ATLAS MATERIAL TESTING SOLUTIONS

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Expert report on weathering tests results on HDPE colored pipes

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Prepared for

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This proposal was developed by Atlas Material Testing Technology GmbH, in the following called ATLAS, for PESTEC GmbH, in the following referred to as PESTEC.

Objective and Scope

The report shall provide an expert opinion on the reliability of accelerated laboratory weathering tests to estimate the long-term durability of HDPE colored cable pipes in end-use conditions, expected to extend for over 50 years in any location worldwide.

In particular, the following questions will be addressed:

- Are PESTEC pipes suitable to comply with the general requirements mentioned in TI 110-2 Edition 0604 page 1?
- Are reported Xenotest® 1200 / Weather-Ometer® Ci4000 test methods state-of-the-art to predict long-term durability for installed HDPE pipes?
- Are executed test evaluation methods (grey scale, colorimetric measurements) state-of-the-art to obtain results relevant to real use?
- Is PESTEC translation chart TI 110-19 Edition 0604 page 5 of result evaluations suitable for evaluating the test results?
- Is PESTEC color recommendation system of TI 110-29 Edition 1104 suitable for decision?

Summary

The results of the technical reports provided by PESTEC have been reviewed. The answer to the initial questions is given in the conclusion.

In general, the author agrees with the conclusions of the various independent laboratories concerning the expected lifetime of tested PESTEC products, which rely on equating radiant exposure between accelerated and real life conditions. However, an important factor that was not taken into account in the interpretation of results is the additional acceleration achieved with higher tests temperatures compared to real life. According to the author, lifetimes longer by at least a factor of two were achieved with these tests.

Background and overview of the reports evaluated

In the years 1990s, PESTEC has undertaken a series of natural and artificial weathering tests to evaluate the durability of their products, HDPE pipes uses for the protection against corrosion of inner strands of stay cable bridges. PESTEC currently provides a warranty of 20 years, although it is desirable that the installed pipes retain their mechanical and appearance properties for over 50 years.

Artificial weathering tests were conducted at recognized independent testing institutes according to international standard (Hoechst Laboratory) and French automotive OEM's test methods (Sercovam, PEP). These tests were characterized by their very long duration, ranging from 5,000 hours up to 20,000 hours.

These laboratory tests described below were carried out in instruments using a filtered xenon arc source which still today represents the best available simulation of natural daylight.

Natural weathering tests were performed in an outdoor site up to 5 years by Hoechst Laboratory, as well as in end-use conditions (bridge in Southern Spain) up to 11 years.

The results of these tests were evaluated according to their visual appearance (grey scale criterion and visual assessment of microcracks), colorimetric assessment (at PEP) and mechanical testing (Hoechst Laboratory and PEP).

Review report

1. Introductory note

Most known polymeric materials, in particular polyolefins, undergo a chemical evolution induced by the effect of the UV radiation ranging from 295 to 380 nm, in combination with atmospheric oxygen, that leads to the decrease in useful properties of the material and ultimately to its failure. Additional factors like temperature increase will affect the rate of the degradation, that can most often be accounted for by the Arrhenius law, while moisture acts primarily as mechanical stress, by swelling and subsequently desorbing from the material in a cyclic manner. In the particular case of PE, in reason of the very low coefficient of adsorption of this material, the effect of moisture will be very limited.

A common practice in using laboratory weathering tests to predict the service life of a material is to equate the radiant exposure of a test to the radiant exposure necessary to obtain the failure of the material in outdoor exposure or in real life. Most often the service life expectancy is unknown, so the test is carried out until the radiant exposure equates the minimum radiant exposure the material should withstand without a unacceptable change in properties. To reduce testing times, a few acceleration techniques can be used.

However, when the expected lifetime of a material is longer than 10 years, it is no more possible to carry out reliable accelerated weathering in a reasonable time compatible with products development cycles. In the case of PESTEC, the tests performed at Hoechst Laboratory and Sercovam are characterized by they extremely long duration and therefore can be referred to as long-term accelerated tests by comparison the average laboratory test duration performed in the plastic industry. In particular, Sercovam tests are among the longest commercial accelerated tests in the filed of weathering.

2. Factors other than light that may influence the actual results

The equivalent real life duration estimated from the tests are only based on the acceleration of the photooxidation reactions, which cause chain scissions, responsible for the decrease in gloss and tensile properties, as well as crosslinking that account for the decrease in elongation at break, making the material more brittle. It does not consider the acceleration of the reactions due to temperature. Since the temperature of the reported laboratory tests is higher than the average temperature measured in Southern and in Central

Europe, it is the author's opinion that these tests simulate longer real life durations than the calculated values indicated in the various reports.[1] A rough although realistic estimate of the acceleration attributable to the temperature effect is given by the author, based on data available in the specialized literature. However, a precise estimation of this effect, which would require a climatic survey of various regions where pipes are used is outside the scope of this report.

Among other potential stress factors that are not taken into account in these tests are compressive or tensile mechanical stress due to temperature cycling, wind, and internal friction force between the pipe and the cable an/or the potential effect of atmospheric pollutants on the oxidized material in highly polluted areas, that would in principle decrease the actual lifetime of pipes. However, these factors occur randomly and cannot be reliably reproduced in either an outdoor or laboratory weathering test.

3. Results of Laboratory Testing

3.1 Tests at Hoechst Laboratory

The early laboratory exposure of white PESTEC pipes were performed between 1991 and 1992 for up to 10,000 hours in a Xenotest 1200 instrument according to the DIN 53387 standard. This standard has since been withdrawn and replaced by the international standard ISO 4892-2, both standards having nearly identical input parameters.[2] The average irradiance was 0.55 W/m² at 340 nm, corresponding to 66 W/m² in the 290-400 nm range (UV range), that is an hourly UV radiant exposure of 237.6 kJ/m². From **table 1** showing the equivalence between the various spectral ranges for different locations, it can be calculated that the radiant exposure received by the samples in the UV range in this test is the same as received after 8 average years in Southern Europe (i.e. ca. 70,000 hours), and 11 average years (i.e. ca. 96,000 hours) in a typical Central European climate (e.g. Frankfurt). The corresponding time factor of this test is ca. 7 relative to Southern Europe and 10 relative to Central Europe.

Region	Langley	295-3000 nm Global	295-800 nm UV + visible	295-400 nm UV	340 nm
Southern Florida (Miami)	140 KLy	5,850 MJ/m²	3,400 MJ/m²	355 MJ/m²	3.2 MJ/m².nm
Central Arizona (Phoenix)	190 KLy	8,000 MJ/m²	4,600 MJ/m²	440 MJ/m²	4.4 MJ/m².nm
Southern Europe (France)	120 KLy	5,000 MJ/m²	2,900 MJ/m²	300 MJ/m²	2.7 MJ/m².nm
Central Europe (Frankfurt)	85 KLy	3,550 MJ/m²	2,050 MJ/m²	215 MJ/m²	1.9 MJ/m².nm

Table 1: Average yearly radiant exposure for various location. The use of Langley unit is only relevant for the global solar radiation range 295-3000 nm. Equivalence: 1 KLy = 41.84 MJ/m².

[1] According to the Arrhenius law, a temperature difference is likely to provide an acceleration of the chemical evolution of the tested products in laboratory conditions, the extent of which depends on the actual value of the temperature difference and the apparent activation energy of the degradation process.
[2] ISO 4892-2:2006 Plastics – Methods of exposure to laboratory light sources – Part 2: Xenon-arc lamps.

A formulation of white pipe was tested. No visible color change was observed. Although not visible with naked eye, micro-cracks developed within a depth of 100 µm, but did not induce any measurable change in mechanical properties.

3.2 Tests at Sercovam

PESTEC pipes were tested against two Renault weathering test methods up to 20,000 hours. At the end of the 1990s, these tests were widely used by Renault and its paints and plastic parts suppliers and represented the state-of-the-art testing procedure.

NOTE #1: To give a comparison between the length of the tests requested by PESTEC and by French OEMs, Renault (as well as PSA Peugeot Citroën) conduct these tests up to between 1,500 and 2,000 hours to validate materials expected to have a 5 to 10 year service life.

NOTE #2: Although D27 1911 and D27 1380 tests look similar, the former one deliver about twice the radiant exposure of the latter one during the same period and uses higher temperature settings. This implies that D27 1911 is expected to provide at least twice the acceleration of D27 1380.

3.2.1 Test D27 1380 [3]

The first test, referred to as D27 1380/E, was conducted in a Xenotest 1200. Since light periods alternated with dark periods of equal duration, the average irradiance was 34 W/m² in the 290-400 nm range (UV range), that is an hourly radiant exposure of 122.4 kJ/m². According to **table 1**, it was calculated that the radiant exposure received by the samples in the UV range after 20,000 hours is the same as received after 8 average years in Southern Europe, and 11 average years in a Central European climate. The corresponding time factor of this test is ca. 3.5 relative to Southern Europe and 5 relative to Central Europe.

Samples 2 to 6 samples underwent a slight color fading, with samples 4 (RAL 9003) and 5 (RAL 9002) showing microcracks. Sample 1 (RAL 3000) underwent an important fading but did not develop microcracks.

3.2.2 Test D27 1911 [4]

The second test was conducted in a Weather-Ometer up to 19,234 hours according to D27 1911. This test method (initial version and subsequent revisions) is based on the standard ISO 4892-2, which is the basis international standard for the artificial weathering of plastics. [2] From **table 1**, the UV radiant exposure delivered by this test is equivalent to the radiant exposure received by samples after 15 years in Southern Europe, and 21 average years in Central Europe. When compared to an end-use location such as Phoenix, in Central Arizona, ranked as Area Section 1 in TI 110-29, the UV radiant exposure delivered by the test is

[3] D27 1380 version E was initially applicable to evaluate the durability of a wide range of material for exterior use, and performed in a Xenotest 1200. In 2002, a revised version has been issued, which mainly differ from the scope. D27 1380 version F (and G since 2003) only applies to coatings and paints, while the testing of plastics has been transferred to another test method, D27 1911. Between versions E and F, the main changes are the irradiance level, the nature of the light filters, and the spray cycle.

[4] Since its introduction in 1995, D27 1911 has been revised 3 times, without significant change in the settings of the parameters.

equivalent to 10 years. The corresponding time factor of this test is the same as the test performed at Hoechst, i.e. 7 relative to Southern Europe and 10 relative to Central Europe.

Only samples 2, 5 and 6 were tested. All three samples underwent fading, to a larger extent than in Xenotest 1200, which is accounted for by the larger radiant exposure received by these samples during Weather-Ometer testing. Only sample 5 (RAL 9002) developed microcracks between 17,800 and 18,500 hours.

3.3 Tests at PEP

The light stability testing performed between 2002 and 2003 consisted of weathering tests in Weather-Ometer up to 5000 hours according to the PSA Peugeot Citroën test method D27 1389, equivalent to the Renault D27 1911, both tests being based on ISO 4892-2. At the time the test was performed, the version E of D27 1389 was current. The tested samples were white, light grey and red formulations. The white sample was only exposed for 4,000 hours. Mechanical tests and colorimetric determination were performed.

On the basis of **table 1**, the UV radiant exposure delivered after 5,000 hours is equivalent to the average UV radiant exposure achieved after 4 years in Southern Europe and 5.5 years in Central Europe (respectively 3 and 4.5 years for the white sample). Again, the corresponding time factor of is 7 relative to Southern Europe and 10 relative to Central Europe.

After 5000 hours, the color of the tested samples did not change significantly. After 4000 hours, microcracks were detected on the white sample. Regarding the evolution of mechanical properties, only the elongation property of the grey sample decrease during the test.

The results are in line with the results found by Hoechst Laboratory, that is the development of microcracks is very limited in depth (only few percents of the total pipe wall thickness), therefore does not influence the mechanical properties of the pipes. The conclusions regarding the expected durability of the tested formulations after 50 to 100 years relies on the assumption of a linear evolution of the change observed after 5000 hours, which is in principle acceptable for mechanical properties but arguable regarding the evolution of color fading.

Additionally, thermal aging has been performed (20 cycles of 2h40 at 60°C and 2h40 at –30°C, i.e. 106 hours in total). No significant changes was observed.

> **NOTE #3:** In the test referred to as thermal aging, the amplitude of the temperature change as well as the total duration of the test (106 hours) are very unlikely to induce any significant change in the mechanical properties. Such tests are usually referred to as thermal cycling, meant to induce mechanical stress to multi-material products, where each material has a specific thermal expansion coefficient. The thermal cycling test of IEC 61215 for the qualification of photovoltaic modules is a typical example, where such modules are exposed to 50 cycles of temperature variation from 85°C to –40°C. [5]

[5] IEC 61215:2005-04 Crystalline silicon terrestrial photovoltaic (PV) modules – Design qualification and type approval, Clause 10.11.

3.4 Conclusion on laboratory testing results

Although the relevance of the microcracks was not discussed in the Sercovam reports, those obtained in Xenotest 1200 are likely comparable to those observed by Hoechst Laboratory, that is reaching a depth of 100 µm with no measurable effect on the mechanical properties. Since formulations RAL 3000, RAL 9016 and RAL 9017 in the one hand and RAL 9002 and RAL 9003 in the other hand behaved similarly upon Xenotest exposure against D27 1380 in terms of microcracks development, it is reasonable to assume that they would have behaved similarly upon Weather-Ometer testing against D27 1911 up to 19,234 hours. The fact that microcracks were only observed with one formulation after ca. 18,000 hours in the D27 1911 indicates that six formulations are expected to retain their mechanical properties after 20 years. [6]

Concerning the visual appearance, formulations RAL 9002, RAL 9003 and RAL 9016 behaved similarly in D27 1380. By assuming similar behaviors in D27 1911 up to 19,234 hours, and according to PESTEC Technical Report TI 110-3, page 3 on the visual evaluation of pipes according to their grey scale grade, a formulation would be rated as very good after 20 years, another one as good to very good and three formulations would lie between fair and good. Formulation RAL 3000 is rated 1 on the grey scale, the lowest grade, after an equivalent 11 years in Central Europe. This illustrates a weakness of the grey scale, since this formulation would still be rated 1 after 20 years, while it is obvious that the color would evolve between 11 and 20 years.

By taking into account the activation effect due to the higher temperature of these laboratory tests compared to outdoor conditions, it is likely that these tests reproduced longer equivalent durations than reported above. In particular, regarding the evolution of mechanical properties, the test D27 1911 can be expected to accelerate by an additional factor of three the reported durations, that is reproduce the aging of about 60 average equivalent years in Central Europe, 45 years in Southern Europe and 30 years in a hot and dry climate such as Phoenix, Arizona. For color fading, characterized by a lower activation energy, a factor of two is still realistic, i.e. the test would represent the fading obtained after 40 average equivalent years in Central Europe, 30 years in Southern Europe and 20 years in Phoenix.

4. Outdoor testing

4.1 Five years outdoors at Hoechst site

After 5 years outdoor exposure of white pipes in a Central European climate type, no micro-cracks nor color change by comparison to the original samples were observed. Based on experience with similar products, Hoechst concluded that the aging of pipes could be performed over several decades without showing an unacceptable change in properties.

[6] The main reason that supports this expectation is the fact the photooxidation rate of polyolefins, which controls the evolution of mechanical properties, is shown to remain rather constant until a significant loss in mechanical properties is achieved. This steadiness generally corresponds to an induction period after which the rate of mechanical properties loss can increase quickly.

4.2 Eleven years in real life in Southern Spain

The follow-up of pipes installed on bridges in Southern Spain (RAL 9016, white and RAL 3000, red) indicated that the red formulation underwent only a slight color change.

4.3 Conclusion on outdoor exposure results

Apart from the confirmation that the dye used to obtain RAL 3000 is challenging to stabilize, no information regarding the long term stability of the color of these formulations can be derived from these series of measurement under real use conditions due to the too short duration.

Conclusions

- The tests performed in the various institute are either international standards or recognized OEMs test methods characterized by their extremely long duration, in particular the tests performed at Sercovam. These tests are designed to reproduce in an accelerated manner the effect of end-use conditions on PESTEC products. Of the four series of laboratory tests, the Renault D27 1911 test method delivered the largest amount of radiant exposure and the highest test temperature.
- By taking into account the thermal activation resulting from higher testing temperature, the test D27 1911 is expected to reproduce the mechanical behavior observed after about 60 and 30 average years of outdoor exposure in respectively Central Europe and Central Arizona. Since the extent of degradation remained very limited, it is likely that PESTEC products will retain acceptable mechanical compressive properties well after these durations. Regarding the visual appearance, the results of D27 1911 give an reliable reproduction of the color change after 40 and 20 average years of outdoor exposure in Central Europe and Central Arizona.
- The outdoor results in Southern Europe have shown that the red formulation, usually found to be lightfast from accelerated testing, withstand 11 years in actual conditions without significant color change.
- At the time the these tests were made, the test methods were state of the art techniques for the testing of polymeric materials for outdoor use. Most of the changes that have been brought to these test methods are a consequence of technical improvements in the devices used to run these tests. Here is a brief account of the state of the art practice in the plastic industry as of 2009:
  - The production of the Xenotest 1200 instrument, used to perform DIN 53387 (at Hoechst) and D27 1380 (at Sercovam) has been discontinued in 1996, and replaced by instruments with additional features and better control of test parameters.
  - The situation is similar with the Weather-Ometer models used to perform the D27 1911 (at Sercovam) and D27 1389 (at PEP), that have been superseded by models with new features and improved control of the parameters.

- To comply with the new instrumental features, the versions of D27 1380 and D27 1911 used by Sercovam have since then been overhauled. However, the main aging parameters such as the spectral power distribution of the light, the irradiance level and the test temperatures did not fundamentally change.
- Standard DIN 53387 used by Hoechst Laboratory has been withdrawn in the 1990s and replaced by ISO 4892-2:2000, both standards have very similar characteristics.

Due to the lack of specific test method for testing the durability of HDPE pipes for stay cables and the outdated character of above referenced tests, any further tests should be performed according to ISO 4892-2:2006, as this standard represents the state-of-the-art testing for plastic parts. Furthermore, this will enable PESTEC to make use of its historical data for comparative purpose, as some of these were obtained with standards based on the conditions of ISO 4892-2.

- The assessment of color changes, as currently performed in the plastic and textile industry relies on two methods, described in two standards. Evidence in the reviewed documents and in this report is given showing that the grey scale evaluation has a number of disadvantages over the colorimetric method. The most remarkable are the non linearity of the scale making extrapolation risky, the lack of sensitivity and the subjective character of the evaluation. The author of this report recommends to prefer colorimetric measurements for evaluating color changes.
- The translation chart in Technical Report TI 110-19 Edition 0604 page 5 provides a way to transcribe standardized criteria for evaluating color differences in terms of perception of color changes in real use conditions by an observer placed at a normal distance from the installed pipes (estimated to a few meters at least), developed from experts advice and PESTEC experience. Since the retention of mechanical properties does not seem to be the main criterion that will determine the durability of PESTEC products, as discussed above, this chart is suitable for use as the main evaluation criterion of test results.
- The Color Recommendation ranking in Technical Report TI 110-29 Edition 1104 indicates that colors ranked as color class 1 are expected to maintain a good appearance for 60 years in all types of climates, ranked by Area Section. Based on the results obtained with D27 1911, the tested formulations, belonging to color class 1 (except RAL 3000) were exposed to conditions equivalent to “only” 20 years in Central Arizona, ranked among climates with the highest yearly radiant exposure, in Area Section 1. However, the acceleration factor due to temperature is only a rough lower estimate, that could prove higher. Finally, although the color recommendations for Area Sections 1 (page 2 of TI 110-29) cannot be proven from the available experimental data, they are reliable regarding the other area sections.

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- Recent publications:
  - Haillant, O., *Photofading of coloured materials*, Polymers Paint Color Journal, 4533, 2009.
  - Haillant, O., *Photoentfärbung gefärbter Materialien*, Welt der Farben, 10, 2008, 12-7.
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- Recent conferences:
  - **PRA Service Life Prediction Symposium**, January 21, 2009: *Contribution of the mechanistic approach to improving the reliability of accelerated weathering testing and service life prediction*.
  - **Third European Weathering Symposium**, September 12-14, 2007, Cracow, Poland: *Natural and artificial photo-aging of a pigmented, HALS-stabilized propylene-ethylene copolymer*.
  - **13th ADDCON World Conference**, September 5-6, 2007, Frankfurt: *Static Weathering and Accelerated Aging of a Stabilized Propylene-Ethylene Copolymer*.
  - **1 jour, 10 ans, 100 ans, … longévité des polymères**, **Les journées de l'innovation du CFP**, October 9, 2007, Paris: *Fiabilité et limites des normes et méthodes d'essai de vieillissement*.