SYSTEMATIC TESTING OF WATER REPELLENT AGENTS

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ABSTRACT

This document describes a systematic test procedure to characterize the category and type of water repellent and to assess the performance of the water repellent treatment in masonry. The authors also illustrate the evolution of the chemical industry of hydrophobic agents. Finally, some results from experimental research are presented.

Key words : Systematic testing - Water repellent - Stone - Analysis

1 INTRODUCTION

Deterioration of buildings, which are exposed to weathering and pollution, is becoming a serious life-cycle problem which is attended with economic and cultural losses. Lifetime and maintenance are the key words in this respect.

Despite all effort that has been paid during many years by the chemical industry for improvement of water repellent agents, the impression remains that there is a lack of knowledge concerning the type of product to be used for conservation with regard to durability.

Water repellent agents for masonry have been available in Northern Europe since the end of the fifties. During this period, the renovation has known an accelerated evolution of the production and commercialization of water repellent agents. Due to the increasing development of new and modified products, a wide variety of hydrophobic agents is available nowadays which makes it difficult for companies involved with restoration to follow up.

From the perspective of current utilizations and further improvements of those products, there is a need to dispose of a simple, fast and standardized test methodology to measure the effectiveness and the durability of the different commercialized formulations, in order to favour an optimal selection related to the material to be treated.

This will enable :

- architects and consulting engineers who are involved with restoration of cultural heritage, to provide a better basis for the choice of treatment,
- application firms to compare performances of different commercialized water repellent agents, based upon objective and comparative values,
- controlling organizations to limit their intervention during the execution of a hydrophobic treatment to the verification of the conformity of the applied product with the tested sample and to the execution according to good practice,
- the EOTA [European Organization for Technical Approval], to publish Technical Agreements for water repellent agents which, according to the results of normalized tests, present a performance level that is superior to a given minimum,
- the manufacturing and formulating industry of water repellent agents to meet the requirements of the sector, as they appear in the required performances of the Specifications.

2 SYSTEMATIC RESEARCH

Within the scope of research projects concentrated upon the techniques to be used for the restoration and renovation of buildings, a systematic investigation on different water repellent treatments has been carried out in the laboratories of the Belgian Building Research Institute (BBRI) and the Royal Institute for Cultural Heritage (IRPA-KIK) since 1978. At this moment, more than 170 formulations have been analysed and tested. The results of the test procedure concerning the evaluation of 80 products has been described in technical official documents and distributed in the United States, Australia, France, the Netherlands and Germany. Besides, it should be remarked that the most important multinational chemical industries producing the base material for water repellent products (e.g. Rhône-Poulenc, Wacker Chemie, Goldschmidt, Bayer, Hüls, ...) submit regularly their basic formulations to our tests. Therefore, the application of a hydrophobic agent on stones is a topic where BBRI and IRPA-KIK have reached a privileged position in Europe.

International contacts, both with the chemical industry as with our colleagues of research centres, participation on seminars and symposia and follow-up of the specialized bibliography seem to confirm that until now this approach of the subject is unequalled, not only regarding the test methodology (which has been proposed to the RILEM [Réunion Internationale des Laboratoires d'Essais et de Recherche sur les Matériaux et les Constructions], in the scope of the working group 59 TPM), but especially concerning the extent of available comparative data.

3 PRODUCT IDENTIFICATION

Water repellent agents, sold as ready to use products, contain an active ingredient, dissolved in a solvent or emulsified in water. The active ingredient is in most cases based on silicium : silicon resins, siloxanes and silanes. Besides, aluminium salts of organic acids, organic fluorine compounds and acrylic resins are available. In a few cases, a mixture of some of these compounds is provided for water repellent treatment. Concerning the type of diluent, almost all water repellents have been dissolved in organic solvents, in general mineral spirits. Due to increasing care for the environment, new products are commercialized based on water as diluent.

In the context of product identification, the chemical analysis should reveal the following :

- the percentage dry weight;
- the chemical composition of the active ingredient;
- the type of diluent;
- the type of catalyst.

3.1 PERCENTAGE DRY WEIGHT

The concentration of the active ingredient can be approximated by determining its dry weight after the evaporation of the diluent, and, eventually, the reaction of the reactive components. This is achieved by placing a small quantity (0.5 g) in an aluminium cup and allowing it to dry under controlled conditions (20° C, 50 % RH).

This technique yields not necessarily information about the concentration of the active ingredient, which is important for conservation purposes. With siloxanes, differences up to 20 % can be obtained between dry weight after evaporation and the actual concentration of the active ingredient.

Concerning silanes, there is a competition between polymerization reaction and evaporation once applied on a porous substrate. For this reason they are generally available as mixtures containing a relatively high concentration of the active ingredient (up to 40 %). If such products are allowed to dry under inappropriate conditions, such as very low relative humidity (R.H.), high wind speed and high temperature, evaporation can gain on polymerization, giving the impression that no solid material will be deposited. A convenient test to avoid such problems involves the filling of the aluminium cup with 1 or 2 g of a standardized stone powder, chemically comparable to the substrate to be treated, and evaluating the deposit of water repellent agent.

3.2 CHEMICAL COMPOSITION OF THE ACTIVE INGREDIENT

A handsome technique to obtain a first screening of the active compounds is X-ray fluorescence (XRF). Depending upon the apparatus available, it can be carried out on either the liquid or the dry material. The analytical technique can be adapted to the type of element present.

Silicon based products :
A wide range of *silicon based products* is used as water repellent :

- silicon resins containing hydrophobic groups, such as methyl, propyl, phenyl, octyl, ...,
- oligomeric siloxanes containing the same hydrophobic groups and with methoxy, ethoxy, a combination of both, propoxy, or higher alkoxygroups,
- silanes containing hydrophobic and alkoxygroups as described above.

For the identification of the nature of the reactive and hydrophobic groups, Fourier Transform Infrared (FT-IR) proved to be a powerful technique. The pattern of the IR-absorption of surface treatment products enables qualitative determination of the solvent, the type of surface treatment product and its functional groupings. According to the sample technique, the analysis is carried out on the liquid solution and dried product. Quantitative analysis is possible if calibration is carried out using well defined reference products.

Since hydrophobic products are mostly commercialized in a diluted from, quantitative accurate analysis of reactive groupings by spectroscopic techniques is limited due to interference with the solvent. A method to determine the amount of alkoxygroups in silicium compounds has been described by J. A. Magnuson[1,2] and P. Dostal and co-workers[3] and is based on an acetylation of the alkoxygroups followed by a titration of the acetic acid formed.
This technique gives an indication of eventually ageing of the water repellent composition, since condensation may occur upon storage by reaction with humid air.

Aluminium salts of organic acids :
Aluminium stearate is the major water repellent compound within the class of aluminium salts of organic compounds . Identification is possible with XRF, Gas Chromatography (GC) and FT-IR.

The techniques described above permits the identification of fluorine and acrylic compounds and mixtures of different types of water repellent products.

3.3 TYPE OF DILUENT

Depending on the apparatus available, the type of the diluent can be determined by GC or by FT-IR.

3.4 TYPE OF CATALYST

XRF and Scanning Electron Microscopy (SEM) is used to reveal the presence of inorganic elements like Sn, Pb or Ti which may be present in the catalyst used.

4 EFFECTIVENESS AND DURABILITY

The effectiveness of the water repellent treatment is evaluated by measuring the water absorption with the "Karsten pipe". In order to evaluate the durability of water repellent treatments, the treated samples are submitted to artificial ageing.

4.1 SUBSTRATES

The systematic investigation of the water repellent agents available on the market has been carried out on four types of substrates : brick, Euville, Massangis and Savonnières. The latter three are French limestones with different porosities. These substrates used for the effectiveness and durability tests are representative for the stone materials currently used in Belgium.

Before application, the samples are submitted to a moistening process by soaking for two hours in water and drying for two days in an environment of 20 °C and 50 % RH. The moisture percentage is calculated by comparing the obtained weight with that of the dry sample.
In order to avoid inhomogeneous treatment, characteristic for brush or airless application, samples are treated in the laboratory by means of a surface contact with the water repellent mixture. The contact time is fixed at 5 seconds and in accordance to the average applied quantities in practice.

4.2 PRINCIPLE OF THE EFFECTIVENESS MEASUREMENT

The methodology to evaluate the water repellent characteristics of the hydrophobic surface treatment is based upon the RILEM [Réunion Internationale des Laboratoires d'Essais et de Recherche sur Matériaux et les Constructions] Recommendations, as noted in the 25-PEM-document of RILEM.
According to these recommendations, the results of water absorption measurements with the "Karsten-pipe" are expressed as water absorption coefficients (WAC), defined as the difference between the observed water level of the pipe after 15 and 5 minutes.

Water absorption measurements are carried out :

- before treatment,
- 1 week after the application of the water repellent agent,
- during artificial ageing (see 4.3),
- after artificial ageing.

4.3 ARTIFICIAL AGEING

The ageing program of the Wheater-Ometer XR-35 used for artificial ageing is in accordance to SAE J 1960, being the most appropriated to simulate natural weathering of substrates treated with water repellent agents. One cycle consists of :

-40 min :	Xenon Temperature : 70 °C* Relative Humidity : 50 %
-20 min :	Xenon Temperature : 70 °C* Front specimen spray
-60 min :	Xenon Temperature : 70 °C* Relative Humidity : 50 %
-60 min :	Temperature 38 °C* Front specimen spray**

* : black panel temperature

**: instead of back specimen spray defined in the original SAE J 1960-procedure.

The total artificial ageing procedure consists of 448 cycles. Water absorption measurements are carried out after 56, 112, 168, 224, 280, 336 and 448 cycles.

4.4 INFLUENCE OF TREATMENT ON WATER VAPOUR CONDUCTIVITY OF THE MATERIAL

The application of a water repellent agent influences the water vapour conductivity of the material. The change of water vapour conductivity due to surface treatment is an important criterion concerning the choice of the type of product. Water vapour conductivity measurements are carried out according to the German norm DIN 52 615 and the specifications of the 25-PEM-document of RILEM, using a well defined type of brick as reference material.

5 SOME RESULTS

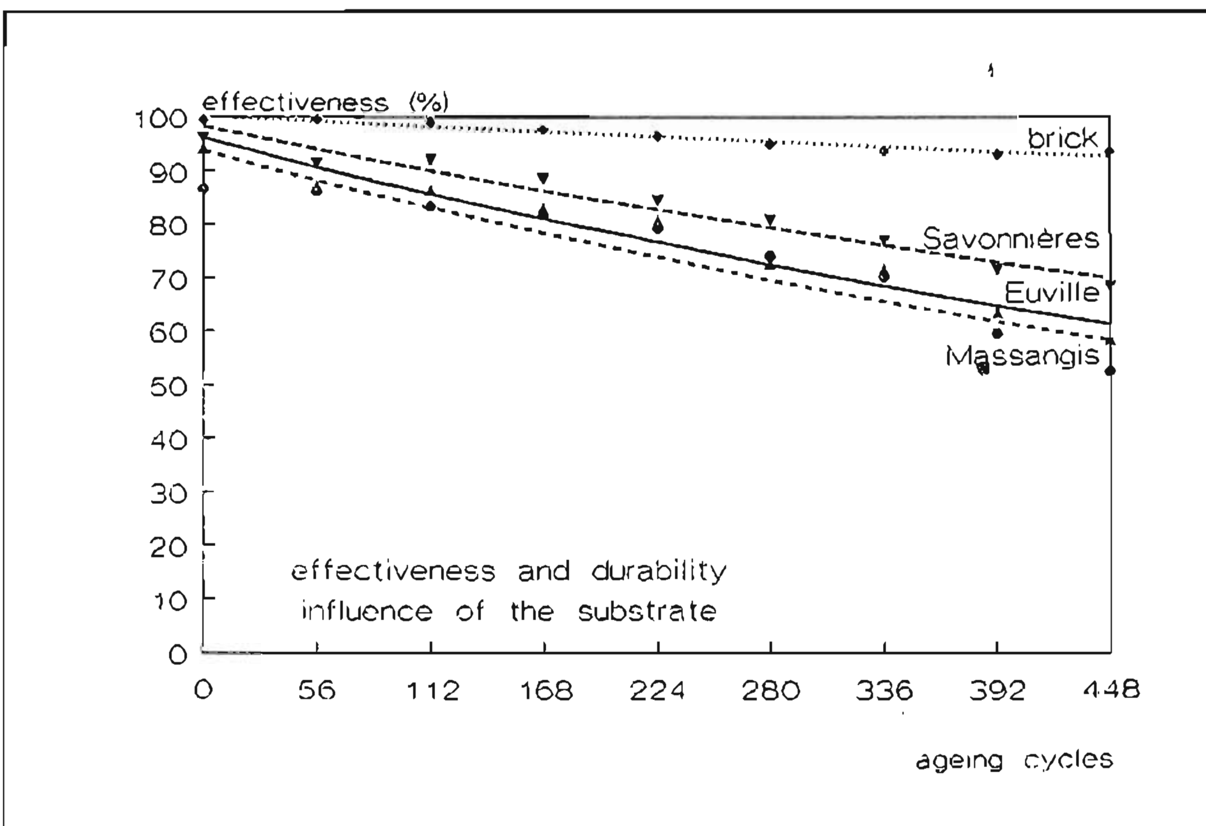
The investigation carried out in BBRI and IRPA-KIK revealed some interesting tendencies towards water repellent treatments, particularly concerning :

- the influence of the type of substrate;
- the influence of the concentration;
- the influence of the type of diluent.

5.1 TYPE OF SUBSTRATE

Results of the effectiveness, based on water absorption measurements, of water repellent treatments on different substrates are presented in figure 1 :

FIG.1
Effectiveness(%) of the water repellent treatment as a function of the number of cycles of artificial ageing on different substrates.



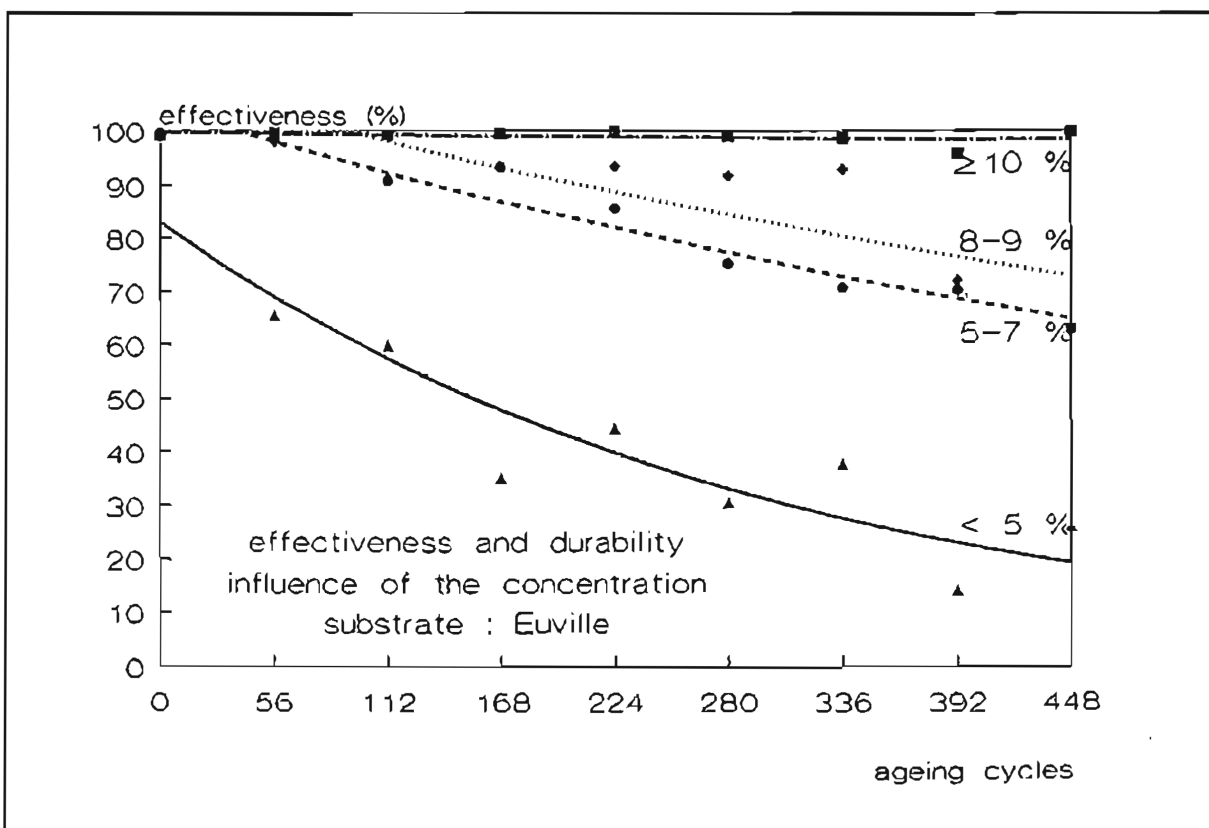
The results presented in figure 1, illustrate that the effectiveness of the water repellent treatment is influenced by the type of surface and indicate that :

- the effectiveness of treatments on brick hardly changes during artificial ageing
- a decreased effectiveness is obtained in case of lime stone as substrate
- there is a strong indication that the total porosity does not play a major role, but rather the amount of pores of a specific diameter, e.g. the pore range between 3.5 and 17 10^{-6} m.

5.2 CONCENTRATION

Figure 2 illustrates the influence of concentration of active ingredient of the water repellent mixture on the effectiveness and durability of the treatment.

FIG.2
Effectiveness (%) of surface treatment as a function of the number of cycles of artificial ageing for varying concentrations of active ingredient of the water repellent mixture.
(type of substrate : Euville)

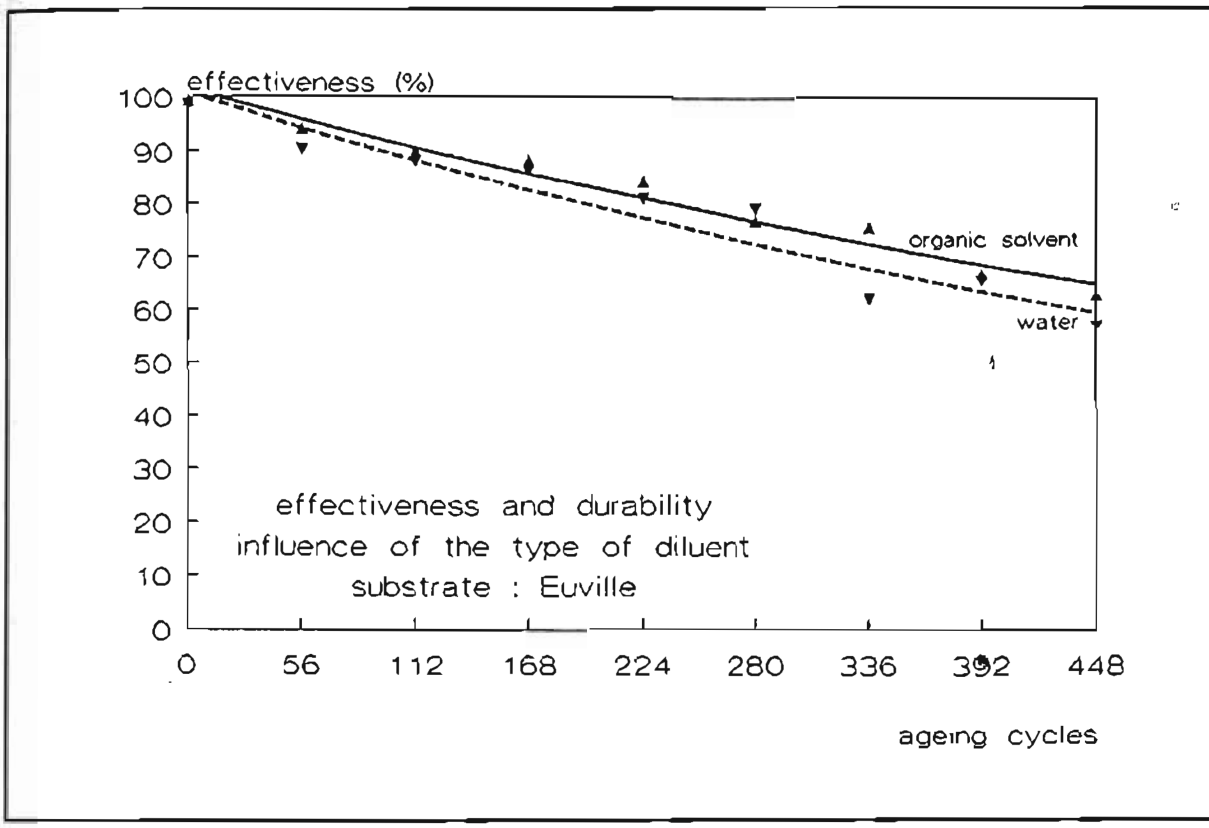


From the results in figure 2 it can be concluded that the effectiveness decreases with decreasing concentration of active ingredient.

5.3 TYPE OF DILUENT

The influence of the type of solvent on the effectiveness of treatment is presented in figure 3.

FIG.3
Effectiveness (%) of surface treatment as a function of the number of cycles of artificial ageing for water repellent mixtures based on organic solvents and water.



From the results in figure 3, it can be concluded that the effectiveness of water repellent mixtures based on water as diluent is comparable with that of water repellents dissolved in organic solvents.

6 CONCLUSIONS

Nowadays, a water repellent treatment is part of almost every restoration or renovation project, and even a lot of new constructions are treated with a hydrophobic protection. The application of high quality products, of which its selection is based on standardized test methods is indirect of economical interest for the maintenance of our cultural heritage.

Although comparative tests, jointly realised by the Belgian Building Research Institute (BBRI) and the Royal Institute for Cultural Heritage (IRPA-KIK) have revealed some interesting tendencies towards water repellent treatments, they have also confirmed that there does not exist any product or family of products which is systematically better than others for current porous materials (natural stone, brick masonry, mortars, ...).

It follows that systematic testing of an individual type of product on a type of substrate remains necessary to predict the effectiveness and the durability of the water repellent treatment.

7 REFERENCES

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