

# **A MORE RELIABLE DETERGENT FOR CONE AND FULL NOTCH CREEP TESTING OF PE PIPE MATERIALS \***

**Frans L. Scholten**

GASTEC N.V., PO Box 137, 7300 AC Apeldoorn, The Netherlands.

**Dominique Gueugnaut and Frédéric Berthier**

GAZ DE FRANCE, Research and Development Division, F-93211 Saint-Denis La Plaine, France

## **ABSTRACT**

Detergents of the type nonylphenol ethoxylate (NPE) are often used in PE pipe tests at 80 °C like the Full Notch Creep Test, Cone test and Constant Load test. However, evidence is presented that this class of detergents is very vulnerable to oxidation by oxygen from the air surrounding the tests baths. This leads to a lower concentration of active detergent and hence to unreliable failure times and failure rates. Although excluding oxygen from the tests baths can stop this oxidation, effective protective chemicals like antioxidants are not available. Moreover, discussions about environmental problems caused by metabolites of NPE detergents in the aquatic environment have caused a very large reduction in the use of these substances. They may become less readily available in future.

An alternative detergent Teepol™ is presented which shows a constant activity in Cone tests on PE pipe materials during more than 1600 hours at 80 °C. Consequently this detergent is recommended for use in FNC, constant load and Cone tests.

A discussion in standardisation committees involved in these types of tests is proposed.

## **INTRODUCTION**

The resistance to slow crack growth (SCG) is one of the most important properties of PE pipes for gas and water distribution. Due to continuing innovation by resin manufacturers and extrusion companies, fuelled by market demands, the last 15 years have seen a large increase in this resistance <sup>[1]</sup>.

This has led to the situation that many PE pipe materials have become so good in this respect, that testing times may increase to impracticably long values, resulting in high testing costs. One way of tackling this problem is to use 'failure accelerators'.

Detergents are such substances. They can be used to accelerate slow crack growth phenomena in PE pipe materials, at temperatures between 50 and 80 °C.

There are 2 types of tests performed on PE pipe materials using detergents dissolved in water, with which are measured, usually at 80 °C:

1. Time to failure of a test bar or rod (constant load tests on butt welds <sup>[2]</sup>, Full Notch Creep tests <sup>[3,4]</sup>)
2. Incubation time and slow crack growth rate (Cone tests <sup>[5-7]</sup> on 20 to 125mm pipes).

*\* Presented at the Plastics Pipes 11 Conference, Munich, Germany, 2001.*

Of course, in all cases the concentration and activity of the detergent should remain constant during the duration of the tests.

Up to now the classical surfactants used are those specified in the SCG related standards [8], noticeably detergents of the class NPE (nonylphenol ethoxylate, with trade names like Antharox™, Arkopal™, Igepal™ and Marlophen™), or to a lesser extent other types of commercial detergents, the most well-known being Teepol™.

However, more than 12 years ago it was published [2] that solutions of NPE detergents in water suffer from oxidation at a test temperature of 80 °C by oxygen from the surrounding air, while exclusion of oxygen from the test bath limits this oxidation.

As a consequence of oxidation, acidification of the test solution takes place, which can be easily measured using a pH meter. Although NPE detergents are non-ionic in nature and its watery solutions therefore have a very low conductivity, ionic reaction products are formed and the conductivity increases markedly.

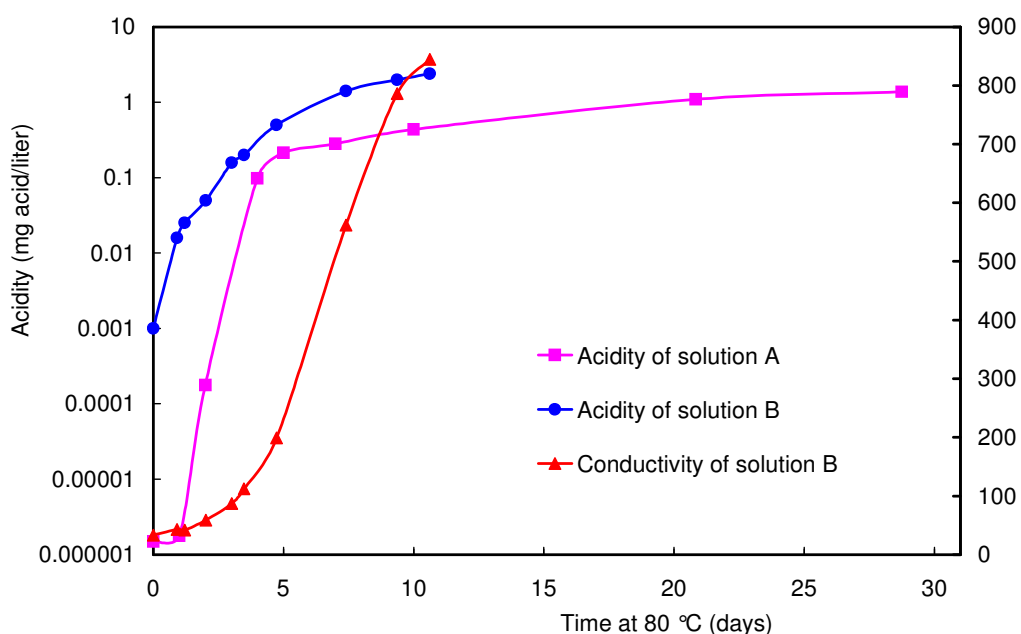


Figure 1. Acidity and conductivity of a solution of 2% Arkopal N110 in de-ionised water at 80 °C (solution B). Solution A: Antharox NPE detergent in drinking water at 80 °C, recalculated from a publication in 1989 [2]. Both solutions in contact with air.

Figure 1 shows that due to oxidation of NPE detergents the acidity, expressed as mg H<sup>+</sup> ions per litre, may increase with a factor of more than 10<sup>5</sup> in only about 10 days at 80 °C. This is accompanied by an increase in conductivity from about 30 to 850 microSiemens/cm in the same time period. These are very large effects that cannot be ignored, because they inevitably lead to a large decrease in the concentration of active detergent in the test solution and consequently to unreliable failure times [2] or crack growth rates. When this happens, much time and money is lost in testing of PE pipe materials. Reliable detergents are needed that produce constant failure times during at least 1 month or preferably longer at 80 °C.

The GERG Materials Bank Group, representing users of PE pipe materials in a number of European countries, has decided to investigate this problem and if necessary present an alternative detergent. The companies that participated in this work are:

ARGB and Electrabel (Belgium)

Ruhrgas A.G. (Germany)

Gaz de France (France)

Gastec N.V. (The Netherlands)

Advantica Technologies Ltd (UK).

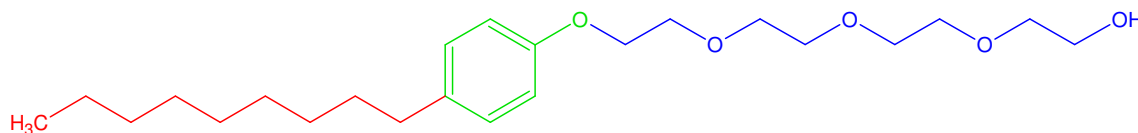
The goal of the work was to investigate which methods exist that can prevent or delay oxidation at 80 °C and to determine whether NPE detergents are still attractive in future for use in Cone and Full Notch Creep testing of PE pipe materials. An alternative detergent, Teepol™, used since the beginning of the 1980s by Gaz de France, was also evaluated.

### **Background of NPE detergents**

The general chemical name of an often-used type of detergent for testing of PE materials is nonylphenol ethoxylate (NPE). The chemical formula is given in Figure 2.

Like most detergents it consists of a ‘hydrophobic’ or water repelling part (nonyl), and a ‘hydrophilic’ or water compatible part, the ethoxylate group on the right.

The aromatic group in the middle including the first oxygen group attached to it is the phenol group, which links the hydrophobic and the hydrophilic parts together.



*Figure 2. Chemical formula of a nonylphenol ethoxylate detergent with only 4 ethyleneoxide groups (on the right). Arkopal N110 however contains 11 of such ethyleneoxide (EO) groups. The hydrocarbon part on the left is a nonyl group. The aromatic phenol group is in the centre.*

### **Oxidation of NPE detergents**

During testing of PE materials, the detergent solution is in constant contact with air, which contains 21% oxygen. Consequently, some oxygen dissolves in the water bath, even at 80 °C. Data provided by Baird<sup>[9]</sup>, shows that the solubility of oxygen strongly depends on temperature. At 80 °C there is still oxygen dissolved in the testing baths (13.8 mg O<sub>2</sub>/litre) that is capable of oxidising the detergent. At 95 °C, oxygen content is estimated by linear interpolation of Baird’s data as 3.9 mg O<sub>2</sub>/litre, which is 28% of the solubility at 80 °C. However at 100 °C, the concentration of dissolved oxygen becomes zero.

In the earlier publication by Scholten et al<sup>[2]</sup> a reaction mechanism was given for the oxidation of the detergent in watery solutions at 80 °C. It was assumed that only the hydroxyl group at the end of the ethoxylate chain would be oxidised into acid. After discussions with specialists however, this mechanism proved wrong. It is now known that the whole ethoxylate chain is split into smaller units (possibly individual ethyleneoxide groups) and that these become oxidised into formic acid and other (partly coloured) products.

This also means that the ethoxylate chain becomes gradually shorter during this oxidation process. Such a process was also measured for bacterial oxidation<sup>[10]</sup> of NPE detergents.

Finally, nonylphenol may be left. Especially this oxidation product raised environmental concerns, as will be discussed later.

## RESULTS

### *Excluding oxygen from the NPE-water solution*

Table 1 shows the effect of reducing the oxygen content of a NPE detergent solution to zero, by testing at 100 °C. It appears that both pH and conductivity are largely unaffected during 5 weeks of testing at this temperature. No PE samples were tested during this experiment.

*Table 1. Acidity, pH and conductivity of de-ionised water with 5% Arkopal N110 exposed to 100 °C.*

<b>Exposure time (days)</b>	<b>pH</b>	<b>Acidity (mg acid/litre)</b>	<b>Conductivity (µSiemens/cm)</b>
0	7.4	$4.0 \cdot 10^{-5}$	
7	8.6	$2.5 \cdot 10^{-6}$	
14	8.6	$2.5 \cdot 10^{-6}$	
32	8.8	$1.6 \cdot 10^{-6}$	182
35	8.9	$1.3 \cdot 10^{-6}$	176

It is also possible to exclude oxygen from detergent solutions by continuously purging the solution with nitrogen gas. As was shown earlier <sup>[2]</sup> this prevents detergent oxidation during at least 600 hours at 80 °C, but probably much longer. Application of nitrogen purge will be mainly governed by practical considerations like costs, ease of operation and possible health hazards (unacceptable expelling of oxygen from the test lab).

Figure 3 shows a comparison between Cone test results obtained with and without nitrogen purge of the testing bath on the same PE100 material. The 2 curves measured without nitrogen purge show an 's-shaped' behaviour. After 30 days, the curves level off, most likely due to oxidation of the detergent. The rate of slow crack growth (Table 2) was only calculated from the highest slope of these curves (between 20 and 30 days).

Although the curves measured with nitrogen purge are not linear over the entire range either, there is no intermediate part with higher slope. That is why the rate of slow crack growth was calculated from the testing period between 30 and 70 days. Lower slopes are found.

Table 2 shows results measured with air contact and with nitrogen purge of the testing baths. In all cases the apparent rate of slow crack growth in the Cone test was calculated from the highest slope of the curve.

The incubation time is defined as the intercept on the horizontal axis when the regression line is extrapolated to zero crack length. Sometimes negative values are found.

The results obtained with nitrogen purge are obviously the more reliable ones.

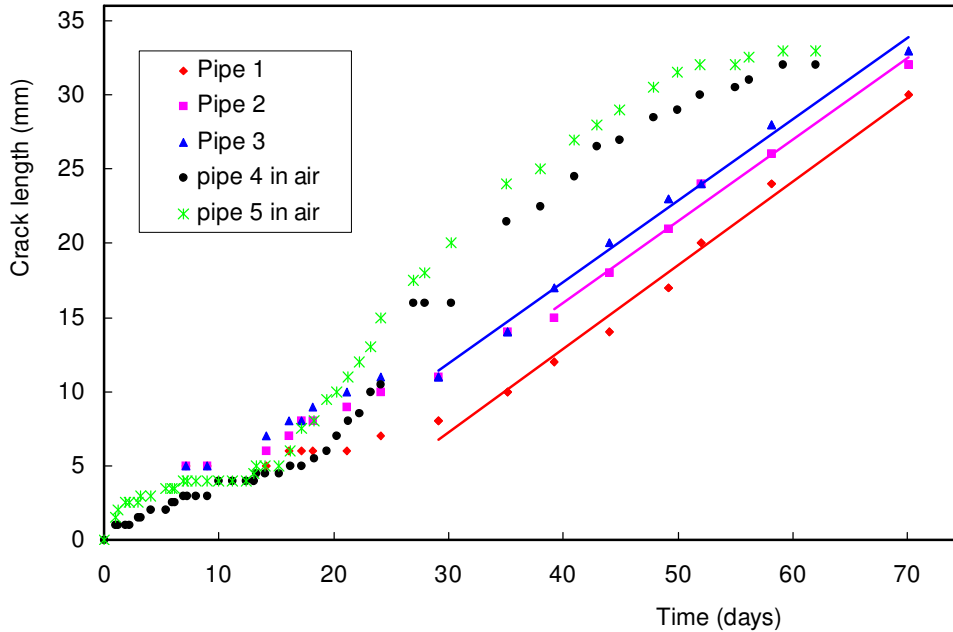


Figure 3. Cone test results on a PE100 pipe material with nitrogen purge (pipes 1, 2 and 3) and without nitrogen purge (pipes 4 and 5).

Table 2. Cone tests with and without nitrogen purge on 32 mm pipes in two- or threefold

Material	N2 purging	Incubation time (days)			Apparent crack growth rate (mm/days)		
A (PE100)	no	10	13		1.01	0.97	
A	yes	17	11	9	0.56	0.55	0.55
B (PE100)	no	8	10		1.59	1.63	
B	yes	- 3	0	- 6	0.70	0.73	0.69
C (MDPE)	no	0	1		0.85	0.96	
C	yes	36	> 70	26	0.85	0.00	0.66
D (PE100)	yes	3	33	2	0.50	0.67	0.58

#### Using a TEEPOL™ -water solution

In Table 3 test results in Teepol™ are compared to results obtained in Arkopal N110™. The materials were selected from the GERG Materials Bank<sup>[1]</sup>.

Those materials that showed no crack growth with Arkopal N110, like O3 and O6 do show failure in Teepol™, although O3 only after a very long incubation time of more than 1200 hours. Also O4 sometimes shows a similar long incubation time in Teepol of more than 1200 hours.

It is emphasised that differences in incubation time are due to crack blunting behaviour of some MDPE materials like O3, O4 and O6. So these differences are not a 'quality parameter' for comparing the reliability of detergents.

*Table 3. Cone test at 80 °C on PE80 materials using 2% Arkopal N110 and 2% Teepol, both dissolved in de-ionised water*

Material	Type	Incubation time (days)		Aver. crack speed (mm/day)	
		Arkopal N110	Teepol	Arkopal N110	Teepol
O1	HDPE	1 – 3	0.3 – 0.5	3.83	14.1
O2	MDPE	1	0.4 – 0.7	4.24	13.8
O3	MDPE		50 – 64	0.00	6.6
O4	MDPE	0.5 – 1	7 – 64	4.83	15.3
O5	HDPE	0.5 – 1	0.3 – 0.4	6.82	16.3
O6	MDPE		0.8 – 1	0.00	5.7

The failure rates in Teepol™ are clearly higher than those in Arkopal N110™. When in Teepol™ failure rates below about 6 mm/day are obtained, no failures occur in Arkopal N110™ (O3 and O6), even after 1470 hours. This can only be due to oxidation of Arkopal N110™. For the other materials the ratio of failure rates ranges from 2.4 to 3.7. This is favourable in view of the testing times and costs.

The above results mean that Teepol™ is an attractive alternative to NPE detergents.

## **DISCUSSION**

First it is discussed which possibilities exist to prevent or limit oxidation of NPE detergents at 80 °C. Purging with nitrogen gas was already proven successful.

### ***Increasing the detergent concentration***

It is possible to increase the concentration of NPE detergent in water from 2 to 5 or 10%. It is thought that at higher concentrations more time will be available during which enough active detergent is present to promote stress cracking in PE materials.

However chemical reaction theory predicts that reaction rates increase with the concentration of the reactants (NPE detergent and dissolved oxygen). Consequently the rate of oxidation will increase rather than decrease. This will counteract the effect mentioned above.

The result will be that the success of this approach may be rather limited. Decreasing the concentration of dissolved oxygen will have a much larger effect, as has already been shown.

### ***Adding antioxidants to NPE-water solutions***

It is not known, which types of antioxidants will act satisfactory, because most types used for plastics are not soluble in water. Consequently it is uncertain what the effectiveness of adding antioxidants to NPE solutions will be.

Moreover, since the Cone test can be used during pipe production as part of French specifications <sup>[7]</sup>, such a test has to be feasible in an industrial environment and one therefore has to minimise any additional actions during the tests (additives or anything else).

***Future availability and environmental issues of NPE detergents***

NPE detergents have been very often used for industrial washing and textile finishes. Some years ago, concerns were put forward <sup>[11-14]</sup>, that their degradation products or metabolites like nonylphenol could act as hormones in animals. Its metabolites can mimic the sex hormone oestrogen in fish living in water containing NPE detergents.

As a result of the debate about this item, large industrial textile fibre producing companies in Germany agreed to a voluntary renunciation of this class of detergents. Detergent producers like Hoechst and Huels have sold their NPE business to other companies.

Due to these developments, NPE detergents may become more difficult to obtain. It is possible that in future this class of detergent will only be produced in remote countries and introduced in more developed countries by traders. Manufacturers may become reluctant to provide technical support, also because the market for testing of PE is futile to them.

A problem is that NPE11 detergent is still recommended in certain ISO standards, for instance the draft ISO standard for the FNC test <sup>[3]</sup>, issued on 24 April 1999.

In view of this there exists a large problem of acceptance that Arkopal N110 may have to be abandoned in future for testing of PE materials.

***Possible reintroduction of the Teepol™ detergent***

The intensive use the Teepol™ detergent since the early eighties at Gaz de France has provided a large amount of experience regarding both the activity of this detergent and the reproducibility of the results obtained in this way.

First of all, the long-term stability - meaning here the related long-term activity - has been proven several times during very long testing periods up to ca. 800 hours <sup>[6]</sup> as shown in Figure 4. It presents a comparison between 2 MDPE materials with similar crack growth rates, but largely different incubation times.

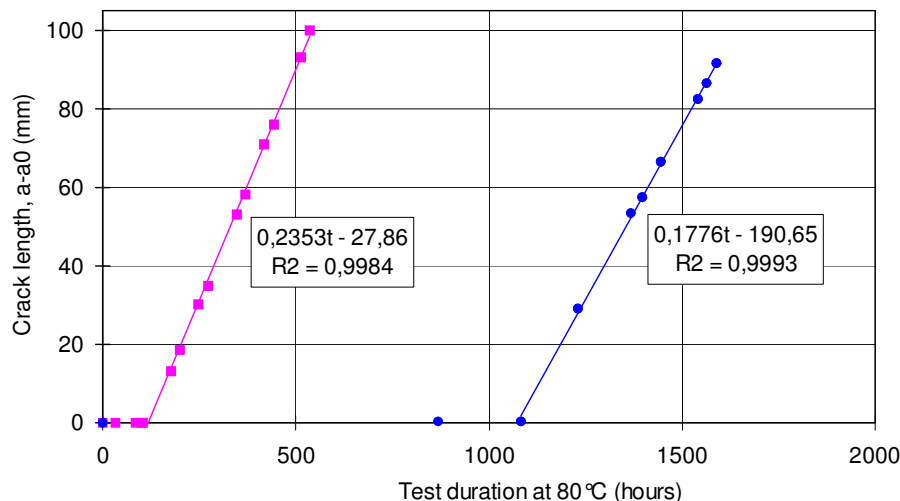


Figure 4. Cone testing at 80°C with a 3% Teepol™ watery solution carried out on 2 SCG resistant PE80 pipe materials (hexene copolymers).

Both curves display a perfectly linear behaviour showing that the solution can be kept very easily at the same activity level even after very long incubation times or crack growth periods. Other studies by Gaz de France on both Cone specimens and pipes show that such a constant activity is achieved if Teepol™ concentrations are beyond ca. 3% (weight). Higher detergent concentrations do not modify both the incubation time and crack propagation. Consequently Cone testing leads to accurate and reproducible data even without refilling the solution since the detergent concentration is constantly increasing during the test period due to water evaporation - which can be further minimised by a correct design of the test baths.

The activity of the Teepol™ detergent was also investigated focusing on its accelerating properties regarding SCG. Cone tests were carried out under both air and 3% Teepol™ watery solution at both 80 and 70 °C.

As shown in Figure 5 established for two ethylene-butene copolymers (5221 and 2477), both incubation time and crack growth rate are clearly modified in the presence of Teepol™ in comparison to air.

Teepol™ causes a large reduction in the incubation times, up to 97%. Large increases in the crack growth rate are observed as high as 86% for both PE materials, even at 70°C.

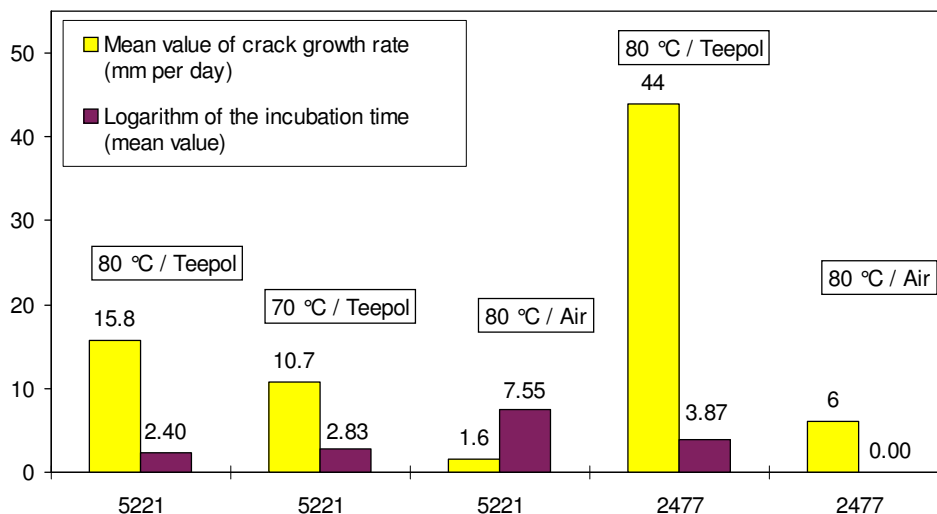


Figure 5. Comparison of the SCG behaviour of butene-type PE63 pipe materials in the Cone test at 80 and 70 °C in Teepol™ solutions and in air.

Microscopic examination of the fractured surfaces obtained by testing in detergent solution and in air at 80 °C reveal different patterns for PE63 #5221 and PE80 #5223. As shown in Figure 6, 80 °C-air testing leads to a less disturbed surface compared to that obtained when the test is carried out in the Teepol™ solution.

This can be explained in terms of both a lubricating role and a surfactant effect of this detergent, phenomena extensively studied and described elsewhere<sup>[15,16]</sup>. Swelling of PE chains by the detergent solution helps in the formation of voids and later crazes and consequently leads to a delayed or postponed crack growth by successive steps as observed on the photographs. These growth steps are mostly visible on an ethylene-hexene MDPE copolymer like #5223 that is more likely to resist SCG by disentanglement.



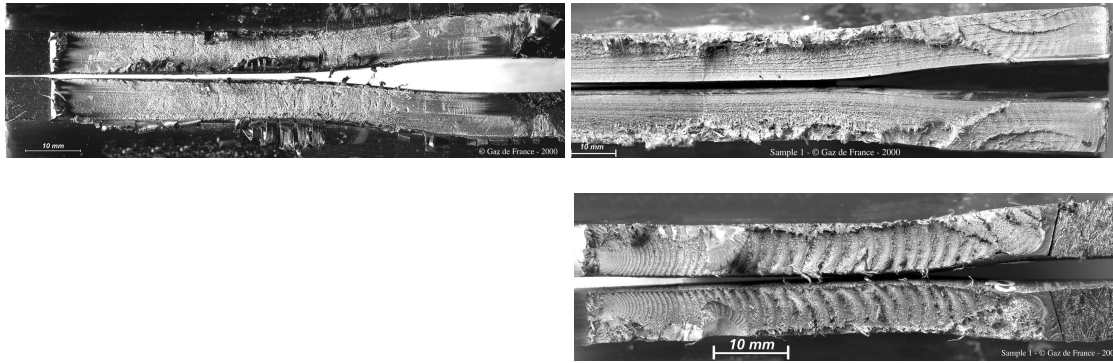


Figure 6. Fractured surfaces of PE #5221 in air (top left) and in 3% Teepol (top right) and PE #5223 in 3% Teepol (bottom) after 80 °C Cone testing.

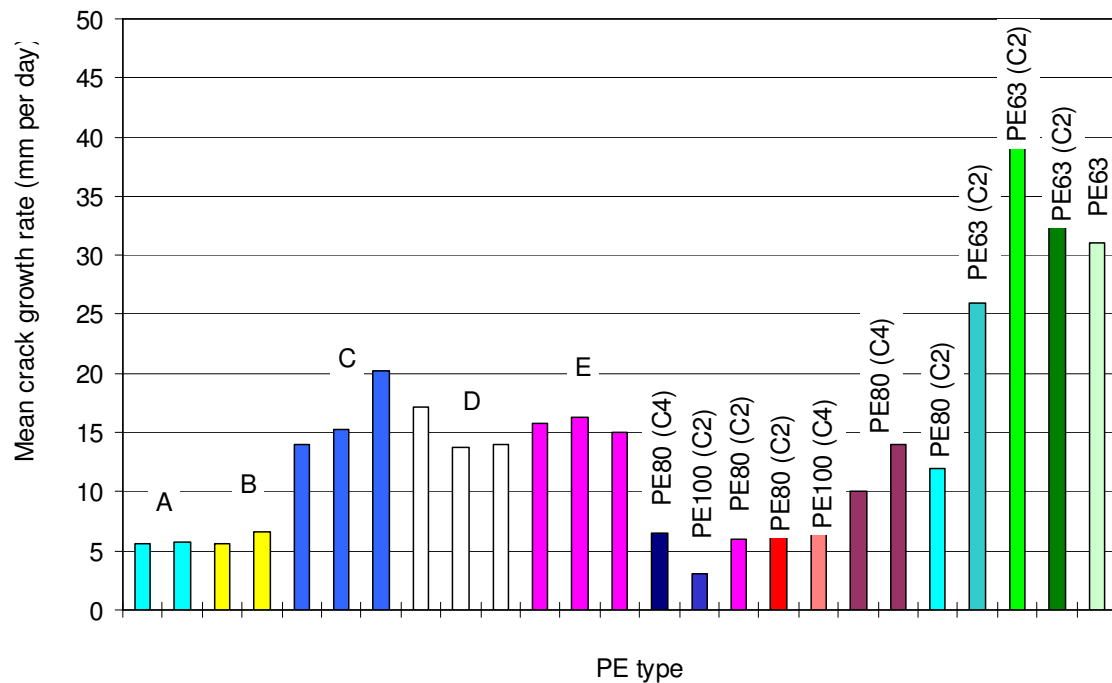


Figure 7. Comparison of the crack growth rates obtained at 80°C in 3% Teepol™ for currently used PE pipe materials

To prove the sensitivity of 80 °C Cone testing in Teepol™ a wide variety of PE resins has been tested. Moreover, the reproducibility of these tests has been verified by multiple runs carried out on several batches from a same PE reference within a ten-year period. Figure 7 presents part of these results.

The reproducibility of the results for 5 representative PE materials shows that the Teepol™ activity is fairly constant over a 10 year period (sets A, B and E), indicating that no major formulation changes have occurred with this detergent. For a given material the fluctuations observed on the crack growth rates can reasonably be attributed to both normal measurement

scatter and batch-to-batch variations (sets B, C and D). Cone testing in Teepol™ is very efficient at revealing significant SCG differences due to processing variations<sup>[17,18]</sup>.

## CONCLUSIONS

- During FNC and Cone testing of PE pipes at 80 °C oxidation of NPE detergents rapidly sets in. This leads to very unreliable failure times and rates of slow crack growth.
- The only possibility to keep using NPE detergents in PE pipe testing is to purge the testing baths with nitrogen continuously, to limit detergent oxidation at 80 °C as much as possible. Protective chemicals like antioxidants have not (yet) been identified.
- Teepol™ was found to be a reliable detergent for testing at 80 °C using the Cone test. A constant activity during at least 1600 hours at this temperature of a 3% solution of this detergent in drinking water was proven. Moreover, using this detergent leads to a reduction in failure times with a factor of 2 or 3 compared to NPE detergents and to a more accurate ranking of PE pipe materials.

## REFERENCES

- [1] Scholten F.L. and Wolters M., 'GERG Materials Bank of PE Gas Pipe Grades - recent developments', International Gas Research Conference, 1998, San Diego, USA.
- [2] Scholten F.L., Pisters J. and Venema B., *Polym. Testing*, **8** (1989), 385-405.
- [3] ISO/CD 16770 'Plastics – Determination of environmental stress cracking (ESC) of Polyethylene (PE) – Full Notch Creep Test (FNCT)' (draft).
- [4] Gueugnaut D., Boytard K., Dang Van K., Ouâkka A., Mamoun M.M., Kanninen M.F., Kuhlman C.J., Popelar C.H., Bernardini G., Frassine, Rink M., Berggren B., Tränkner T., International Gas Research Conference, pp. 471, Cannes, France, 6-9 Nov. 1995.
- [5] Gueugnaut D., Marty F., Bon J., Dang Van K., Ouakka A., *Plastics Pipes IX*, pp.561 Edinburgh (Scotland), UK, 18-21 Sept.1995.
- [6] Gueugnaut D., Rousselot D., 16th International Plastic Pipes Fuel Gas Symposium, pp. 113, New Orleans (LA), USA, 1-4 Nov.1999.
- [7] French Standard NF T54077, published December 1992.
- [8] ISO Standard FDIS 13480 : 1997 (F).
- [9] Baird J.C.: <http://jcbmac.chem.brown.edu/myl/hen/oxygenHenry.html>, Brown University.
- [10] Corti A., D'Antone S., Solaro R. and Chiellini E., *J. Environ. Polym. Degrad.* **6** (1998), 121.
- [11] Soto A.M., Justicia H., Wray J.W. and Sonnenschein C., *Environmental Health Perspectives*, **92** (1991), 167-173.
- [12] Jobling S, Sumpter J.P., *Aquatic Toxicology*, **27** (1993), 361-372.
- [13] White R., Jobling S, Hoare S.A., Sumpter J.P. and Parker M.G., *Endocrinology*, **135** (1994), 175-182.
- [14] Sherman J.D., *Toxicology and Industrial Health*, **10** (1994), 163-179.
- [15] Soares J.B.P, Abbott R.F., Kim J.D., *J. Polym. Sci., B: Polym. Phys.*, **38**, (2000), 1267.
- [16] Wright D., "Environmental Stress Cracking of Plastics", Rapra Technology Ltd, ISBN 1-85957-064-X, 1996.
- [17] Gueugnaut D., Relet P., Rousselot D., Polymer Processing Society, International Regional Meeting, pp. 271, Palermo, Italy, 15-18 Sept. 1991.
- [18] Gueugnaut D., Rousselot D., Polymer Processing Society, European Meeting, 6.18, Stuttgart, Germany, 26-28 Sept.1995.