Evaluation of the mixing ratio in I.G. polysulphide sealants

Sealants are an important part of the I.G. market, and polysulphide is, at present, more and more frequently used. This article takes a look at the different compounds that can be used as hardeners, and the correct dosage of these two products, providing interesting information to sealant suppliers and customers, in order to obtain the optimal usage of today's two-component polysulphide sealants.

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Oxford Lab X 3000 XRF analyser and extruded polysulphide sealant samples

INTRODUCTION

Polysulphide sealants are products based on aliphatic polymers, which are classified as elastomers. Two-component polysulphide sealants consist of a base - component A, containing the polymer, and of a hardener - component B, containing the oxidative agent.

A wide range of compounds, both organic and inorganic, can be used as oxidative agents. Among inorganic agents, manganese dioxide, lead dioxide, metallic peroxides and perborates are the most common used as hardeners.

Today, activated manganese (IV) oxide (MnO_2) is the most used cross-linking agent for two-component polysulphide sealants. MnO_2 has a series of advantages over PbO_2 as a curing agent, such as improved pot life stability, better resistance to light, and a clearly reduced level of toxicity.

Referring to insulating glass manufacturing in glass for architecture (see European Standard for I.G. Units, EN 1279 series) the correct mixing ratio and mixing quality between Part A and Part B components are critical and relevant factors to reach the best sealant performance.

PURPOSE

This article describes a useful method to characterize the quality of a mixture of two components in a polysulphide system, providing interesting information to sealant suppliers and customers, in order to obtain the optimal usage of the product.

Manual and automatic machines are often used by I.G. manufacturers to mix the base and hardener before sealant application. Dosage systems, which are suggested by suppliers, provide the correct matching ratio in machine mixers. After extrusion and catalysis, there is the possibility to check their correct working by means of laboratory analysis on the extruded sealant samples.

Using a modern technique based on X-ray Fluorescence (XRF), a fast and extremely precise determination of manganese content in extruded samples can be obtained.

As a base component for Fenzi THIOVER catalyst, manganese dioxide quantification allows mixing ratio determination in usage.

Besides, repeated analysis on successive sample portions identifies anomalous fluctuations in the mixing ratio, which are symptoms of incorrect extruder working.

Scope of this study is to achieve a helpful method of analysis for polysulphide sealant samples coming from manual and automatic I.G. lines. A correct interpretation of results could give proper suggestions on corrective actions to be taken in the case of imperfect working of machines.

EXPERIMENTAL

Instrument description

The Oxford Lab-X 3000 is a bench-top analyser using the principle of Energy-Dispersive X-rays Fluorescence (EDXRF) spectrometry to determine concentrations of various elements in a range of materials.

Operator input is accomplished via software control and is activated using the integral keypad. Software results are shown on the liquid crystals display.

In order to determine the correct metal (or metal oxide) concentration in a particular sample, a regression curve of calibration is needed for every requested element analysis.

Calibration standards and curve

Preparation of calibration standards was carried out by means of the following specimen preparation procedure.

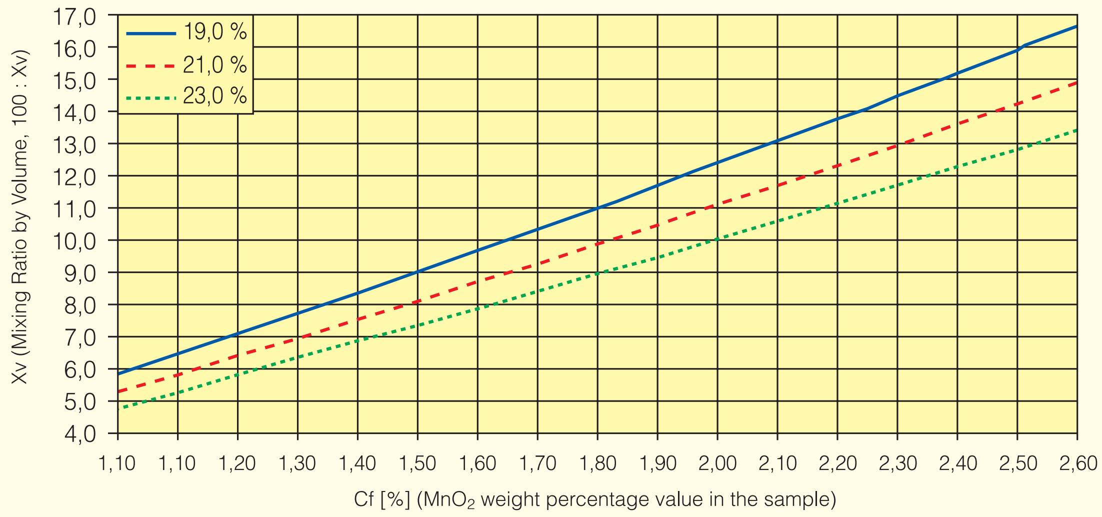
Before starting calibration, a set of parameters has to be fixed in order to reach the correct and most accurate analysis, and to avoid evaluation errors.

This setting, which involves the right energy range choice, the suitable tube voltage and current, the correct filter (if requested) and the element specific channel region, has to be kept for every further analysis of that particular chemical element in the same matrix.

In our case, the standards are disks of mixed polysulphide sealant containing a specific manganese concentration which corresponds to a certain X-ray intensity (counts per second).

A regression curve can be drawn once sequential samples at different Mn concentration have been analyzed by spectrofluorimeter. A blank sample (without manganese) constitutes the zero Mn concentration level. The curve is fixed by the internal programme of the instrument and, whenever calibration has been performed, a sealant sample can be analyzed to determine its manganese content, which is directly related to CPS.

MIXING RATIO BY VOLUME VS MNO_2 WEIGHT PERCENTAGE VALUES AT DIFFERENT INITIAL HARDENER MNO_2 WEIGHT PERCENTAGE. F=1,05



Suggested mixing ratio for Fenzi THIOVER polysulphide sealant is 100 Base parts to 10 Hardener parts by volume and 100 Base parts to 9.5 parts by weight.

Standards have been prepared referring to initial concentration of manganese in the hardener and mixing the two components in several mixing ratios (from 100:6 to 100:14 by volume), which correspond to a final concentration of manganese in the mixed product. Conventionally, the manganese dioxide (MnO_2) content was considered for analysis and will be referred to in our calculations.

Specimen preparation

Customers interested in this kind of service, must give the technical office of sealant supplier at least four plastic glasses containing the extruded product.

Samples must be numbered in sequence, and the sealant must be compressed to avoid air inclusions, which disturb analysis. For better accuracy of final results, customers should also communicate the catalyst production code number. In this way, the technicians can calculate the mixing ratio, as they know the initial manganese dioxide concentration in the hardener (Ci).

After receiving the samples, the same specimen preparation has to be carried out for each glass and each customer, in order to avoid random errors.

Each glass type glass has to be cut into sections, creating from four to seven disks (depending on the quantity of filled sealant) of about five to ten millimetres in thickness. Disk diameter side must be smaller than the Lab X cell diameter and larger than the X-ray analyzing area. The section plane must be as flat and horizontal as possible, to allow maximum analysis accuracy.

Example: if glasses are divided into five disks, the first disk of the first glass represents the initial point of extrusion sequence, the fifth disk on the top corresponds to the fifth point, the first disk of the second glass is the sixth point, and so on. Each numbered disk represents a point of the extrusion.

Analysis and Calculations

Each disk is analyzed by XRF analyser and its MnO_2 value reported.

MnO_2 value is strictly related to mixing ratio by following considerations and formulas:

if mixing ratios are denoted by

100 : Xv (100 base volume parts to X hardener volume parts)

100 : Xw (100 base weight parts to X hardener weight parts)

Xv is correlated to Xw by a factor depending from densities of base and hardener at 20 °C:

Xv = F • Xw (1)

and $F = d_A/d_B$ (2)

knowing Ci (weight percentage of MnO_2 in the hardener) and Cf (MnO_2 weight percentage value detected by the instrument in the sample), Xv comes from the following:

$$Cf = \left[\frac{Ci \cdot Xw}{100 + Xw}\right] \quad (3)$$

In fact, if we suppose that Ci = 20 per cent and mixing ratio by weight is 100:11.0

$$Cf = \left[\frac{20 \cdot 11}{100 + 11}\right] = 1.98\%$$

which is the sample MnO_2 value detected by XRF Lab X 3000.

From equation (3)

$$Xw = 100 \cdot \left[\frac{Cf}{Ci - Cf}\right]$$

and, from equations (1) and (2)

$$Xv = F \cdot Xw = 100 \cdot \frac{d_A}{d_B} \cdot \left[\frac{Cf}{Ci - Cf}\right] \quad (4)$$

Example: a sample coming from a mixture with a hardener at 20 per cent MnO_2 weight content, gives Cf=1.80 per cent. Base and hardener have densities by 1.77 gr/cm^3 and 1.69 gr/cm^3 respectively.

From (4) it is simple to calculate the mixing ratio by volume, which is 100:10.4.

Analysing every sample of the sequence, we get a complete mixing profile of the entire extrusion, from beginning to the end of filled glasses preparation.

The average value of all Cf will give the average mixing ratio by volume and by weight of the extrusion. The graph on page 116 shows the relationship between Cf and Xv for several initial MnO_2 contents and for F=1.05.

Remarks

Total weight content in manganese before oxidative reaction with polysulphide and after does not change. Of course, manganese dioxide reacts according to the following general formula:

$$2R - SH + MnO_2 \longrightarrow R - SS - R + MnO + H_2O$$

Having prepared calibration standards referring to MnO_2 concentration and assigning to every CPS value a MnO_2 value (coming from calculation of MnO_2 in hardener formula), the instrument returns a MnO_2 concentration, although CPS refers only to manganese content.

If Ci is expressed in manganese concentration, then Cf also has to be expressed. Our weight concentrations are specified in MnO_2 content. In order to correlate our values to manganese weight percentage contents, the following formula has to be applied:

$$Mn(Weight\%) = 0.63 \cdot MnO_2(Weight\%)$$

which considers atomic and molecular masses of manganese and manganese dioxide respectively.

RESULTS

An oscillating curve showing the "mixing ratio by volume" values and a straight line corresponding to the "average mixing ratio by volume" versus "extrusion sequence" (as explained in specimen preparation) represent the mixing profile of a given customer's sealing machine.

In the case of Fenzi THIOVER polysulphide sealant, the following considerations are to be respected in order to reach optimum performances of the product:

optimal average mixing ratio by volume is 100:10 ± 1

Fluctuations around the nominal value (100:10) should be within 20 per cent.

Mixing Ratio Profiles

In the five examples below, we will consider different cases of mixing profiles, coming from XRF analysis of several customers' samples:

1 Correct average mixing ratio, good behaviour;
2 Low average mixing ratio, good behaviour;
3 High average mixing ratio, good behaviour;
4 Correct average mixing ratio, "up and down" behaviour;
5 Correct average mixing ratio with decreasing mixing ratio at the beginning followed by good behaviour.

One optimal extrusion performance is represented by "Mixing Profile 1". Average mixing ratio is very close to nominal value and fluctuations around that are minimal. Such conditions constitute two main factors for optimum sealant performance.

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"Mixing Profile 2" shows a fine behaviour in terms of fluctuations, but mixing ratio average is low. Corrective action will increase hardener incoming by modifying the setting of the dosage system.

The dual case of example two is shown in "Mixing Profile 3"; the average mixing ratio is quite high. However, behaviour looks like acceptable. Fluctuations rise above 20 per cent more than nominal value for half of extrusion, because of high average. The dosage system is set wrongly but the valves are working correctly. Action must be taken in order to decrease the ratio.

An example of incorrect working of valves can be seen in "Mixing Profile 4". Although mixing ratio average is right (the customer could not identify the problem, since hardener drum consumption is correct), an "up and down" mixing ratio does not ensure optimal performance of the product. Incomplete catalysis in spots containing low hardener concentrations and high hardener content areas may result in adhesion, hardness, mechanical properties and mixing quality problems. A complete check of dosage and mixing systems is needed.

In "Mixing Profile 5", the average mixing ratio is good and behaviour is optimal from the centre of the second glass to the last one. The beginning part of extrusion is affected by a lack in hardener concentration. This machine may have a problem in the dosage system, and bad working of a valve responsible of part B incoming does not allow a right mixing ratio in initial phase.

Further examples

In the previous paragraph we considered the common and most experienced cases of mixing ratio profiles. Other examples include:

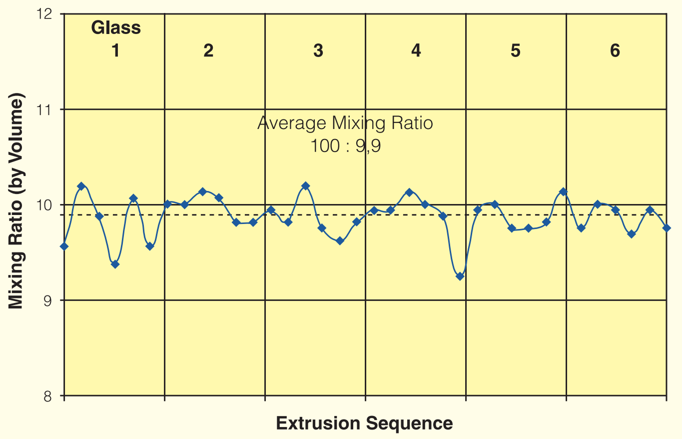
very high mixing ratio (more than 100:12) - good or bad behaviour;

very low mixing ratio (less than 100:8), - good or bad behaviour; and

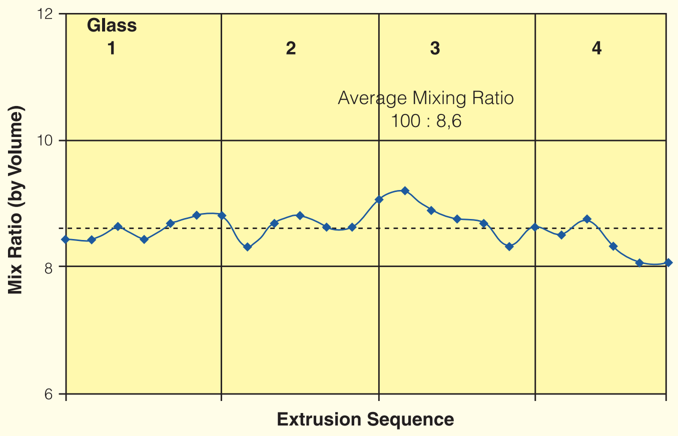
low or high mixing ratio with up and down behaviour.

All these cases can be considered as amplified aspects of the previous ones. Machinery technical assistance is suggested in order to investigate, verify and correct the anomalous working of the lines.

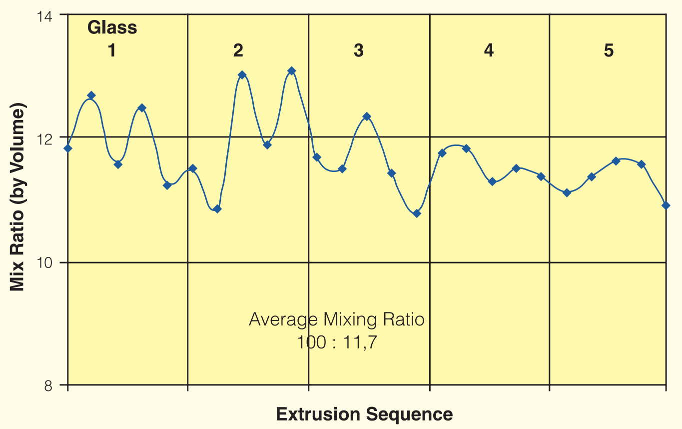
MIXING PROFILE (1) - CORRECT MIXING RATIO AVERAGE, GOOD BEHAVIOUR



MIXING PROFILE (2) - LOW MIXING RATIO, GOOD BEHAVIOUR



MIXING PROFILE (3) - HIGH MIXING RATIO AVERAGE, GOOD BEHAVIOUR



Remarks

During specimen preparations, a visual analysis of sample mixing quality must be performed. In this phase, the technician evaluates possible anomalies such as veins, non-homogenous mixing, non-catalyzed spots, white parts, oiled sections and other causes of bad mixer-working or dosage errors.

Reports for customers will also contain this useful information.

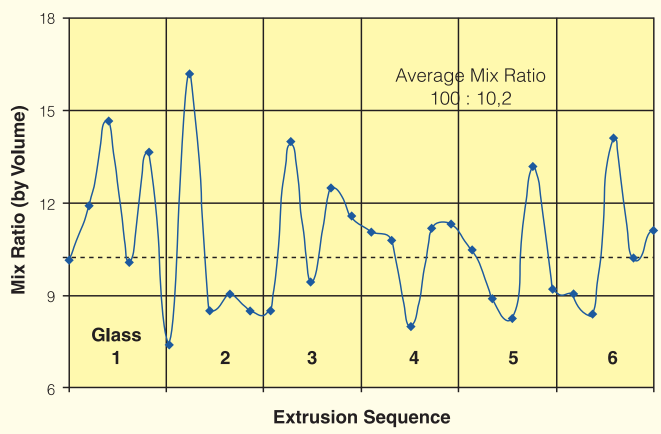
Average Shore A hardness evaluation (DIN 53505) will add further valuable information about sample examination and will complete an overall analysis.

CONCLUSIONS

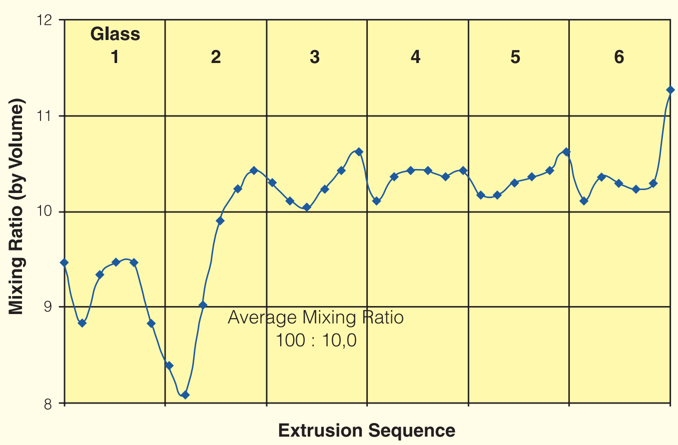
The usage of a modern technique based on X-ray Fluorescence (XRF) accomplishes a fast and functional method to analyse I.G. polysulphide sealants mixing ratio and offer to I.G. manufacturers a useful service.

After a brief explanation of XR Fluorimeter working, specimen preparation has been illustrated and some typical examples of mixing ratio profiles have been explained and discussed. Then, further information about overall analysis closes this study, which could provide interesting information to sealant suppliers and customers, in order to obtain optimal usage of the product.

MIXING PROFILE (4) - CORRECT MIXING RATIO AVERAGE, UP AND DOWN BEHAVIOUR



MIXING PROFILE (5) - CORRECT MIXING RATIO WITH AN INITIAL LACK OF PART B



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