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The Long-Term Stability of Sodium Percarbonate in Presence of Zeolite

Stability testing of sodium percarbonate is required in order to predict the performance of the product. The results in this note demonstrates that microcalorimetry can be used to assess the stability of mixtures of SPC and Zeolite in terms of heat flow. The results were found to be in agreement with conventional stability testing including analysis of the hydrogen peroxide content by iodometric titration.

Introduction

Sodium percarbonate (SPC) is used as an oxidising bleaching agent in many application, e.g. laundry and automatic dishwasher detergents. Detergents usually include a variety of ingredients such as tensides, enzymes and perfumes. In order to increase the efficiency of tensides inorganic absorbers such as Zeolite are commonly added to trap Ca^{2+}/Mg^{2+} in the washing water. However, Zeolite can also trap Fe^{2+}/Fe^{3+}as well as H_2O and both of these might reduce the stability of SPC although the main destabilising effect is probably caused by water. A number of patents on coating procedures and manufacturing conditions can be found in the literature.The purpose of this study was to evaluate microcalorimetry as a tool for studying the stability of SPC samples.

Background

SPC is an adduct between sodium carbonate and hydrogen peroxide. The overall decomposition of SPC is highly exothermic. In the presence of water dissolution of SPC occurs under formation of sodium carbonate and liquid hydrogen peroxide (reaction 1). The hydrogen peroxide formed is unstable and will decompose under formation of water and oxygen (reaction 2). For this reason the decomposition of SPC can be regarded as autocatalytic. The decomposition of hydrogen peroxide is wanted during use but must be avoided during transportation and storage. This is done by keeping the relative humidity low.

The hydrogen peroxide is an acid that will dissociate to HOO^- and H^+ (pKa=11.62 at 25°C). The HOO^- formed can oxidise double bonds of chromophoric groups responsible for yellowing of textile fibres. This reaction is termed the bleaching step and the amount of oxygen available for bleaching is termed active oxygen.

Conventional stability testing versus microcalorimetry

Conventional stability testing of SPC includes oven aging at an elevated temperature and controlled relative humidity and regular removal of samples for analysis of hydrogen peroxide content by

$$2\,Na_2CO_3 * 3\,H_2O_2(s) \rightarrow 2\,Na_2CO_3(s) + 3\,H_2O_2(l) \quad k_1, \Delta H_1 \quad (1)$$

$$3\,H_2O_2(l) \rightarrow 3\,H_2O(l) + 1.5\,O_2(g) \quad k_2, \Delta H_2 \quad (2)$$

$$Na_2CO_3(s) \rightarrow 2\,Na^+(aq) + CO_3^{-2}(aq) \quad k_3, \Delta H_3 \quad (3)$$

$$H_2O_2(l) \leftrightarrow HOO^-(l) + H^+(l) \quad pKa=11.62 \quad (4)$$

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Field of application
Material Sciences

Instrument configuration
3101 TAM III Thermostat
3208 Multicalorimeter
Equipment for ampoule calorimetry
0.3 ml microhygrostats

References

1) M. Dreja and W. von Rybinski; "Microcalorimetric investigations of detergent ingredients"; Tenside Suf. Det. 39 (2002)

2) Greenwood, N.N. and Earnshaw, A. in Chemistry of the Elements, Reprint 1989, Pergamon Press, Oxford, New York, Beijing, Frankfurt, Sao Paulo, Sydney, Tokiyo, Toronto, pages 706 - 712.

Applicant Solvay-Interox; Patent number: EP1007474, EP0891417, EP0850192 (US6228342); EP0731774 (WO9515292) and EP0624549 (US5478488)

Applicant Degussa; EP1419104 and WO0226623

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iodometric titration. In contrast to this technique microcalorimetry makes use only of one sample and stability data is obtained continuously in terms of heat flow, i.e. from start of reaction throughout the test.

Calorimetry is a non-specific technique and thus, the monitored heat flow reflects contributions from all physical processes and chemical reactions. For this reason the monitored heat flow will reflect the influence of manufacturing conditions (granular size, surface coating etc) as well as experimental parameters (sample amount, atmosphere, temperature etc).

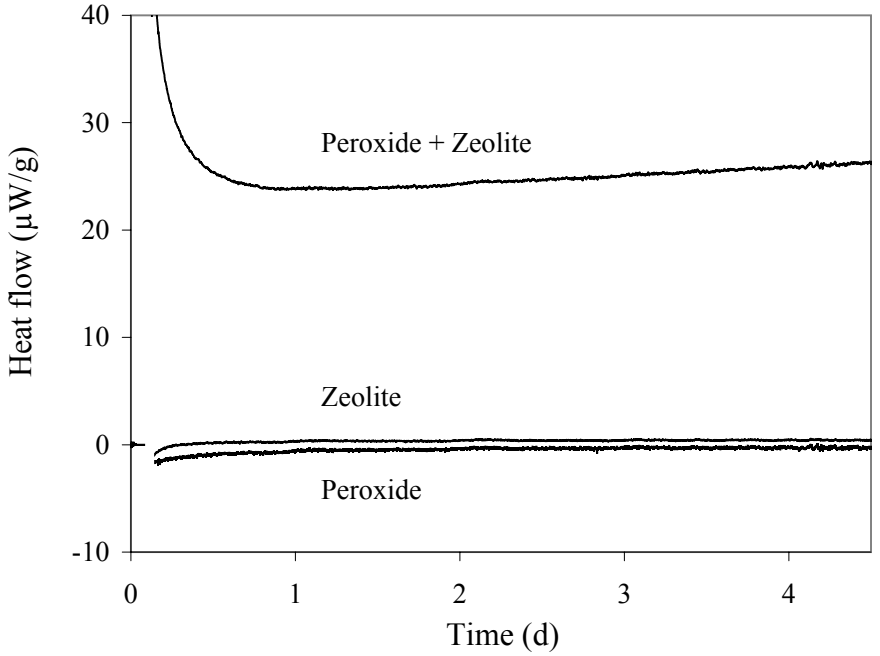

Figure 1. *Influence of Zeolite on the stability of SPC at 30˚C. The ampoules were sealed under ambient atmosphere. Heat flow normalised with respect to the total amount of sample is shown versus time.*

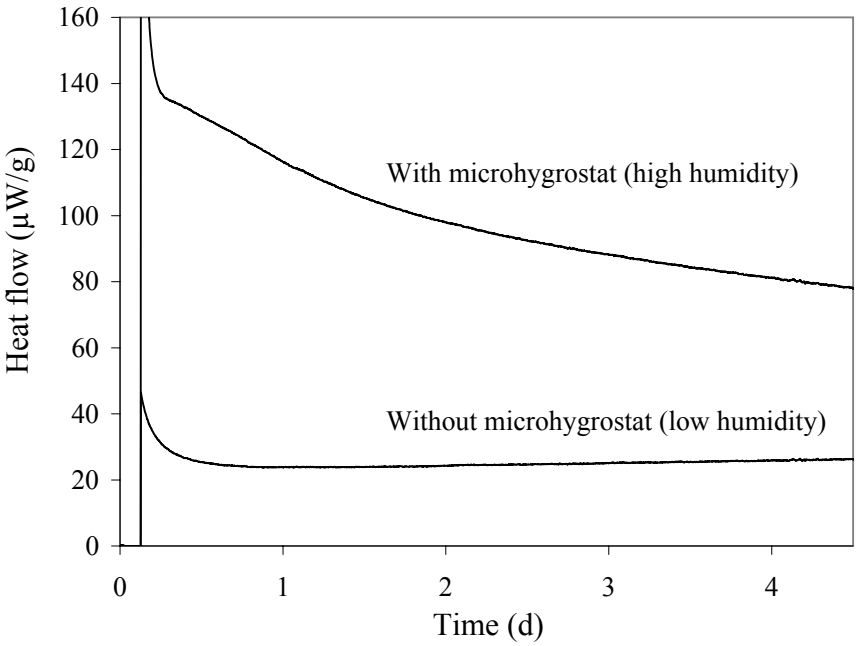

Figure 2. *Influence of humidity on the stability of SPC samples (1:1 mixtures per weight of SPC and Zeolite) at 30˚C in ambient atmosphere. The microhygrostat was partly filled with a saturated cupper chloride solution. Specific heat flow (normalised with respect to the total amount of SPC) is shown versus time.*

Experimental

Samples consisting of 1:1 mixtures by weight of SPC and Zeolite were used for all measurements if other not indicated. SPC differing in granule size and surface coating were used. 0.5 g of SPC and 0.5 g of Zeolite was loaded into 4 ml disposable glass ampoules which were subsequently sealed using a standard lid. Mixing was done by shaking the ampoules for 2 minutes. Small 0.3 ml glass vials (microhygrostats) partly filled with saturated cupper chloride solution were inserted into the ampoules in order to control the relative humidity close to 70 % at 30°C. Precautions were taken to avoid any contamination of the SPC sample with the salt solution.

Microcalorimetric measurements were performed with TAM III - a multichannel microcalorimetric system that allows up to 48 samples to be studied in parallel. 4 ml minicalorimeters were used for the measurements.

The microcalorimetric measurements were run continuously at 30°C. After one week the samples were moved to a block heater kept at the same temperature. After 2 and 3 weeks respectively the ampoules were moved back to the calorimeters for continued measurements. These measurements were run for shorter periods.

Results and Discussion

The influence of Zeolite on the stability of SPC was tested by performing a set of three experiments. SPC, Zeolite and a 1:1 mixture of SPC and Zeolite were loaded into glass ampoules which were sealed at ambient atmosphere and subsequently loaded into the calorimeters.

Figure 1 shows the response in heat flow at low relative humidity from SPC, Zeolite and a mixture of the two. The mixture shows a much larger response compared to the pure samples indicating the destabilising influence of Zeolite on the SPC. The heat flow shows a small autocatalytic effect indicating the

influence of water formed during decomposition of hydrogen peroxide. It is concluded that Zeolite has a destabilising effect on SPC.

The influence of humidity on the stability of SPC was studied by preparing two 1:1 mixturs of SPC and Zeolite. A microhygrostat partly filled with saturated cupper chloride solution was loaded into one of the ampoules in order to control the relative humidity close to 70 %. The second ampoule was closed in ambient atmosphere.

Figure 2 shows that the stability of the SPC sample exposed to increased humidity from the microhygrostat is reduced significantly compared to the sample which was prepared under low relative humidity (ambient atmosphere). The results shows that in order to prolong the life time of SPC the relative humdity must be kept low.

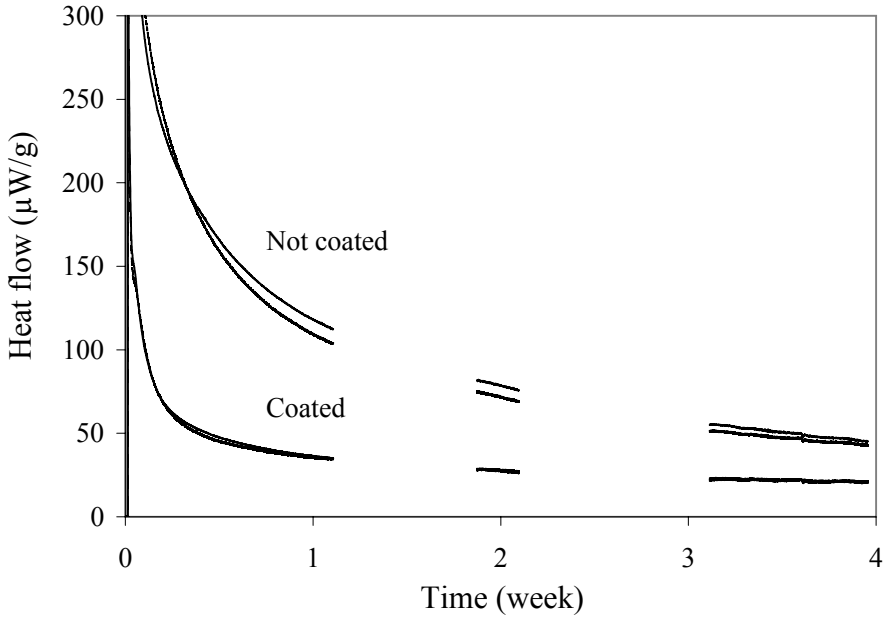

Figure 3. *Influence of a protecting surface coating on SPC samples (1:1 mixtures per weight of SPC and Zeolite) at 30˚C under humid conditions. Specific heat flow (normalised with respect to the total amount of SPC) is shown versus time. The double curves represents repeated experiments.*

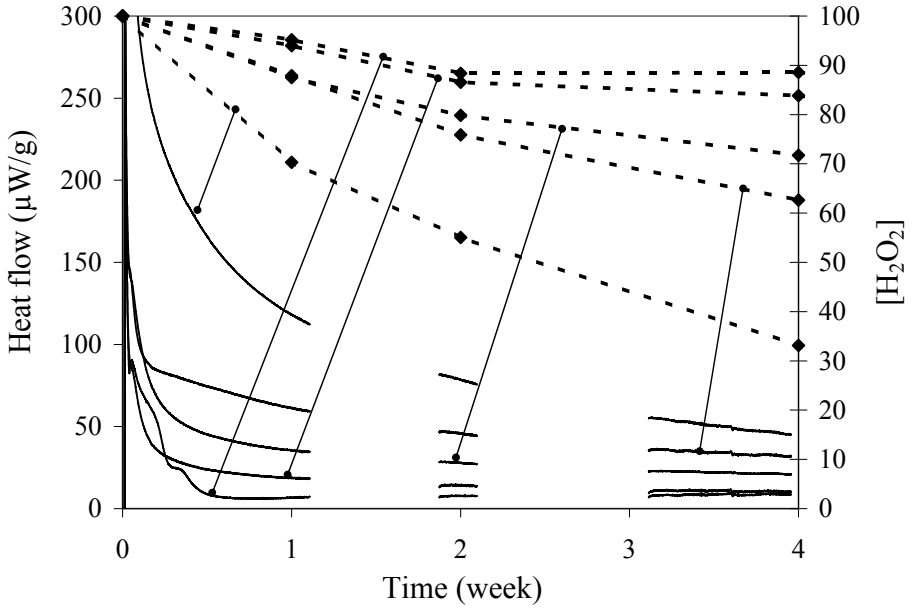

Figure 4. *Comparison of the stability of various SPC samples in terms of heat flow and residual amount of hydrogen peroxide. Specific heat flow (normalised with respect to the total amount of SPC).*

In order to increase the stability of SPC it is common to apply a surface coating on the percarbonate granules. The main purpose is to prevent the granules for exposure to water vapour and catalytic impurites. Two different grades of SPC were used, one without coating and one with a protective surface coating of sodium sulphate. Two experiments were performed in order to check the repeatbility; 1:1 mixtures of each of the two grades of SPC and Zeolite were prepared and loaded into glass ampoules. Microhygrostats were added to all ampoules in order to control the relative humidity close to 70 %.

Figure 3 shows that the magnitude of the heat flow curves is lower for the coated sample indicating the protective influence of the coating. Furthermore, the almost overlapping curves of each experiment indicates an excellent repeatability. The somewhat less repeatability of the non coated samples is in agreement with similar variations in the peroxide content of non-coated samples subjected to oven ageing.

To check the reliability of microcalorimetry as a tool for stability testing of SPC samples a set of samples (1:1 mixtures of SPC and Zeolite) representing different manufacturing and experimental conditions were prepared. A similar set of samples were prepared and stored in an oven at 30°C and 70 % relative humidity during a four week period. Samples were removed after 1, 2 and 4 weeks and the hydrogen peroxide content was determined using iodometric titration .

Figure 4 shows that a close relation between the microcalorimetric response and the hydrogen peroxide

content was found for all samples studied. SPC samples showing a high hydrogen content, after storage in hot and humid climate, are considered to be more stable than samples containing a lower content of hydrogen peroxide. These samples did also exhibit heat flow curves of lower magnitude. The close relation between the hydrogen peroxide content and the magnitude of the heat flow indicates that the heat flow monitored reflects the rate of decomposition of the hydrogen peroxide. Furthermore, the microcalorimetric data shows that the stability of SPC can be predicted from microcalorimetric data after only a few hours/days of measurement.

Conclusions

Microcalorimetry has proved to be a well suited technique for multi sample stability testing of sodium percarbonate samples.

The influence of humidity, surface coating, and granular size on the stability of various sodium percarbonate samples could all be determined.

The microcalorimetric results obtained for a range of different samples were all in agreement with results obtained by conventional stability testing including oven aging and analysis of the hydrogen peroxide content.

Several advantages of using TAM III for stability testing of sodium percarbonate compared to conventional stability testing can be distinguished. A major advantage is that the same sample is used during the entire measurement. Another advantage is that TAM III offers multi sample stability testing - up to 48 samples can be studied in parallel. Furthermore, microcalorimetry offers stability data to be monitored continuously from start of reaction throughout the test.

The excellent long-term stability of the calorimeter makes it possible to perform also long-term measurements for extended periods, e.g. weeks although the stability in the present study could be predicted after only a few days.

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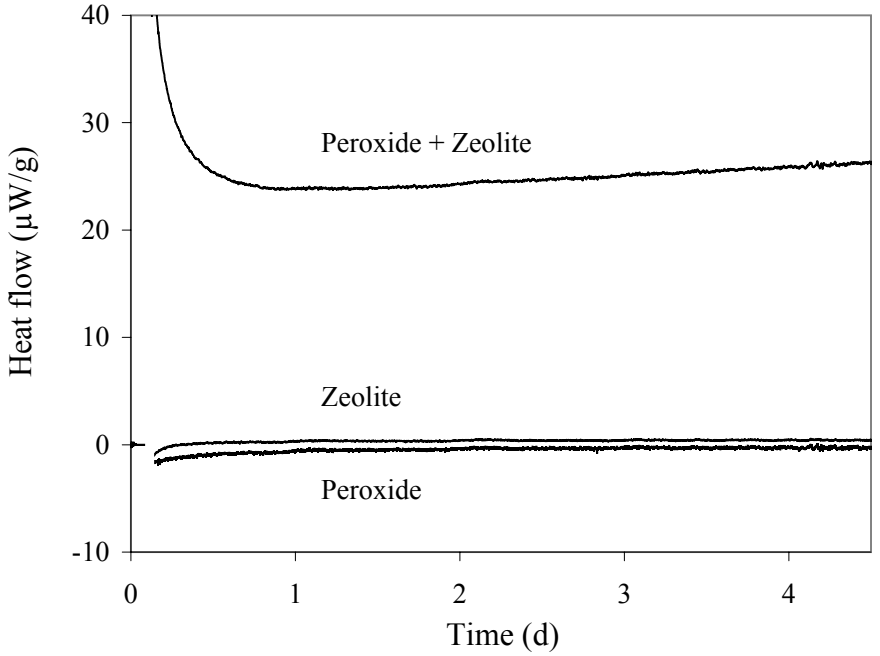

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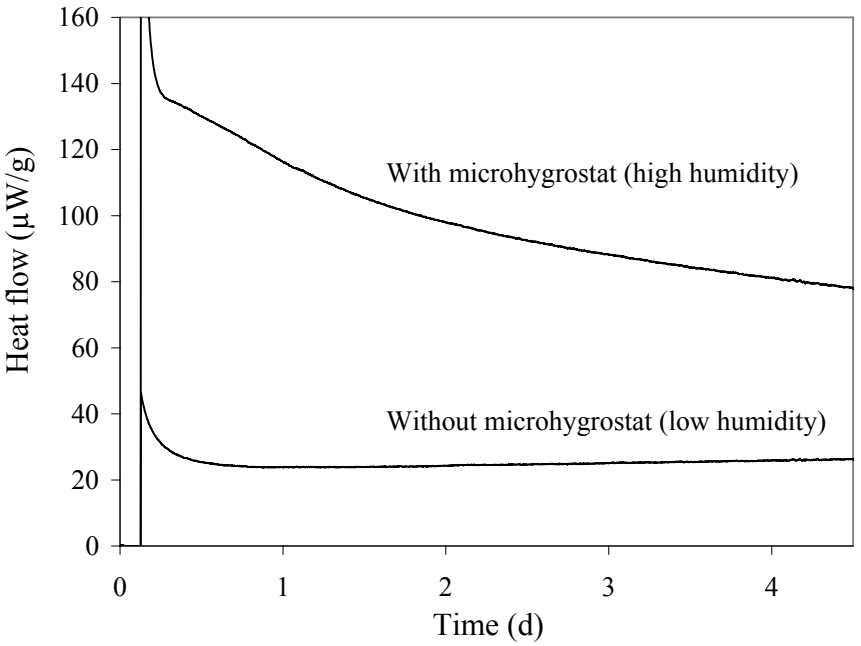

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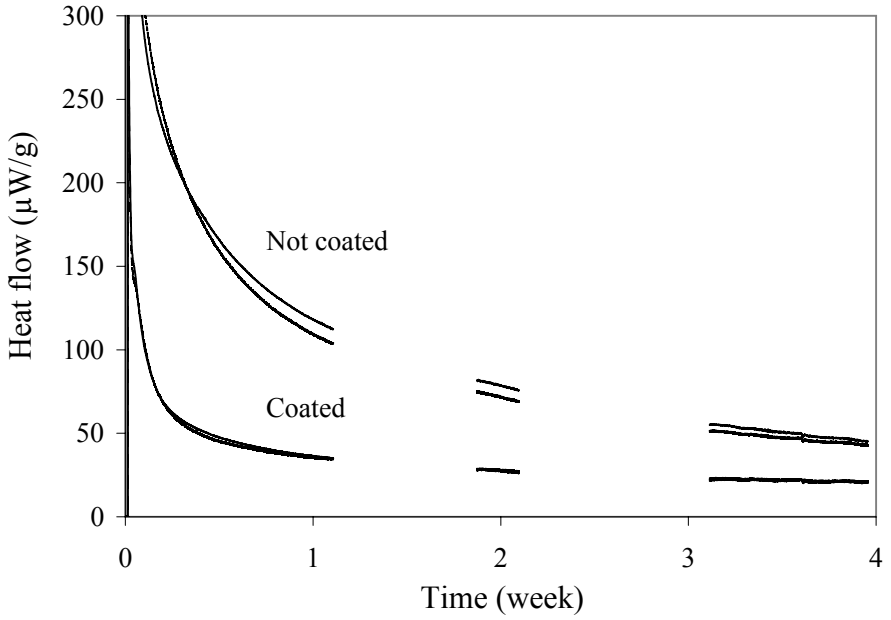

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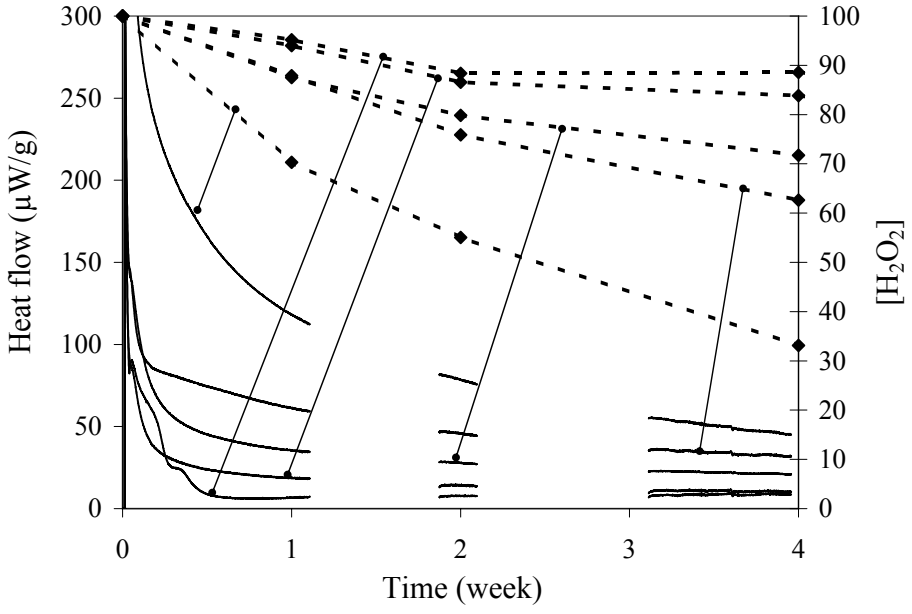

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