OXIDATIVE DEGRADATION OF POLYPROPYLENE IN SANITARY HOT WATER ASSOCIATED WITH *LEGIONELLA* PREVENTION MAINTENANCE

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Summary: Polypropylene has been and still is a great material that can be usedin hot and cold water installations for a few years. Due to its many advantages, polypropylene is used in the construction design of domestic hot water generation facilities. However, treatments to prevent Legionnaire's disease combined with the operating conditions at the sanitary installation can produce irreversible oxidative degradation (OD) of this polymer. Therefore, the effect of this water and the temperature on the polypropylene behavior was studied along one year operation. The present study concludes that the use of propylene in hot water circuits can be depreciated mainly by the effect of temperature both in thermal disinfections and in temperatures above 60ºC in accumulators.

Key words: Polypropylene, antioxidants, oxidative degradation, *Legionella spp*, domestic hot water, chloramines

1.- INTRODUCTION.

The use of polypropylene is becoming more common in domestic water circuits, both hot and cold, due to its many advantages (among others, its mechanical and chemical resistancethat makes it agood substitute for metal materialsin water circuits), and it is relatively inexpensive [1-2].

It is important to note that the characteristics of these circuits as well as their preventive maintenance are regulated by Royal Decree 865/2003, of 4 July, which establishes the hygiene-sanitary criteria for the prevention and control of Legionnaires' disease [3] as well as by Royal Decree 140/2003, of 7 February, which establishes the sanitary criteria for the quality of water for human consumption [4]. The former regulates everything related to chemical treatments and periodic maintenance to avoid the development and proliferation of the pathogenic agent, while the latter places special emphasis on the need to use approved materials that are compatible with each other and do not affect the chemical quality of the water.

Over the years, many installed polymeric materials such as polypropylene have suffered degradation at critical points in the installation. That sometimes happens at certain times or over long periods of time due to temperature and/or chlorination conditions, highly damaging [5]. An example of this would be the process of generating hot water for the circuit with accumulation and return of water.

Expansion phenomena, resulting from high thermal expansion coefficients, leads to leaks at hot-melt or flange points, with the possibility of large leaks as a result of irreparable longitudinal fragility.

The resistance of this kind of materials is influenced by the presence of antioxidants (AO) of different natures, which on many occasions can produce either a migration in the material itself or an irreversible degradation and loss of it. Most studies related to migration and degradation have been focussed on food-grade polymers. Garde [6] carried out AO migration tests on polypropylene in food containers, observing concentration gradients of polypropylene into the food, concluding that the migration depends on several factors, such as temperature, but it doesnot depend on the material used.

Forrester et al. [7] evaluated the importance of the polymerisation process, including the catalyst doses forthe reactions and the agitation conditions for the success of the Ziegler-Natta catalyst. The stability of many antioxidants can be affected by the polymer extrusion process which is subjected to high temperatures and shearing processes [8].

Dopico [9] analyzed the influence of the most relevant antioxidants, including those of primary character formed by the phenol family (primary antioxidants that trap free radicals) as well as phosphite, which acts as a hydroperoxide deactivator. Both types of antioxidants showed a relationship with polymer resistance that can be optimized by modifying the dose of both AO and polymer, as well as the relationship between them.

However, the characteristics and mechanisms of this type of compounds are complex to find in the literature, particularly, the influence of sanitary water and temperature on polypropylene that are theobjective of this study. In order to do that, the Oxidation Induction

Time (OIT) was selected as a simple and standardized test to assess the performance of polypropylene [10].

2.-EXPERIMENTAL PROCEDURE.

The water supplied by the municipal network, which was already subjected to monthly physical-chemical control, was analysed by measuring Langelier index [11]. All the measuring instruments were provided by HANNA INSTRUMENTS (Spain).

For temperature control, data was taken using the daily integral control system, with measurements every 8 hours in triplicate, obtaining the range interval at the output of the accumulator along one year.

The polymer samples were taken vertically at the immediate outlet of the hot water tank and sent directly to all the distribution uprights. Single-layer food grade polypropylene quality certificated for domestic hot water with 70ºC maximum supported temperature, PN10 and DN90, was used for the circuit installation during two years.

Cleaning treatments were carried out on a monthly basis, raising the set temperature to 70ºC for two hours in the recirculation process. Only one annual cleaning and disinfection has been carried out by means of hyper chlorination at 20 mg/l of free chlorine in the accumulator, monitoring at distant terminal points at approximately 2 mg/l.

Oxidation induction times were determined in the in polypropylene (PP) pipe according to Standard UNE-EN ISO 11357-6:2013 [10], using differential scanning calorimeter DSC PT 1000 from Linseis (Germany).

3.-RESULTS AND DISCUSSION.

Figure1 shows the maximum and minimum interval of the Langelier index of the supply water at different temperatures, observing that its low organic matter content and pH close to neutral result in an eminently corrosive character.

Feed water is generally characterized by low organic carbon content with electrical conductivity close to 200 µS/cm and hardness < 8ºF. Its sulphate concentration does not exceed 5 mg/l with a low total alkalinity (<40 mg/l). The pH varies in the range [6.80 - 7.65]. The above-mentioned values mean that the behaviour of the water is eminently corrosive throughout the entire temperature range analysed.

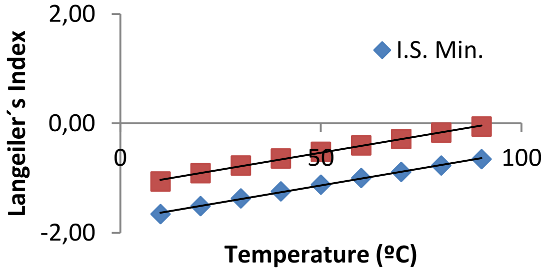

Figure 1. Langelier Index interval over the one-year period of the water supply.

In the case of hot water, the temperature values are those shown in figure 2. As can be seen, the average value is close to 60ºC, the value established by current legislation, which indicates correct maintenance and compliance with current legislation.

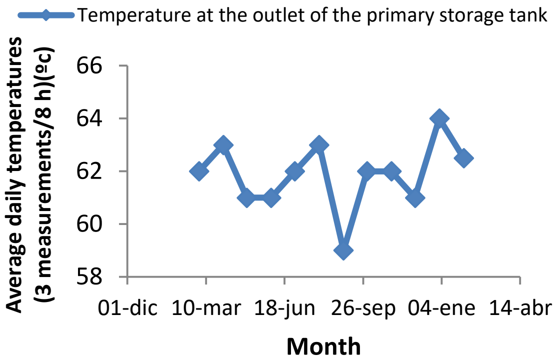

Figure 2. Monthly evolution of water temperature in storage.

With regard to the qualitative analysis of the material, it can be seen that two years after its installation, the interior surface of the sample is completely cracked: longitudinal cracks parallel to the axis of the tube run from end to end on the interior surface of the tube; in the cut it can be seen how some of these cracks penetrate deeply into the wall of the tube (Figure 3). However, the outer appearance remains unchanged at its largest surface (Figure 4).

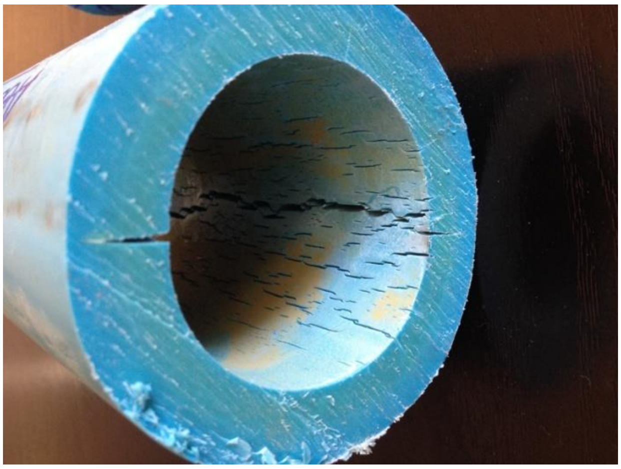

Figure 3. Internal qualitative analysis.

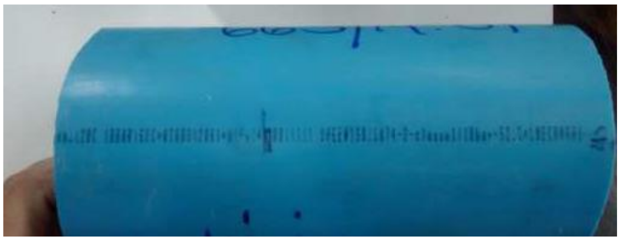

Figure 4. External qualitative analysis.

In order to be able to determine the degree to which the material is affected, the OIT study has been carried out for different radii. Table 1 shows the results for each of the radii (external, intermediate, internal), with a drastic reduction in the results considering that the standard of this type of polymer has an associated OIT of 24.98 minutes.

Table 1. OIT gradients.

	Internal radius	Medium radius	External radius
Sample mass (g)	14.00	14.08	14.03
O.I.T (Min)	0.43	6.38	24.55
Standard OIT (min) 24.98			

Figure 5 shows a degradation of the material due to the losses of antioxidants. Comparing with the standard OIT, there is no increase of OIT values in any of the studied radii, so the possibility of radial migration of the antioxidants due to the effect of water and/or temperature was ruled out.

The degradation inside the pipe (Position 1) is the most accentuated, observing a reduction in the stability of the material by 98.3%, leaving the material obsolete in terms of its functionality. For this reduction, it should be considered that this section is the one that is closest in contact with the fluid, as well as the one that has the greatest thermal jump. In the middle part, a 74.5% reduction in the O.I.T. is observed, which, combined with the previous degradation, makes the section studied more fragile. For the outermost radial section (section 3) there is no apparent variation in antioxidant properties, only a slight reduction with respect to the standard (1.7% reduction).

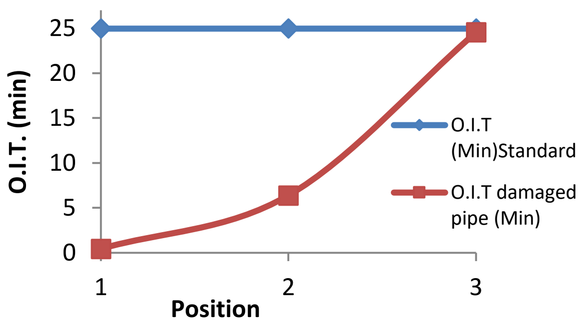

Figure 5. O.I.T. radial gradient.

4.- CONCLUSIONS.

Preventive maintenance in domestic hot water circuits with accumulation and return, classified as higher risk installations according to the Royal Decree, requires preventive maintenance, especially to ensure the constant 60ºC setpoint in the last accumulator. The design of hot water generation rooms is pre-determined on certain occasions by the costsof the project and the type of water, which is generally chosen for polymeric materials such as PP to avoid the proliferation of *legionella*. At this point, a depreciation of materials in this category can be found as a consequence of the thermal disinfection treatment that increases the process temperature to 70ºC for a determined time. Technicians from biocide service companies, as well as those responsible for maintenance, opt on multiple occasions for shock treatments with greater frequency and shorter application times, with the aim of avoiding unwanted *Legionella* positives. This aspect makes, as shown in the present investigation, that certain materials of the market that fulfil the pre-established requirements and quality are depreciated by this aspect.

The chemical influence of the circulating water is ruled out for the losses of quality and properties of the polymerin this case because it contains a very low salt content as well as close to neutral pH. Likewise, the possible damage of annual punctual hyper chlorination is ruled out (moderate dose of chlorine, two hours and with room temperature to avoid evaporation). Therefore, it is concluded that damage is due to high temperatures and thermal disinfection processes with monthly frequency. The selection of materials in hot water circuits is recommended in each case depending on the energy conditions of operation, opting for high quality metal materials. Therefore, a balance of treatments must be achieved in each installation with regard to the prevention of Legionnaire's disease, with criteria and decisions being agreed upon by the owner of the installation and the technical manager of the installation.

5.- ACKNOWLEDGEMENTS.

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