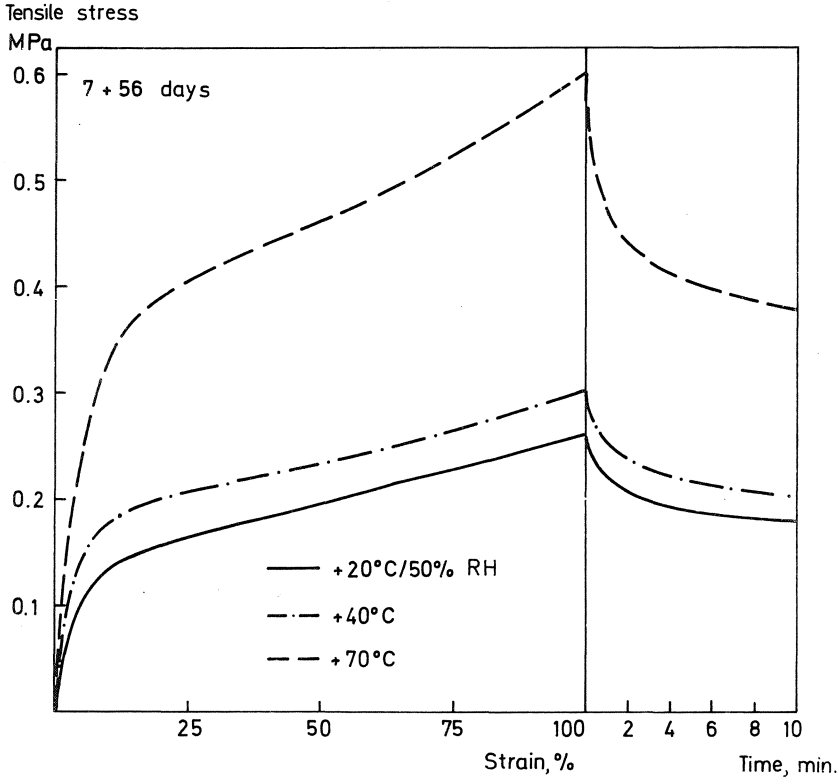


FIG. 4.18 Stress-strain curves for Material No. 3 after heat-ageing at different temperatures. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

In Fig. 4.18 examples are given of the stress-strain curves after 56 days at different temperatures. The corresponding curves after about three years at +20 or +40°C are shown in Fig. 4.19. The sealant stored at +70°C during this period was very brittle due to an increased cross-linking, and showed dis-colouration and a high degree of shrinkage. From Fig. 4.19 it is evident that the sealant has become very elastic and it also shows a strain-hardening effect at higher elongation.

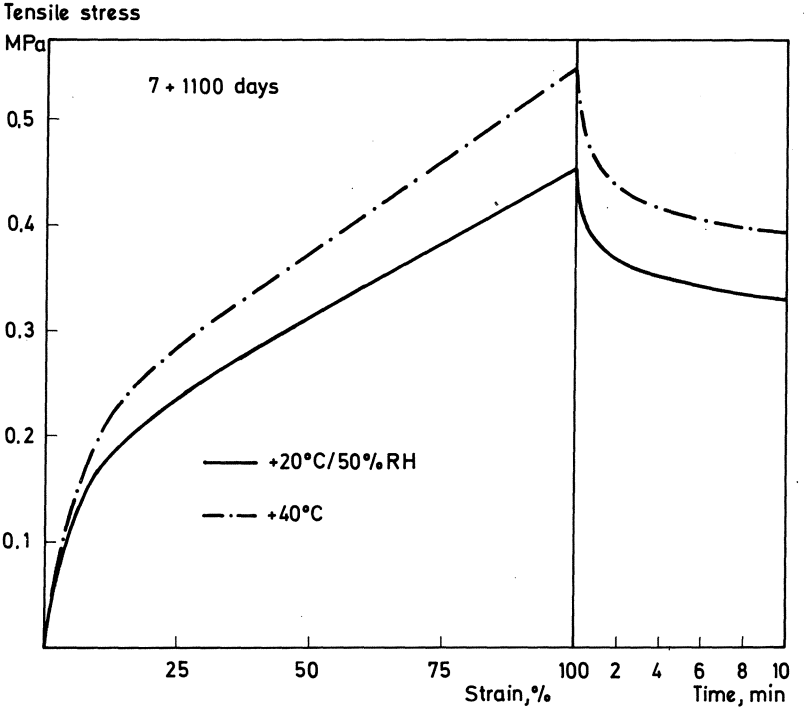


FIG. 4.19 Stress-strain curves for Material No. 3 after about three years at different temperatures. Compare Fig. 4.18! Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

Material No. 4 is a two-component sealant based on a polyurethane-polyepoxide co-polymer. Some results are shown in Fig. 4.20 after heat ageing at different temperatures. After storing in a climate of +20°C/50% RH the sealant shows a small continued increase in hardness during a long period of time. The heat ageing has a very slight effect on Material No. 4. But if the heat ageing continues too long at +70°C chemically changes occur in the sealant. Thus, after almost three years at +70°C the sealant was reverted.

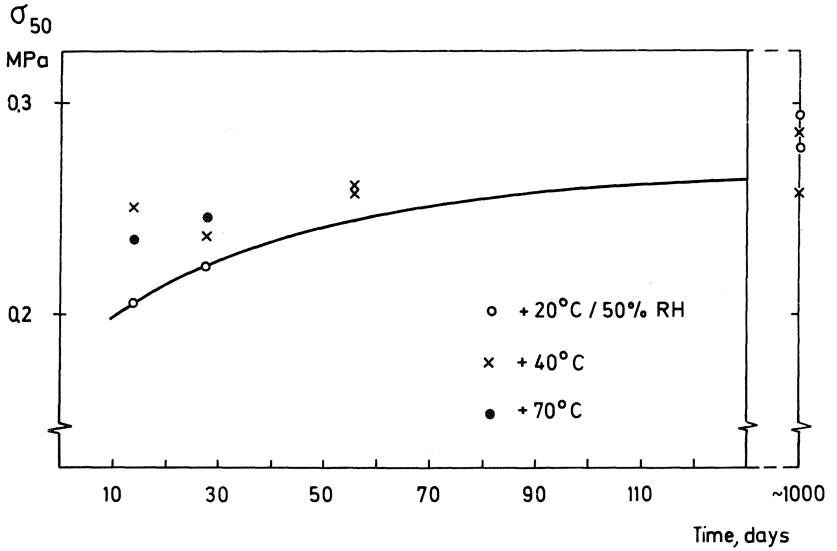


FIG. 4.20 Tensile stress at 50% elongation (= σ_{50}) for Material No. 4 as a function of storing time at different temperatures. Initial storing: 7 days at +20 °C/50% RH.

Stress-strain curves after heat ageing for 28 days at different temperatures are shown in Fig. 4.21.

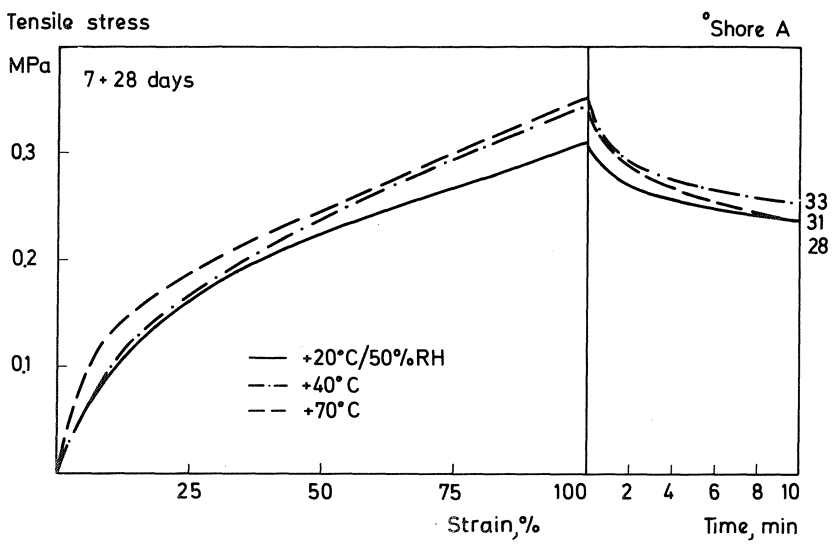


FIG. 4.21 Stress-strain curves for Material No. 4 after heat-ageing at different temperatures. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

Material Nos. 5 and 6 are both acrylic sealants, type solvent release. However, the polymers differ greatly in structure and properties. They cure or harden chiefly because of the evaporation of their solvent content. This is particularly true where Material No. 5 is concerned. For Material No. 6 it is claimed that a portion of the cure is a result of the chemical reaction; a continued polymerization of the binder.

Both these sealants are thermoplastics. They become considerably harder at low temperatures and reveal the typical stress-strain curve of a plastic sealant. Fig. 4.22 shows this for Material No. 5. Naturally the stress relaxation is also very pronounced.

In this case, the heat ageing started after 7 days at +20°C/50% RH. At that time the material still contained a large quantity of solvent, cf. Chapter 4.9. When the heat ageing started, the solvent evaporated rapidly thus forming many large pores, cf. Fig. 4.23. This probably means that the stress-strain curve for the heat aged material in reality is higher than that shown in Fig. 4.22.

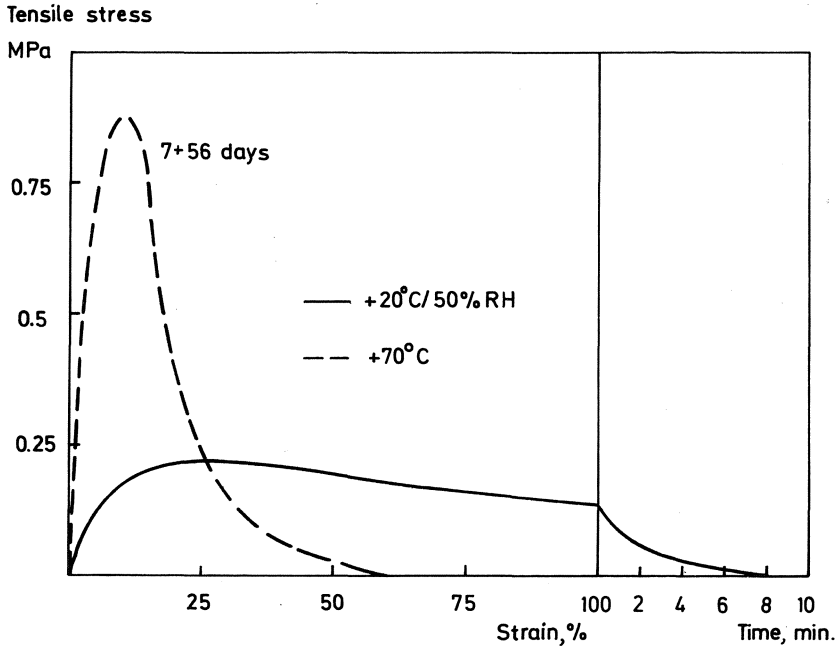


FIG. 4.22 Stress-strain curves for Material No. 5 after heat-ageing at different temperatures. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

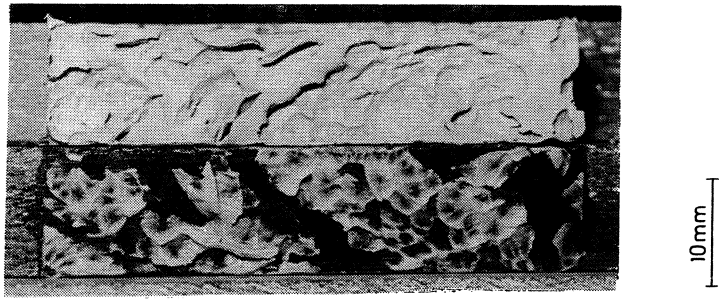


FIG. 4.23 Fracture surface of a specimen of Material No. 5 (acrylic based, solvent release) heat aged 56 days at +70 °C. Initial storing: 7 days at +20 °C/50% RH.

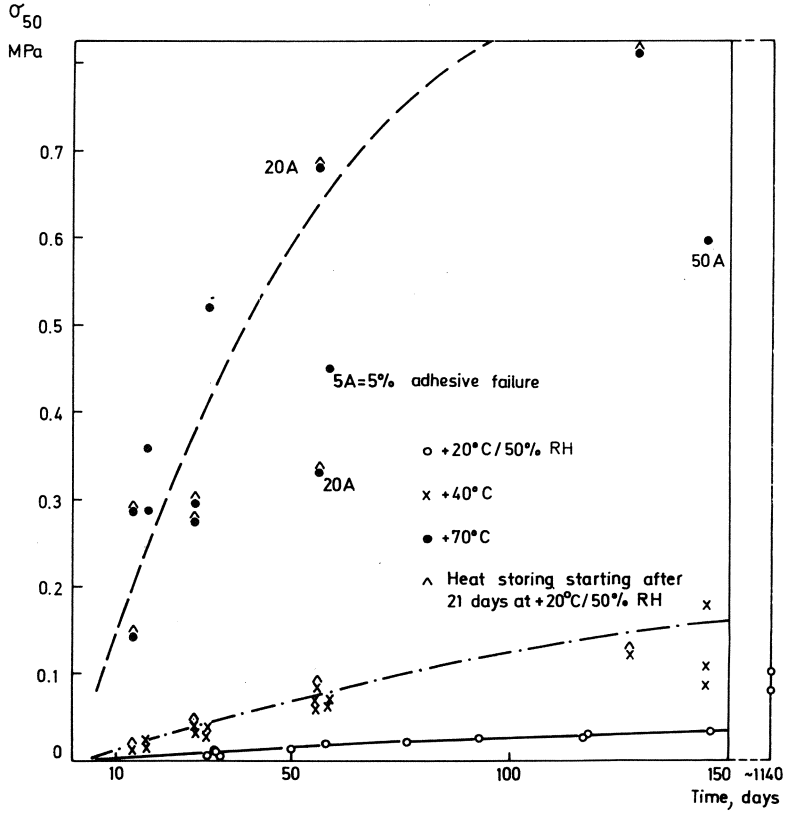


FIG. 4.24 Tensile stress at 50% elongation (= σ_{50}) for Material No. 6 as a function of storing time at different temperatures. Initial storing: 7 or 21 days at +20 °C/50% RH.

The other acrylic sealant, Material No. 6, also showed a considerable increase in deformation resistance after heat ageing. Fig. 4.24 summarizes the results from the stress-strain determinations. The tensile stress at 50% elongation is plotted as a function of time in different climates. At +20°C/50% RH there is a very slow increase in the elongation resistance.

Heat ageing at +40°C increases the hardness to a certain extent, while heat ageing at +70°C has a considerable effect upon the tensile stress at 50% elongation. However, there is a large scatter among the values. This depends mainly on adhesive cracks and to some extent on cohesive cracks which occurred after a long period of storage at +70°C. These types of cracks occurred when heat storage started after 7 and after 21 days at +20°C/50% RH.

Fig. 4.25 shows stress-strain curves after 14 days of heat ageing and after about three years in a climate of +20°C/50% RH. No stress-strain curves are shown after 56 days of heat ageing at +70°C. This is because partial adhesive failure usually occurred after such a lengthy heat ageing, irrespective of whether the heat ageing started after 7 days or after 21 days in a normal climate.

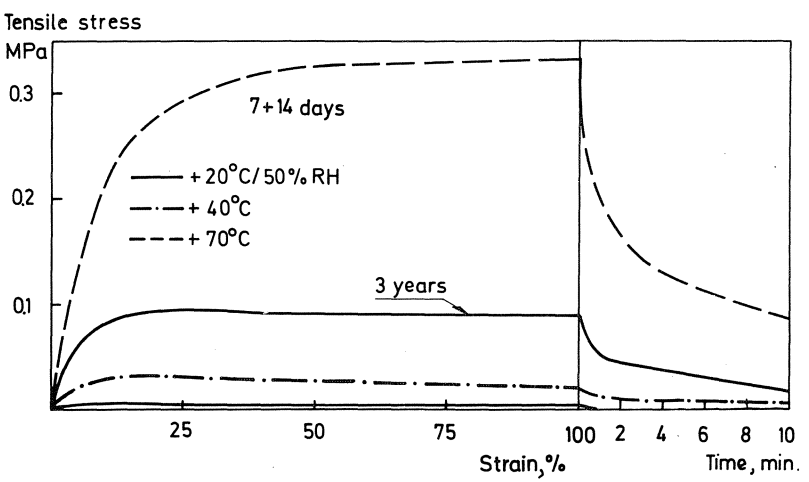


FIG. 4.25 Stress-strain curves for Material No. 6 after heat-ageing at different temperatures. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

Comparing Fig. 4.25 to Fig. 4.22, it is obvious that the different binders in the two acrylic-based sealants No. 5 and No. 6 also greatly affect the stress-strain properties of the sealants. Though both sealants can be characterized as being plastic sealants (cf. Chapter 1), Material No. 6 does not show such a large necking as Material No. 5. Furthermore, the stress-relaxation is great, but not as great as that for Material No. 5.

Material No. 7, a water dispersed acrylic sealant, differs considerably from both of the solvent based sealants which were discussed above. This sealant has a pronounced elastic behaviour, see Fig. 4.26. However, the great relaxation also reveals a large plastic portion in the sealant. The increase in hardness after storing for a long time in the normal climate is probably due to loss of water and plasticizer, cf. Chapter 4.9. This change is almost the same when the material is stored at +40°C. But if the sealant is heat aged at +70°C the elongation resistance is almost doubled.

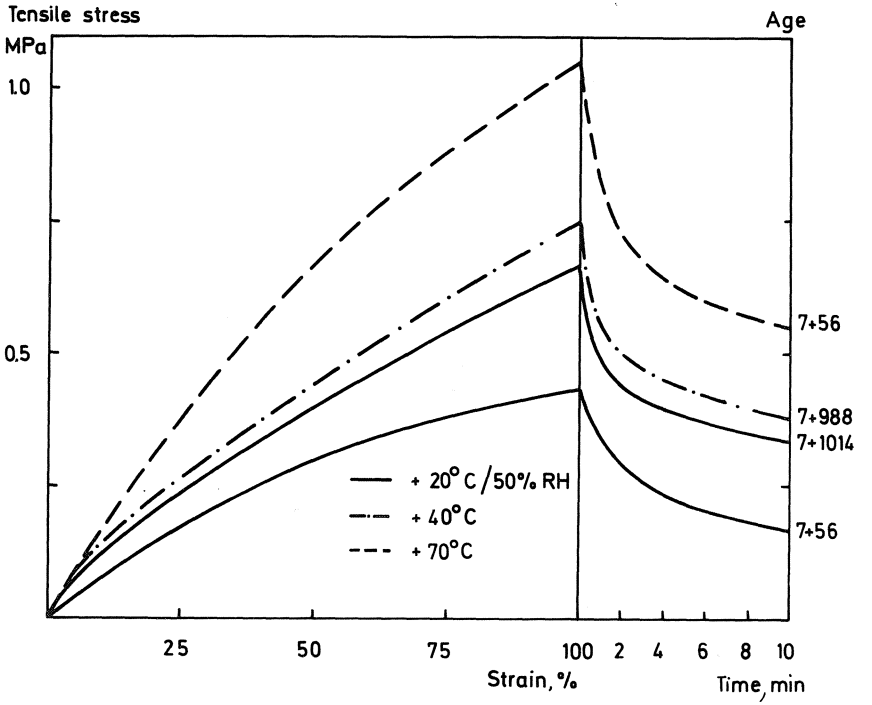


FIG. 4.26 Stress-strain curves for Material No. 7 after heat-ageing at different temperatures. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

A great many results from work carried out on this sealant were spoiled due to poor adhesion properties. Particularly when aluminium was used as a substrate.

However, this material is sufficiently elastic for the hardness values in °Shore A to be important. At the same time one can avoid the adhesion problems. Therefore, in Fig. 4.27 the Shore A values are shown after different times in a variety of climates. When stored at +20°C/50% RH the hardness of the sealant continues to increase as the water evaporates. This increase continues for a long period of time.

When the temperature is raised, the evaporation is naturally quicker. Therefore the hardness is increased when the sealant is heat aged at +40°C or +70°C. But, in the long run, an asymptotic value seems to have been reached.

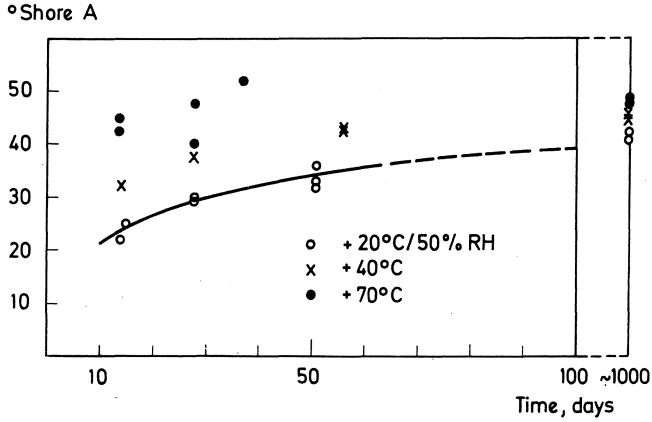


FIG. 4.27 Instantaneous Shore A-value for Material No. 7 as a function of storing time at different temperatures. Initial storing: 7 days at +20 °C/50% RH.

Material No. 8 is an oil based sealant. Most of its properties differ considerably from those shown for the previous materials. For example the curing time, the curing mechanism, the way in which the material fulfills its sealing function are different. These facts also mean that it is rather a complicated matter to carry out laboratory tests with this kind of sealant.

After the application, oxidation starts on the surface and a somewhat

ductile skin is formed. During varying joint movements the skin surface becomes wrinkled, and works like concertine bellows. The material functions well as long as this skin remains intact as it prevents continued oxidation of the inner part of the sealant.

The effect of heat ageing is shown in Fig. 4.28. As the curing rate is very slow, stress-strain curves after 91 days of heat ageing are shown. The position of the stress peak has moved towards a somewhat lesser elongation after heat ageing. This is due to the fact that the rise in temperature increased the thickness of the skin at the same time as a certain oxidation took place in the centre of the sealant. The skin cracks at a certain elongation. This means that the continued elongation of the joint width will take place in the part of the centre where the surface crack entered. Furthermore, the heat ageing also caused oxidation to a certain extent in the centre. Therefore its ability to distribute the elongation decreased.

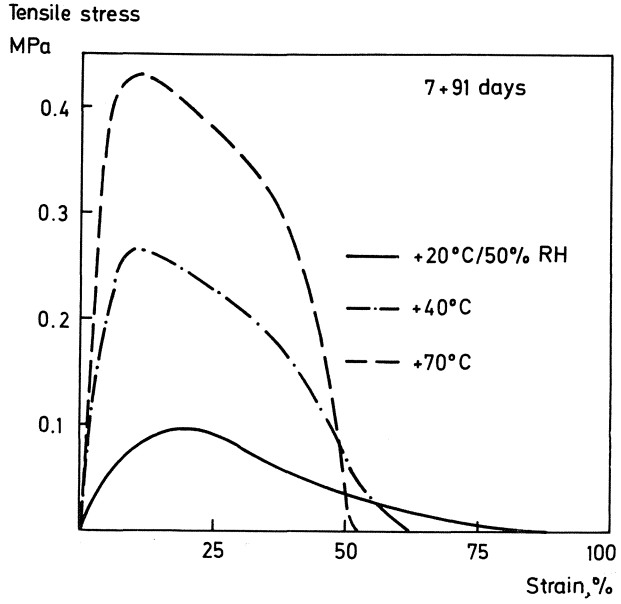


FIG. 4.28 Stress-strain curves for Material No. 8 after heat-ageing at different temperatures. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

The ability of an oil based sealant to function is, apart from the ductility of the skin, also greatly dependent on the fact that the thickness of the surface skin does not increase too quickly.

The thickness of the skin was therefore determined at different times and after storage in different climates. A scalpel cut was made through the sealant. By using a magnifier the skin thickness was determined to an accuracy of 0.05 mm.

Fig. 4.29 shows the skin thickness as a function of time. For material stored at +20°C/50% RH the relation is approximately a straight line in the log-log diagram. Empirically the equation of this line is $S \approx 0.03 \cdot t^{0.48}$. The exponent agrees with the well-known relation $x = c \cdot \sqrt{t}$ where c is a constant and t the time. This expression is approximately valid for chemical attack, e.g. carbonatization of concrete.

When storing the sealant at an increased temperature oxidation naturally takes place quicker. Consequently the thickness growth of the skin is also quicker.

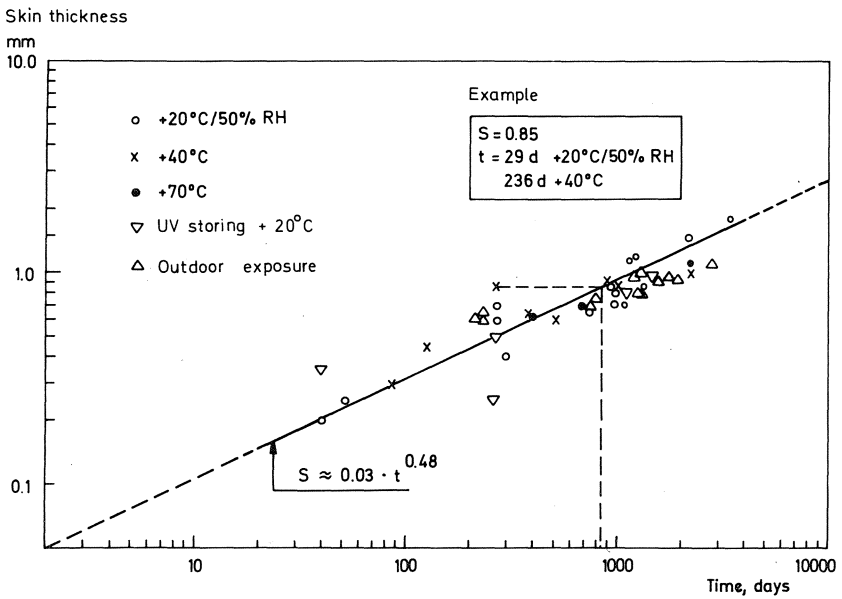


FIG. 4.29 Surface skin thickness as a function of storing time at +20 °C/50% RH for Material No. 8. Example of calculating the equivalent time at +20 °C/50% RH for material stored at +40 °C. The values of material stored at +40 and +70 °C are calculated values to equivalent times at +20 °C/50% RH according to the example in the Figure.

With the aid of the skin thickness, measured after storage at +40°C and +70°C, the real storage times at respective temperatures were recalculated to the equivalent times at +20°C/50% RH. The calculations are shown in one example in the Figure. The point S = 0.85/t = 265 (29 days at +20°C/50% RH and 236 days at +40°C) has, according to the Figure, an equivalent hardening time of about 850 days at +20°C/50% RH. Suppose that the skin growth is x times quicker at +40°C than at +20°C/50% RH, then

$$29 + x \cdot 236 = 850$$
$$x \approx 3.5$$

The average value for the corresponding calculations for a number of other points was about 4. The calculations for specimens stored at +70°C resulted in a growth factor of about 22.

The heat ageing of Material No. 8 causes an increased rate of oxidation. As this is a chemical process, the values 4 and 22 could be compared to those one obtains when using the thumb-rule: The reaction rate of many chemical processes is doubled when the temperature is raised about 10°C. Using this simple rule one obtains a surprisingly good correlation as the values are 4 and 32 respectively!

Having recalculated the actual times in the different climates to equivalent times, the values of the heat aged specimens were plotted (x and •) in the Figure.

Consequently it is possible to say that heat storage at +40°C results in ageing which is 4 times faster than storage at +20°C/50% RH. The factor 22 is valid for heat ageing at +70°C. However, the time at +70°C must be limited to approximately 100 days. Because in the long run, such a high temperature will result in an oxidation and a considerable increase in the viscosity at the centre, regardless of the growth of the thickness of the skin. This does not occur in a normal climate.

4.4.3 Discussion

As has been shown, all sealants, except Materials Nos. 1 and 2, show a varying increase in the hardness after different forms of heat ageing. Usually, this effect is due to either a loss of plasticizer or a chemical change of the binder (Chapter 2.2).

Regarding Material No. 1 there is an evident decrease in the hardness. This unexpected change is difficult to explain. Usually "Thikol LP-32" or "Thiokol LP-2" is used as a binder or sometimes a mixture of the two. In previous investigations concerning polysulfide sealants from other manufacturers it has been quite clear that heat ageing causes an increase in the hardness. Also in Peterson et al (1976) results with both these polymers show an increase in the hardness.

For Material No. 1 there might have been a depolymerisation or another chemical change of the binder. However, the reason for this is difficult to find without knowing the formulation of the sealant.

Material No. 2 is also based on a polysulfide binder. The polymer content is higher compared to Material No. 1. The effect of heat ageing is not quite clear, but the main conclusion must be that this sealant is almost completely unaffected by heat ageing.

Material No. 3 showed a great increase in hardness after heat ageing. This was to some extent probably due to an increased cross-linking of the polymer. But other results also occur during the heat ageing. In Chapter 4.9.2 a rather large shrinkage is revealed. This could be due to a loss of solvent and/or a loss of plasticizer.

Material No. 4 showed a moderate increase in the hardness. On examining the curing as a function of time at +20^{o}C/50% RH it was found that it was not quite completed after 28 days. Therefore, the increase in the hardness after heat ageing could be due to an accelerated curing.

Material No. 5 contains 14% solvents. In Chapter 4.9.2 it is shown that this amount evaporates very slowly at +20^{o}C/50% RH. Thus, the remaining amount acts as a plasticizer. That is why the sealant is so soft when tested after storing in a normal climate.

It is the same where Material No. 6 is concerned. Apart from this, the heat ageing may also have accelerated the chemical curing of the sealant.

Where both these acrylic sealants are concerned, it must be pointed out that the heat ageing ought not to start too early. 21 days at +20^{o}C/50% RH is not sufficient. Maybe they should be stored for almost 56 days in a normal climate before the heat ageing is started. The young sea-

lant has too much solvent left and a low viscosity. This combination may very easily result in cracks and bubbles if the temperature is raised. Therefore, these sealants should not be used in a soutern or western facade on a sunny summer day.

Material No. 7 hardens when the water evaporates. The equilibrium moisture ratio is naturally higher when the sealant is stored at +20°C compared to +70°C. The water acts as a plasticizer after storing at the lower temperature. Another mechanism is that at the higher temperature a type of sintering of the polymer particles may occur forming a closer structure of the sealant which to a certain extent also explains the steep increase in the hardness after heat-ageing (Figs. 4.26 and 4.27). A loss of plasticizer is a third explanation.

As has previously partly been discussed, where Material No. 8 is concerned, the rate of oxidation takes place more rapidly when the temperature is increased. This oxidation forms a thicker and harder skin, Fig. 4.29, which explains the higher levels of the heat-aged curves in Fig. 4.28. The sealant contains vegetable oil as a binder and there could also be some solvent in the material, (cf. Chapter 4.9.2). The loss of solvent naturally contributes towards a harder material.

The use of heat storing as a means of accelerating the ageing of the different sealants has proved to be useful in some cases. For example, for Material Nos. 3 and 8 connections have been observed between natural and accelerated ageing. However, there are some pitfalls present (Material No. 1). These make general conclusions dangerous. Questions regarding these matters are discussed in Chapter 7.

4.5 The effect of moisture and alkaline action on sealants

4.5.1 Introduction

The action of moisture and alkali was studied by storing the specimens at +20°C on a sponge saturated with de-ionized water or a $Ca(OH)_2$ solution. This procedure could, for example, be similar to when a back-up material for some reason or other becomes saturated with water. The alkalic environment could arise in practice if a joint is located between concrete elements.

The pH-value of the de-ionized water was kept at 4-6 while the intended

value of the alkalic solution was 11. According to Grunau (1968) this could be a reasonable value similar to that of a concrete surface. However, the value dropped a little during the experiments. On the average the pH-value for the alkaline baths was 9-10.

The sealants were initially cured/hardened for 7 or 21 days at +20°C/50% RH before storage in the baths started. Testing was carried out after 14, 28 and 56 days of storage.

4.5.2 Results

All sealants showed a varying degree of water absorption and swelling during storage in the water or alkaline water environment. It was about the same level in both cases, cf. Chapter 4.9.2. In some cases this water absorption resulted in a softening of the sealant. The water acted as a plasticizer.

However, for Material Nos. 1 and 2 there were no significant effects of water and alkali exposure. Fig. 4.30 shows the stress at 50% elongation as a function of time in water or alkaline water for Material No. 1. This Figure may be compared to Fig. 4.11. It is obvious from the Figures that there are no significant differences in the results.

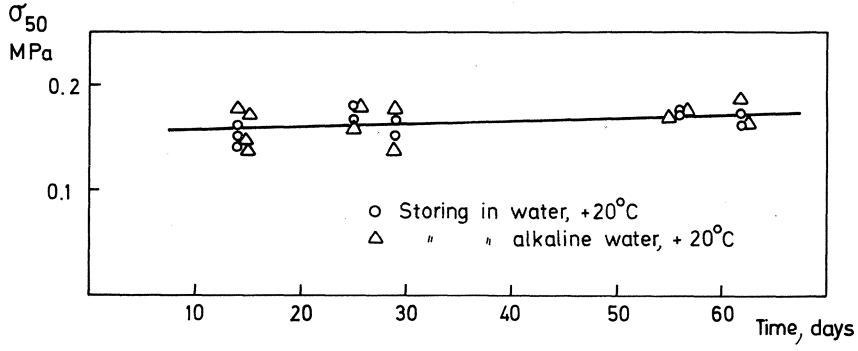


FIG. 4.30 Tensile stress at 50% elongation (= σ_{50}) for Material No. 1 as a function of storing time on water and alkaline water. Initial storing: 7 days at +20 °C/50% RH.

Material No. 3 showed a large swelling caused by water absorption (Chapter 4.9.2). This resulted in a softening of the sealant. If the material had been allowed to dry out, the previous water and alkaline storage would have resulted in a considerably larger increase in hardness than, for example, heat ageing at +40°C, Fig. 4.31 compared to Fig. 4.18.

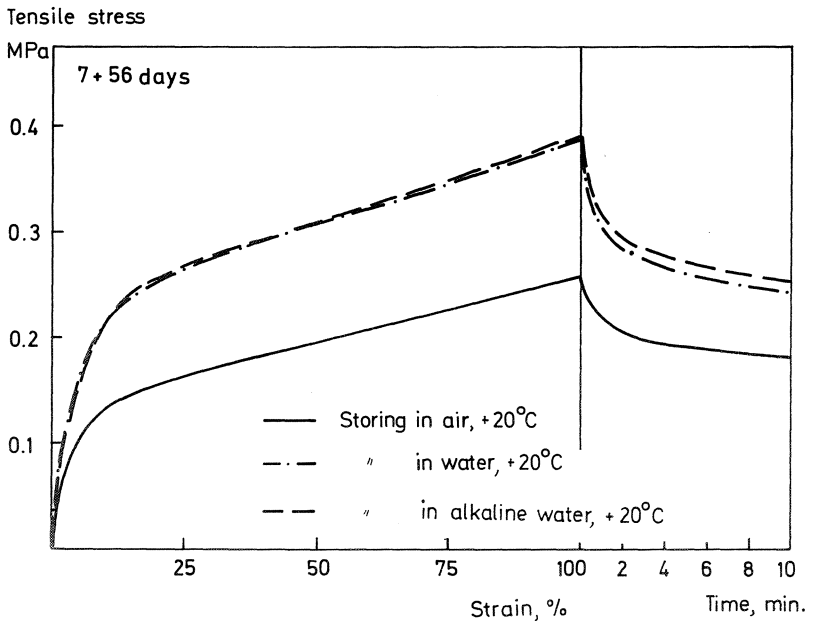


FIG. 4.31 Stress-strain curves for Material No. 3 after storing at +20 °C/ /50% RH, on water and alkaline water. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

As Material No. 3 is cured by the air humidity it is natural that the water storage decreases the curing time.

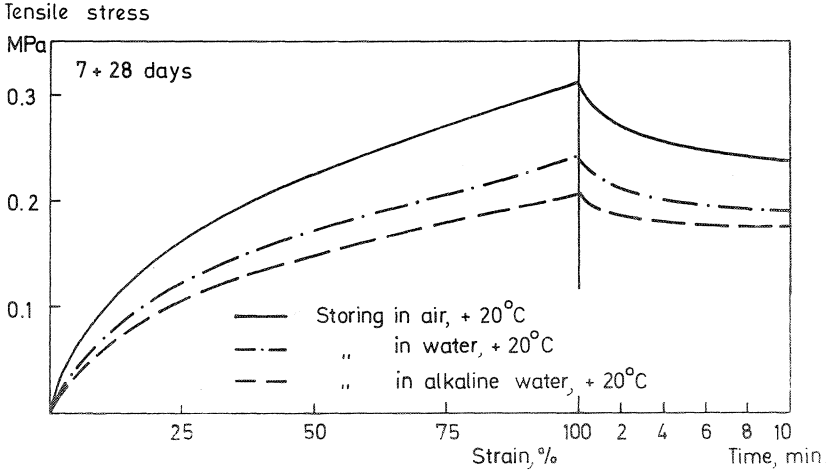


FIG. 4.32 Stress-strain curves for Material No. 4 after storing at +20 °C/ /50% RH, on water and alkaline water. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

For Material No. 4 storage in water and alkaline baths resulted in a certain softening. This is shown in Fig. 4.32. It depends on the fact that the material absorbs a certain amount of water during storage, Chapter 4.9.2. When the sealant was allowed to dry out it regained its "normal" elongation resistance.

There are no stress-strain curved to be shown for Material No. 5. This is due to the plasticity of the material and the fact that the material produces such a small deformation resistance that any possible differences are difficult to evaluate in this way. In Chapter 4.9.2 a certain amount of swelling is revealed when the sealant was stored in an alkaline bath.

Material No. 6 is also mainly plastic, but in Fig. 4.33 stress-strain curves are shown after storage in water and alkaline. If the curves are determined immediately after storage, it is obvious that the sealant has softened. This depends on the water absorption. An ocular inspection also showed that the joint profile had expanded and that the surface had started to break up. The latter was the case particularly where alkaline storage was concerned. If the specimens were allowed to

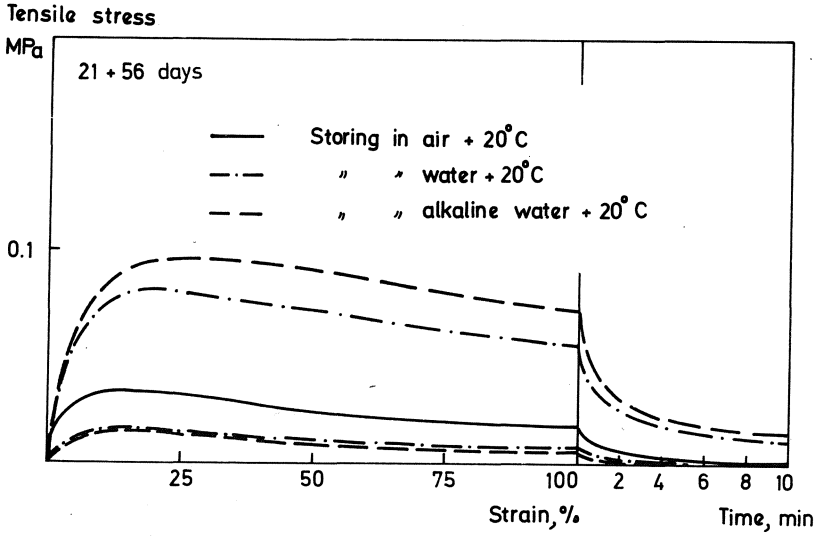


FIG. 4.33 Stress-strain curves for Material No. 6 after storing at +20 °C/ /50% RH, on water and alkaline water. The both upper curves are valid for specimens which were allowed to dry three weeks after the water and alkaline water storage. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

dry out, the result was an increase in hardness of the sealant instead (Fig. 4.33).

Material Nos. 7 and 8 were both found to be very sensitive to storage in water and alkaline water. They showed a very rapid water absorption, cf. Chapter 4.9.2. Therefore there was no point in determining stress-strain curves for these materials.

4.5.3 Discussion

It is evident that water, the element which sealants are supposed to protect us against, has a great effect on most sealants. Therefore, sealants must be protected against long-time contact with water. In the design of a joint, back-up materials which might absorb water should be avoided.

For many sealants contact with water led to a water absorption and a softening which were reversible. However, Material Nos. 6-8 should not be used even where there is a risk for just a short-time contact with water, especially if there an alkaline influence is present.

Today, sealants similar to Material No. 7 are marketed as suitable for most types of joints. As is the case where all building materials are concerned, this universal use is not to be recommended.

4.6 The effect of radiation action on sealants

4.6.1 Introduction

When observing the effect of radiation, the purpose was to examine only the effect of UV radiation on the sealants. However, most of the available UV sources had a large part of their energy outside the UV range. Therefore a low effect lamp was chosen (type OSRAM HNS 15 W, ozone free).

Six of these light sources were placed in a cylinder where specimens could be fixed on the inner wall. The temperature in the cylinder was maintained constantly at about +20^{o}C.

Storage in UV light was started after 7 days initial curing/hardening at +20^{o}C/50% RH. For some of the sealants testing was carried out after 14, 28 and 56 days in UV light. Some sealants were also stored for a longer period of time.

4.6.2 Results

Generally speaking, the UV radiation only slightly affected the sealants. For example, this was in the form of a change in colour, a dull surface, wrinkling and in certain cases cracking.

As an example of the latter, Fig. 4.34 shows a SEM photograph of a polysulfide sealant exposed to UV radiation for 21 days. The cracking

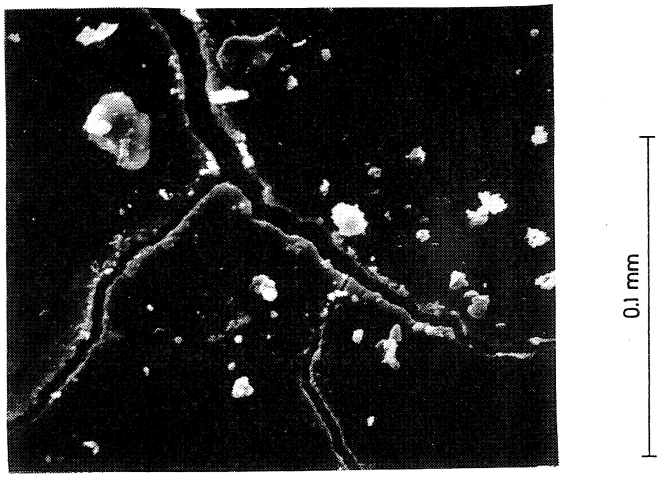


FIG. 4.34 SEM-photograph of the surface of a polysulfide-based sealant UV-irradiated for 21 days. Enlargement 600x. Photo: The Zoological Institution of Lund University.

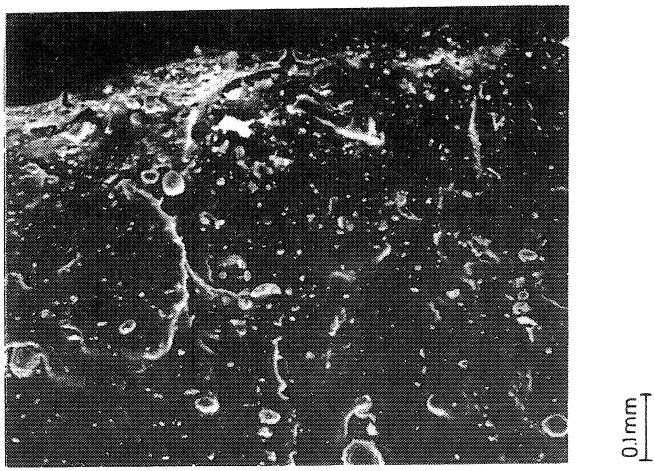


FIG. 4.35 SEM-photograph of a cut through a UV-irradiated polysulfide sealant according to Fig. 4.34. Enlargement 120x. Photo: The Zoological Institution of Lund University.

appears to go deep into the sealant. A cut through the material, Fig. 4.35, shows that the effect of the UV radiation is of a very superficial nature. However, it is both possible and probable that this effect contributes in the long run to an increased cracking when UV light is combined with varying joint movements, cf. Chapter 5.3.

Using the stress-strain curve as an evaluation method, it was not possible to reveal any crackings. The cracks were probably too shallow to be seen on the stress-strain curve.

However, an example of the results will be given. Fig. 4.36 shows the stress at 50% elongation after different periods of UV light exposure. This Figure should be compared to Fig. 4.11. There is no significant difference between the measured stresses even after long periods of UV exposure.

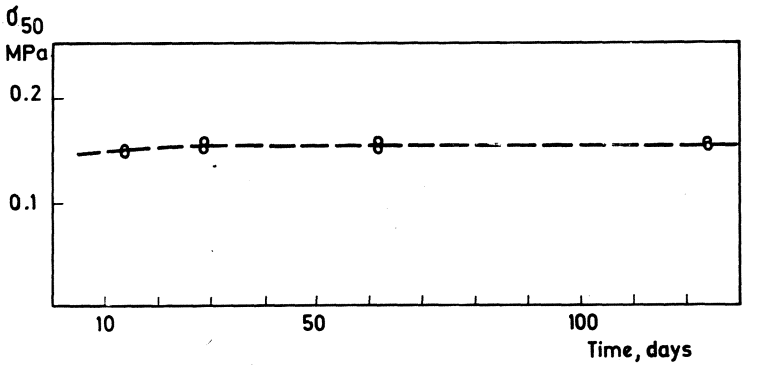


FIG. 4.36 Tensile stress at 50% elongation (= σ_{50}) for Material No. 1 as a function of storing time in UV-light. Initial storing: 7 days at +20 °C/50% RH.

Ocularly, there were some surface changes on all sealants. These changes are described in Table 4.2.

The sealant which showed the smallest changes due to the UV exposure was Material No. 4. Therefore some SEM photographs were taken of the surface of a specimen exposed to UV radiation during 28 days, see Fig 4.37. The sealant was tested, i.e. elongated to 100%, before the picture was taken. There is an obvious crack pattern due to the UV exposure.

TABLE 4.2 The effect of UV radiation on the sealants

Material No.	Surface change
1	Dullness
2	Dullness
3	Dullness; cracking visible with the naked eye
4	Dullness
5	Dullness; formation of a skin; small cracks
6	" " " " " " "
7	Dullness; very small cracks
8	Dullness; formation of a wrinkled skin

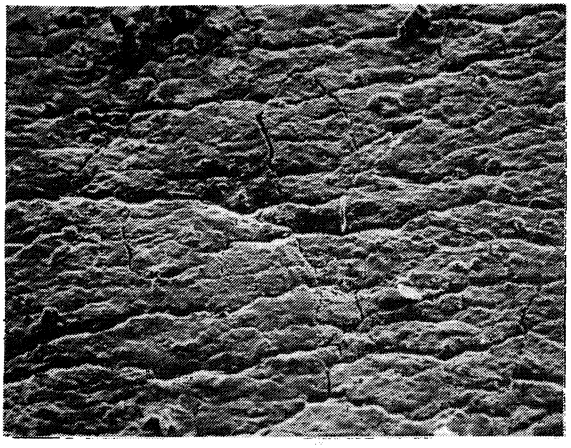


FIG. 4.37 SEM-photograph of the surface of Material No. 4 after UV-irradiation for 28 days. Initial storing: 7 days at +20 °C/ /50% RH. The specimen has been elongated 100% before photographing. Enlargement 240x. Photo: The Zoological Institution of Lund University.

4.6.3 Discussion

As has been shown the effects of the UV irradiation itself are very small, almost negligible. But, when choosing appropriate UV sources for studying the effect of UV radiation, it is important to choose a reasonable UV source. Different types of materials absorb radiation of diffe-

rent wavelengths. Therefore, it is possible that an incorrectly chosen UV source hits some types of material unnecessarily hard or, on the other hand, favours some UV-sensitive materials. Because of this, it would be interesting to try other UV sources as well and furthermore, also combine the UV light with e.g. water, cf. Chapter 4.8.

4.7 The effect of ozone action on sealants

4.7.1 Introduction

The effect of ozone has been studied on all the sealants shown in Table 4.1. In literature it has been pointed out that ozone cracking only occurs if a rubber material is elongated, that is, it has an internal tensile stress. Some of the chosen sealants were regarded as being much too plastic for the elongation to be of any value. For this reason, the sealants were divided into two groups, according to Table 4.1:

Group I, comprising mainly elastic sealants, consisted of Materials Nos. 1-4 and Material No. 7.

Group II, comprising mainly plastic sealants consequently consisted of Materials Nos. 5-6 and Material No. 8.

In spite of group II comprising sealants without tensile stresses it was considered to be of interest to study if any other effects of ozone might occur.

The other test conditions had to be adapted to the standards valid for this range. These included e.g. ozone level, time and storage temperature (+30^{o}C). The test plan for the effect of ozone is shown in Table 4.3.

The specimens which were to be stored under tensile stress were elongated in the laboratory before they were transported to the rubber factory where the ozone exposure was carried out. Where these specimens were concerned, it meant that the stress built up in the sealants had time to relax to a certain extent before the exposure began. In order to estimate the amount of stress relaxation, dummy specimens elongated 25 or 50% were used.

TABLE 4.3. Test of ozone resistance, experimental plan

VARIABLES	LEVELS	NOTE
Ozone content	50 pphm 200 pphm	
Age	35 days	Half the number of specimens were heataged 14 days at +70°C
Time	1x96 h	
Deformation	0% 25% 50%	Sealants in group No. I and II Sealants in group No. I Sealants in group No. I

After the exposure the specimens were inspected ocularly. Stress-strain curves were determined and some SEM photographs were taken for a couple of the sealants.

4.7.2 Results

Adhesive failure was frequent on specimens which were kept under elongation during the exposure. This was especially the case for Material Nos. 1, 2 and 7. Of these specimens, those which were heat aged in advance usually showed better adhesion.

No effects of the ozone on materials that were not elongated were observed. Of the elongated specimens only both the polysulfide sealants were affected by ozone, and the tendency was fairly evident: The largest cracks and the most frequent ones appeared in the harder sealant, Material No. 2. Furthermore, the most severe effect occurred at 50% elongation and at an ozone concentration of 200 pphm.

Fig 4.38 valid for specimens of Material No. 1 elongated 50% during the ozone exposure, shows a certain decrease in the deformation resistance to the highest ozone content. The reason for this is shown in Fig 4.39. The specimen shows typical ozone cracks oriented at right angles to the direction of the elongation.

Fig. 4.40 shows that ozone cracks in Material No. 2 occurred both at 25 and 50% elongation at 200 pphm.

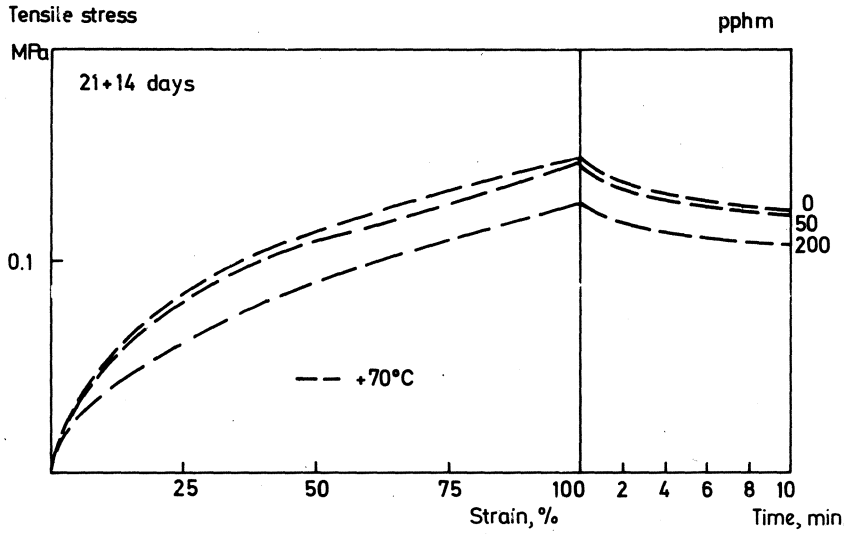


FIG. 4.38 Stress-strain curves for Material No. 1 after storing at 50% elongation and different ozone levels. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

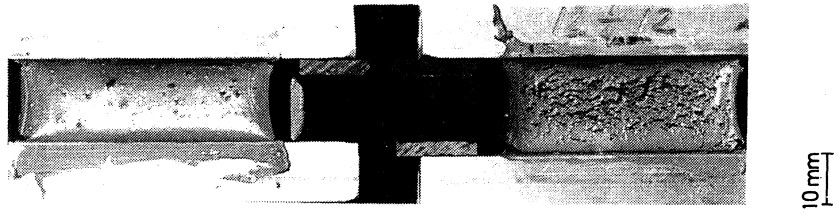


FIG. 4.39 Heat aged specimens of Material No. 1 after storing at an ozone concentration of 200 pphm. The specimen to the left elongated 25% and the specimen to the right 50% at the ozone exposure.

FIG. 4.40 Heat aged specimens of Material No. 2 after storing at an ozone concentration of 200 pphm. The specimen to the left elongated 25% and the specimen to the right 50% at the ozone exposure.

Some SEM photographs were taken of a couple of sealants in order to see if any changes in a micro scale could be detected. As an example Fig. 4.41 shows the surface of Material No. 4. The sealant was stored elongated 50% at 200 pphm. After that the stress-strain curve was determined in the usual way, i.e. up to 100% elongation. Ocularly, the sealant did not show any cracks or failures. Apparently some cracks did occur and they passed between the small "mountains" as seen on the Figure. These mountains consist of filler particles. The cracks are not caused by ozone exposure, as corresponding photographs of specimens not exposed to ozone showed the same crack pattern.

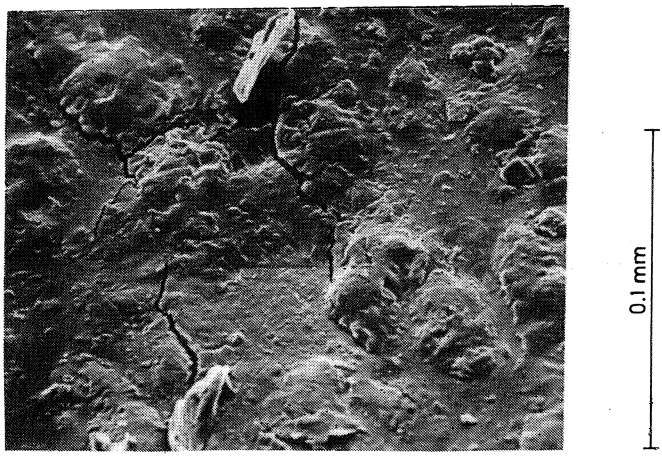


FIG. 4.41 SEM-photograph of the surface of Material No. 4 after storing at 50% elongation and an ozone concentration of 200 pphm. The specimen has been elongated 100% before photographing. Enlargement 600x. Photo: The Zoological Institution of Lund University.

4.7.3 Discussion

The only sealants which were found to be affected by ozone exposure were Material Nos. 1 and 2. These sealants both contain polysulfide as a binder. In Damusis (1967) it is said "that polysulfide sealants have excellent resistance to ozone, ageing, ...". In spite of this, results of ozone exposure have been found here.

It is not impossible that the ozone exposure also affected other sealants. According to Dolezel (1978) a brittle surface layer forms on many polymeric materials during ozone influence. This layer prohibits further diffusion of the ozone into the material, and therefore the attack

ceases. However, with the evaluation methods used here, the results have not been possible to detect and are therefore negligible.

As has been shown, both the degree of elongation and the ozone concentration as well as the type of polymer affect the results. The chosen levels of both can naturally be discussed. However, elongations of 25 and 50% are fairly reasonable and may occur in practice. An ozone content of 50 pphm may also occur in practice, cf. Chapter 2.6.

It has been discussed in literature whether or not any threshold value of the stress exists, i.e. the lowest value for cracks to occur. In Dolezel (1978) such a value is given for one quality of rubber. However, some people say that such a value does not exist. It is just a question of time if the material has a molecular structure that is sensitive to ozone attack. Generally speaking, the greater the amount of elongation the shorter the time until ozone cracks occur. The ozone cracks occur not only at static, but also at dynamical deformations. However, the ozone crack formation is smaller under dynamical stresses compared to equal large static ones.

The time required until the first crack occurs depends upon the ozone concentration according to the connection (Dolezel (1978))

$$\tau = k/C^{\alpha}$$

where τ = time until the first crack occurs

C = ozone concentration

k, α = coefficients

Examples of values of the coefficients are not given. The test material in this investigation is too small to be applied where this is concerned. But it should be possible to obtain such a connection for a polysulfide sealant in a more comprehensive study.

Of the ozone sensitive sealants, Material No. 2 was found to be more sensitive than Material No. 1. The explanation for this is that Material No. 2 has a considerably higher polymer content and is also harder. If the polymer itself is also sensitive to ozone attack, then both these facts contribute to more ozone cracks: A higher polymer content gives more

sensitive bonds per unit volume of the sealant, and in a harder sealant greater stresses occur compared to a soft sealant with the same deformation.

In Table 4.4 the stresses at 25 and 50% elongation are shown for the elongated sealants. As can be seen the stresses are considerably greater for Material No. 2 compared to Material No. 1, even after a long period of stress relaxation. Material Nos. 3 and 4 did not appear to be sensitive to ozone in spite of greater stresses being built up during elongation and relaxation.

TABLE 4.4. Stress relaxation at +22°C and different levels of deformation and curing

Material No.	σ_{25} MPa		σ_{50} MPa		% Remaining stress after t hours			
					σ_{25t} MPa		σ_{50t} MPa	
	+20°C 50% RH	Heataged at 70°C	+20°C 50% RH	Heataged at 70°C	20/50	Heataged	20/50	Heataged
1	adhesive failure	0.07	adhesive failure	0.10	-	46 (t=25)	-	52 (t=65)
2	adhesive failure	0.34	adhesive failure	0.46	-	58 (t=46)	-	cohesive failure
3	0.10	0.27	0.15	0.29	52 (t=61)	33 (t=17)	49(t=53) 46(t=143)	41 (t=42)
4	0.09	0.14	0.15	0.16	62 (t=60)	44 (t=20)	54(t=50) 50(t=143)	52 (t=43)
7	0.05	0.22	0.12	0.34	19 (t=61)	15 (t=17)	17(t=53) 14(t=143)	16 (t=42)

4.8 Synergistic effects on sealants

In practice the previously mentioned weathering factors cooperate in a very complex pattern. The total effect can be very difficult to estimate as this cooperation may cause synergistic effects (Chapter 2.9).

There is a lot of equipment available on the market for accelerated ageing tests. A survey is given in Dolezel (1978). This equipment often combines heat, radiation and moisture in certain programs.

In Gjelsvik (1975) the specially built equipment is described, where low temperatures are also included in a certain cyclic program.

These types of apparatus often produce very valuable information, as some synergistic effects may also be revealed. However, if the proportions or concentrations of the factors are chosen wrongly misleading results may arise. Therefore, it should be interesting to know the action of the different factors separately.

In this investigation the effects of one action of the different factors have been studied. Just in a few cases combinations of different factors have been used. E.g. mechanical stress and ozone, heat and ozone. Naturally outdoor exposure has also produced a combination of all the factors in a slightly accelerated way, Chapter 5.

In spite of this, more combinations would be of interest and should be examined. Such combinations are e.g. heat plus radiation, moisture plus radiation. Due to lack of time it has not been possible to carry out these studies.

4.9 Shrinkage and shrinkage stresses in sealants

4.9.1 Introduction

As previously mentioned (Chapter 4.1) the determination of weight- and volume-loss was used as a method of evaluation when determining changes in the sealants after different forms of ageing.

A large amount of shrinkage may affect the function of a sealant considerably. E.g. a large amount of shrinkage may be followed by a great increase in the hardness. Furthermore, in Agri et al (1973) it was pointed out where water-dispersed acrylic sealants are concerned a large amount of shrinkage causes tensile stresses in the joint. Whether or not this is true, some sealants used in manufacturing of insulated glass revealed very high tensile stresses due to shrinkage and curing. In some cases these stresses were so high that the edges of the glass were also broken!

In ordinary building joint sealants a moderate shrinkage may have a positive effect: From a movement capability point of view the sealant has a better profile, the bi-concave cross-section, cf. Fig. 4.42.

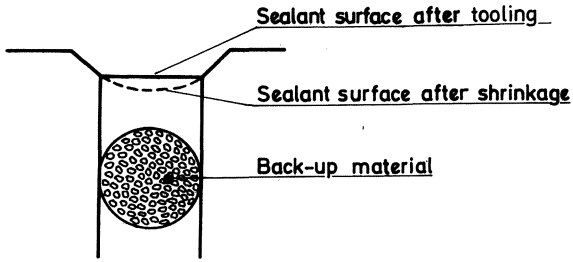


FIG. 4.42 A certain amount of shrinkage gives a better profile from the movement capability point of view.

The shrinkage and weight-loss were determined for all the sealants according to Table 4.1. The different types of storage were:

- +20°C/50% RH
- +40°C
- +70°C
- water +20°C
- alkaline water +20°C pH 9-11
- UV radiation +20°C

Storage in these conditions was usually started after storage for 7 days at +20°C/50% RH. However, heat storage at +40°C and +70°C was also started after 21 days in a normal climate, +20°C/50% RH.

The investigation was started in a Master thesis (Nimmermark et al (1976)) and was later completed by the author.

The measurements of shrinkage stresses that might occur were made in the equipment according to Fig. 4.1 and in a specially built frame, Fig. 4.43. Measurements were carried out for Material Nos. 1, 3, 7 and 8. The temperature was +22 ± 1°C.

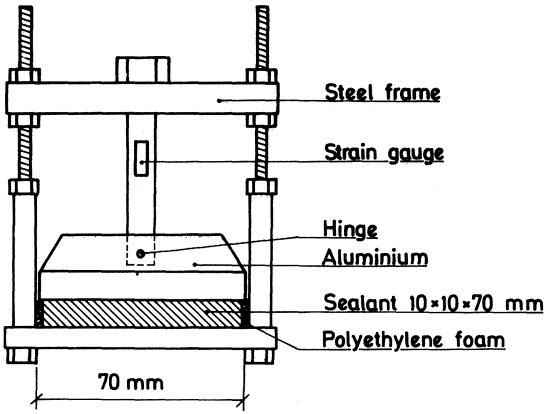


FIG. 4.43 Device for measuring of shrinkage stresses.

4.9.2 Results

Figs. 4.44-4.46, 4.48-4.52 show the results of the measurements of the volume loss for all sealants after storage in different climates. Each point is the mean value of two specimens.

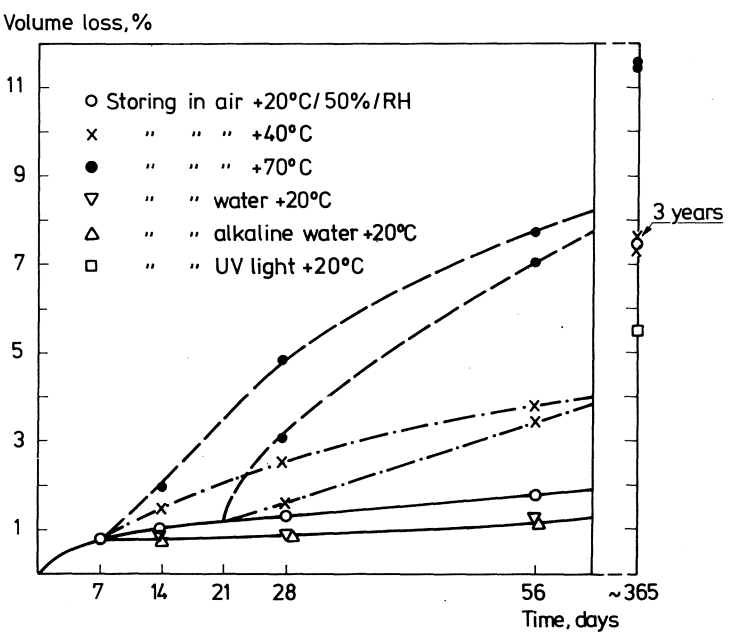


FIG. 4.44 Shrinkage as a function of storing time in different environments for Material No. 1.

Fig. 4.44 gives the results for Material No. 1. In a normal climate +20°C/50% RH there is a continued decrease in volume. Note the high amount after three years! When comparing weight and volume loss it is possible to calculate the density of the component of the sealant that disappeared. This density was 130 kg/m^3 and disagrees with the densities of any volatile components, solvent and plasticizer, which may have disappeared. Evidently there must have been a chemical change in the sealant which caused a contraction of the bulk.

It appears from the Figure that the time necessary to reach the volume loss 7.5% is considerably shorter if the temperature is raised. This level is reached after about one year if the temperature is +40°C and after about 42 days if the temperature is +70°C. The well-known rule of thumb, saying that a temperature increase of 10°C doubles the rate of a chemical reaction can be applied also in this case: A temperature increase from +20 to +40°C increases the reaction rate by a factor 4 (in this case 3) and an increase from +20 to +70°C increases the rate by a factor 32. The factor found here is about $3 \times 365/42 \approx 26$.

Thus, it should be possible to accelerate this spontaneous curing and shrinkage by means of a simple heat ageing of the sealant.

If the heat ageing continues for a long time there is a great loss of plasticizer. The shrinkage after about one year is 11.5%.

If the sealant is stored in water or alkaline water the liquid is absorbed and the volume loss decreases.

The conclusions drawn for Material No. 1 are, with one exception, also valid for Material No. 2, Fig. 4.45. The heat ageing at +70°C does not produce the same rapid volume loss in this case. However, after one year the levels are almost the same. This difference might be due to the fact that the plasticizer is caught within a denser molecular structure in Material No. 2, and therefore it evaporates more slowly.

Fig. 4.46 shows the results for Material No. 3. There is a large volume loss even when the sealant is stored in a normal climate, but most of it is completed already after 8 weeks. The rule of thumb regarding the heat ageing is probably also valid in this case.

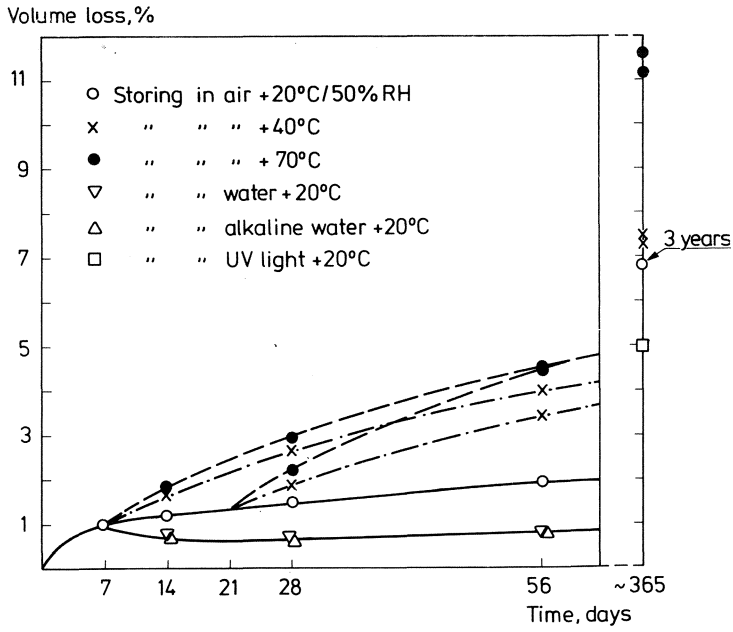


FIG. 4.45 Shrinkage as a function of storing time in different environments for Material No. 2.

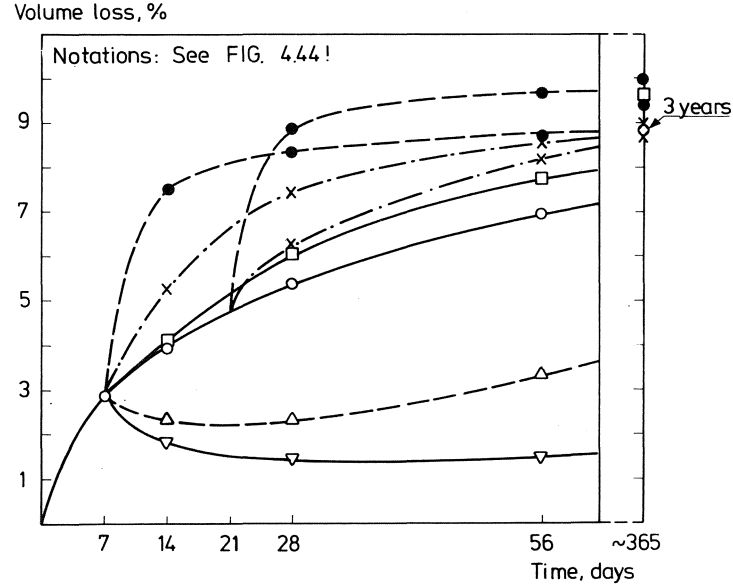


FIG. 4.46 Shrinkage as a function of storing time in different environments for Material No. 3.

However, if heat storage at +70°C is started later, there is an increased volume loss. Considering the weight loss as a function of time, Fig. 4.47, it is obvious that this is the same in the both cases. Evidently, there is a pore formation in the sealant due to rapid evaporation of the solvent if the heat ageing is started too early.

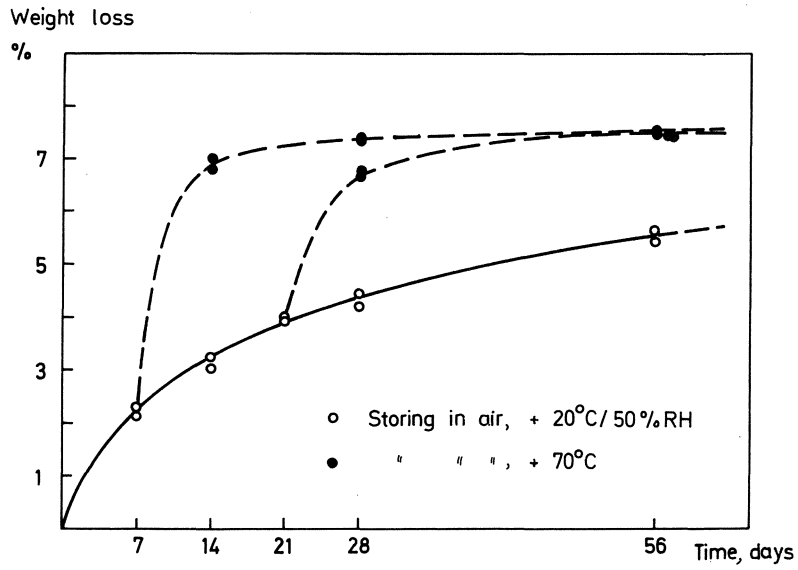


FIG. 4.47 Weight loss as a function of storing time at different temperatures for Material No. 3.

When calculating the density of lost substance this is found to be about 910 kg/m^3 in a normal climate. This corroborates with the density of solvent. If the heat ageing at +70°C is started after 7 days the density is 977 kg/m^3 and after 21 days 896 kg/m^3. The "true shrinkage" is evidently obtained in the latter case.

Storage in water and alkali results in considerable absorption of the liquid. The degree is higher where storage in water is concerned.

Exposure to UV radiation caused a higher volume loss compared to storing in a normal climate. The UV light made the surface brittle and cracks occurred which might explain the greater amount of shrinkage.

The results for Material No. 4 are shown in Fig. 4.48. The volume loss in a normal climate is to a large extent completed within eight weeks. When heat ageing at +70°C the shrinkage increases very quickly and therefore the rule of thumb is not valid in this case. This is due to the shrinkage caused by the evaporation of a plasticizer and not a chemical reaction.

This sealant is sensitive to moisture storing as there is rather a large amount of water absorption.

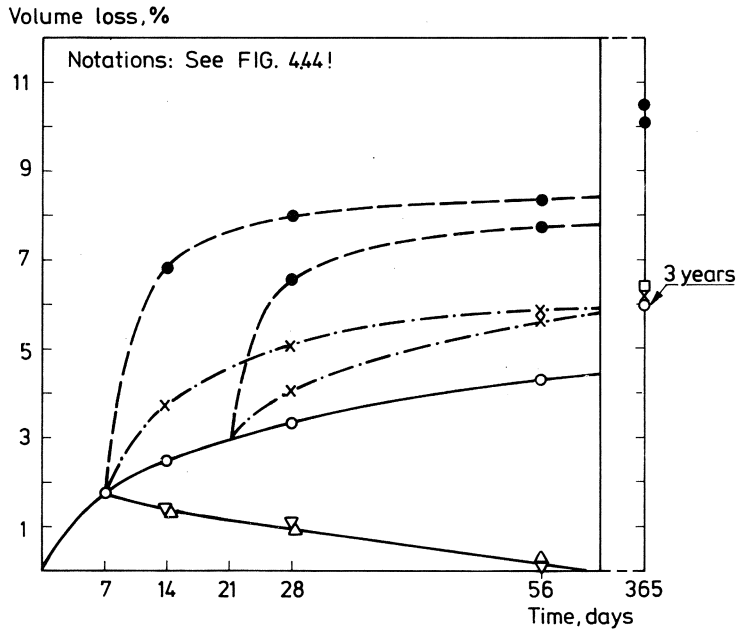


FIG. 4.48 Shrinkage as a function of storing time in different environments for Material No. 4.

The results of Material No. 5 are shown in Fig. 4.49. The volume loss after storage at different temperatures depends on the solvent loss. If the heat ageing at +70°C is started too early one obtains a false volume loss due to the formation of pores within the sealant. The sealant absorbs water during storage in alkaline water.

Almost the same conclusions are valid for Material No. 6, Fig. 4.50. However, sensitivity to an early start of the heat ageing is more pronounced. Furthermore, there is more water absorption during storages in water and alkaline water.

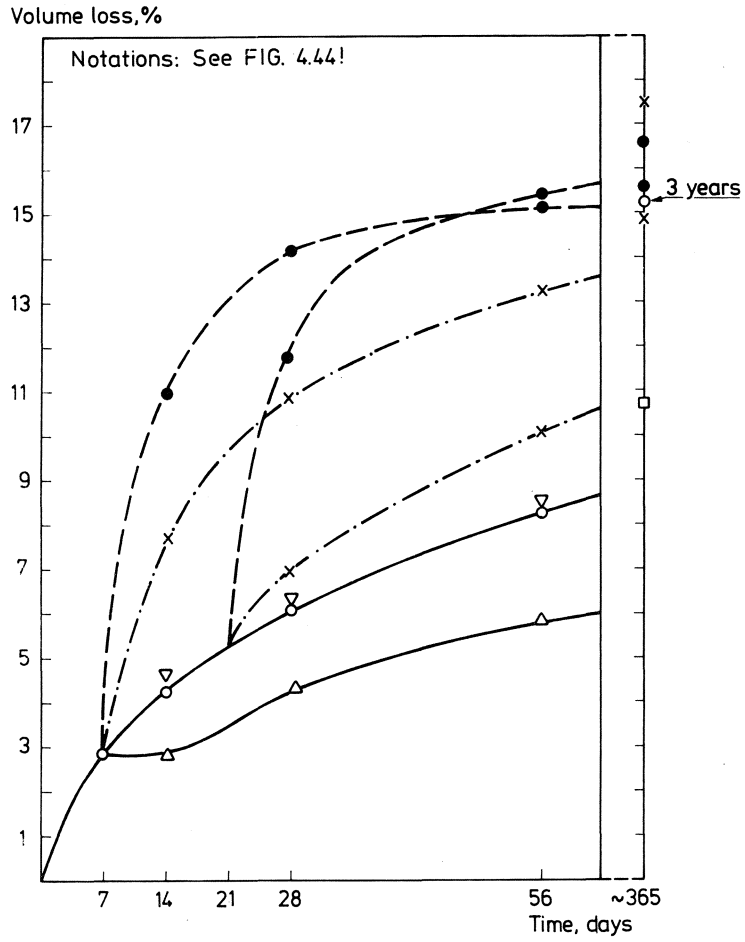


FIG. 4.49 Shrinkage as a function of storing time in different environments for Material No. 5.

Material No. 7 is a water-dispersed acrylic sealant. The results are shown in Fig. 4.51. The sealant hardens during the evaporation of water. The water content is about 24% by volume. Most of it vanishes very quickly. There is a tendency to a formation of pores if the sealant is heat aged too rapidly. This explains why the volume loss is higher if the heat ageing is started after three weeks at +20°C/50% RH compared to one week in the same climate.

Storage in water or alkaline water is fatal for the sealant. The moisture storage began after one week. Very shortly after that, the sealant absorbed water and was destroyed.

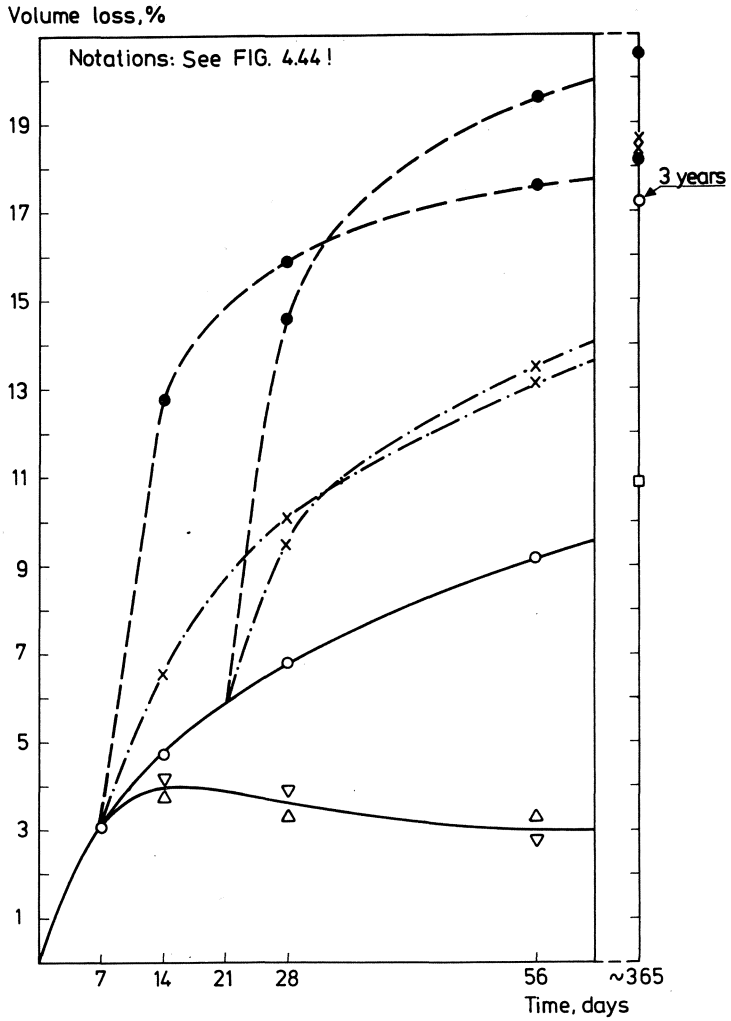


FIG. 4.50 Shrinkage as a function of storing time in different environments for Material No. 6.

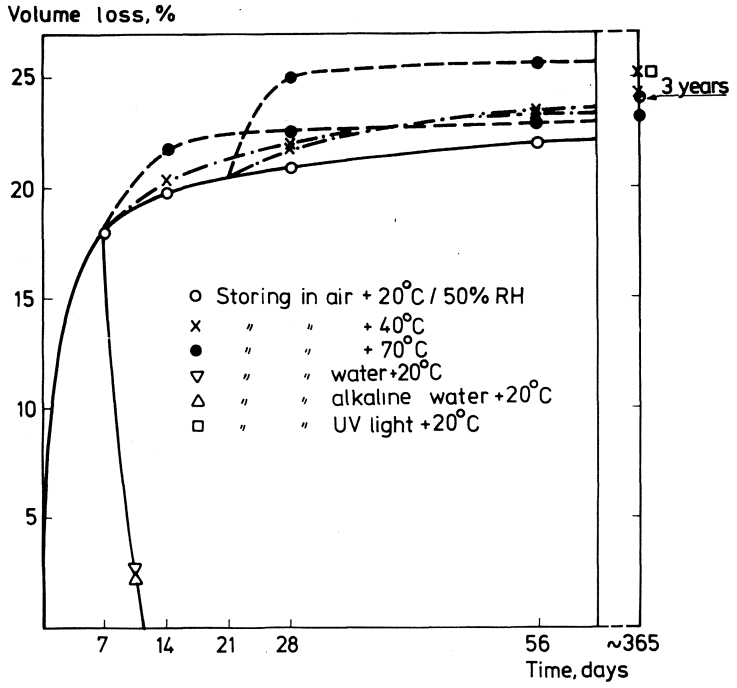


FIG. 4.51 Shrinkage as a function of storing time in different environments for Material No. 7.

For Material No. 8 the results of the volume loss as a function of time are shown in Fig. 4.52. The shrinkage continues for a long period of time in a normal climate. The processes going on are mainly the evaporation of the solvent and oxidation of the binder. The more the oxidation progresses the denser the sealant becomes and therefore the rate of evaporation diminishes. An increase in the temperature speeds up these processes. The rule of thumb previously mentioned applies quite well in this case.

As can be seen there is a large amount of water absorption during the moisture storage. This is surprising, as the binder is a vegetable oil which should be hydrofob. Obviously, other components in the sealant contribute to this sensitivity to water.

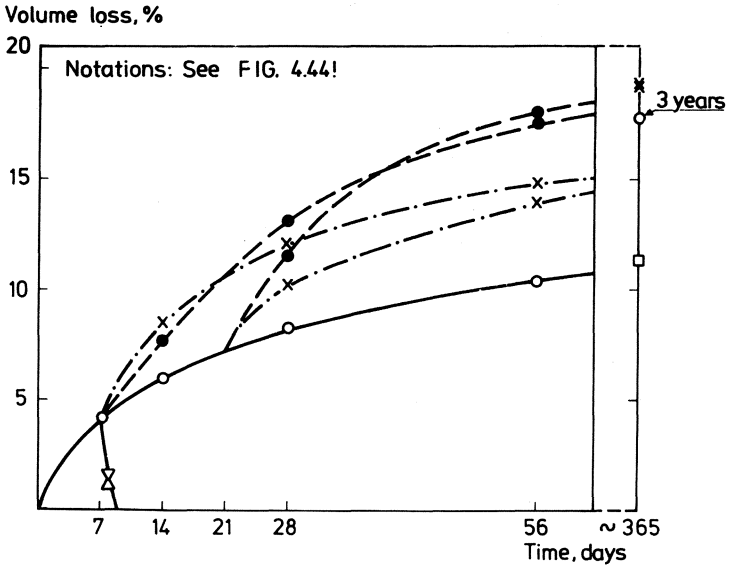


FIG. 4.52 Shrinkage as a function of storing time in different environments for Material No. 8.

The results of the measurements of the shrinkage stresses are summarized in Table 4.5.

TABLE 4.5. Shrinkage stresses after different times of ageing

Material No.	Age days	Shrinkage vol-%	Measured stress MPa	Maximum error in measurements MPa	Maximum shrinkage stress MPa
1	12	1	0	$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$
3	27	5.5	$3 \cdot 10^{-3}$	"	$5 \cdot 10^{-3}$
3	27	5.5	$6 \cdot 10^{-3}$	10^{-4}	$6.1 \cdot 10^{-3}$
3	46	6.5	$12 \cdot 10^{-3}$	10^{-4}	$12.1 \cdot 10^{-3}$
7	31	21	$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$4 \cdot 10^{-3}$
7	46	22	$<5 \cdot 10^{-3}$	10^{-4}	$5.1 \cdot 10^{-3}$
8	46	10	0	10^{-4}	$0.1 \cdot 10^{-3}$

As it was a question of measuring very small stresses there was some uncertainty regarding the measurements. The equipment according to Fig. 4.43 is sensitive to changes in temperature etc. Therefore an approximation of the measuring accuracy was made. This resulted in a general addition ($=2 \cdot 10^{-3}$ MPa) to the measured values.

Measurements were also made with the help of the equipment shown in Fig. 4.1. The measuring accuracy was then less than 10^{-4} MPa

Consequently the results obtained from the measurements showed that the shrinkage stresses due to shrinkage are very small. The shrinkage stress is greatest for Material No. 3. The value $12.1 \cdot 10^{-3}$ MPa could be compared with the tensile stresses occurring in the material at a very low deformation (Fig. 4.18). At 1% deformation the tensile stress was about the same as the shrinkage stresses that occurred.

Corresponding comparisons for the other sealants resulted in even smaller deformations.

4.9.3 Discussion

All sealants show a considerable volume loss even after storing in a normal climate. The results are summarized in Table 4.6. The values given by the manufacturers are also shown. The differences are considerable in some cases.

TABLE 4.6. Weight and volume loss after 3 years at $+20^{\circ}C/50\%$ RH

Material No.	Weight loss %	Volume loss %	Density of lost substance kg/m^3	Volume loss according to the manufacturer
1	0.6	7.6	130	"negligible"
2	0.9	6.8	200	"no shrinkage"
3	6.8	8.8	910	no information
4	3.7	6.0	730	"7%"
5	9.8	15.2	870	"moderate"
6	11.1	17.2	910	"10%"
7	15.8	23.7	1000	no information
8	8.0	17.7	680	"15%"

A rough approximation of the density of the lost substances is obtained by means of the weight and volume loss. The calculated densities of the lost substances agree well with the anticipated values. E.g. the value for Material No. 5 is 870 kg/m^3. The density of Toluol is 890 kg/m^3 and of Xylol 870 kg/m^3. For Material No. 7 the lost substance is evidently water. However, the densities of the lost substances of other sealants are too low. This must be explained by a contraction of the structure due to a continued chemical curing. This is particularly true where Material Nos. 1 and 2 are concerned. It is therefore possible to determine such changes by using this very simple method.

Furthermore, it is possible to accelerate the mechanism by heat ageing the sealants. The processes concur fairly well the thumb of rule regarding the chemical reaction rate, i.e. heat ageing increases the changes by a factor of about 2 for every increase in the temperature of 10^{o}C.

5. OUTDOOR EXPOSURE OF SEALANTS

5.1 Introduction

The purpose was to compare the results obtained from the accelerated ageing in the laboratory with ageing results closer to reality. This can of course be done by comparing laboratory tests with tests on sealants used in buildings. However, problems arise regarding the evaluation of changes and the formulation of the sealants might also have changed during the time when the tests were being carried out. It is also important to carry out the outdoor tests during conditions which can easily be controlled and at the same time as they accelerate the degradation. But, the comparisons with buildings are both interesting and important and must not be neglected.

In order to expose the sealants to almost natural weathering conditions and at the same time as they were tensioned/compressed, special equipment was built.

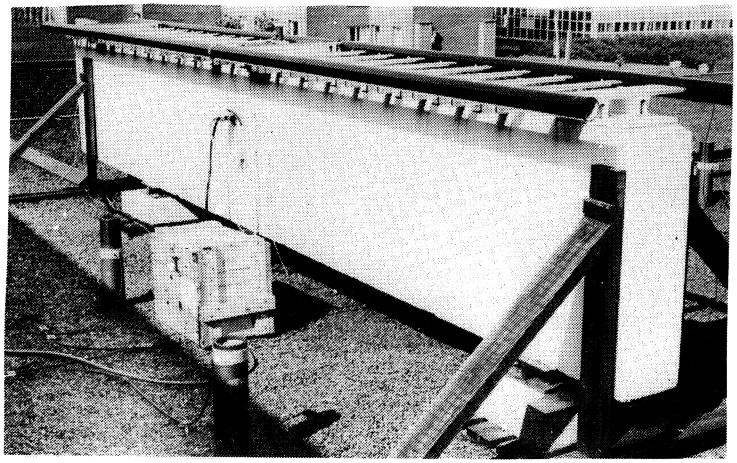


FIG. 5.1 A survey of the testing equipment for outdoor exposure of specimens.

5.2 Equipment for outdoor exposure of joint specimens

A survey of the equipment is shown in Fig. 5.1. The equipment consists of an aerated concrete element (250 x 900 x 6000 mm) placed on one fixed and one rolling bearing respectively. Two aluminium tubes, connected with "rungs" of aluminium, are placed on this element. This "ladder" is fixed to the aerated concrete at one end and to a roller bearing at the other end.

Specimens can be fixed between this ladder and the aerated concrete element. This means that the joint width of each specimen will change according to the changes in the humidity and temperature of the white painted element and the temperature of the black painted aluminium ladder. The fixation of the specimens is made in such a way that the specimens are compressed when the temperature increases.

Assuming that

- the variation in temperature of the aluminium ladder is within the range -20 - +50°C
- the variation in temperature of the aerated concrete is within the range -20 - +35°C
- $\alpha_{\text{aerated concrete}} \approx 8 \cdot 10^{-6}$ m/m°C
- $\alpha_{\text{aluminium}} \approx 24 \cdot 10^{-6}$ m/m°C
- the moisture depending movements of the aerated concrete could be neglected

the maximum difference in length could be about 7.0 mm. This change in dimension will decrease linearly towards zero, where the aluminium ladder is fixed to the aerated concrete.

Thermo couples were placed on the construction, which is located in a north-south direction. Thermo couples were also placed in sealants of different colours. The maximum difference in movement was measured by means of an inductive deformation gauge. The light intensity, i.e. the amount of sunshine, was measured with a photoelement. All measured values were registered on a 12-channel point recorder.

At least eight specimens of each sealant were exposed in the outdoor equipment. Regardless of the curing or hardening mechanism each material was kept 7 days at +20°C/50% RH before being applied. This meant that the hardening of the chemically curing sealants and the water-dispersed acrylic sealant was fairly advanced, even if these were far from being fully cured, cf. Chapter 4.4.

Materials Nos. 5-6 and 8 were extremely plastic when placed outdoors.

Half the specimens had asbestos cement as a substrate and the other half aluminium. This was done in order to combine the climatic influence with a certain alkaline influence. The pH-value of water pouring over the asbestos cement was 9-10.

The specimens were applied at +5 - +10°C in the autumn. With a supposed maximum variation in temperature of -20°C - +50°C, this meant that the specimens would be compressed to a greater extent than elongated, which was also the intention. There are indications which show that compressive movements cause greater strain on a sealant than a corresponding elongating movement (Andersson and Hasselblad (1972), Hockman (1975)). This depends on the fact that large local deformations occur during compression and that stress relaxation is greater at higher temperatures (the temperature is often higher when a sealant is compressed).

Concerning the chemically curing elastic sealants, Material Nos. 1-4, another application of specimens was made during the spring and at a temperature of about +12°C. These specimens were cured longer before installation: About 100 days in a normal climate and one week at +40°C.

When choosing the position on the aluminium ladder, the basis used was the movement capability stated by the manufacturers. From the largest to the smallest joint movements, the order of the sealants was consequently: Material Nos. 4, 6, 3, 8, 1, 2, 7, and 5.

Specimens of each sealant were also applied where they were exposed to about half the maximum joint movement for the respective material used.

5.3 Results

Fig 5.2 shows examples of measured joint width variations on a sunny day with great temperature variations. The joint movement noted is the maximum joint width variation in the construction, i.e. at the end where the aluminium ladder is placed on movable bearings.

On this day the joint width changed by 3.35 mm. The speed of the joint movement according to the Figure is about 10^{-3}-10^{-2} mm/min. During a given time the joint width remained almost unchanged.

The change in temperature in the centre of the 250 mm thick aerated concrete element was naturally slower. The maximum atmosphere temperature in this case was around mid day while the highest temperature in the aerated concrete occurred about 6 hours later. The gradually increasing temperature inside the aerated concrete resulted in a subsequent change in joint width in spite of the ladder temperature remaining at about the same high level.

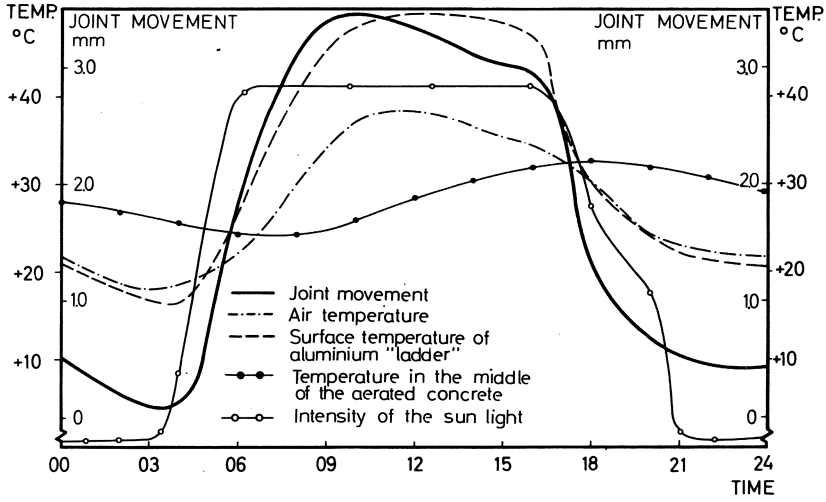


FIG. 5.2 An example of a day (750809) with large measured temperature variations and in connection to that joint movements in the outdoor equipment for exposure of specimens.

Fig. 5.3 shows a photograph of a chart from the point recorder. Note the partial drops during the intensity of the sunlight (channel 7). These are due to clouds passing by. The clouds change the temperature of the black aluminium ladder immediately (channel 5). This is directly followed by a change in the joint movement (channel 12), i.e. the sealants are exposed to rapid dimension changes.

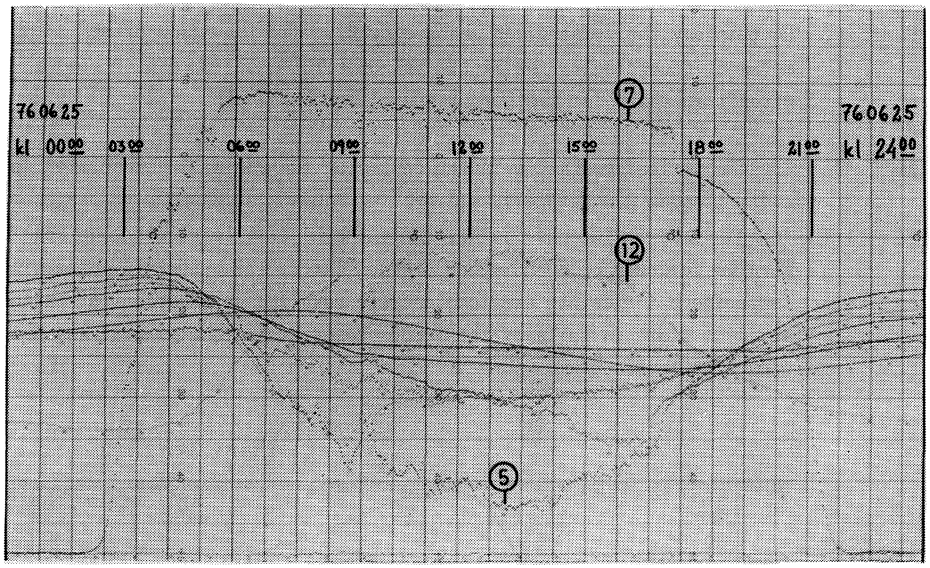


FIG. 5.3 Photo of a chart from the point recorder.

The rapid changes in temperature measured in the aluminium construction and the slow changes measured in the aerated concrete are very important in practice. This means that sealants between aluminium constructions will be exposed to a large number of joint width variations at a comparative high deformation rate. For example, the joint width will change when the sun is temporarily hidden behind clouds. When sealants are used between concrete or aerated concrete elements they will mainly be exposed to a fairly regular, approximately sinusoidal joint movement, varying over a period of 24 hours.

The variations of the maximum differences in length between the aerated concrete and the aluminium ladder at the end of the construction are shown in Fig. 5.4. The situation when the first series of specimens was installed is considered as origo. Length changes which cause elongation of the sealants are considered as a positive movement.

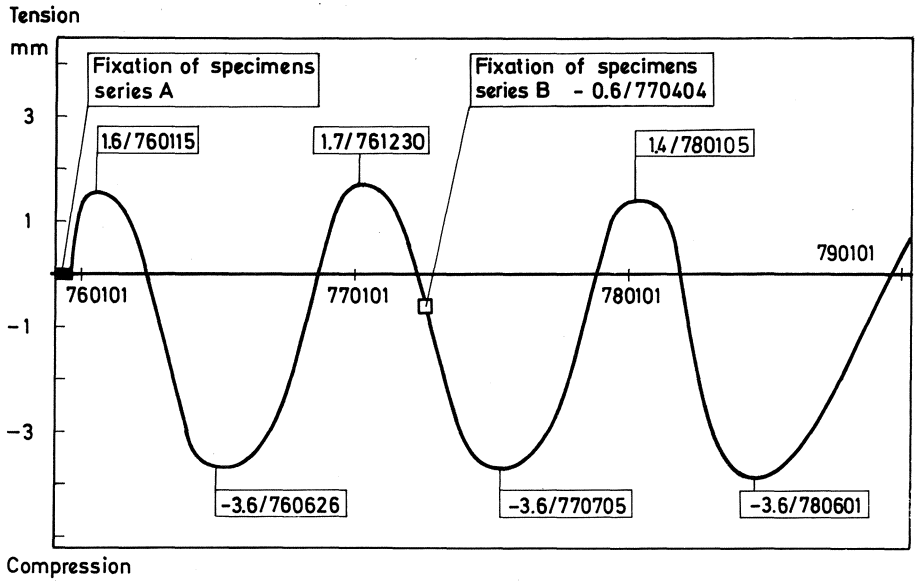


FIG. 5.4 The variations of the "joint" movements at the end of the outdoor equipment.

The deformation pattern can be described as a sine curve over a period of one year. Comparing Fig. 5.4 to Fig. 5.2, it is obvious that a daily dependent movement is superimposed on this season dependent movement. The latter sometimes shows great amplitudes. This movement pattern coincides with the movements measured in real buildings, cf. Chapter 8.2.

Fig. 5.4 shows that the sealants were compressed to a greater extent than they were elongated. This is particularly the case where the specimens in series A are concerned.

The results of the observations for the different sealants after varying times of outdoor exposure are summarized in Tables 5.1 - 5.8. "Testing" in these Tables indicates that the stress-strain curve was determined.

TABLE 5.1. Material No. 1 (soft, polysulfide-based), results of outdoor exposure

Specimen No.	Curing conditions before fixation	Date of fixation	Time of exposure months	Max. tension/ compression %	Observations
1261	7 days 20/50	751208	7	8.9/20.6	Surface cracks. Compressed profile. Testing
1262	7 days 20/50	751208	7	8.9/20.6	Surface cracks. Start of adh. failure
			14	9.7/20.6	Surface cracks. 100 A. Compressed profile
1263	8 days 20/50	751209	7	3.5/8.0	Surface cracks. Compressed profile. Testing
1264	8 days 20/50	751209	7	3.5/8.0	Surface cracks
			14	3.7/8.0	Surface cracks. 10 A
			23	3.7/8.1	Surface cracks. 10 A
			37	3.7/8.3	Surface cracks. 10 A
			39	"	Surface cracks. 40 A
1266	7 days 20/50	751208	7	8.9/20.6	Surface cracks. Compressed profile. Testing
1267	8 days 20/50	751209	7	3.5/8.0	Surface cracks. Compressed profile. Testing
1268	8 days 20/50	751209	7	3.5/8.0	Surface cracks.
			14	3.7/8.0	"
			23	3.7/8.1	" 2 A
			37	3.7/8.3	" 5 A
			39	"	" 50 A
12 1/6 9 and 12 1/6 10	108 days 20/50 7 days +40 °C	770404	7	2.6/17.3	Surface cracks. 5 A
			21	11.2/18.2	Surface cracks. 100 A. Compr profile. Cf. Fig. 5.5
12 1/6 11 and 12 1/6 12	108 days 20/50 7 days +40 °C	770404	7	1.0/6.7	Surface cracks.
			21	4.4/7.0	"
			23	5.0/7.0	" Testing

Note: 100 A means 100% adhesive failure.

The results of Material No. 1 are shown in Table 5.1. It is evident that this polysulfide-based sealant is sensitive to UV irradiation especially in combination with joint movements. Surface cracks occurred within 7 months of exposure. These cracks were frequent only on the surface facing the sun.

Adhesive failures, partly or completely, were also very frequent in spite of the maximum deformations being within the 33% deformation allowed (according to the manufacturer). This might be due to the type of movements the sealant was exposed to; more compressing than elongating movements. The common opinion was that the elongating movements are more severe for the sealants. However, from Table 5.1 it is evident that the compressing movements have caused plastic deformations of the sealant, thus forming a new stress-free profile. The following elongating movement must now be taken by a narrower profile, Fig. 5.5. This leads to a higher percentage of tension and consequently higher stresses and possible cohesive or adhesive failure (Cf. also Chapter 8). This mechanism has occurred in Material No. 1 both when the sealant was installed rather fresh or when well cured.

The results of the outdoor exposures thus indicated, that Material No. 1 probably functions as a plastic sealant where seasonal movements are concerned and as a mainly elastic sealant where daily movements are concerned! Anyway, this was true where the used distribution of movements, i.e. more compressing than elongating movements, was concerned.

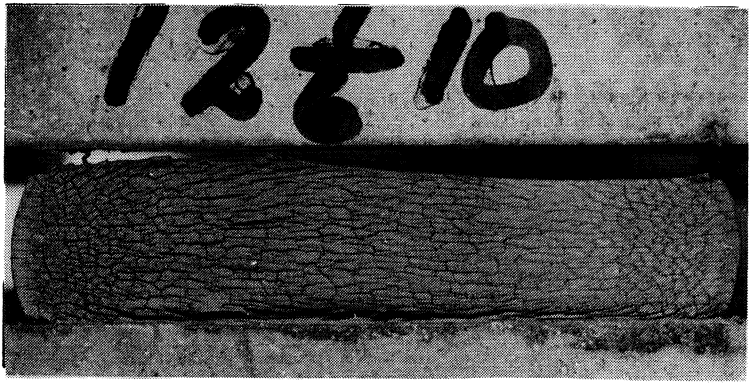


FIG. 5.5 Photo of specimen No. 12 1/6 10 after 21 months of outdoor exposure. The specimen has been elongated 11.2% and compressed 18.2% (cf. Table 5.1).

TABLE 5.2. Material No. 2 (hard, polysulfide-based), results of outdoor exposure

Specimen No.	Curing conditions before fixation	Date of fixation	Time of exposure months	Max.tension/ compression %	Observations
2361	7 days 20/50	751208	7	8.3/19.2	Compressed profile. 20 A. Testing
2362	7 days 20/50	751208	7	8.3/19.2	Compressed profile. 100 A
2363	8 days 20/50	751209	7	2.8/6.6	Compressed profile. Testing
2364	8 days 20/50	751209	7	2.8/6.6	
			14	3.1/6.6	Small surface cracks. 10 A
			23	"	" "
			37	3.1/6.9	" "
			39	"	" " Compr.prof. 50 A
2366	7 days 20/50	751208	7	8.3/19.2	Compressed profile. 100 A
2367	8 days 20/50	751209	7	2.8/6.6	Compressed profile. Testing
2368	8 days 20/50	751209	7	2.8/6.6	
			14	3.1/6.6	Small surface cracks.
			23	"	Small surface cracks. 2 A
			37	3.1/6.9	Small surface cracks. 5 A
			39	"	Small surface cracks. 20 A
23 1/6 9 and 23 1/6 10	108 days 20/50 7 days +40 °C	770404	7	2.4/16.2	Small surface cracks. Compr. profile. 100 A
23 1/6 11	108 days 20/50 7 days +40 °C	770404	7	0.8/5.6	Small surface cracks
			21	3.6/5.8	"
			23	4.2/5.8	" Testing
23 1/6 12	108 days 20/50 7 days +40 °C	770404	7	0.8/5.6	Small surface cracks
			21	3.6/5.8	" 1 A
			23	4.2/5.8	" 10 A

Note: 20 A means 20% adhesive failure

The corresponding results for Material No. 2 are shown in Table 5.2. Almost the same conclusions as those for Material No. 1 are valid for this sealant. But Material No. 2 has a better resistance against UV light. In spite of smaller movements, adhesive failure was also more frequent. This is naturally because higher stresses are induced in this sealant during elongation.

Table 5.3 shows the results for Material No. 3. This sealant showed a characteristic crack pattern on the surfaces after a relatively short time of outdoor exposure. These cracks were rather difficult to see with the naked eye at the beginning, but they gradually increased in size, Fig. 5.6. They were present on all surfaces, and not only on the one facing the sun. Apparently, they are not the result of pure UV irradiation.

After some time the surfaces started to chalk too. Therefore, degradation must be taking place in the binder on the surfaces. This degradation is probably the result of combined heat, water, radiation and movements.

This sealant was found to function mainly as an elastic material both where seasonal and daily movements were concerned.

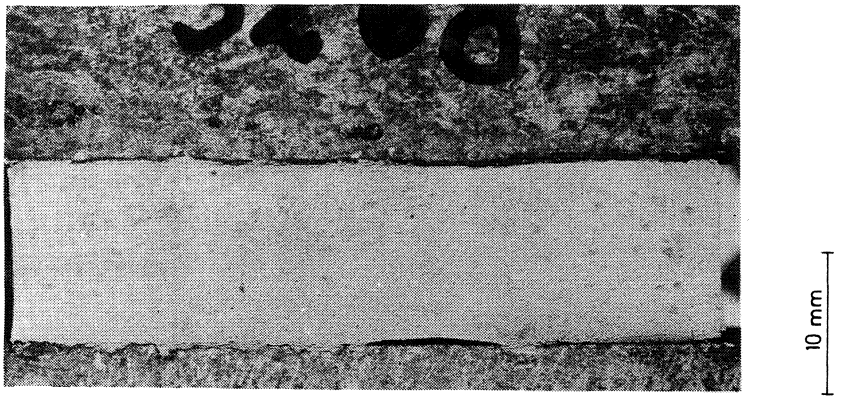


FIG. 5.6 Photo of specimen No. 3268 after 39 months of outdoor exposure. The specimen has been elongated 5.7% and compressed 12.8% (cf. Table 5.3).

TABLE 5.3. Material No. 3 (1-component polyurethane-based), results of outdoor exposure

Specimen No.	Curing conditions before fixation	Date of fixation	Time of exposure months	Max.tension/ compression %	Observations
3261	7 days 20/50	751203	7	10.1/23.4	Very small surface cracks. Testing
3262	7 days 20/50	751203	7	10.1/23.4	Very small surface cracks
			14	11.0/23.4	"
			23	11.0/23.5	" 15 A
			37	11.0/24.4	" 100 A
3263	8 days 20/50	751204	7	5.3/12.3	Very small surface cracks. Testing
3264	8 days 20/50	751204	7	5.3/12.3	Very small surface cracks.
			14	5.7/12.3	Very small surface cracks.
			23	"	Small surface cracks. Chalking. 5 A
			37	5.7/12.8	Small surface cracks. Chalking. Testing
3266	7 days 20/50	751203	7	10.1/23.4	Very small surface cracks. Testing
3267	8 days 20/50	751204	7	5.3/12.3	Very small surface cracks. Testing
3268	8 days 20/50	751204	7	5.3/12.3	
			14	5.7/12.3	Very small surface cracks
			23	"	Very small surface cracks. Chalking
			37	5.7/12.8	Very small surface cracks. Chalking. 2 A
			39	"	Very small surface cracks. Chalking. 20 A Cf. Fig. 5.6. Testing
32 1/6 9	105 days 20/50	770404	7	2.9/19.7	Slight chalking
	7 days +40°C		21	12.7/20.6	" 5 A
			23	14.8/20.6	" 5 A
32 1/6 10	105 days 20/50	770404	7	2.9/19.7	Slight chalking
	7 days +40°C		21	12.7/20.6	Small surface cracks. Testing
32 1/6 11	105 days 20/50	770404	7	1.5/10.4	
	7 days +40°C		21	6.7/10.8	Very small surface cracks. Testing
32 1/6 12	105 days 20/50	770404	7	1.5/10.4	
	7 days +40°C		21	6.7/10.8	Very small surface cracks
			23	7.7/10.8	Very small surface cracks. Chalking. 25 A. Testing

Note: 15 A means 15 adhesive failure

TABLE 5.4. Material No. 4 (polyurethane-polyepoxide-based), results of outdoor exposure

Specimen No.	Curing conditions before fixation	Date of fixation	Time of exposure months	Max.tension/ compression %	Observations
5561	7 days 20/50	751216	7	11.9/27.7	Testing
5562	7 days 20/50	751216	7	11.9/27.7	
			14	12.9/27.7	
			23	"	Slightly dirty. 5A
			37	12.9/28.9	" . 5A
			39	"	" . 5A
5563	7 days 20/50	751216	7	6.5/15.1	Testing
5564	7 days 20/50	751216	7	6.5/15.1	
			14	7.0/15.1	
			23	7.0/15.2	Slightly dirty. 2A
			37	7.0/15.7	" . 2A
			39	"	" . 2A
5566	7 days 20/50	751216	7	11.9/27.7	Testing
5567	7 days 20/50	751216	7	6.5/15.1	Testing
5568	7 days 20/50	751216	7	6.5/15.1	
			14	7.0/15.1	
			23	7.0/15.2	Slightly dirty
			37	7.0/15.7	Dirty
			39	"	Partly dirty. Fig. 5.7. Testing
55 1/6 9	108 days 20/50	770404	7	3.4/23.3	Slightly dirty
	7 days +40 °C		21	15.0/24.4	"
			23	17.4/24.4	" Testing
55 1/6 10	108 days 20/50	770404	7	3.4/23.3	Slightly dirty.50A
	7 days +40°C		21	15.0/24.4	" .50A
			23	17.4/24.4	" .100A
55 1/6 11	108 days 20/50	770404	7	1.9/12.7	Slightly dirty
	7 days +40°C		21	8.2/13.3	"
			23	9.5/13.3	"
55 1/6 12	108 days 20/50	770404	7	1.9/12.7	Slightly dirty. 100 A
	7 days +40°C				

Note: 5 A means 5% adhesive failure

Material No. 4, see Table 5.4, functioned rather well during the outdoor exposure. In spite of being forced to accommodate the largest movements, most of the specimens functioned well.

The sealant showed a tendency to become dirty, partly because it was pigmented white and partly because the sealant remained slightly tacky for a long time.

Material No. 4 also showed a certain sensitivity to UV radiation in sunlight, see Fig. 5.7. Only the surface facing the sun showed this pattern. Fig 5.7 can be compared to Fig. 4.37 showing the same sealant when UV irradiated in the laboratory. Almost the same type of crack pattern can be seen in both cases.

This sealant proved to be extremely elastic both where seasonal and daily joint width variations were concerned.

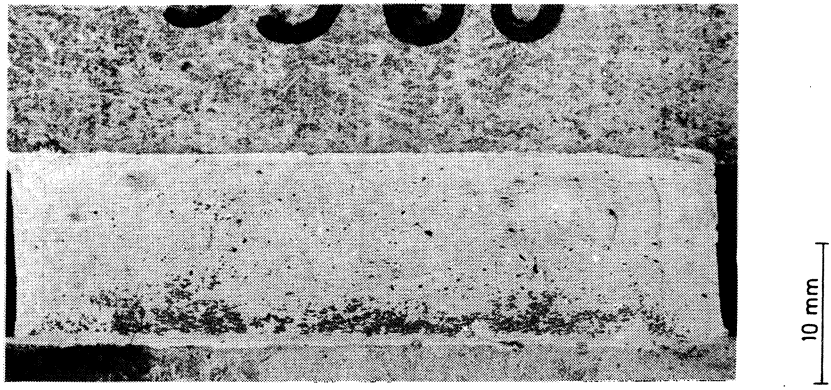


FIG. 5.7 Photo of specimen No. 5568 after 39 months of outdoor exposure. The specimen has been elongated 7.0% and compressed 15.7% (cf. Table 5.4).

The results of Material No. 5, one of the acrylic-based sealants of type solvent release, are shown in Table 5.5. The thermoplasticity of this sealant was quite evident; the sealant became folded and very dirty. However, there was no cohesive or adhesive failure in any of the cases. As there was no information regarding movement capability from the manufacturer, this sealant was placed where the smallest movement occurred. But the sealant functioned well from the point of view of keeping the joint tight.

TABLE 5.5. Material No. 5 (acrylic based, solvent release), results of outdoor exposure

Specimen No.	Curing conditions before fixation	Date of fixation	Time of exposure months	Max.tension/ compression %	Observations
6261	7 days 20/50	751120	7	7.2/16.6	Folded. Dirty. Testing
6262	7 days 20/50	751120	7	7.2/16.6	Folded. Dirty.
			14	7.8/16.6	" "
			23	7.8/16.7	" "
			37	7.8/17.3	" "
			39	"	" "
6263	7 days 20/50	751121	7	1.7/3.9	Folded. Dirty. Testing
6264	7 days 20/50	751121	7	1.7/3.9	Folded. Dirty
			14	1.8/3.9	" "
			23	"	" "
			37	1.8/4.1	" "
			39	"	" "
6266	7 days 20/50	751120	7	7.2/16.6	Folded. Dirty. Testing
6267	7 days 20/50	751121	7	1.7/3.9	Folded. Dirty
6268	7 days 20/50	751121	7	1.7/3.9	Folded. Dirty
			14	1.8/3.9	" "
			23	"	" "
			37	1.8/4.1	" "
			39	"	" "

The results of Material No. 6 are shown in Table 5.6. This sealant was forced to accomodate large movements. This was because the movement capability was 50% according to the manufacturer. The sealant managed to keep the joints tight but the profile became folded during the varying movements, Fig. 5.8. The surfaces also became rather dirty, but to a

TABLE 5.6. Material No. 6 (acrylic based, solvent release), results of outdoor exposure

Specimen No.	Curing conditions before fixation	Date of fixation	Time of exposure months	Max.tension/ compression %	Observations
7561	7 days 20/50	751124	7	10.8/25.0	Folded. Dirty. Testing
7562	7 days 20/50	751124	7	10.8/25.0	Folded. Dirty
			14	11.7/25.0	" "
			23	11.7/25.1	" "
			37	11.7/26.0	" "
			39	"	" "
7563	7 days 20/50	751126	7	5.9/13.8	Small folds. Dirty. Testing
7564	7 days 20/50	751126	7	5.9/13.8	Small folds. Dirty
			14	6.4/13.8	" "
			23	6.4/13.9	Folds. Dirty
			37	6.4/14.4	" "
			39	"	See Fig. 5.8
7566	7 days 20/50	751125	7	10.8/25.0	Folded. Dirty. Testing
7567	7 days 20/50	751126	7	5.9/13.8	Small folds. Dirty. Testing
7568	7 days 20/50	751126	7	5.9/13.8	Small folds. Dirty
			14	6.4/13.8	" "
			23	6.4/13.9	Folds. Dirty
			37	6.4/14.4	" "
			39	"	" "

lesser extent compared to the relative, Material No. 5. It is apparent that the different types of acrylic polymer used in both these sealants result in end products with different properties.

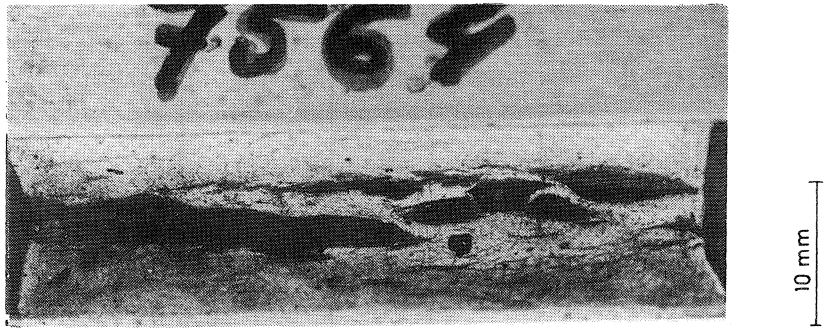


FIG. 5.8 Photo of specimen No. 7564 after 39 months of outdoor exposure. The specimen has been elongated 6.4% and compressed 14.4% (cf. Table 5.6).

The results of Material No. 7 are summarized in Table 5.7. The sealant itself has functioned surprisingly well during exposure. Only a slight brittleness of the surface facing the sun was detected. This is probably due to UV irradiation. The surfaces also turned dirty to some extent. However, there were adhesive problems regarding the very tight substrate, aluminium, while adhesion was better for asbestos cement. The great amount of shrinkage of the sealant has probably contributed to a reduction of adhesion problems.

In some cases the material showed small folds. Consequently, it worked partly as a plastic material where seasonal movements were concerned and partly as an elastic material where daily movements were concerned.

The results of the oleo-resinous sealant can be seen in Table 5.8. The sealant was forced to accomodate very large movements and consequently became folded. But the most important part of this type of sealant, the surface skin, remained essentially intact.

TABLE 5.7. Material No. 7 (acrylic based, water-dispersed), results of outdoor exposure

Specimen No.	Curing conditions before fixation	Date of fixation	Time of exposure months	Max.tension/ compression %	Observations
8261	8 days 20/50	751204	7	7.7/17.8	Testing
8262	8 days 20/50	751204	7	7.7/17.8	10A
			14	8.4/17.8	10A
			23	8.4/17.9	Dirty. 10A
			37	8.4/18.6	Dirty. 10A
			39	"	Slightly dirty. 30A
8263	8 days 20/50	751204	7	2.3/5.2	Testing
8264	8 days 20/50	751204	7	2.3/5.2	Slightly dirty
			14	2.4/5.2	Dirty
			23	"	"
			37	2.4/5.5	"
			39	"	Slightly dirty. Testing
8266	17 days 20/50	751127	7	7.7/17.8	Slightly folded. Testing
8267	17 days 20/50	751127	7	2.3/5.2	Testing
8268	17 days 20/50	751127	7	2.3/5.2	Dirty
			14	2.4/5.2	"
			23	"	"
			37	2.4/5.5	"
			39	"	Slightly dirty. Testing

Note: 10A means 10% adhesive failure

TABLE 5.8. Material No. 8 (oleo-resinous based), results of outdoor exposure

Specimen No.	Curing conditions before fixation	Date of fixation	Time of exposure months	Max.tension/ compression %	Observations
9561	11 days 20/50	751116	7	9.4/21.7	Folded. Testing
9562	11 days 20/50	751116	7	9.3/21.5	Folded
			14	10.1/21.5	Folded. Small surface crack
			23	10.1/21.6	"
			37	"	" "
			39	10.1/22.4	Folded. Small surface crack. Fig.5.9
9563	14 days 20/50	751119	7	4.1/9.4	Slightly folded. Testing
9564	15 days 20/50	751120	7	4.1/9.4	Slightly folded
			14	4.4/9.4	"
			23	4.4/9.5	"
			37	4.4/9.8	"
			39	"	Slightly folded. Very small surface cracks
9566	11 days 20/50	751116	7	9.2/21.3	Folded. 5A. Testing
9567	14 days 20/50	751119	7	4.1/9.4	Slightly folded. Testing
9568	14 days 20/50	751119	7	4.1/9.4	Slightly folded
			14	4.4/9.4	"
			23	4.4/9.5	Slightly folded. Very small surface cracks
			37	4.4/9.8	Slightly folded. Very small surface cracks
			39	"	Slightly folded. Very small surface cracks. Fig. 5.10

Note: 5A means 5% adhesive failure

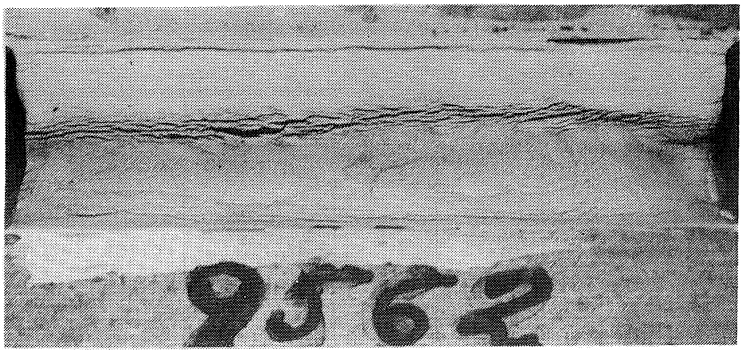


FIG. 5.9 Photo of specimen No. 9562 after 39 months of outdoor exposure. The specimen has been elongated 10.1% and compressed 22.4% (cf. Table 5.8).

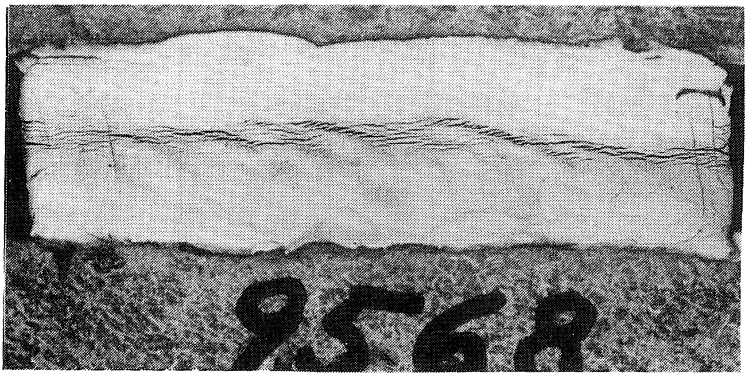


FIG. 5.10 Photo of specimen No. 9568 after 39 months of outdoor exposure. The specimen has been elongated 4.4% and compressed 9.8% (cf. Table 5.8).

5.4 Comparisons between accelerated ageing tests and results from outdoor exposure

Where a couple of the sealants are concerned, adhesive failures made it difficult to compare the stress-strain curves after accelerated ageing with those after outdoor exposure. However, it was possible to determine the instantaneous values in Shore A with the restrictions previously mentioned.

The values for the mainly elastic sealants are shown in Fig. 5.11. All the sealants show an increase in hardness with an increasing time out-

doors. Where a couple of sealants are concerned some dots do not adhere to the pattern. In the case of Material No. 3, the one-component polyurethane sealant, three dots after 21 and 23 months respectively are well below the curve. These dots are valid for specimens which had been cured longer when placed outdoors.

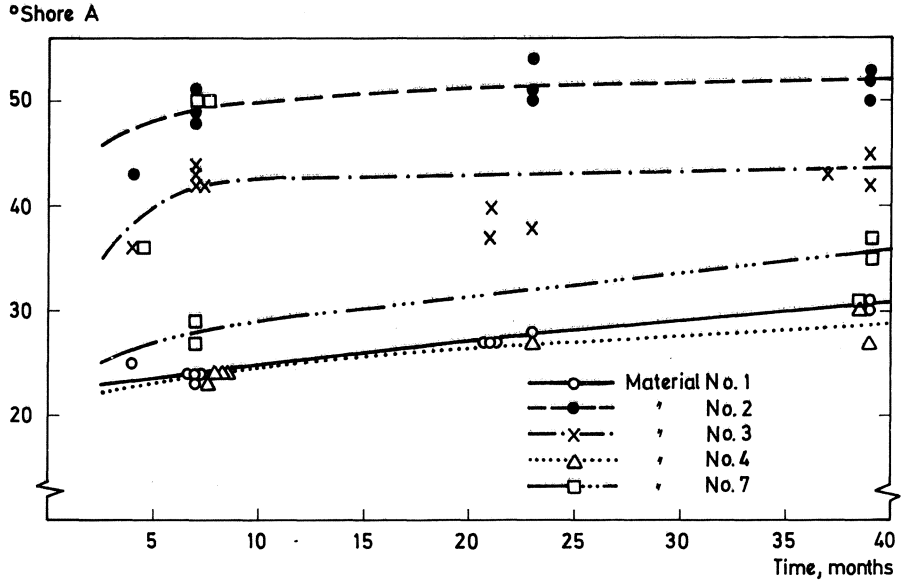


FIG. 5.11 Instantaneous Shore A-values for the mainly elastic sealants as a function of time outdoors.

Where Material No. 7 is concerned three dots are also away from the drawn curve. These are after 4 and 7 months and are valid for specimens with asbestos cement as a substrate. Evidently there is an alkaline action where this water-dispersed acrylic sealant is concerned.

At least two sealants, Material Nos. 4 and 7, show a tendency to absorb water during outdoor exposure (cf. Chapter 4.9, too). The water acts as a plasticizer and consequently when these sealants were allowed to dry out indoors the hardness increased about 3 degrees.

The values of Shore A under different conditions are given in Table 5.9. It is apparent that the values given by the manufacturers are far too low in comparison to those determined. On the other hand, the values after about three years of outdoor exposure correspond surprisingly well with those obtained after the same time in the normal climate +20°C/50% RH!

TABLE 5.9. Instantaneous Shore A-hardness under different conditions

Material No.	According to the manufacturer	+20°C/50% RH		7 days +20°C/50% RH +56 days at		Outdoors
		63 days	3 years	+40°C	+70°C	3 years
1	13	26	26	28	25	30
2	40	47	50	46	47	52
3	25	36	40	38	44	44
4	18	28	32	32	31	29
7	15	34	42	41	48	35

Where Material Nos. 1-3 are concerned there is only a slight increase in the hardness after three years outdoors compared to the same time indoors. The previously mentioned water absorption in Material Nos. 4 and 7 has also shown a lower value after outdoor exposure.

However, ocular changes have been observed regarding some of the sealants. For example a comprehensive cracking of the surface of Material No. 1 and a cracking and chalking of the surface of Material No. 3. These types of changes cannot be revealed by measuring the instantaneous hardness. By using the stress-strain curves there is a possibility that such changes might be detected.

For example, in Fig. 5.12 the stress-strain curves for Material No. 1 are shown after varying times of outdoor exposure. The hatched surface indicates the curves of a total of six specimens with exposure times from seven to eleven months. According to Table 5.1 these specimens are 1261, 1263, 1266, 1267 and two specimens from an earlier investigation. In spite of the hardness in Shore A having increased, Fig. 5.11, the 23 months of exposure caused the stress-strain curve to drop (12 1/6 11 and 12 1/6 12). This is due to UV action on the sealant. The UV irradiation has made the surface brittle. Together with varying joint movements cracks have occurred (cf. Fig. 5.5). These cracks increase during elongation, thus diminishing the registered force.

In comparison to Fig. 4.12 the curve for storage in a normal climate corresponds extremely well with the curves shown in Fig. 5.12 after seven to eleven months of outdoor exposure. I.e. if there are only small changes in the sealant due to UV irradiation, for example, the deformation properties of the sealant are about the same as when the sealant is exposed outdoors or indoors.

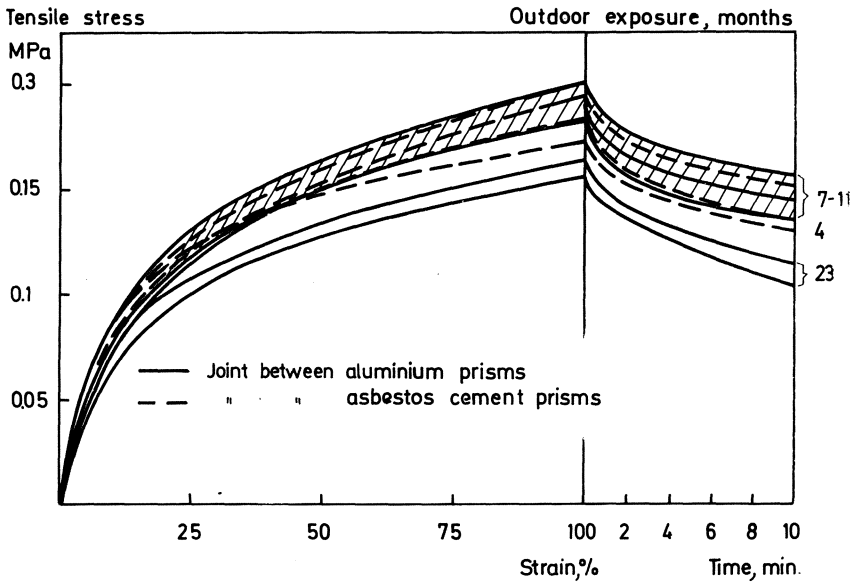


FIG. 5.12 Stress-strain curves for Material No. 1 after different times of outdoor exposure. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

Fig. 5.13 shows the corresponding curves for Material No. 2. This sealant was found to be less sensitive to UV attack than Material No. 1. Therefore the "expected" increase in hardness was found. In a case such as this the elongation resistance, determined via the stress-strain curve, correlates very well with the hardness determined by a Durometer (Fig. 5.11 and Table 5.9).

Material No. 3 showed a rather slow curing mechanism in the normal climate, cf. Fig. 4.17. The results of the determination of stress-strain curves after different times of outdoor exposure are shown in Fig. 5.14. The hatched surface indicates the curves of four specimens (3261, 3263, 3266-7) with an exposure time of seven months. Evidently, most of the

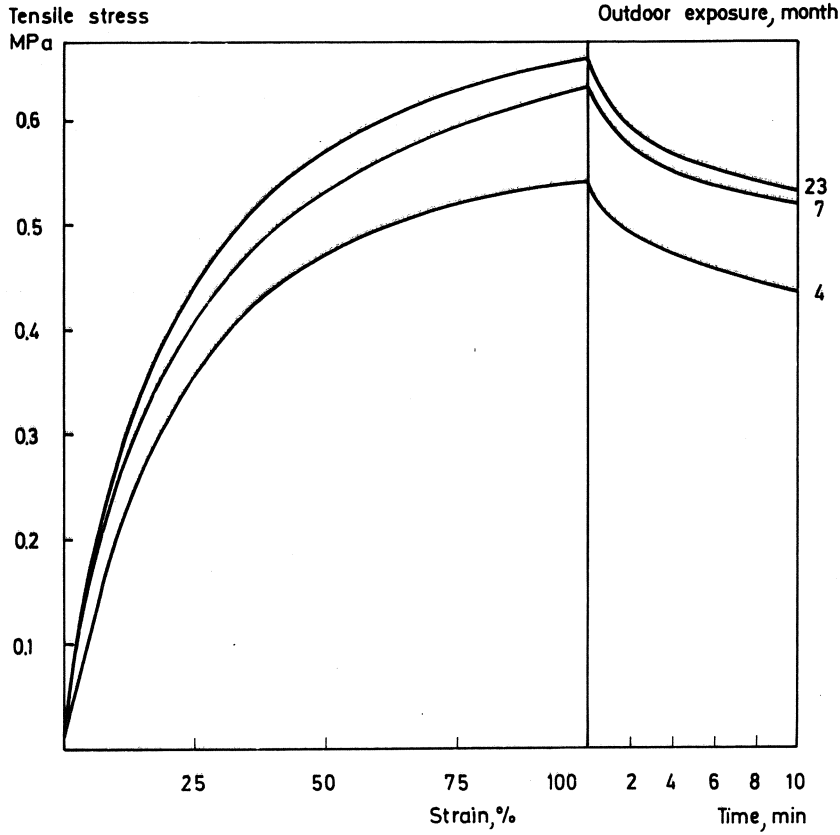


FIG. 5.13 Stress-strain curves for Material No. 2 after different times of outdoor exposure. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

curing have taken place within seven months, but there is still a continuing increase in hardness. The curve after 37 months of outdoor exposure is higher and steeper in spite of the specimen having showed a partial adhesive failure (about 5%) and small cracks on the surfaces before the testing (specimen 3264).

The dotted line curve represents a specimen (32 1/6 11) which was well cured before being installed outdoors. This softer material is also to be found in Fig. 5.11. The final properties of the sealant, hardness and elongation resistance, evidently depend upon the curing climate. A better cured sealant when placed outdoors results in a softer final product. In practice the sealants naturally cure outdoors, thus forming a harder sealant.

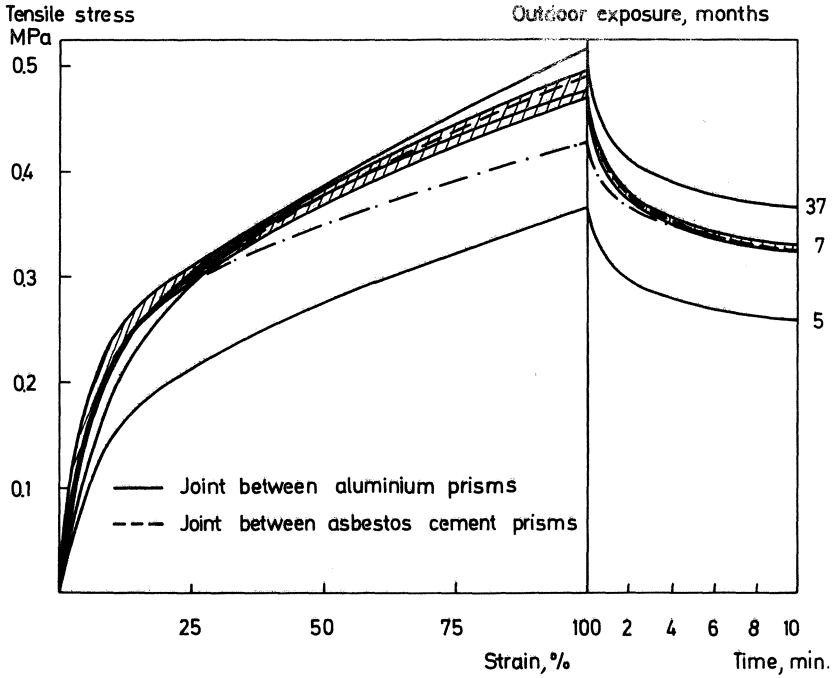


FIG. 5.14 Stress-strain curves for Material No. 3 after different times of outdoor exposure. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

When comparing the stress-strain curves after five and seven months of outdoor exposure, it is apparent that a continuing increase in hardening took place. However, Fig. 4.17 showed, that this increase occurred more quickly when the sealant was heat aged at +70°C. The value of the tensile stress at 50% elongation after seven months outdoors is about 0.375 MPa (= σ_{50} MPa). This value corresponds to about 10 days heat ageing at +70°C (Fig. 4.17). This means that heat ageing at +70°C for about 1/21 ($\frac{7 \cdot 30}{10} = 21$) of the time results in having about the same effect on the deformation resistance as outdoor exposure.

Using this factor, a 37 months outdoor exposure period should correspond to $\frac{37 \cdot 30}{21} \approx 53$ days at +70°C. From Fig. 4.17 it can be seen that this results in a σ_{50} value of about 0.45 MPa. The obtained value in Fig. 5.14 is about 0.38 MPa. The difference may well be explained by the previously mentioned partial adhesive failure and the present surface cracks.

Fig. 5.15 shows the stress-strain curves for Material No. 4. The hatched surface indicates the stress-strain curves for 4 specimens (5561, 5563, 5566-7 according to Table 5.4) with an exposure time of about 7 months and with different degrees of deformation. The dispersion is very small.

After 39 months of outdoor exposure specimens Nos. 5564 and 5568 were tested. These curves also fell within the hatched surface! However, the latter specimens showed less stress relaxation, i.e. the sealant had became slightly more elastic.

The dotted line curve represents a specimen (55 1/6 9) which was well-cured before being placed outdoors. Therefore the curve is slightly steeper and the sealant shows less stress relaxation.

When comparing normal and heat stored specimens in Fig. 4.20 to the values from Fig. 5.15 it is evident that the outdoor exposed material is considerably softer! A reasonable explanation for this is that the outdoor material absorbed small amounts of water. As previously mentioned the water acts as a plasticizer.

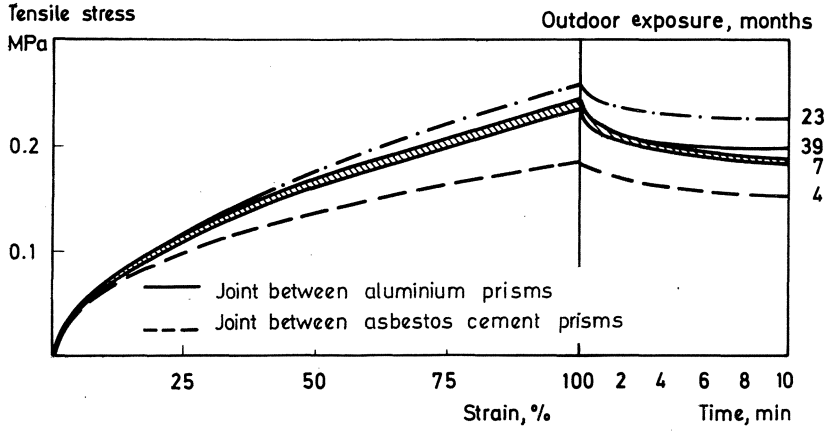


FIG. 5.15 Stress-strain curves for Material No. 4 after different times of outdoor exposure. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

The stress-strain curves for Material No. 6 after varying times of outddor exposure are shown in Fig. 5.16. Material Nos. 5 and 6 are plastic sealants. However, as far as Material No. 6 is concerned, the elastic properties increase slowly with time. The plastic behaviour

has caused wrinkling in the joint profile. This made it difficult to measure cross sections before stress-strain curves were determined and therefore the results showed a great dispersion.

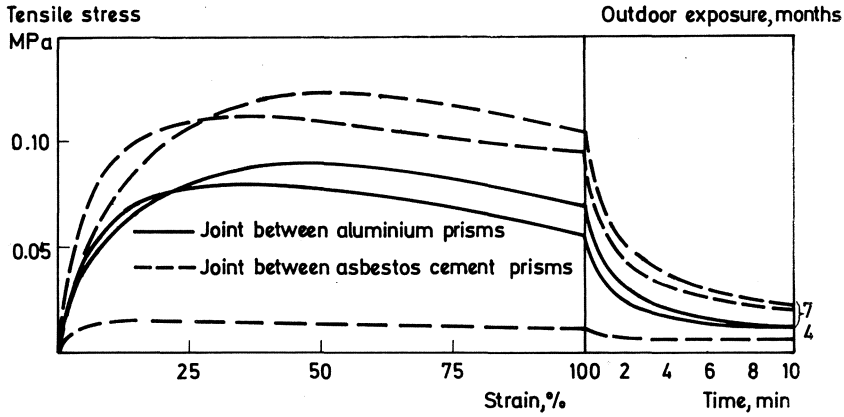


FIG. 5.16 Stress-strain curves for Material No. 6 after different times of outdoor exposure. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

The comparisons with the results of heat ageing indicated that heat ageing at +70°C seemed to result in a rather hard ageing. Compare for example Fig. 5.16 to Fig. 4.25. Just two weeks at +70°C resulted in an increase in hardness far greater than the one obtained after seven months outdoors. However, a suitable length and level of heat ageing should be useful when making accelerated ageing tests on this type of sealant.

Fig. 5.16 shows the difference between specimens with aluminium and asbestos cement as substrates. In Chapter 4.5.2 the effect of the alkaline action was also revealed. This effect was only apparent if the sealant was allowed to dry after alkaline exposure. The great difference between the stress-strain curves after four and seven months of outdoor exposure depends to a great extent upon the fact that the former specimen was tested in the spring after a rainy period, while the latter were tested during the summer.

The stress-strain curves for Material No. 7, after outdoor exposure, are shown in Fig. 5.17. The figures indicate the specimen numbers. One curve without such a number represents two specimens from a pre-

vious investigation. With one exception, the curves only concern joints between asbestos cement prisms. When using aluminium, most of the specimens failed, showed adhesive failure during the test. On the other hand, when asbestos cement was used, the adhesion was excellent. The water dispersed sealant obviously requires a fairly absorbant substrate in order to obtain good adhesive capacity or alternatively, primer treatment.

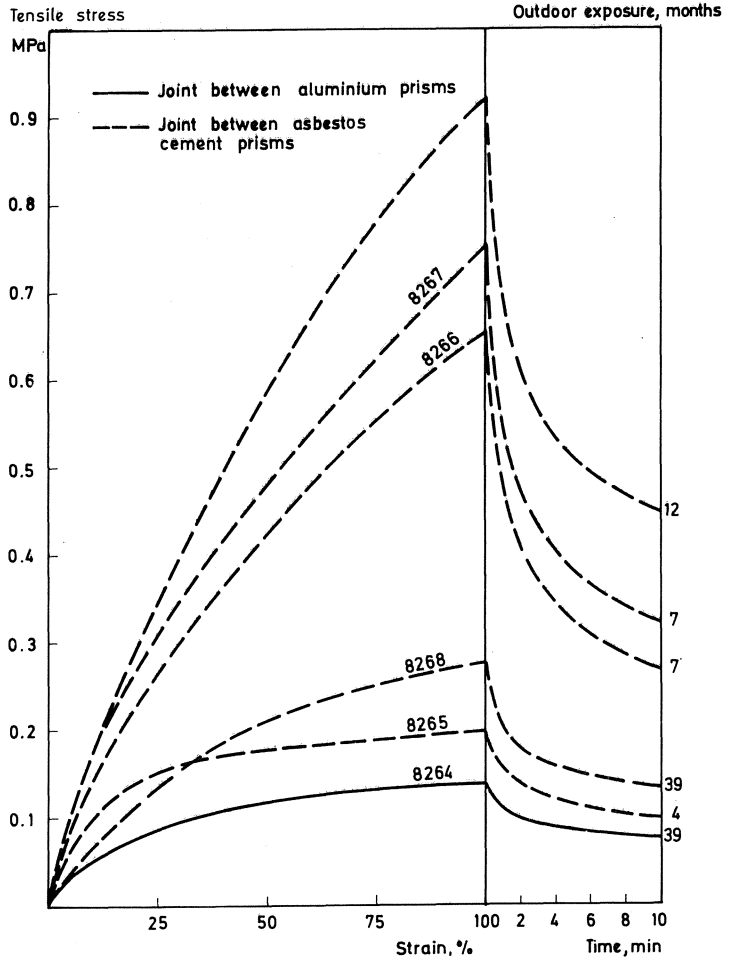
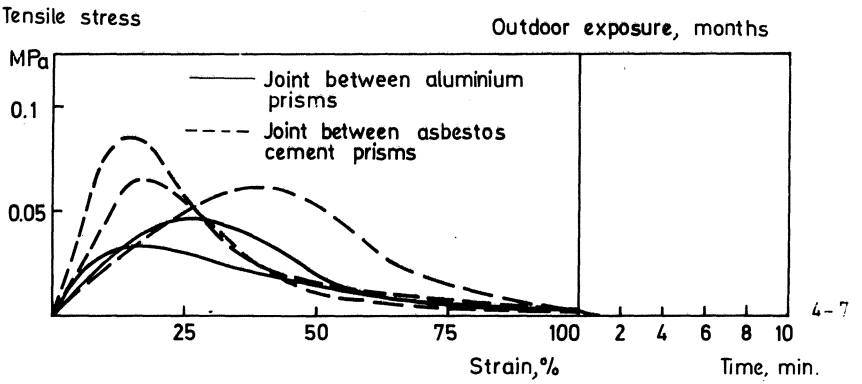


FIG. 5.17 Stress-strain curves for Material No. 7 after different times of outdoor exposure. Deformation speed: 1.5 mm/min. Testing temperature: +2 ^{o}C.

At a first glance at Fig. 5.17, the tendency is very irregular. However, after studying all the variables a little closer, two main conclusions can be drawn:

Firstly, the properties of the sealant itself are dependent only to a small extent, on the time outdoors. The differences seen between the curves depend mainly on the water content, i.e. the storing conditions before testing. The highest curve represents two specimens which were stored indoors for about four months before testing. Specimen Nos. 8266 and 8267 were tested immediately, but the outdoor climate had previously been rather warm and dry. 8268, 8265 and 8264 were taken and tested in March after a cold and wet period.



4-7

FIG. 5.18 Stress-strain curves for Material No. 8 after different times of outdoor exposure. Deformation speed: 1.5 mm/min. Testing temperature: +2 °C.

Secondly, there is an apparent tendency towards an alkaline effect on Material No. 7. Specimen Nos. 8264 and 8268 differ only where the substrate is concerned. The same tendency was found when using the Durometer for all specimens (including the adhesively failed ones).

As there were only small surface changes of the sealant it should be possible to obtain a connection between accelerated heat ageing and the time of outdoor exposure. When comparing Fig. 4.26 to Fig. 5.17 it is apparent that heat ageing for 56 days at +70°C results in a greater increase in the hardness than twelve months outdoors. However, the comparison material is too small and the stress-strain curves after outdoor exposure should be determined according to the same type of drying which would make comparisons possible.

Material No. 8 showed a plastic behaviour and maintained a very soft consistency for a long time. Therefore it was difficult to determine the stress-strain curves with acceptable accuracy. However, Fig. 5.18 shows the stress-strain curves after varying degrees of outdoor exposure. With an increased length of time outdoors, there was a tendency to a decrease in the elongation at which the maximum stress occurs. This stress occurs where the surface skin cracks. Fig. 4.28 together with other results also showed a very clear tendency for the stress peak to move to the left after heat ageing. The stress level is however considerably higher after heat ageing according to Fig. 4.28 compared to the outdoor specimens. But it should be possible to obtain a correlation between outdoor exposure and simple heat ageing for this sealant as well.

As previously discussed, in Chapter 4.4.2, the ability of an oil based sealant to function, apart from the ductility of the skin, is also greatly dependent on the growth of the surface skin. The skin thickness as a function of time was found to follow a straight line in the log-log diagram (Fig. 4.29). If the corresponding values for material stored outdoors (Δ) are plotted in this Figure, it is apparent that the outdoor storage causes about the same thickness growth as the climate +20°C/50% RH does. For example, one point relates to a sample from an approximately eight year old joint (2920 days) between elements of concrete, 2.7 m long. The joint faces southwest and is consequently sometimes exposed to high temperatures. In spite of this, the point falls just below the straight line.

According to Figs. 4.28 and 5.18 the stress-strain curves and the stress peaks are very similar regardless of whether the sealant is stored for 98 days in a climate of +20°C/50% RH or seven months outdoors. This should indicate, together with Figure 4.29, that Material No. 8 ages in the same way both indoors and outdoors! It is possible to accelerate the ageing by means of heat storing. As pointed out in Chapter 4.4.2 heat ageing at +70°C results in a thickness growth which is 22 times faster than at +20°C/50% RH. It is therefore reasonable to use this factor as an accelerating factor for Material No. 8.

As in the case of Material Nos. 4 and 7, water absorption also takes place during the outdoor exposure of Material No. 8.

5.5 Discussion

There is a great variation of properties in the eight sealants investigated. Therefore it is impossible to obtain a unique correlation between laboratory accelerated ageing and the results from outdoor exposure. However, a correlation was obtained for some essential properties of a couple of the sealants. By means of a simple heat ageing it is possible to obtain a fairly good correlation, for example, for Material Nos. 3 and 8.

From the comparisons of the results it is also apparent that some effects which might occur in practice cannot be revealed in a laboratory ageing test. For example the cracks in the surfaces of Material No. 1, and to some extent Material No. 2. These were found to be the result of a combined action of UV radiation and varying joint movements: The cracks were deeper and more common in the specimens of Material Nos. 1 and 2 which were exposed to the largest movements.

Apart from adhesive or cohesive failure, there was no clear connection between the degradation of the sealant itself and the increasing joint movements for the other sealants. For example in Tables 5.1-5.8, the results could be used to estimate the movement capability of the different sealants.

6. ACCELERATED AGEING OF SEALANTS COMPARED TO PRACTICAL EXPERIENCE

6.1 Introduction

If an accelerated ageing and an estimation of the durability of sealants is to be of any value, the results should be compared to the experiences from the practical use of the sealants.

Some comparisons have been made in Chapter 5.4 between accelerated ageing in the laboratory and the results from outdoor exposure of joint specimens during well registered conditions. Then, the next step should be to compare these results with experiences of sealants in actual buildings. Naturally problems arise concerning the fact that the formulations of the sealants may have changed, and the time of their practical use may be rather limited etc. etc. However, such comparisons will be made in this Chapter.

6.2 Previous investigations

An interesting investigation made by Grunau (1976) was briefly reviewed in Chapter 3, also compare Table 3.1. The polysulfides were found to produce the longest expected lifetime (22 years) and the largest allowable deformations (20%). Many examples from around 1960 were said to have indicated these values. These sealants contained a relatively high content of binder, 40 to 50% by weight. Compared to the formulations of today they were harder (about 50^{o} Shore A) and showed a high recovery.

According to Grunau, the formulations of today contain 30 to 40% by weight of polysulfide binder and these are said to be even better. Some examples of outdoor exposed polysulfide sealants with binder content from 19 to 35% by weight are shown. The one with the highest polymer content showed the best resistance to exposure.

These results concur fairly well with the results found in Chapter 5 regarding Material Nos. 1 and 2, both polysulfide based sealants. The polymer content is higher in Material No. 2. This sealant was considerably harder and also showed the greatest resistance to environmen-

tal conditions. However, Material No. 2 was so hard that adhesive problems arose in many cases. The formulation of this sealant probably correlates well with those used in the 60's.

It is obvious that the formulation changes from a higher to a lower polymer content also changed the nature of the problems which might arise. The higher polysulfide content resulted in a more durable sealant but on the other hand, also caused more adhesive problems. Today, the softer sealants give better protection against adhesive failure, while the sealant itself shows a higher degree of degradation. These contrasts naturally constitute an optimization problem.

The maximum allowable deformation was said to be 20% of the original joint width for polysulfide sealants. This seems to be a reasonable value if the joint is accurately designed and the sealant is applied properly. However, limitations must be made regarding the distribution of the joint movements. As discussed in Chapter 5.3 the stress relaxation of the polysulfides is very high at higher temperatures. As the sealants are mostly compressed at these temperatures, this may lead to large plastic deformations if too high a part of this 20% is compressed. The results in Tables 5.1-5.2 showed these indications very clearly where total deformations were concerned even less than 20%. However, the cross-section of those specimens was rather unfavourable. Nevertheless, a caulking at a temperature of about $+5^{o}C$ is not unusual. In some constructions this could cause an unfavourable distribution of the movements leading to large plastic deformation during compression and adhesive or cohesive failure during the following elongation at a lower temperature.

Grunau is very positive regarding the polysulfides but at the same time he is rather negative regarding other types of sealants, for example all kinds of oil based products and also where the expected lifetime and allowable deformations of the polyurethanes are concerned. The expected lifetime is about 10 years and the allowable deformations 5-10%.

The polyurethane sealants appeared in the late 60's. The previous formulations were insufficient. They showed a continuing increase in hardness and a poor climatic resistance. This may explain the low values

given. However, there has been a very intensive development in this field. New and better formulations have appeared.

The results shown in Chapter 5.3 for the two polyurethane sealants, Material Nos. 3 and 4, indicated longer lifetime and also greater allowable deformations than stated by Grunau (1976).

In the investigation carried out by Andersson and Hasselblad (1972), mentioned in Chapter 3, valuable information is given regarding the practical use and experiences of different sealants especially those concerning facade panels of concrete.

The most frequent problems were cohesive failure followed by adhesive failure. Cracking was also rather common. The frequency of the damages was greatly dependent upon the geographic orientation. The joints facing south-west showed the most common damages. Naturally this could be explained by the great effect of the sunlight and the heavy rain in the area investigated.

Surface cracking on polysulfide sealants was rather frequent. These cracks were usually located in a direction parallel to the joint. These must be due to the varying joint movements together with the attack by UV and/or ozone on the surface. The same pattern was found on the polysulfide specimens according to Chapter 5.3. This type of cracking is very common on the softer polysulfide sealants which are used today. These crackings occur rather early. For example compare with Fig. 6.1 showing a soft polysulfide sealant two years after application. Note the difference in UV action. The upper part of the joint is mostly shaded by part of the wall.

In one case a very strong and deep type of cracking was reported. It was thought that this might be due to the effect of snow on the sealant. However, large cracks can also occur in a polysulfide sealant without any special environmental action. In Fig. 6.2 a 12 year old joint with a polysulfide sealant (about 50^{o} Shore A) is shown. The joint is located indoors at a constant temperature of about $+22^{o}$C! There must have been some chemical processes continuing within the sealant, thus forming a shrinkage and eventually cracks.

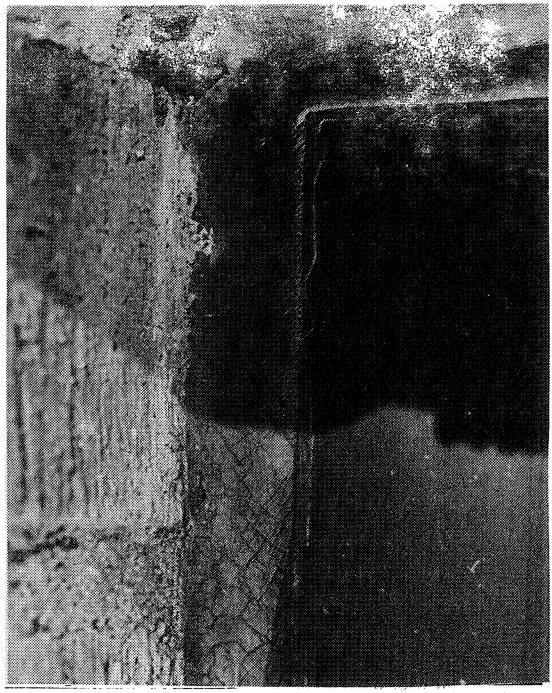


FIG. 6.1 UV-action on a two year old polysulfide-based sealant. The upper part of the joint is mostly shaded. Therefore, the UV attack is considerably lesser on this part of the sealant.

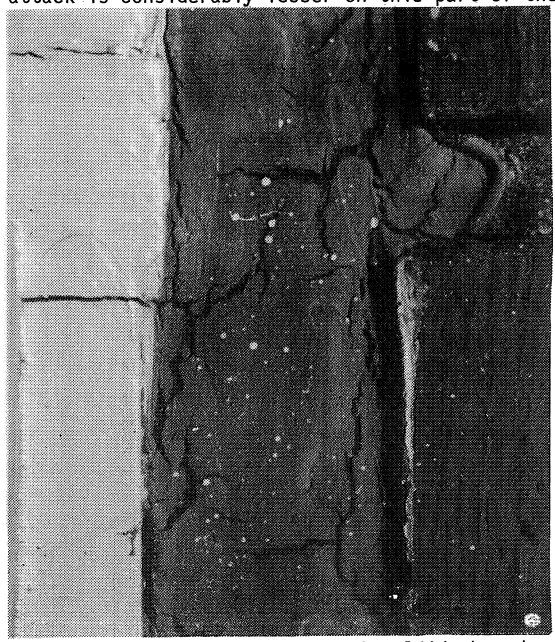


FIG. 6.2 Deep cracks in a 12 year old polysulfide-based sealant (50^{O} Shore A). The joint is located indoors at a constant temperature of about +22 ^{O}C.

The acrylic sealants reported by Andersson and Hasselblad (1972) naturally showed wrinkled surfaces after large movements. In some cases an alkaline action was found to destroy the acrylic sealants (cf. Chapter 4.5). The formation of pores and bubbles shown in Fig. 4.23 was also found in one case.

The oleo resinous sealants which were used showed a great variation in properties. One sealant between room sized concrete panels was in excellent condition after twelve years. On the other hand, some sealants were in very poor condition after only a few years. Material No. 8 was also used in a couple of buildings with good results (cf. Chapter 5.3).

It was also supposed that most sealants in the long run cannot withstand a deformation of ±25% of the original joint width. This value has been used for a long time where so-called elastic sealants are concerned. This assumption also agrees very well with the results in Chapter 5.3.

Material Nos. 2 and 8 were included in the previously mentioned work by Nylund (1964), Chapter 3, together with 23 other sealants. The observations made and reported after about 28 months also agree well with the findings according to Chapter 5.3. For example, Material No. 2 showed small crackings. It is of course plausible that changes in the formulations have been made since then but the main formulation should still remain.

The previously mentioned tendencies regarding different kind of sealants were confirmed in an investigation by Stridh and Östlund (1974).

6.3 Discussion

It has been shown above, that there are great similarities between the practical experiences of different kinds of sealants and the results which can be obtained by rather simple laboratory tests in combination with equipment for outdoor exposure, for example, according to Chapter 5.2.

The tendencies and the results of the outdoor exposure can be obtained within a rather short time. Within less than a year there are preliminary results which are usually only reinforced after a longer period of time, cf. Tables 5.1-5.8.

This should mean that, when introducing a new sealant on the market, a good estimation of the long-time properties of the sealant could be made before it is used in buildings. Today, some manufacturers recommend their products too early and before any outdoor testing has been carried out.

Today, we recommend the elastic sealants for maximum joint movements of ±25%, cf. for example HusAMA (1972). The results from Chapter 5.3 and the results from practical experience discussed in Chapter 6.2 clearly indicate that the given value is far too high. The reason being that in spite of the fact that most sealants work well, the joint movements in practice were less than those calculated. When failures occur, the movements may have reached the estimated value!

7. WAYS OF ESTIMATING THE DURABILITY OF SEALANTS

7.1 Introduction

The ultimate aim of testing ageing properties of building materials is of course to obtain a method for estimating the durability of the materials in different environments.

As far as the group of the sealants is concerned this group is not homogenous and it is therefore necessary to make a sub-division.

In this concluding chapter concerning the ageing of sealants, some attempts will be made to draw up lines of direction for making estimations of the durability of different groups of sealants possible. These lines will be put together with the sealants used according to Chapter 4.3.

The ageing of the sealants, i.e. the changes in the materials due to environmental influence, naturally depends to some extent upon the amount of varying joint movements taking place at the same time, cf. Chapter 5.3-5.4. The question regarding the movement capability of sealants however is treated in Chapter 9.3.

When dealing with the question regarding the estimation of the durability of different sealants, it will therefore be assumed that the sealants are only exposed to "normal" amounts of varying joint movements. In other words the movements which each respective sealant is designed to be able to accomodate, cf. Chapter 9.

7.2 Different types of curing/hardening systems

All building joint sealants can roughly be divided into three different groups according to their way of curing/hardening. These groups are:

1. Chemically curing sealants for which the curing mechanism enables a material to retain the same properties throughout the whole cross-section. Oxidation is excluded.

   This group may comprise sealants which are 1-, 2-, or multi-component. The binder could for example be silicone, polyurethane or

polysulfide. Among those sealants in Table 4.1 Material Nos. 1-4 should belong to this group.

2. Sealants which to a major extent harden by vaporization of a component in the fresh, liquid sealant. During this hardening the sealant gains the same properties throughout the whole cross-section.

   The function of the volatile component is to give the sealant a gunnable viscosity. This component is normally a type of solvent or water. Examples of sealants belonging to this group are Material Nos. 5-7 according to Table 4.1. The non-drying sealants, for example some butyls, should also belong to this group.

3. This group comprises sealants which are cured by oxidation of the binder, which is normally a vegetable oil or a mineral oil.

   The oxidation starts from the surface of the sealant. Therefore a surface skin may develop, which protects the inner part of the sealant from oxidation. In that case the cured sealant consists of two parts, a ductile surface layer and a viscous semi-liquid inner part.

   Sealing materials known as "mastics" and "putties" should also belong to this group, in spite of usually being oxidized almost equally through the whole cross-section.

   Material No. 8 in Table 4.1 should belong to this group of sealants.

7.3 Chemically curing sealants

With the results of the investigations above, described in Chapter 4-6, and bearing in mind the assumption in Chapter 7.1, it should be possible to try to draw up a line of directions for estimating the durability of sealants belonging to the group of "chemically curing sealants".

The first step is to expose the sealants to the isolated environmental factors as shown in Chapter 4.4-4.7, 4.9. Any specific weakness of a sealant may then be revealed.

For example, Material Nos. 1-2 are sensitive to ozone attack. Material No. 3 is sensitive to thermal action and shows a rather high degree of water absorption. Material No. 4 also shows a rather high degree of water absorption.

These results could be used as advice against recommending the sealant in question in a case where there is a great risk for a specific environmental factor.

Among the environmental factors given in Chapter 4.4-4.7, heat is usually found to have the greatest effect on the deformation properties of chemically curing sealants. Of course there are exceptions, cf. for example Material No. 1, which showed a completely unexpected response to heat ageing.

But, if there is an evident thermal action, it is also possible to obtain a fairly good correlation between heat ageing and the effect of storage in a normal climate, +20°C/50% RH. By means of determining the stress-strain curves for Material No. 3, it was shown in Chapter 4.4.2 that heat ageing at +40°C resulted in an increase in hardness four times faster compared to the normal climate +20°C/50% RH, i.e. an application of the rule of thumb regarding temperature and reaction rate was possible. To be able to estimate this should be the second step.

The third step should be to try to correlate outdoor exposure to heat ageing in the laboratory. Once again, by means of determining the stress-strain curves for Material No. 3, it was shown in Chapter 5.4 that heat ageing at +70°C accelerated the increase in hardness by factor 21 compared to outdoor exposure.

With these comparisons available it is possible to estimate the effects over a longer period of outdoor exposure where the deformation properties are concerned.

It is possible to obtain connections similar to the above for all chemically curing sealants, if the effect of thermal action clearly preponderates over the effects of other environmental factors.

But there are pitfalls of course. In many test methods some type of heat ageing is used to accelerate the ageing of the sealant. And as heat ageing and outdoor exposure are not the same thing the manufacturer would be able to make a formulation suitable for the test method, while practical experience could be completely different.

Material No. 1 showed an obvious decrease in hardness after heat ageing while outdoor exposure showed a slight increase.

When determining the stress-strain curves after outdoor exposure it must also be observed that some sealants absorb water during the exposure. Therefore, if comparisons are to be made, the specimens have to be conditioned equally before testing.

Some kind of outdoor exposure is also recommended from another point of view. The effect of UV irradiation in the laboratory is never the same as the combined effect of UV irradiation from the sun and varying joint movements, cf. for example the results of Material Nos. 1 and 2. Furthermore, the preliminary results, which are also usually valid after longer periods of time, are obtained within a rather short time.

7.4 The hardening of sealants by vaporization of volatile components

The first step when estimating the durability of sealants belonging to this group is the same as for the chemically curing sealants.

Material Nos. 5-7 were found to be very sensitive to thermal action, and Material Nos. 6-7 were found to be sensitive to moisture and alkaline action.

Where thermal action is concerned it has quite a different effect on this group of sealants compared to the former group. Therefore, it is not possible to obtain a simple connection between heat ageing and normal ageing, either at +20°C/50% RH or outdoors. This is because heat ageing does not mainly have a chemical action on this type of sealants. During heat ageing the volatile components vanish rapidly, thus forming a more porous structure compared to the one which is obtained during slower evaporation. Heat ageing should therefore take place at a lower temperature (+40°C). If a higher temperature is to be used, the sealants should be stored in a normal climate for almost 56 days before

the heat storage starts (cf. Fig. 4.49-4.51).

The results of a step outdoors for this group of sealants are difficult to evaluate. These sealants are usually fairly resistant to the weathering factors. Stress-strain curves can be difficult to determine but in spite of this outdoor exposure is recommended. In any case this will give an estimation of the behaviour during varying joint movements.

As some sealants may reveal water absorption during exposure outdoors one must be observant during the determination of stress-strain curves for example. The specimens must be stored to equilibrium in the same climate if comparisons are to be possible.

7.5 Oxidizing sealants

The investigation of the effect of the different weathering factors used for the other sealants should also be carried out for this group of sealants.

As an example, thermal action was found to have a great effect on Material No. 8. The action of water and alkaline water caused swelling and destruction, the UV irradiation caused wrinkling of the surface skin.

Where the skin forming oxidizing sealants are concerned it is possible to obtain a correlation between the growth of the skin thickness and the time at +20°C/50% RH. An example of this was shown for Material No. 8 in Fig. 4.29. There was also a connection between the growth and the time if the temperature was raised to +40 or +70°C. One day at +40 or +70°C corresponded to 4 and 22 days respectively at +20°C. Consequently, the rule of thumb mentioned above can also be considered to be valid in this case.

As the skin forming rate is a very essential property of this type of sealant, this rate and its connection with heat ageing should be determined for all similar products. If these connections are outlined it is possible to make rather definite extrapolations.

Another essential property of skin forming sealants is the ductility of the skin. If the skin cracks due to overload the oxidation continues

into the center after which the core becomes harder and looses its ductility. This mechanism is shown in Fig 7.1. The sealant contained a small bubble through which oxygen was able to diffuse.

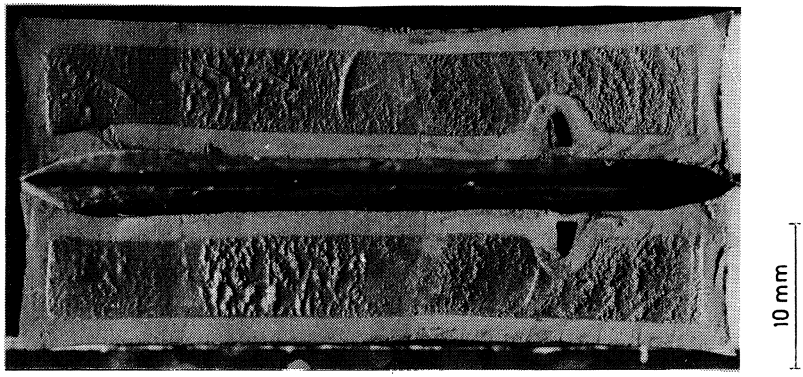


FIG. 7.1 Photo of a cut through a 9 year old specimen of Material No. 8. The specimen contains a bubble, with an outer skin which has been completely oxidized. Then the oxidation has continued within the sealant.

It is therefore important to know the limit to which this surface skin can be elongated. This limit determines the movement capability of a skin forming sealant. This matter is therefore discussed in Chapter 9.

By carrying out outdoor exposure tests it is possible to correlate the skin forming rate outdoors to the rate in a known climate. Where Material No. 8 was concerned it was found that this rate was almost the same at +20^{o}C/50% RH as outdoors!

Apart from that it is naturally possible to compare the movement capability found outdoors to the that found during tensile tests.

In the case of oxidizing sealants which do not form an obvious surface skin, for example a putty, it should be possible to use the correlations shown above. I.e. heat ageing at +40^{o}C or +70^{o}C cures the material 4 respectively 22 times faster as compared to +20^{o}C.

8. DEFORMATION PROPERTIES OF SEALANTS

8.1 Introduction

"A sealant is a material which is applied to a joint in an unformed state and which constitutes a seal by adhering to appropriate surfaces within the joint".

This definition according to the International Organization for Standardization reveals some of the demands made upon a sealant: After application, the sealant must immediately prevent the penetration of moisture and/or draughts between the elements or components. The sealant must adhere to the surfaces during the changes in the joint width.

Consequently, the deformation characteristics of a sealant are a very important property. It is not only the properties in the fully cured state but also during the curing and in the aged state that are of importance.

These questions will be dealt with in this chapter. The effects of the most essential factors affecting the deformation properties will be investigated.

8.2 Joint movements

When referring to joint movements in connection with sealants there are two particular aspects which are most important.

Firstly, the amplitude of the movements, i.e. the maximum increase and decrease in the joint width calculated at one particular time. This time usually being the time of sealant application.

Secondly, the rate of the joint movements is of great importance.

With an increased knowledge of these matters it should be possible to simulate in the laboratory the conditions to which sealants are subjected in practice.

There are many research workers, who have studied joint movements. The first systematical approach was made by Nylund (1968). He introduced a geometrical and mathematical ground for the division of the movements of concrete elements. The movements were divided into one temperature- and one moisture-dependent part.

The temperature-dependent movement could be subdivided into one long- and one short-term movement. The first one was assumed to follow the yearly variation of mean temperature in the air. The second one superimposed the yearly movements and comprised movements because of the air temperature deviates from the mean temperature and because of temperature variations caused by radiation.

The moisture-dependent movements were caused by an irreversible shrinkage of the concrete and a shrinkage/swelling between the limit curves. The latter was due to the yearly variations in the relative humidity of the air.

Taking these movements into consideration mathematical expressions were formulated from which it was possible to calculate the movements.

Apart from the analytical descriptions of the movements, practical measurements of movements between concrete elements were also carried out.

Since then, a great deal of information has been published regarding measurements of joint movements in actual buildings. Compare for example Ryder and Baker (1970), Diergarten (1973), and Karpati and Sereda (1976 a and b).

However, the results obtained were sometimes contradictory. Ryder and Baker examined the extent of movements in three different types of buildings. One building was a fifteen storey tower construction with aluminium and glass cladding. The second had reinforced concrete cladding panels forming the external walls. The third building consisted of a concrete wall-frame tower block. The joints were open and drained.

The movements showed a diurnal pattern which was approximately sinusoidal. Superimposed on this pattern was a seasonal pattern of progressive opening

of the joints during the autumn and winter and progressive closing during the spring and summer.

In a case of joints between equal components not subjected to moisture movements it might be expected that there would be a simular response to the same changes in temperature. However, the results showed an appreciable difference in diurnal movements and in the seasonal range for joints which were apparently similar.

Comparisons with calculated unrestrained thermal movements showed that the majority of measured movements did not exceed the calculated ones, while the measured movements were appreciably greater for a few joints! Bowing of the components could be a possible explanation for this.

Diergarten (1973) measured the movements between four identical precast concrete panels on a western facade. The amount of movement differed considerably from joint to joint. The corresponding measurements carried out another year produced even more confusing results. A joint, which the year before, had showed practically the largest movements did not show any movement at all the following year! Measurements of movements in another concrete panel construction showed no movements at all. The moisture-dependent movements were found to counteract the temperature-dependent movement completely.

Karpati and Sereda (1976 a) reported measurements of joint movements in precast concrete panel cladding. They found that for most of the joints, it was possible to calculate the movements by using the linear coefficient of thermal expansion of concrete. However, in one case the movement was about 20 % greater.

In another investigation dealing with expansion joints in two different buildings, Karpati and Sereda (1976 b), it was found that the joint movements correlated well with the temperature changes measured at the surface of the wall. However, the change in the width of the joints, measured at the top of two buildings, was about half that predicted from the coefficient of thermal expansion. The movement was reduced to a negligible size at the bottom, where the wall was restrained by the foundation.

In Nylund (1975) a method was described for calculating the temperature-dependent movements of facade panels. He also claimed, that for precast concrete panel cladding the yearly dependent changes in length, caused by shrinkage/swelling and temperature respectively, are roughly equal and counteract each other. This applies where a normal yearly variation of temperature and relative humidity in non-maritime or non-tropical climate is concerned.

The same conclusion was arrived at by Beijer (1976) who calculated the moisture-dependent movements of facade panels of concrete with assumed material characteristics.

Summing up the information from these practical measurements, the results are to some extent confusing. Evidently, there are great variations regarding the mechanical restraints of the components. Sometimes the moisture- and temperature-dependent movements counteract each other completely. If the irreversible shrinkage is negligible then a reasonable approximation would be to design the joint only with respect to the short-time thermal movements.

The other important question of joint movements is the rate. Ryder and Baker (1970) reported a step-like pattern of the movements. This could be a so called slip-stick-movement, i.e. a movement which is restrained by friction and then suddenly becomes free to move. These jerks could cause a major disaster especially where plastic sealants are concerned.

However, Andersson and Hasselblad (1972) made some measurements in order to detect these movements, but they were impossible to find. Instead it has been suggested that the step-like pattern is due to the equipment used. The measurements were made using potentiometers with wire diameters of 0.025 mm. This dimension could possibly explain the pattern which was found. However, Nylund (1975) also claimed the existence of these movements.

There are very few measurements of continous joint movements which have been reported. Apart from these step-like movements Ryder and Baker also reported rates of movements lasting 12 minutes or longer (this is due to the equipment). The maximum rate of the concrete cladding panel building was about $2 \cdot 10^{-2}$ mm/min.

From a recorderchart, shown in Andersson and Hasselblad, it was possible to calculate the maximum rate of joint movement in a facade facing south-west. This rate was found to be about $2 \cdot 10^{-3}$ mm/min. Consequently, most joint movement rates in concrete facades are rather slow.

8.3 Factors affecting the deformation properties of sealants

8.3.1 Introduction

When a joint is closing due to increasing temperature the sealant is then consequently compressed, Fig. 8.1. The deformation properties of the sealant at that movement are to a great extent dependent upon the amplitude and the rate of the joint movement, the temperature, the duration of the movement, the age of the sealant etc. There is a complex co-operation between these variables. Stresses are induced within the sealant, and stress relaxation occurs during a resting time.

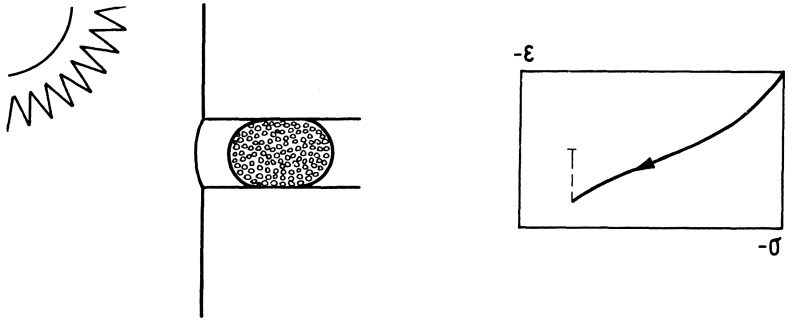


FIG. 8.1 Joint closing and a consequence of that compressive stresses in the sealant.

At a subsequent opening of the joint when the temperature drops, the sealant moves back to the original width and is later elongated to a certain amplitude. Tensile stresses are induced in the sealant, Fig. 8.2.

This pattern is repeated day after day. In some cases the sealants are not only exposed to these elongation/compression movements, but also to shear deformations. The shear may occur along the joint or perpendicular to the joint. It can easily be shown that a shear movement compared to an equal percentage of elongation/compression movement causes a much lesser strain on the sealant.

Therefore, the tests carried out concerning deformation properties of sealants have been concentrated on pure elongation or compression.

In this chapter examples will be given of how some main variables affect the deformation properties of different types of sealants.

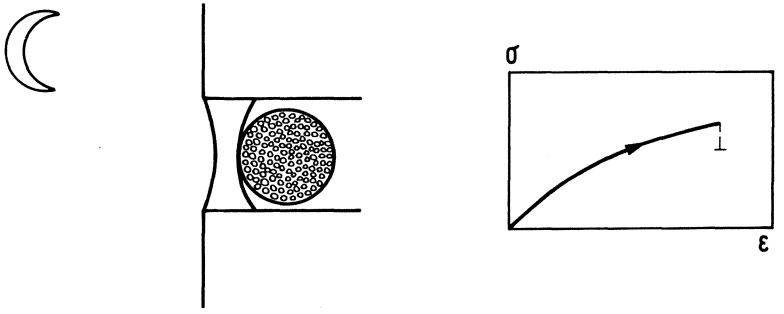


FIG. 8.2 Joint opening and tensile stresses are induced.

8.3.2 The effect of the temperature

From literature it is commonly known that the deformation resistance of sealants generally increases in a decreasing temperature. However, the temperature-dependence varies greatly between different materials.

For example, the silicone-based sealants are known to be practically unaffected by changes in temperature in normal use. On the other hand, acrylic-based sealants, type solvent release, are known to be thermoplastics in behaviour, i.e. the hardness increases considerably at a low temperature and softens when the temperature is raised.

In an investigation started by the author and later continued by Blomsterberg and Holmberg (1974), amongst others, the remaining deformation after different degrees of deformation at different temperatures was examined. The tests were carried out on three different sealants, one acrylic-based (solvent release), one polysulfide-based (25^{o} Shore A) and one silicone-based (20^{o} Shore A). Specimens were elongated 10, 25, 40 and 50% and compressed 10, 20, 25 and 30% at a rate of 0.001 mm/min. The temperature at the elongation was +23 ^{o}C, -5 ^{o}C and -25 ^{o}C, while at compression it was +23 ^{o}C and +55 ^{o}C. The recovery was measured during one hour.

Figs. 8.3 - 8.5 summarize the results for the different sealants. It is evident that the lower temperatures lessened the remaining deformations for all the sealants, including the very plastic acrylic sealants.

In other words, the lower temperatures increase the elasticity of the sealants at the same time as the adhesive stresses are increased. The higher temperatures, on the other hand, increase the plastic deformations even for the highly elastic silicone-based sealant.

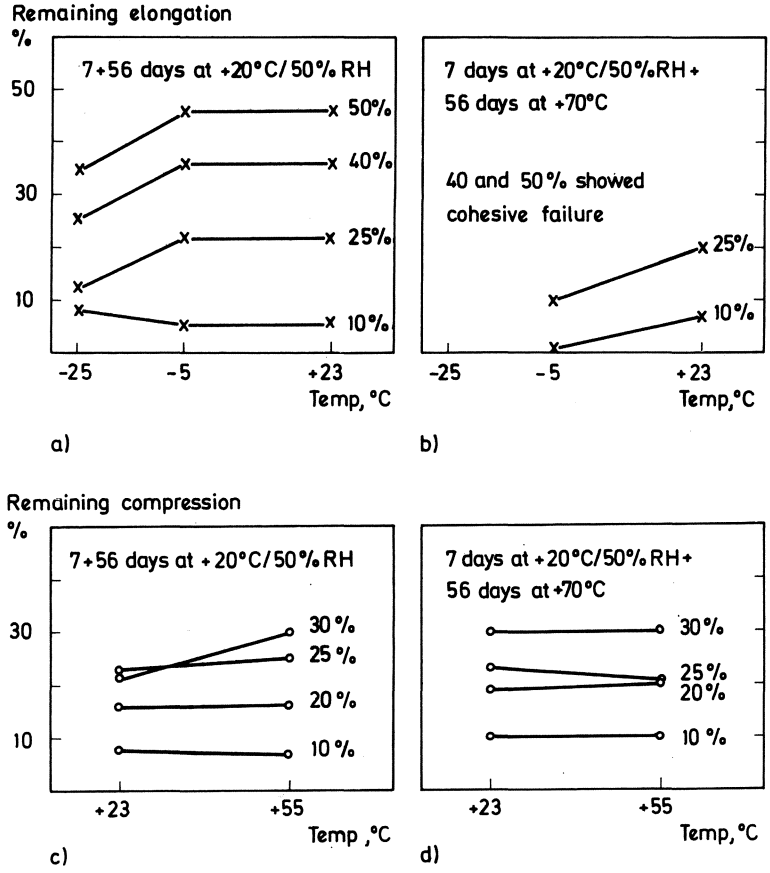


FIG. 8.3 Remaining deformations as a function of temperature for an acrylic-based sealant (solvent release). Specimens have been elongated 10%, 25%, 40% and 50% or compressed 10%, 20%, 25% and 30% at a rate of 0.001 mm/min. 7 + 56 days at +20 °C/ /50% RH etc. indicates the curing conditions before testing.

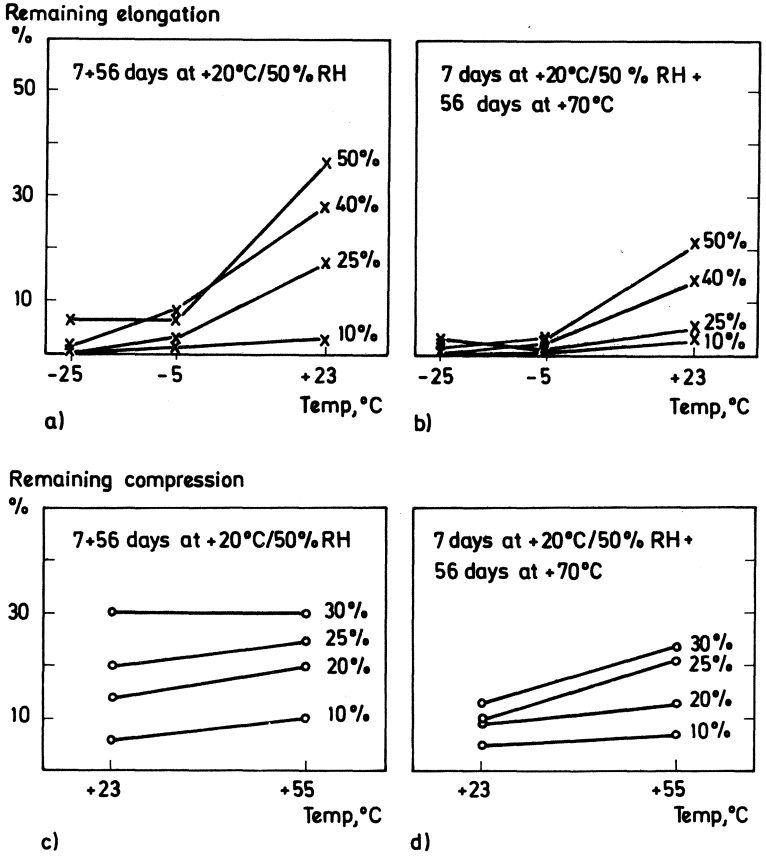


FIG. 8.4 Remaining deformations as a function of temperature for a polysulfide-based sealant (25° Shore A). Compare Fig. 8.3!

8.3.3 The effect of the joint movement rate

Usually the rate of deformation has a great effect upon the deformation properties of sealants. If the sealant is fairly elastic the stress-strain curve, for example, would be almost entirely independent of the deformation rate. But, because of the viscous elasticity of the polymers, the deformation of a sealant is usually connected with a delayed elastic and viscous deformation. The latter is sometimes explained by irreversible slidings between the molecular chains.

The extent of these irreversible deformations in a sealant is of great importance for the function of the material during repeated movements. It is essential to know this when testing the materials in the labora-

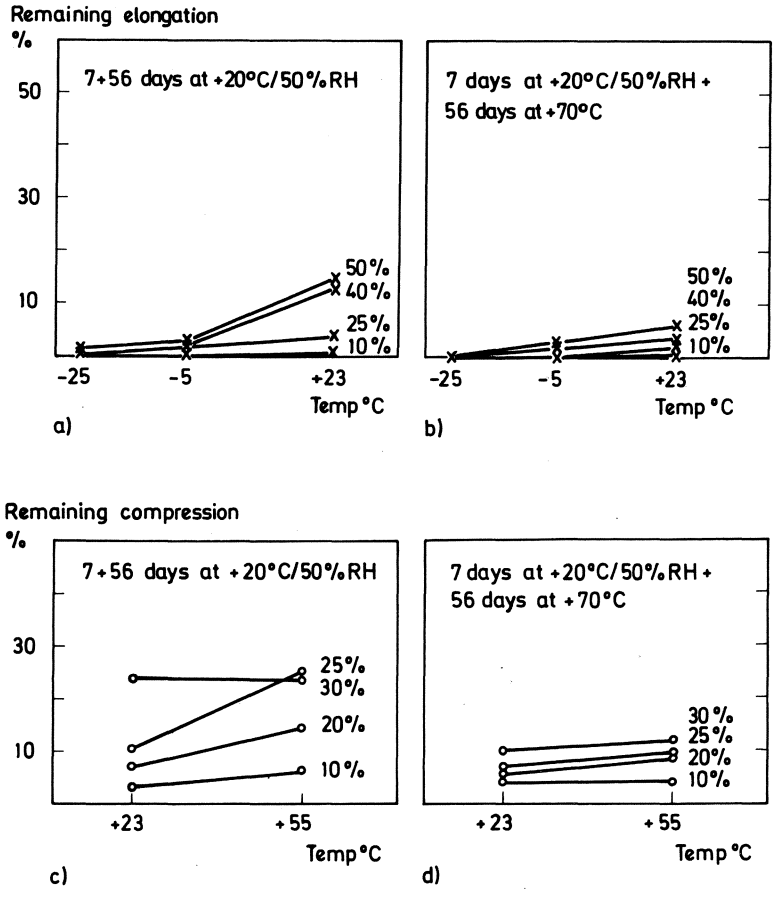


FIG. 8.5 Remaining deformations as a function of temperature for a silicone-based sealant (20° Shore A). Compare Fig. 8.3!

tory. If too high a deformation rate is used, then the viscous deformation is not developed and a wrong picture of the sealant is obtained. Therefore, one reason why such great efforts are made to determine real joint movement rates (cf. Chapter 8.2) is to obtain as reasonable testing rates as possible.

An example of how the testing rate affects the result for an "elastic", polysulfide-based, sealant is shown in Fig. 8.6.

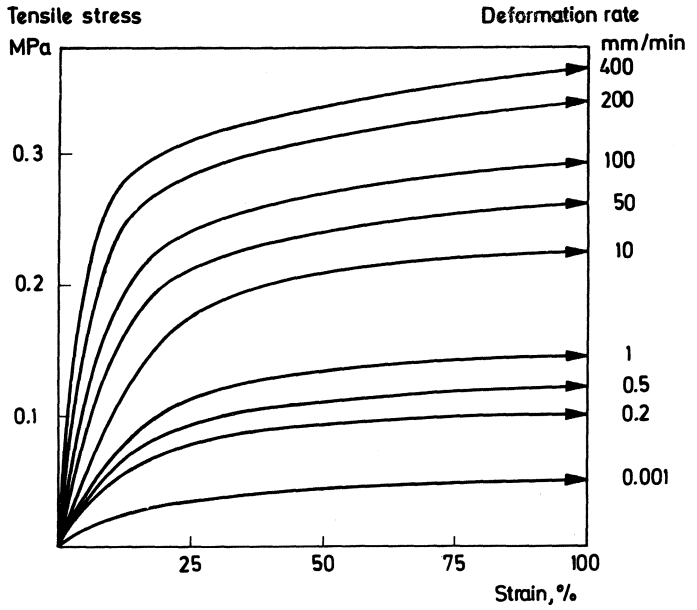


FIG. 8.6 The effect of the deformation rate upon the stress-strain curve of a polysulfide-based sealant, 22° Shore A. Testing temperature: +20 °C.

The tensile stress at 25% elongation (= σ_{25}) can be plotted as a function of the deformation rate. This is shown in Fig. 8.7 for the polysulfide sealant according to Fig. 8.6. Apart from this, the corresponding values are also plotted for a silicone- and an acrylic-based sealant. The greatest effect of the deformation rate, as expected, is found in the plastic acrylic-based sealant. At higher deformation rates, about 400 mm/min, the curves in Fig. 8.7 seem to converge towards almost the same tensile stress.

Several independent investigations have shown that the joint movement rate in actual buildings are mostly very slow, Chapter 8.2. However, it is time-consuming and expensive to test sealants at these low rates in the laboratory. With the help of curves, similar to those shown in Fig. 8.7, it should be possible to obtain an estimation of the fault, if a tensile test is carried out at a higher rate. For example, consider the stress at a deformation rate of 0.001 mm/min as the "true stress" (= 0.036 MPa) for the polysulfide sealant. If the test is carried out at 1 mm/min then the obtained stress is about 0.107 MPa, i.e. about 200% too high.

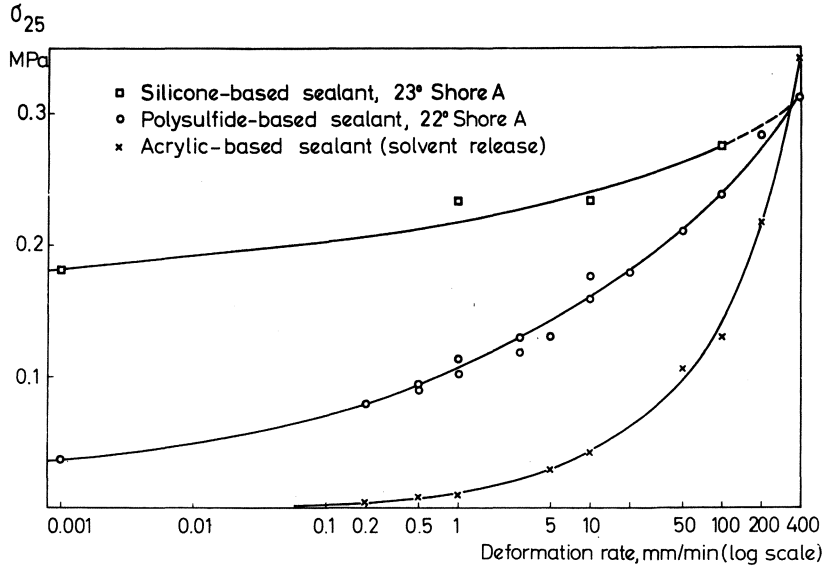


FIG. 8.7 Tensile stress at 25% elongation (= σ_{25}) as a function of deformation rate for three different types of sealants.

If a sealant is exposed to the so-called slip-stick movements (Chapter 8.2) very high instantaneous stresses are induced within the material. An estimation of the amplitude of these jerks is made in Andersson et al (1972). These were about 0.0025 mm.

Some slip-stick tests have been carried out where the amount of the movement varied within 0.01 - 0.03 mm. These movements were obtained by means of compressed air cylinders. As an example, for an acrylic-based sealant a tensile stress peak of 0.13 MPa was obtained at a movement of 0.03 mm. These stresses are relaxed comparatively quickly, but depending on the frequency of these kind of movements, the total stress can of course sometimes reach high levels. In order only to illustrate the level of the stress 0.13 MPa it can be compared to a more "normal" deformation rate. The same stress is obtained at about 40% elongation at a deformation rate of 100 mm/min.

Thus, a high frequency of this type of movements can build up high stresses in a sealant. These may be dangerous both for the sealant itself and for the adhesion of the sealant.

8.3.4 The effect of the cyclic joint movements

Sealants are normally exposed to cyclic joint movements and usually at a rather slow rate. The moving periods are interrupted by resting periods when stress-relaxation may occur. It is important to be able to simulate these kinds of movements in the laboratory in order to get an idea of the movement capability of the sealants.

Some attemps can be found in literature where these matters have been handled, cf. for example Matsumoto et al (1978). However, in most cases the deformation rates were too high. If the rates chosen are too high, the viscous deformations may not be allowed to develop.

In Fig. 8.8 an example of a cyclic test on a polysulfide sealant is shown. The rate is too high and therefore this kind of test is of no real value.

Instead it should be possible to develop suitable testing methodics, in which the joint movements are simulated and combined with appropriate temperatures. By using such a method it could be possible to predict the function of the sealant in practice.

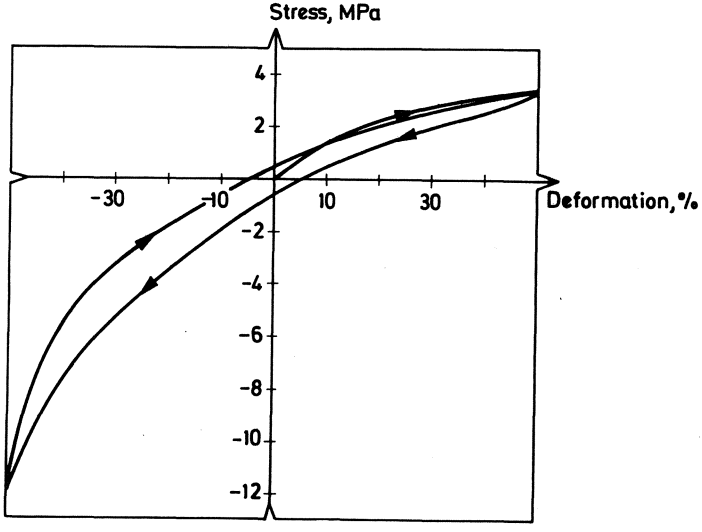


FIG. 8.8 The effect of cyclic joint movement on a polysulfide-based sealant. Deformation rate: 10 mm/min. Testing temperature: +20 °C.

8.3.5 The effect of the sealant age

It has been shown previously, for example in Chapter 4.2.2, that the curing or hardening of most sealants continues for a long time. As far as Material No. 3 was concerned there was still a continous curing after three years in a climate of +20 ^{o}C/50% RH. This means that the deformation properties of the sealant are changing at the same time. Usually the sealants grow more elastic during curing. Therefore, large movements which arise when the sealant is young may cause large plastic deformations which later on can be fatal for the sealant.

An example of a polysulfide sealant is given in Fig. 8.9. According to the data sheet from the manufacturers, this type of sealant is usually said to be fully cured within a week. If the sealant is heat-aged, which amongst others increases the curing of the sealant, then the plastic deformations are dramatically decreased when the material is elongated or compressed. I.e. from this point of view the sealant becomes better after a heat-ageing. Now the question arises, when should the sealant be tested? Nevertheless, joint movements start as soon as the liquid sealant is applied to the joint.

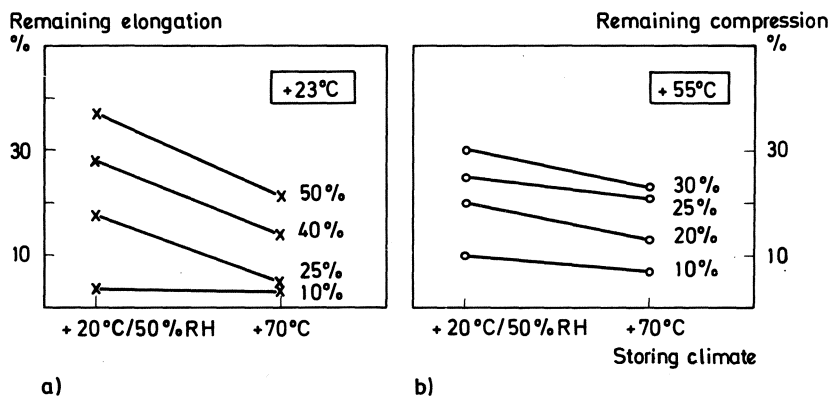


FIG. 8.9 Remaining deformation as a function of curing conditions for a polysulfide-based sealant (25^{o} Shore A). Specimens have been elongated 10%, 25%,40% and 50% at a temperature of +23 ^{o}C (Fig. 8.9a) compressed 10%, 20%, 25% and 30% at a temperature of +55 ^{o}C (Fig. 8.9b). The time at +20 ^{o}C/50% RH has been 63 days while the time at +70 ^{o}C has been 56 days after 7 days at +20 ^{o}C/50% RH. Deformation rate: 0.001 mm/min.

8.3.6 Creep and stress relaxation properties of sealants

The phenomena of creep and stress relaxation in materials are interrelated and can therefore be treated together. Creep is the increasing deformation at a constant load, while stress relaxation is the decrease of stress at a constant deformation.

The amount of stress relaxation is important for a sealant. During resting periods of the joint movements, stress relaxation occurs and thus causes plastic deformations in the sealant.

Stress relaxation tests have been carried out by Nimmermark and Olsson (1976). Three different sealants were investigated. These were Material Nos. 1, 3 and 4 according to Table 4.1. The sealants were cured for 7 days at +20 ^{o}C/50% RH and for 21 days at +70 ^{o}C before testing. The specimens were elongated 5, 10, 15 and 25% when the stress relaxation was measured. The results are summarized in Table 8.1.

TABLE 8.1 σ_1/σ_0-values * for Material Nos. 1, 3 and 4

Deformation	Elongation rate = 1.5 mm/min			Elongation rate = 0.001 mm/min		
%	Material No. 1	Material No. 3	Material No. 4	Material No. 1	Material No. 3	Material No. 4
5	0.54	0.52	0.55	0.97	0.93	0.79
10	0.61	0.55	0.60	0.98	0.95	0.85
15	0.62	0.56	0.60	0.93	0.92	0.93
25	0.64	0.60	0.64	0.97	0.98	0.95

* σ_1 = tensile stress after 1 hour of relaxation
σ_0 = tensile stress at the respective maximum deformation

Obviously, almost the same values are arrived at independent of the maximum deformation, i.e. up to 25% elongation at least the stress relaxation is independent of the amount of elongation for these three types of sealants. It is also found, that a considerable relaxation occurs already during the elongation if this takes place at a very low rate.

When examining the relaxation curves it was found, that about the same absolute stress level was obtained after one hour of relaxation regard-

less of whether the sealants were elongated at 1.5 mm/min or at 0.001 mm/min. Thus, an estimation of the absolute stress levels at a stress relaxation can be obtained in a shorter time, if the sealants are elongated at a higher rate.

According to Cook (1967) the relaxation curve followed the expression

$$\sigma = \sigma_0 \exp\left(-\frac{t}{\tau}\right)$$

where

σ = stress at any time

σ_0 = initial stress

t = time

τ = stress relaxation time

The stress relaxation time is defined as the time necessary for a specimen to decay to $\frac{1}{e}$ or 36.8% of its initial value.

When using the data found in Nimmermark and Olsson (1976) the stress relaxation time for the polysulfide sealant (Material No. 1) is about 64 hours at a rate of 0.001 mm/min. Checking the equation above with the experimental values results in the following:

8 hours: $\sigma_0 = 25.9$ kPa

$\sigma = 25.9 \exp(-\frac{8}{64}) = 22.9$

experimentally value found = 20.6

24 hours: $\sigma = 25.9 \exp(-\frac{24}{64}) = 17.8$ kPa

experimentally value found = 15.4 kPa

Thus, the given equation fairly accurately describes the stress relaxation of this polysulfide sealant. The relaxation of the two other sealants after 64 hours was not sufficient for the stress relaxation time to be reached. Therefore, it was not possible to make the corresponding calculations.

Evidently there are many factors affecting the relaxation properties of sealants. For example, an increased deformation rate or an increased temperature increases the stress relaxation, while the amount of deformation up to at least 25% does not affect the amount of stress relaxation.

There are also other, specific properties, which affect the relaxation properties. In an investigation of sealants for insulated glass manufacturing the stress-strain and the stress relaxation behaviour were examined. One sealant was softer and at the same time showed a "brittle" behaviour and a quick stress-relaxation. A SEM-photograph of a fracture surface, Fig 8.10, showed a lot of small pores within the sealant. Thus, stress concentrations in these pores caused cohesive cracks in the sealant.

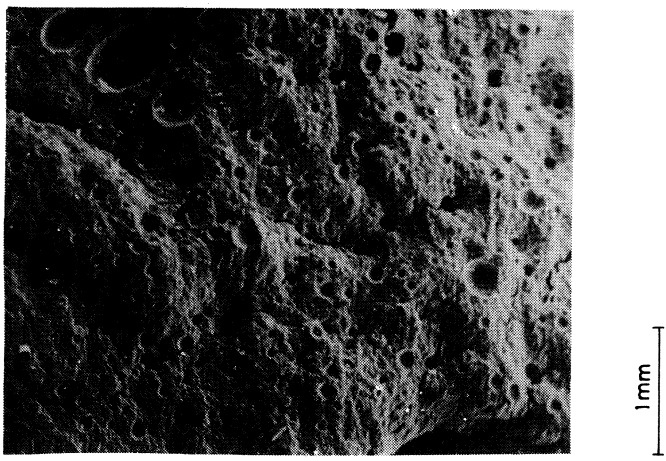


FIG. 8.10 SEM-photograph of a fracture surface of a polysulfide-based sealant for insulated glass manufacturing. Note the high amount of small pores within the sealant. Enlargement 24x. Photo: The Zoological Institution of Lund University.

Creep properties of sealant may be of interest when a sealant is forced to accommodate a constant load. For example, some sealants have been used as a glue where glass sheets are concerned. As many sealants are rather soft for conventional creep experiments to be carried out, another method can be used.

In Nimmermark and Olsson (1976) stress-strain curves were determined at various rates (from 0.2 - 400 mm/min). From these curves it is possible to calculate the time necessary to reach a certain stress at a certain rate. When plotting the times and the deformations connected to these a creep curve is obtained for a certain stress. Examples of such creep curves are shown in Fig. 8.11.

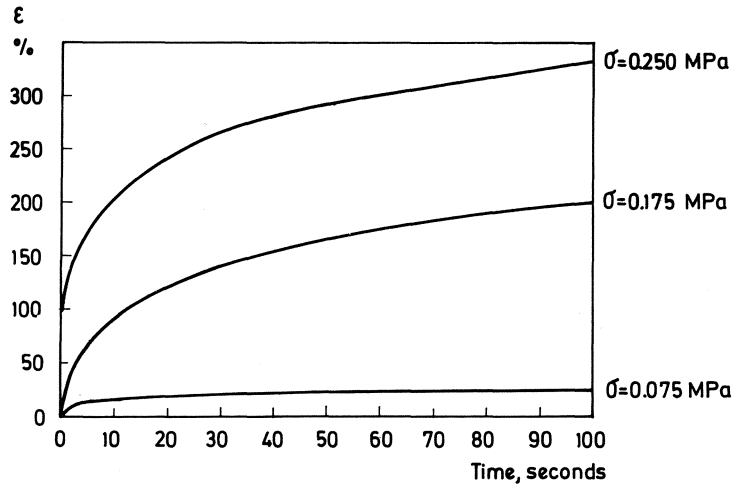


FIG. 8.11 "Creep curves" of Material No. 1 after 7 days at +20 °C/50% RH + 21 days at +70 °C. A constant deformation rate is assumed when calculating this type of creep curves. Testing temperature: +20 °C.

9. MOVEMENT CAPABILITY OF SEALANTS

9.1 Introduction

Over the years the use of sealants in building constructions has led to great failures in many cases. One reason for this is that the movement capability of the sealants has been overestimated. Therefore, in spite of the progress in making new and better polymers and formulations, the permitted movements of the sealants have successively been decreased. Naturally, the problem is to be able to make reasonable estimations of the movement capability of the sealants taking into consideration all the variables which affect the sealants: Type of polymer, formulation, age, stress, temperature, environmental influence, joint movement rate, joint movement pattern, etc. etc.

However, there are some factors which are more essential than others. These are stress, deformation, time (= deformation rate) and temperature. These factors must be considered independent of the age of the sealant, the environmental influence and so on.

The factors depend on each other in one principal way as shown in Fig. 9.1. An increasing deformation rate raises the curve, while an increasing temperature lowers the curve.

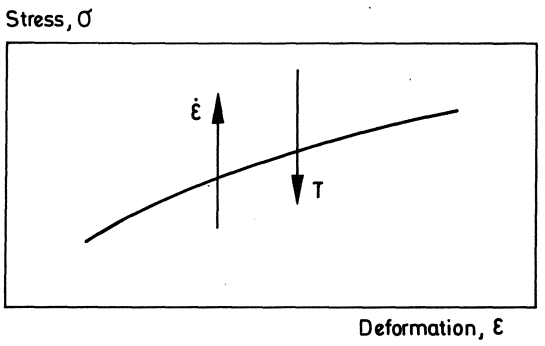


FIG. 9.1 Principal connection between stress (σ), deformation (ε), time (= deformation rate, $\dot{\varepsilon}$) and temperature (T).

9.2 What is happening in the joint?

As has been shown previously (Chapter 8.2), the joint movements are yearly and daily dependent. For hygroscopic materials the yearly moisture depending movements in some cases seem to nullify the temperature depending movements. At that case, only daily temperature depending movements should arise, while where other materials are concerned both types of movements are apparent.

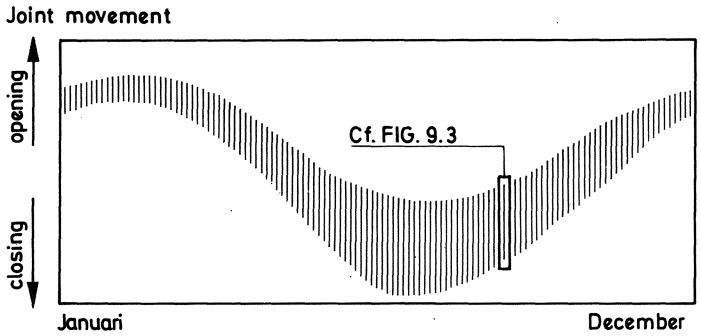


FIG. 9.2 Yearly and daily dependent movements in a joint.

In a case of both yearly and daily movements the picture could be the same as in Fig. 9.2, where the vertical lines represent the daily movements. When looking at part of this Figure and at the same time concentrating upon what happens in a predominantly elastic sealant this could be visualised as in Fig. 9.3.

Stresses are built up in the sealant at an elongation, relaxation and compression and relaxation occur until the sealant is elongated once again. These consecutive movements and relaxation periods successively increase the plastic deformations of the sealant. The growth of these deformations is particularly pronounced during the warmer seasons, as the amplitudes are greater and higher temperatures increase the amount of stress relaxation.

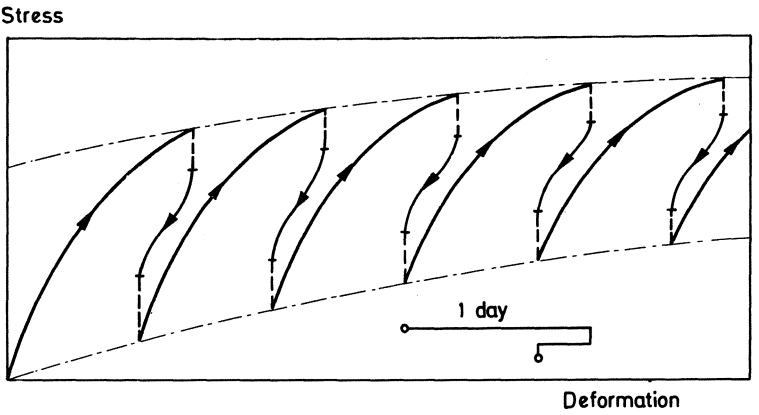


FIG. 9.3 Principal connection between stresses induced in a sealant due to daily and yearly movements. The vertical dashed lines indicate stress relaxation in the sealant.

When the temperature drops successively during autumn and winter, the joint opens. The deformation now has to be accomodated by a narrower sealant profile. This gives rise to higher stresses in the sealant. If they are high enough the sealant will fail cohesively or adhesively.

If, during a joint opening period, the total of all increments of tensile stresses minus all reductions of compressive stresses is formed according to Fig. 9.3, then a resulting stress-strain curve is obtained. If the stress relaxations are also summed up then a curve according to Fig. 9.4a can be drawn. If the same calculations are made during a joint closing period, then the curve according to Fig. 9.4b is arrived at.

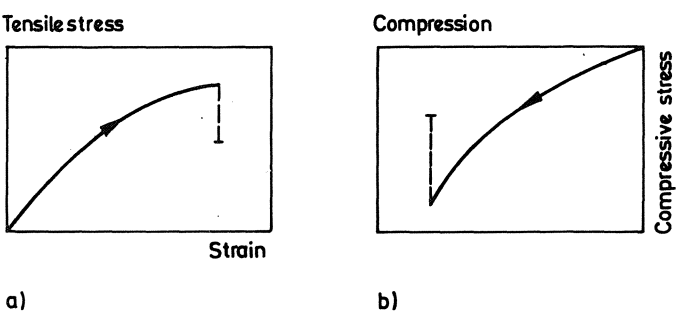


FIG. 9.4 a) The total of all increments of tensile stresses minus all reductions of compressive stresses and the total of stress relaxation according to Fig. 9.3 form a resultant stress-strain-relaxation-curve.
b) The same calculation as in 9.4a but during a joint closing period.

The discussion above can be exemplified in the following way:

* Take a joint where the yearly depending movements vary according to Fig. 9.5. A sealant with a movement capability of ±25% is chosen and applied in the autumn, point A in Fig. 9.5. To simplify matters, this point is supposed to be where equal movements occur (25%).

  During a decrease in temperature the joint opens to point B where the sealant is elongated 25% (calculated according to the original sealant width = 20 mm). The joint width at this point is consequently 25 mm.

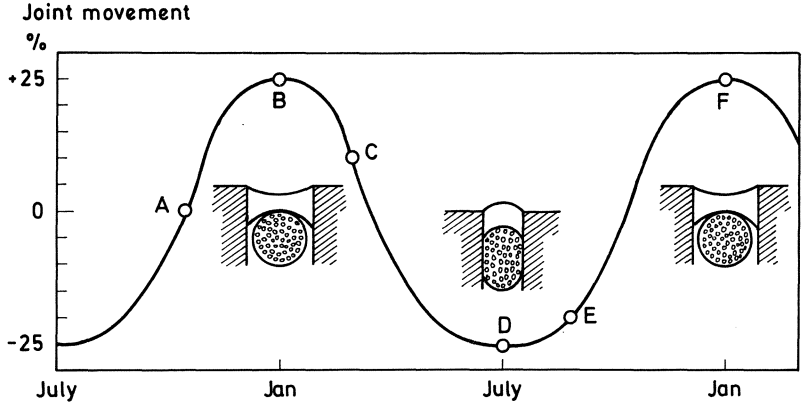


FIG. 9.5 Examples of yearly dependent joint movements. Cf. Fig. 9.6a and b.

Where the "stress-strain-relaxation-curve" that has been formed during the joint movement A-B is concerned, it can be seen in Fig. 9.6a.

During an increase in temperature the joint starts to close and the sealant starts to be compressed. At a certain level, e.g. ε = 10%, zero stress in the sealant is reached (the dotted line in Fig. 9.6a).

Thus, a new sealant width is formed (= 20 + 2 = 22 mm). This happens in point C in Figs. 9.5 and 9.6a.

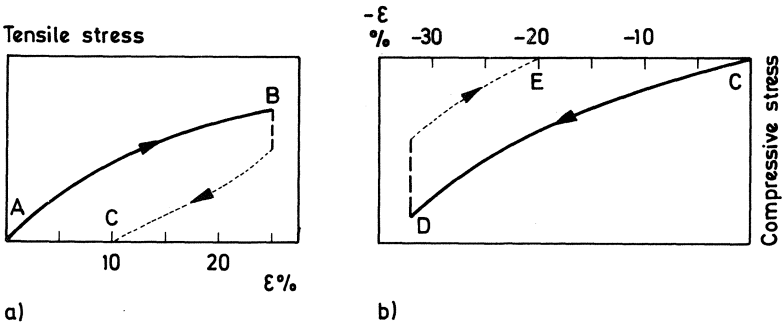


FIG. 9.6 a) Tensile stresses induced in a sealant and remaining deformations according to the example in Fig. 9.5.
b) Compressive stresses induced in a sealant and remaining deformations according to the example in Fig. 9.5.

The joint continues to close and reaches its narrowest value at point D where the original joint width is compressed 25%. However, the new sealant width will now be compressed 2 + 5 = 7 mm and the percentage compression is consequently $\frac{7}{22} \cdot 100\% = 32\%$. The corresponding "stress-strain-relaxation-curve" can be seen in Fig. 9.6b.

During the following opening of the joint the sealant is allowed to elongate, but zero stress is reached at, e.g. 20% compression (point E in Figs. 9.5 and 9.6b). Thus, the new sealant width is now $22 - \frac{20 \cdot 22}{100} = 17.6$ mm. Therefore, the elongation up to point F in Fig. 9.5 is = (20 - 17.6) + 5 = 7.4.

Now, the sealant is forced to accommodate a percentage elongation of $\frac{7.4}{17.6} \cdot 100\% = 42\%$, etc.

Practical experience shows that if failures occur in a sealant, these will usually appear within about two years. This fact, together with the example above, should indicate that the yearly depending movements cause the greatest strain on a sealant.

Therefore, it should be valuable to try and simulate these kinds of strain in a sealant.

9.3 Methods of estimating the movement capability of sealants

As pointed out previously, the basis of this work was to examine the ageing and deformation properties of the sealants themselves. The adhesive problems were said to be managed by the manufacturers. However, this investigation could illuminate the demands made on the adhesion of the sealants concerned.

Then, when estimating the movement capability of sealants, a criterion should first be stated. Such a criterion could be a tight joint. This means that no cohesive failure would be allowed to occur, but the sealant could become wrinkled. The latter is essential especially for skin-forming oleo-resinous sealants.

It is also essential to make some kind of sub-division of the inhomogenous group of sealants. A basic could, in this case, be the shape of the stress-strain curve formed by the materials. Thus, one group consists of sealants with a stress-strain curve showing a maximum point of the stress, cf. Fig. 4.5. Consequently, the other group consists of sealants which do not show a maximum point before failure. This basis of division is roughly the same as that previously defined for plastic and elastic sealants (Chapter 1).

However, the group of stress-peak-curves should also be sub-divided into two groups. Firstly, sealants which are inhomogenous through the cross-section, for example skin-forming sealants. Secondly, sealants which are homogenous through the cross-section.

Summing up, when making a simple estimation of the movement capability, the sealants could be divided into three groups:

1 a. Sealants, which are inhomogenous through the cross-section and are forming stress-strain curves with a maximum point approximately according to Fig. 4.5. A typical example is a skin-forming oleo-resinous sealant.

1 b. Other types of sealants which are forming stress-strain curves with a maximum point approximately according to Fig. 4.5. A typical example is an acrylic-based sealant, type solvent release.

2. Sealants which are forming an ever increasing stress-strain curve until failure.

As far as skinforming sealants are concerned, one critical point is the permanent strain after rupture of the surface skin. The other is the growth rate of the skin, but this can be checked according to Chapter 4.4.2.

The permanent strain after rupture of the skin can be determined for example by making specimens, according to Chapter 4.2. In order to reduce the cross-sectional necking, it could be reasonable to make the cross-section rectangular. For example 12 x 8 mm (width x depth). The specimens are heat aged 56 days at +70 ^{o}C. The stress-strain curve is determined at a reasonable rate and temperature according to the practical function. Appropriate levels are 0.001 mm/min respectively -5 ^{o}C. If the deformation rate is too high, the tensile strength of the skin will be reached at a much lower elongation, cf. Chapter 9.4. The strain at which the maximum point occurs on the curve could be called the permanent strain after rupture of the skin.

For practical use, the total movement capability of this type of sealants (elongation and compression) is equal to the permanent strain after rupture of the skin.

For the other groups of sealants showing a stress-strain curve according to Fig. 4.5, the movement capability can be determined in a similar way. These kinds of sealants are homogenous through the cross-section. Consequently, there is no need to determine any surface characteristics.

The stress-strain curve is determined on specimens according to Chapter 4.2. The specimens are stored in a climate of +23 ^{o}C/50% RH for 56 days followed by heat ageing at +70 ^{o}C for 56 days. The stress-strain curves are determined at a rate of 0.001 mm/min and a temperature of -5 ^{o}C. The strain where the maximum stress occurs is the movement capability of the sealant. Above this strain, large, local deformations will occur.

These types of sealants show a high degree of stress relaxation. Therefore, when designing the joint width the movement capability of the

sealant should be used from the narrowest calculated joint width, i.e. the original joint width at application minus the calculated closing movement. See the example in Chapter 9.4.

As discussed in Chapter 9.2 the critical mechanism of an elastic sealant is the stress relaxation periods which occur during the elongations and compressions of the sealant. These relaxations cause permanent deformations of the cross-section. If a high movement capability of a sealant is to be obtained, then these permanent deformations should be minimized.

An estimation of the amount of these deformations can be obtained by simple elongation and compression tests to various degrees of deformation and at various temperatures. The remaining deformations are then measured in each case. The sum of these deformations should not exceed a certain level, say 15%. If this is not complied with, then the elongations and compressions are decreased. A proposal for methodics is determined below.

Specimens are manufactured according to Chapter 4.2. These are cured at +23 ^{o}C/50% RH for one week and then heat aged at +70 ^{o}C for 56 days. Three specimens are elongated to 50% and three compressed to 30% at a rate of 0.001 mm/min and a temperature of -5 ^{o}C respectively +55 ^{o}C. The deformations are maintained for one hour during which the stress relaxation is registered. Then the specimens are released and the remaining deformations are determined after one hour. If the sum of these deformations divided by three is less than 15% then the movement capability of the sealant is ±15%. This value is obtained by comparing laboratory values with practical experiences.

If the remaining deformations are greater than 15%, then the elongation and compression values should be decreased to 40 respectively 20%. If the sealant satisfy the demand in that case, then the movement capability is said to be ±10%. The testing values for a third group are 30%/10% (elongation/compression) which should give ±5% movement capability.

It should also be pointed out that the tests could be carried out at a higher rate. In that case the relaxation times are prolonged before releasing the specimens. The stresses arising in the sealant in question at lower rates could then be estimated with the help of diagrams as shown in Fig. 8.7.

9.4 Examples

Oleo-resinous sealant

Suppose the movement capability of the oleo-resinous sealant, Material No. 8 according to Table 4.1, is to be determined.

The growth of the skin thickness is found to be very low, cf. Fig. 4.2.9. The permanent strain after rupture of the skin is determined according to Chapter 9.3. The results are shown in Fig. 9.7. The maximum stress, the point where the skin cracks, occurs at a strain of about 20%, which should be the movement capability of this sealant. This movement should be calculated from the narrowest joint width, cf. the example below!

The value agrees with the results in Chapter 5.3 and also with practical experiences.

If the tensile tests are carried out at a higher rate, the stress peak is moved towards smaller strains, cf. Fig. 4.2.8.

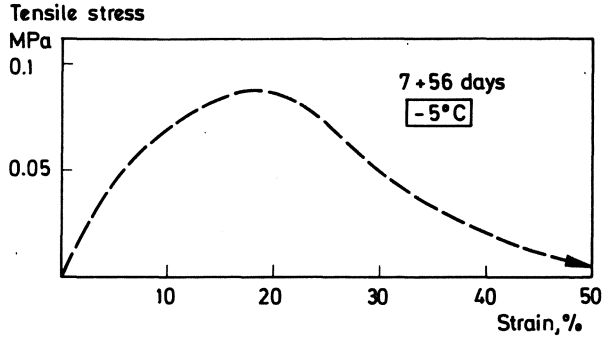


FIG. 9.7 Example of the determination of the movement capability of a oleo-resinous sealant (Material No. 8).

Acrylic-based sealant, type solvent release

Consider Material No. 6 according to Table 4.1. This material is acrylic-based, type solvent release. The stress-strain curve is determined according to Chapter 9.3. The results are shown in Fig. 9.8. The maximum stress is reached at about 15% elongation, which is the movement capability of the sealant.

As stated in Chapter 9.3 the permitted movements should be calculated from the narrowest joint width.

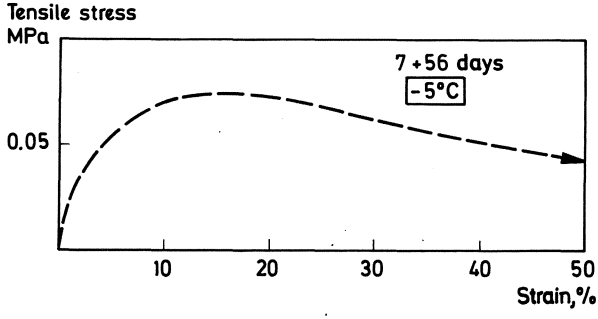


FIG. 9.8 Example of the determination of the movement capability of an acrylic-based sealant (Material No. 6).

Suppose that Material No. 6 is going to be used in a joint where the closing movements are calculated to be 2 mm and the opening movements 1 mm. How wide should the joint be?

Suppose the joint width = B mm.

$$\therefore \frac{1 + 2}{B - 2} \cdot 100 = 15$$

$$B = 22$$

If the oleo-resinous sealant above had been chosen instead, then the joint width would have been = 17 mm ($\frac{1 + 2}{B - 2} \cdot 100 = 20$).

Polysulfide-based sealant

A couple of polysulfide sealants have been examined according to the proposal in Chapter 9.3. An example is given for one polysulfide sealant, Shore A-hardness about 28.

The stress-deformation curves are shown in Fig. 9.9. At this deformations, this sealant did not satisfy the demand "remaining deformation < 15%". The movement capability of the sealant is thus less than ±15%, say ±10%.

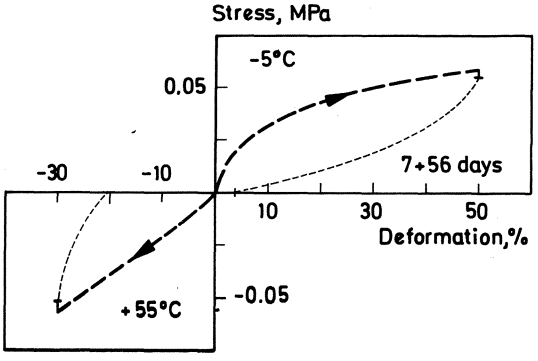


FIG. 9.9 Example of the determination of the movement capability of a polysulfide-based sealant (25° Shore A).

REFERENCES

Agri, O., and Holmlund, U., Joints in Exterior Walls (in Swedish). Information sheet B 12:1973 from the Swedish Council for Building Research.

Andersson, K.A., and Hasselblad, V., 1972, Joints in Facades made up of Precast Concrete Sections (in Swedish). The Swedish Council for Building Research. Report R 42:1972. Stockholm.

Ashton, H.E., 1969a, Weathering of Organic Building Materials. Canadian Building Digest 117, NCR, Ottawa.

Ashton, H.E., 1969b, Accelerated Durability Tests for Organic Building Materials. Canadian Building Digest 118, NRC, Ottawa.

Ashton, H.E., 1970a, Irradiation Effects on Organic Materials. Canadian Building Digest 121, NRC, Ottawa.

Ashton, H.E., 1970b, Radiation and other Weather Factors. Canadian Building Digest 122, NRC, Ottawa.

Beijer, O., 1976, Temperature and Moisture Movements in External Wall Panels of Concrete. Research 8:76, Swedish Cement and Concrete Research Institute at the Royal Institute of Technology, Stockholm.

Bendel, E., 1974, Degradation of plastic and paints surface (in Swedish). The Swedish Council for Building Research. Report R14:1974, Stockholm.

Binder, L., and Sultan, S., 1973, Methods of determining the degree of degradation of polyethylene and ageing properties of some films of polyethylene (in Swedish). Unifos Kemi AB, Sweden.

Blaga, A., and Yamasaki, R.S., 1977, Outdoor durability of a common type fire retardant glass fiber reinforced polyester sheet. Vol. 10, No. 59, Materiaux et Constructions.

Blomsterberg, Å., and Holmberg, L.E., 1974, Investigation of a Proposal to Classification System for Sealants (in Swedish). Lund Institute of Technology, Division of Building Materials.

Burström, P.G., 1977, Durability and Ageing of Sealants. Report TVBM-3003 from Division of Building Materials, Lund Institute of Technology, Sweden.

Cook, J.P., 1965, The Effects of Specimen Length on the Laboratory Behaviour of Sealants. Highway Res. Record, No. 80.

Cook, J.P., 1967, Polysulfide Sealants. Pp 175-195 in Sealants. Reinhold Publishing Corporation, New York.

Cook, J.P., 1970, Construction Sealants and Adhesives. John Wiley and Sons, Inc., New York.

Damusis, A., 1967, Sealants. Reinhold Publishing Corporation, New York.

Diergarten, B., 1973, And they move or still they do not? Measurements of joint movements (in German). Thiokol GmbH, Mannheim-Waldhof.

Dolezel, B., 1978, The Durability of Plastics and Elastomers (in German). Carl Hanser Verlag, München.

Evans, R.M., and Green, R.B., 1976, Urethane Sealants. Pp 112-133 in Building Seals and Sealants. ASTM STP 606, Philadelphia.

Foghelin, M., and Pattyranie, C., 1978, Investigation of the status regarding weather durability of paint and plastic products (in Swedish). The Swedish Council for Building Research. Report No. R19:1978. Stockholm.

Friberg, G., 1970a, Environmental Action on Polymeric Materials (in Swedish). Plastvärlden No. 3, 1970.

Friberg, G., 1970b, Ozone (in Swedish). Modern Kemi 12, 1970.

Gjelsvik, T., 1975, The Effect of the Outdoor Climate upon Materials and Constructions in Facades (in Norwegian). The Norwegian Building Research Institute, off-print No. 234, Oslo.

Gjelsvik, T., 1976, Building joint sealants (in Norwegian). Report O 5046A, Norwegian Building Research Institute, Oslo.

Grunau, E.B., 1968, Joints in Buildings (in German). Verlagsgesellschaft Rudolf Müller, Köln-Braunsfeld.

Grunau, E.B., 1976, Life Expectancy of Sealants in Buildings (in German). Das Baugewerbe, Heft 5/76.

Hockman, A., 1975, Private Communication.

HusAMA 72 (in Swedish). Stockholm 1972.

Höglund, I., 1974, Calculating extreme surface temperatures. Building Research and Practice Nov/Dec 1974.

Jagfeld, P., 1968, Alternating storage tests on joint-sealing compounds for precast concrete construction (in German). Betonstein-Zeitung, Heft 2/1968.

Karpati, K.K., 1968, Literature Survey of Sealants. Journal of Paint Technology, Vol. 40, No. 523, August 1968, pp. 337-347.

Karpati, K.K., and Sereda, P.J., 1976a, Joint Movement in Precast Concrete Panel Cladding. Journal of Testing and Evaluation, Vol. 4, No. 2, March 1976, pp. 151-156.

Karpati, K.K., and Sereda, P.J., 1976b, Measuring the Behaviour of Expansion Joints. Building Research and Practice, Nov/Dec 1976, pp. 346-355.

Karpati, K.K., Solvason, K.R., and Sereda, P.J., 1977, Weathering Rack for Sealants. Journal of Coatings Technology, Vol. 49, No. 626, March 1977, pp. 44-47.

Karpati, K.K., 1978 Device for Weathering Sealants Undergoing Cyclic Movements. Journal of Coatings Technology, Vol. 50, No. 641, June 1978, pp. 27-30.

Künzel, H., and Gertis, K., 1969, Thermal Deformation in Outer Walls (in German). Betonstein-Zeitung, Heft 9/1969.

Künzel, H., et al, 1975, Investigations in Sealants and Ageing Durability of Hard-PVC (in German). Berichte aus der Bauforschung Heft 98, Verlag Wilhelm Ernst & Sohn KG, Berlin.

Lerchenthal, H., and Rosenthal, I., 1972, Changes in some characteristics of polysulfide-based joint sealants in accelerated ageing tests. Vol. 5 - No. 29 - 1972 - Matériaux et Constructions.

Lucke, H., 1973, Sealants - Sealing Problems (in German). Bertelsmann Fachzeitschriften GmbH, Berlin.

Matsumoto, Y., et al, 1978, Fatigue and Movement Capability of Field-Molded Sealants. Paper to The First International Conference on Durability, Ottawa, August, 1978.

McCarty, W.M., 1972, Sealers for Longitudinal Joints. National Technical Information Service, U.S. Department of Commerce, Springfield Va.

Nimmermark, S., and Olsson, G., 1976, Shrinkage, Creep- and Relaxation-Properties of Sealants, (in Swedish). Lund Institute of Technology, Division of Building Materials.

Nylund, P.O., 1964, Sealants as seal in concrete facades (in Swedish). Reprint 2:1964 from the Swedish Council for Building Research.

Nylund, P.O., 1968, Movements in Joints. Bulletin 61, Division of Building Technology, the Royal Institute of Technology, Stockholm.

Nylund, P.O., 1975, Thermal Movements of Facade Panels (in Swedish). The Swedish Council for Building Research. Report R 60:1975, Stockholm.

Panek, J.R., 1979, Private communication.

Peterson, E.A., et al, 1976, Polysulfide Rubber. Pp. 11-39 in Building Seals and Sealants, ASTM STP 606, Philadelphia.

RILEM Committee 8-SR, 1975, Bibliography on the long-term weather resistance of plastics. Vol. 8, No. 44, Materiaux et Constructions.

Rosato, D.V., and Schwartz, R.T., 1968, Environmental Effects on Polymeric Materials. John Wiley & Sons, Inc., New York.

Ryder, J.F., and Baker, T.A., 1970, The Extent and Rate of Joint Movements in Modern Buildings. Report to the International Symposium for the Construction Industry. Joint Movement, Design & Materials, Brighton.

Saare, E., 1960, Ageing and Durability of Building Materials of Plastic (in Swedish). Teknisk Tidskrift h 32 1960.

Stridh, Å., and Östlund, S., 1974, Examination of Sealant Failures in Construction Joints (in Swedish). Lund Institute of Technology, Division of Building Materials.

Schröderheim, G., 1971, Life Length of Rubbery Materials (in Swedish). Korrosion & Ytskydd No. 5, 1971.

Tons, E., 1962, Geometry of Simple Joint Seals Under Strain. Publication No. 1006, Building Research Institute, Washington.

Wright, J., 1972, Outdoor and Accelerated Weathering of Elastomers and Plastics: The Assessment of an Accelerated Weathering Test Chamber. Explosives Research and Development Establishment, Waltham Abbey, England.

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