

The Ageing of PA-11 in Flexible Pipes

API TECHNICAL REPORT 17TR2
FIRST EDITION, JUNE 2003



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Upstream Segment

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The Ageing of PA-11 in Flexible Pipes

1 Introduction

In the construction of a flexible pipe, an inner polymeric pressure sheath is the only layer which seals the conveyed fluid within the pipe structure. Therefore, its integrity is crucial to safe and reliable operation. Polyamide 11 (PA-11) is the most commonly used pressure sheath material⁽¹⁾, other options being polyvinylidene fluoride and polyethylene.

This document provides comprehensive guidance on materials and pipe issues regarding the use and operation of PA-11 in flexible pipe applications, typically in production and gas handling applications up to 100°C.

The document concentrates on the use of PA-11 in the internal sheath of flexible pipes, although similar considerations may also apply to other uses of PA-11 within flexibles, e.g., anti-wear layers, intermediate sheathes and outer sheathes.

The collective goal of this document is to prevent failure of the internal pressure sheath, as a result of ageing and associated loss of mechanical properties, by determining and disseminating the necessary scientific and practical information. API Specification 17J and Recommended Practice 17B^(2,3) contain only limited information with respect to these phenomena, and this report supplements and updates the data in the Third Edition of API RP 17B⁽³⁾.

PA-11 is also used in umbilicals. However, the exposure temperatures are frequently lower than production temperatures. In cases of higher temperature exposure, the information contained in this document applies.

2 The Ageing of PA-11

2.1 BACKGROUND

The main ageing concern regarding PA-11 in flexible pipe applications, in the absence of oxygen in the bore fluids, is the effect of water at elevated temperature. The hydrolysis reaction breaks the polyamide links within the polymer, and leads to embrittlement of the material. There is a long history of detailed study of this process, and key references are listed in Appendix A.

Pipe manufacturers all use slightly different grades of RilsanTM PA-11. These differences mainly concern the product specifications and processing parameters defined by each manufacturer. It should be noted, however, that two antioxidant packages have been used within RilsanTM PA-11 over the years, both having been fully qualified according to API Specification 17J requirements. All data included in this document is based on experience with PA-11 with the old antioxidant package. The industry expects that the working life of the PA-11 with the new antioxidant package is expected to be at least comparable to that with the old package, as the basic polymer remains unchanged. The ageing and definition of

appropriate acceptance criteria for the PA-11 with the new antioxidant are currently subject to further investigation and quantification to assure at least equivalent ageing performance. Therefore it is assumed that the same service life prediction method can be used for all PA-11 pipe.

The rate of the PA-11 ageing reaction is highly dependent on a number of operational factors including the water content of the fluid, temperature, acidity (due to carbon dioxide, hydrogen sulphide, organic acids, inorganic acids), oil composition, and presence of oilfield treatment chemicals, such as methanol. Considerations regarding the chemical ageing of PA-11 are detailed in Appendix A, and summarised in the sections which follow. Outline guidelines for conducting laboratory ageing experiments are given in Appendix B.

It should be noted that other aspects of performance, unrelated to chemical ageing, may influence the use of any polymeric material in a flexible pipe, e.g., mechanical properties, fracture toughness, creep, blistering performance, coefficient of friction, thermal expansion, dynamic properties, etc. These other aspects of performance are outside the scope of this document.

2.2 THE EFFECT OF WATER IN SATURATED & UNSATURATED CONDITIONS

Experimental results derived through JIP projects and in-house research along with fundamental chemistry considerations confirm that the process affecting the ageing of PA-11 in a water environment is reduction in the molecular weight due to hydrolysis. This process is independent of the sheath thickness in typical pipe designs. There is now good agreement on this aspect of ageing from different sources. The chemical mechanisms are discussed in Appendix A.

If there is free water in a production stream, the PA-11 will age as if immersed in 100% water. It has also been found that a free water phase is not necessary for such ageing to occur. Conditions should be regarded as “wet” for the consideration of PA-11 ageing if water levels are > 80% of saturation in any given liquid or gas environment flowing within the pipe⁽³⁾.

2.3 THE EFFECT OF THE pH OF WATER

The ageing of PA-11 is accelerated in the presence of acid, under typical field operating conditions. Again, the chemical mechanisms are discussed in detail in Appendix A.

The effect of carbon dioxide is to lower the pH of produced water, and so this must be taken into account in PA-11 ageing. The effect of H₂S on pH can be similarly accounted for. pH can be both calculated and measured. There are several reliable industry and proprietary programs for calculation of pH, based on partial pressures (fugacity), temperature and water chemistry. Direct pH measurement can be very complicated. To

reflect in-situ operating conditions it must be carried out under pressure in order to account for the effect of the acid gases.

Consideration of using either the partial pressure (and/or fugacity) of acid gases or pH of the water phase in determining the effect of acid gases on PA-11 ageing is currently under further investigation. Within this document, pH calculated using full water analysis is employed.

There may also be a contribution to the pH of the water phase from acids in the oil phase, although there may also be other effects of such acids, as described in the following section.

2.4 THE EFFECT OF DIFFERENT CRUDES

Different crude compositions may affect PA-11 differently. The most important ageing effect is derived from the so-called TAN (Total Acid Number) of the crude, rather than pH, which applies only to the water phase. TAN is a gross measure of the amount of organic acids, typically naphthenic carboxylic acids, within the crude⁽⁴⁾.

The effects of TAN are generally secondary relative to the effects of water and pH. The principal effect of these high molecular weight acids, which are not soluble in water, is to give an extra “skin” effect, effectively a highly aged surface layer, on top of the pH effect. Specific ageing testing may be required for very highly acidic crudes (TAN > 3.5).

In order to quantify the effect of a specific crude on PA-11 it may be necessary to gain a more detailed knowledge of the acid species. Different ageing effects have been observed at similar TAN numbers.

2.5 THE EFFECT OF HYDRATE TREATMENT CHEMICALS

Hydrate treatment chemicals may affect the ageing of PA-11.

Pure, liquid methanol diffuses easily and quickly through PA-11 and very effectively extracts plasticiser and swells the material.

As a hydrate prevention and remediation measure, methanol is typically introduced either by continuous injection or in batch treatments. In continuous injection, the temperature is typically high, e.g., the production temperature if injected at a production wellhead, but the concentration is low. In batch treatments, the average exposure temperature may be lower than the production temperature, but the methanol is in high concentration. It should be noted that methanol used in the field varies in its water content, and is typically only specified to be > 95% methanol. The contribution of methanol to the ageing of a PA-11 internal pressure sheath must take account of all these factors.

For continuous injection, at low concentrations, typically 10 to 200 ppm, field experience suggests that methanol is not a problem. For PA-11 pressure sheath service life prediction under these conditions the effect of methanol can be neglected.

For batch treatment, an estimation of cumulative exposure time and temperature must be made. Until other data

becomes available, extrapolation of high temperature test data to lower operating temperature can then be used to give a conservative indication of the effect of the batched methanol on a PA-11 pressure sheath.

The detailed effects of methanol are subject to further investigation.

Glycols are also widely used offshore, e.g., MEG for hydrate inhibition and TEG for gas drying. Glycols do not diffuse into PA-11 as quickly as methanol, and do not cause major swelling. Conservatively, the ageing effect is comparable to water at pH = 7. Operators should be aware of the potential effects of acids created during glycol regeneration.

2.6 THE EFFECT OF TREATMENT CHEMICALS

Many different types of production chemical can be deployed in the oilfield, some of which can have an effect on PA-11. The method of deployment is important. Table 1 has been prepared by considering data derived mainly from testing of umbilicals. It should be taken as giving preliminary guidance only. If there is any doubt about compatibility with production chemicals, then specific evaluation should be carried out.

2.7 OTHER EFFECTS ON CHEMICAL AGEING

2.7.1 Wax and Scale

The effect of wax and scale is as yet undefined, although there is some evidence to suggest that they may increase pressure sheath life, e.g., as thermal barrier. This is, however, difficult to consider in either initial pipe design or operation.

2.7.2 The Effect of Treatment Fluids Trapped Behind the Carcass

It has been shown that in some circumstances, fluids can be trapped behind the internal steel carcass giving a localised environment. While this is not thought to be a problem in liquid service, gas pipes may need to take account of this. For example, in a gas pipe batch treated with methanol, the ageing effect of the methanol must take account of the time needed to evaporate methanol trapped behind the carcass. Heavier alcohols such as MEG may never evaporate from behind the carcass once there.

2.7.3 Effect of Fluids Absorbed During Storage and Hydrotest

The ageing effect of water absorbed during storage and hydrotest will be minimal, as PA-11 naturally saturates under ambient conditions, natural absorption being 1 to 2 %, dependent on temperature. The potential effects of any chemical package, e.g., corrosion inhibitors, biocides, glycols, added to the water should be considered.



Documents

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Table 1

Production Chemical	Chemical Nature	Continuous Injection	Effect of Neat Chemical
Scale inhibitor	Acrylate polymers or phosphates/phosphonates in aqueous solution, with ether and alcohol additions. Generally acidic.	No effect	PA-11 pressure sheath not normally in contact with neat chemical, but phosphonates can be aggressive.
Pour point depressants/wax inhibitors	Ethylene Vinyl Acetate copolymers in solvents	No effect	No effect. PA-11 pressure sheath not normally in contact with neat chemical.
Demulsifier	Alkoxylated phenol formaldehyde, in solvents	No effect	PA-11 pressure sheath not normally in contact with neat chemical.
Aromatic solvents	Benzene, toluene, xylene	No effect	Swelling above 40°C. Minimise exposure.
Drag reducing agents	Very high molecular weight polyalphaolefins and polyacrylamides.	No effect	No effect. PA-11 pressure sheath not normally in contact with neat chemical.
Ca carbonate scale dissolver	Strong inorganic acids, Na EDTA and alternatives	Not used in dilute form	Strong inorganic acids should not be used in PA-11 pipe.
Ba sulphate scale dissolver	Strong alkalis	Not used in dilute form	Strong alkalis above pH = 10 should not be used in PA-11 pipe.
Wax & asphaltene dissolvers	Aromatic solvents, e.g., xylene, or terpene based solvents, e.g., based on leminene	No effect	Aromatic solvents can cause swelling above 40°C. Minimise exposure.
Hydrate inhibitor	Neat alcohol, normally methanol or glycol, but may be ethanol	See section 2.5	See section 2.5.
NaOH	Hydrate inhibition	Not used in dilute form	Strong alkalis above pH = 10 should not be used in PA-11 pipe.
Corrosion inhibitor	Ethoxylated and quaternary amines in aqueous glycols or alcohols. pH in range 4 – 8	No effect	PA-11 pressure sheath not normally in contact with neat chemical, but will be aggressive and should be avoided.

Note: Storage of umbilicals containing glycol or methanol at high ambient temperature has resulted in plasticiser extraction, which was later observed in the fluid⁽⁵⁾.

2.7.4 The Consequences of Outer Sheath Damage

Mechanical damage of the outer sheath may expose the internal or intermediate pressure sheath to seawater, and any fluids used to treat the flooded annulus for anti-corrosion purposes. Where outer sheath damage occurs, there is therefore a need to evaluate the effect of seawater and any other chemicals in the pipe annulus.

Typically, where a pipe is being used to handle wet fluids, seawater will not affect the ageing process on the internal surface of the pressure sheath, but may effect the ageing profile across the sheath. Where a pipe is being used to handle dry fluids, an ageing profile will be created across the sheath,

with the most highly aged material within the pressure sheath thickness rather than on the internal surface.

2.8 DETERMINATION OF AGEING

The chemical ageing of PA-11 can be followed in a number of ways. In common with other semi-crystalline polymers, for PA-11 grades employed in flexible pipes, there is a critical average molecular weight (MW) range over which there is a transition in mechanical properties. Above this molecular weight range, the material behaves in a highly ductile fashion. Below it, it is much more brittle. As a result, chemical ageing of PA-11 can be followed by tracking molecular weight^(6–9).

Mechanical properties, such as elongation at break, have been used to follow the ageing of PA-11, and indeed API RP 17B suggests a minimum acceptable elongation to break of 50%. However, measurement of elongation at break in this material is subject to a number of difficulties, including the

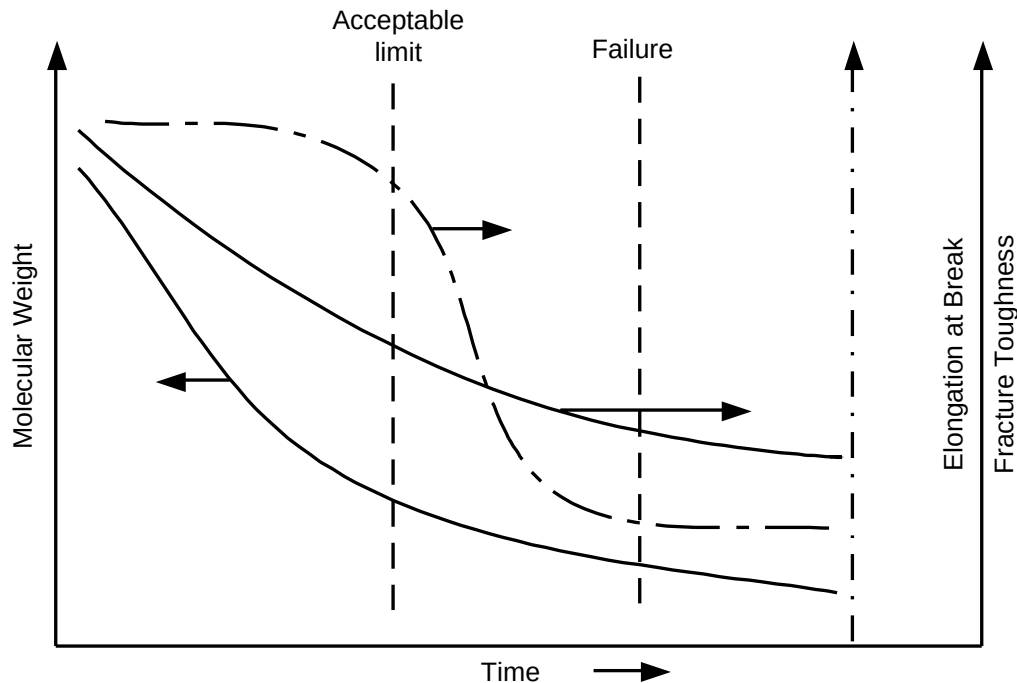


Figure 1—Illustration of the Transition in Mechanical Properties and MW with Time

need to use numerous, large samples, the fact that the tests are destructive, and the fact that test samples are very susceptible to mechanical damage during machining. However, the biggest problem with this method is that it does not detect the extent of ageing until the material has entered the stage where it begins to experience the sharp change in properties at the ductile-brittle transition. Other mechanical property measurements, such as fracture toughness, have been much less studied in flexible pipe applications, but may offer advantage over elongation at break.

In contrast, molecular weight, and its associated experimentally measured properties, are able to detect changes throughout the ageing period from new material up to and through the ductile-brittle transition. This is illustrated in Figure 1.

Therefore, the current state-of-the-art is such that molecular weight has been adopted for service life assessment. A number of MW characterisation techniques exist, such as viscosity, size exclusion chromatography, light scattering, osmotic pressure or with instruments which use multiple methods and detectors. A comparison of methods for determining molecular weight can be found in Appendix C.

Inherent viscosity represents a simple, readily standardised measurement method. A test protocol for MW determination by measurement of Inherent Viscosity is to be found in Appendix D. This method was subject to a “Round-Robin” evaluation, the results of which are described in Appendix E.

3 Service Life Prediction Models

3.1 GENERAL

The service life prediction models consist of tools for predicting the ageing of PA-11 with time over field exposure, and initial acceptance criteria, based on corrected inherent viscosity, as described in 2.8.

Service life prediction tools can be used to predict changes in molecular weight and correlated properties over field life.

Typically at the preliminary design stage, where relevant operational parameters are not completely defined, as a first approach, a Miner’s type rule is assumed for accumulated operational history, such as changes in temperature, water production, methanol injection etc. In this instance, the appropriate ageing curves from 3.4 can be employed.

Much more comprehensive models exist for use during detailed design and operation, which predict PA-11 pressure sheath life, based on detailed planned or actual operational exposure. These models are based on the rigorous chemical and physical considerations outlined in Appendix A.

3.2 INPUT PARAMETERS

In order to utilise the models, both material and operational data are needed.

For design of new pipes, a corrected inherent viscosity of 1.8 dl/g should be used as the initial value. An end user may accept the use of a higher initial value for design after

detailed review of the manufacturing history of a specific flexible pipe supplier.

For evaluation of manufactured or aged pipes, the initial molecular weight or inherent viscosity should be that measured on the manufacturing run of the actual pipe in question, according to procedures in Appendix D.

Operational data must be provided, in as much detail as possible. For example, at the design stage, a typical data set might include: temperature; water cut with time; CO₂ levels; pressure; predicted downtime; crude acidity; hot oil regime; etc. It is also necessary to include estimated cumulative exposure to production chemicals, e.g., methanol, acid etc. Temperature gradients across the pressure sheath thickness should not be considered.

Given the sensitivity of the service life models to temperature, inclusion of the temperature profile of the development over field life in any analysis can improve the reliability and accuracy of the predictions derived.

As a project moves into the operational phase, the extent and accuracy of this data should increase and PA-11 service life verification can form part of the overall flexible pipe integrity assurance process.

3.3 INITIAL ACCEPTANCE CRITERIA

The initial acceptance criterion for PA-11 pressure sheathes is based on the corrected inherent viscosity of the most highly degraded material on the inside bore of the sheath reaching a certain defined level.

It is acknowledged that in practise there may be a gradient of corrected inherent viscosity across the wall thickness of the pressure sheath. Therefore, depending upon the failure mode, consideration of only the most highly degraded material is a conservative approach.

Once the initial acceptance criterion is reached, the pressure sheath has aged significantly, as illustrated in Figure 1. In order to continue using the pipe, an analysis of potential failure modes should be performed. This will aim to evaluate the margin of safety and address risk and criticality, in a remnant life assessment, considering recovery and re-use if applicable.

The initial acceptance criteria is based on a failure criterion derived and validated from both the examination of pipe retrieved from service, detailed in Appendix F, and from laboratory mechanical property, fatigue and crack growth testing, detailed in Appendix G.

The failure criterion for a PA-11 pressure sheath is a corrected inherent viscosity of 1.05 dl/g. Therefore, the initial acceptance criterion is set at a corrected inherent viscosity of

1.2 dl/g. This initial acceptance criterion typically includes a time based safety factor of 1.6 or more over failure, e.g., 1.64 at pH = 4, 1.75 at pH = 5, and 2 at pH = 6.

It is recognised that this initial acceptance criterion is not based on a large statistical base. However, from the field failure results indicate it is conservative, and it is consistent with laboratory experience.

It should be noted that there is potentially a good case for reducing the initial acceptance criterion to 1.1 dl/g in case of static applications. There are several reasons for this:

a. *Stress levels*—In static applications, a pressure sheath is typically only subjected to thermal stresses which are lower than 3 MPa, e.g., in the case of cool down from 75°C to 20°C. In a dynamic application, stresses as a result of vessel motion, typically range from 6 to 26 MPa, ignoring thermal stresses.

b. *Number of cycles*—A static pipe is typically subjected to 1000 to 5000 temperature and pressure cycles over its life-time, whereas a dynamic pipe will see a much larger number of stress cycles, typically 10⁸.

c. *Low strain rate*—In static applications, strains rates are typically very low. There is a growing body of evidence to suggest that under such circumstances the ductile / brittle transition occurs at temperatures below those encountered in typical field conditions.

d. *Field experience*—As shown in Appendix F, all the failures of static lines have involved PA-11 material with corrected inherent viscosity lower than 0.95 dl/g.

This case for setting a reduced initial acceptance criterion for static pipe is currently undergoing further refinement.

3.4 AGEING CURVES

The prediction curves in Figure 2 are derived from the initial acceptance criterion of CIV = 1.2 dl/g.

The mathematical relations for these curves are tabulated in Table 2.

The API RP 17B relations have been taken from close examination of Figure 21 in the Third Edition⁽³⁾. The “unsaturated” RP 17B curve is still to be employed in dry service, as defined in 2.2.

The “Batched methanol treatment” relation can be used to give a conservative indication of the effect of the batched methanol on a PA-11 pressure sheath, by considering cumulative exposure time and temperature for methanol batch treatments.

A worked example of service life prediction using these curves is included as Appendix H.