

### **Introduction**

Prof. Lemaire from CNEP laboratory invented the SEPAP 12-24 weathering device about 20 years ago. Focus was the prediction of long term polymer stabilization based on this new short time test. The SEPAP test is based on an ultra photo-oxidation acceleration of polymer materials and was originally designed for testing of thin films (up to 50  $\mu\text{m}$ ). In most cases polymer oxidation is evaluated with IR analysis by screening the C=O value. Specimens from the test under discussion were microtome cuts from the pipes surface with 50 – 100 microns thickness.

The SEPAP Test did not reach international acceptance up to now and has not been approved from experts for an international norm caused by following reasons.

### **Polymer Oxidation and UV Light properties**

Light, heat and shear are initiators which lead to the oxidation of polymers by air.

The rate of this process depends on the type of polymer, its quality and stabilization.

By polymer oxidation the original molecular structure is decomposed leading to typical alterations in material brittleness and appearance.

The most harmful part of the natural sun is the UV light. Although its share is just about 6.8 %, UV is more or less responsible for 100 % degradation of organic materials, in particular polymers.

The shortest wave length of sun-light reaching the earth's surface by passing the atmosphere is about 290 nm (shortwave UV light). This correspond to an energy content of approx.  $410 \text{ kJ} \times \text{Einstein}^{-1}$  as the longest wave of sun-light, at the end of the UV range at 400 nm, still comprises energy content of approx.  $300 \text{ kJ} \times \text{Einstein}^{-1}$ .

<b>wave length [nm]</b>	<b>energy [kJ Einstein<sup>-1</sup>]</b>	<b>kind of bond</b>	<b>bond energy [kJ mol<sup>-1</sup>]</b>
290	419	C-H	380-420
300	398	C-C	340-350
400	300	C-N	320-330

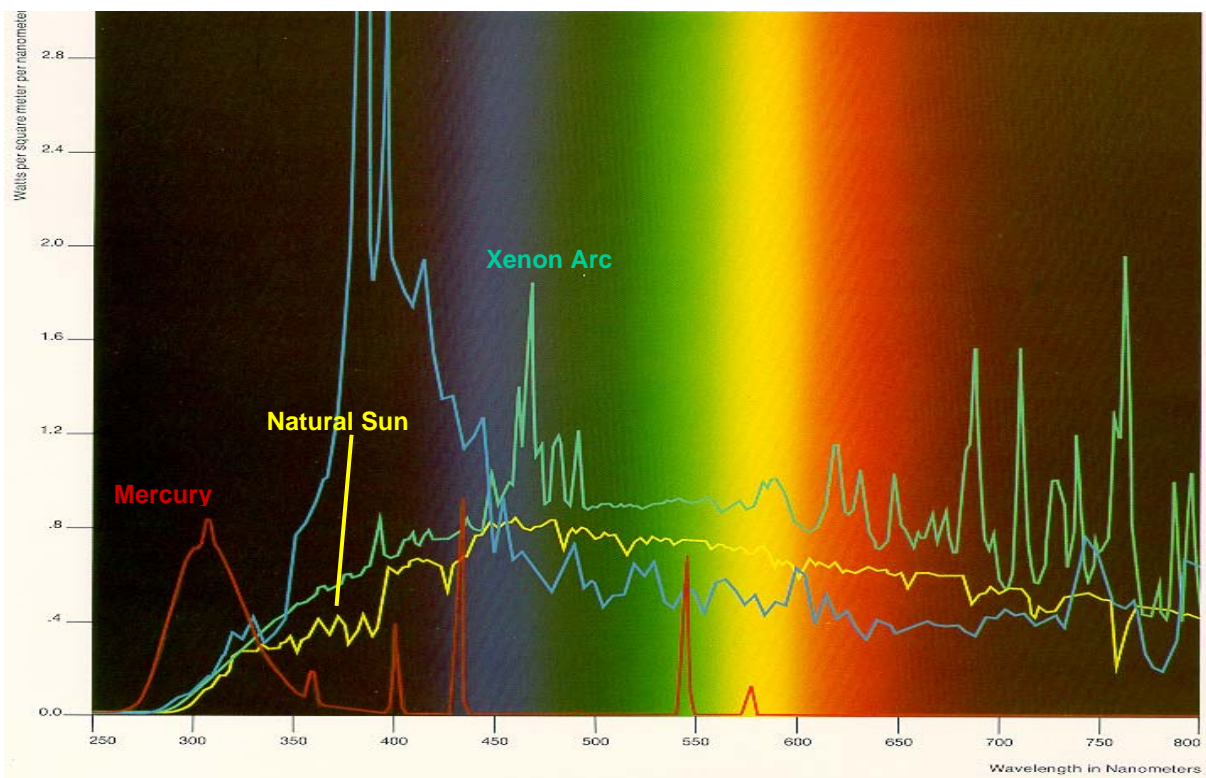
In comparison with the bond energies of the most common types of polymer bonds, the UV share of the sun-light is effectual to cleave these bonds and to form radicals, means the start of polymer degradation.

To simulate sun light by artificial weathering devices, two main aspects need to be considered.

First is the range of UV irradiation (290 – 400 nm) and second the spectral energy distribution has to be as close as possible to natural UV. Therefore Xenon Arc (used in Xeno and WOM tests) is very accepted as it is in line with these requirements. This underlines that most international standards for accelerated weathering are based on Xenon Arc irradiation.

### Sunlight vs. Artificial Light sources

Comparison of Spectral Energy Distribution in different artificial weathering devices



Green = Xenon-Arc Lamp (Xenon/WOM Test), Red = Mercury-Arc Lamp ( SEPAP Test)

Mercury irradiation is known in the market since decades. Although its importance as artificial weathering device is low, it still is applied as it has the capability to induce very fast photo-degradation.

The main differences vs. Xenon irradiation are:

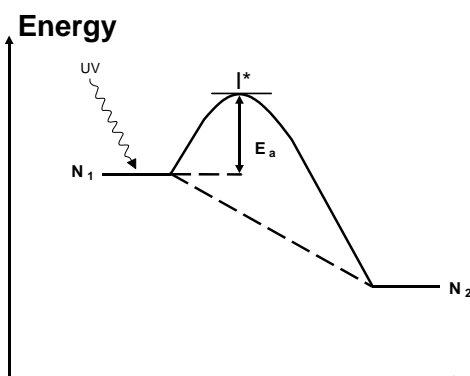
UV emission starts already at approx. 270 nm and the energy distribution (spectral distribution) in the UV range differs as the energy level @ 290 - 310 nm is extraordinary high and not in line with the sun-light.

In conclusion, the high acceleration factor is achieved by non-realistic high energy levels as demonstrated by the table below. Users are aware about these problems and in order to eliminate the UV below 290 nm often filter systems are installed. Presumed these filter systems work properly, the non-realistic high energy from 290 – 310 nm remains.

wave length [nm]	energy [kJ Einstein <sup>-1</sup> ]	kind of bond	bond energy [kJ mol <sup>-1</sup> ]
270	445	RO-H	420-470
280	430	H-H	435
290	419	C-H	380-420
300	398	C-C	340-350
400	300	C-N	320-330

The mercury irradiation energy conditions, whether the one below 290 nm and/or the one from 290 – 310 nm cause non-realistic degradation of the polymer, pigments and stabilizers. Some pigments (e.g. organic red colour) and additives can absorb UV light between 270 and 300 nm. Exposing these compounds to mercury light provokes their excitement and finally their decomposition after the activation energy was overcome.

Principle demonstration



- $I$  = excited state prior to decomposition;
- $E_a$  = activation energy, e.g. by UV radiation
- $N_1$  = energy level of virgin polymer
- $N_2$  = energy level of degraded polymer

### **Principles on IR Analysis (FTIR/IRTF)**

Polymer and additive analysis in principle is very complex and the results always depend on the use of suitable methods.

SEPAP uses IR-Light analysis method not generally suitable to detect all kind of polymers and stabilizers. Since there is no overall method available, adequate methods are required to be considered to identify all additive/stabilizer/polymer of a Master batch / Pipe.

IR is a non-destroying and fast analysis method to identify and quantify additives, or to screen the rate of polymer degradation. In most cases the carbonyl index (C=O value) of the polymer degradation can be determined and in many cases it is proportional to polymer degradation.

Some additives might be evaluated by the C=O value, too, but in particular in altered polymers IR might not any longer suitable to trace additives since the C=O rate of polymer degradation is higher and overlay the additives, so they will not be detected.

Since there is no overall method available, one has to take care to apply adequate methods for polymer degradation and additive/ pigment determination.

Following effects might falsify the evaluation results.

- not all additives, UV stabilizers and/or antioxidants are detectable with this method
- not all pigments are detectable with this method (mainly caused by absorption in the visible light range)
- only virgin polymers and polymer compounds reveal reliable results
- some additives contain C=O groups leading to a C=O index right from the beginning

### **Result evaluation from cutted micro tomes**

It has been demonstrated from other laboratories that the additive migration depends on the material wall thickness and the thickness of oxidized layer (TOL) which varies with the chemical formula of each polymer.

SEPAP simplify the result by measurement of only 50-100  $\mu\text{m}$  of total minimum pipe wall thickness of 5.000  $\mu\text{m}$  including 1.500  $\mu\text{m}$  of coloured co extrusion – layer in the project and so does not reflect the real pipe stabilization due to the different additive migrations.

### **PESTEC NOCX Pipe Tests**

PESTEC NOCX pipes with 7 different colours in 4000 hrs SEPAP 12.24 test (corresponding to 20 years) executed in 1997 and 2006 varied in result from good for colour "light grey" to completely determined for colour "red" after test time of already 200 hrs. (corresponding to 1 year exposure) versus same PESTEC NOCX pipes in 20000 hrs Xenotest 1200 and W-O-M Test (corresponding to 20 years exposure) show very good uv-stabilization results for all colours.

Due to the fact that exactly the same red pipe has been installed 15 years ago on a bridge in Southern Spain and the colour and surface still remain in very good conditions we can not accept the SEPAP test a realistic prediction of long term polymer stabilization.

More than this, SEPAP did not detect our uv-stabilizers (HALS), obviously caused by one of the above mentioned test method falsification.

Even if Prof. Lemaire confirms all test methods should finally result in same predictions they do not.

### **Conclusion**

The SEPAP Test did not reach international acceptance up to now and has not been approved from experts for an international norm.

Main reason seems to be

- Use of non-natural light radiation with very high energy causing molecule absorptions, polymer and additive damages and excessive polymer oxidation
- IR evaluation method not generally suitable to detect all kind of polymers and additives
- Thin film layer evaluation only
- Different test results by comparison of acceleration tests

PESTEC propose to refer to standard Xenotest 1200 or W-O-M Test acc. international accepted ISO and ASTM norms as a reference test for accelerating photo-aging test for long term uv-stability prediction of HDPE pipe products.