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Stabilised hydrogen peroxide



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Description

The invention relates to a modified hydrogen peroxide and to its use in the chemical sterilisation of packaging materials.

The chemical sterilisation of packaging materials nowadays makes it possible to make foodstuffs such as milk, yoghurt or fruit juices available to the end user in simple, user-friendly packaging, without treating or impairing the respective foodstuff itself in any way.

The high degree of acceptance of the user-friendly packaging referred to above results in the filling capacity of the filling machines constantly being increased, which simultaneously is often accompanied by shortening of the filling cycles.

In the chemical sterilisation of packaging materials, the chemicals which can be used are limited by food regulations. Only those chemicals or mixtures which are permitted on their own or - in the case of mixtures - the individual constituents of which are permitted under food regulations are permitted.

It has been shown in the past that hydrogen peroxide, owing to its high oxidising capacity, is a very effective germicidal medium and therefore has now been used successfully for years in almost all aseptic packaging plants in the milk-processing industry and also in juice production etc..

Compared with other germicidal substances or comparable oxidising agents, hydrogen peroxide has the great advantage of not leaving any residues other than water behind on the packaging materials as a result of the product and of the process, apart from the slight traces of stabiliser.

In the chemical sterilisation of packaging materials, nowadays essentially two processes have become established on the market, the dip bath process and the spray process. In both processes, nowadays hydrogen peroxide is used as germicidal chemical at elevated temperatures, the demands made on the material-specific properties of the hydrogen peroxide depending on the process in question.

Thus for example in the spray process the hydrogen peroxide used should for process-related reasons contain only few "inert materials", which very largely originate from the stabilisers used: in the spray process the "inert materials" result in incrustations in the evaporator or spraying section, which necessitates cleaning and ultimately reduces the filling capacity.

In the dip bath process the germicidal process takes place in a bath filled with hydrogen peroxide. For this, the packaging material is passed through a temperature-controlled bath and during the later course of the process is mechanically separated from adhering hydrogen peroxide residues. As a result of the process, therefore, the hydrogen peroxide used must be more highly stabilised than the product used in the spray process referred to above.

In order to extend the useful life of the hydrogen peroxide used, foodstuff-compatible stabilisers are added to the hydrogen peroxide. It is for example known to use

pyrophosphates/phosphoric acid in combination with stannates for stabilisation.

The increases in filling capacity described above, with substantially unaltered dip bath geometries, are accompanied substantially by a reduction of the dwell time of the packaging material in the dip bath. In order nevertheless to maintain the sterilisation effect, the operating temperature in the dip bath must be increased.

The object of the invention then consists in modifying hydrogen peroxide such that it is possible to use it in high-speed aseptic packaging plants at higher temperatures than have been possible hitherto without shortening the filling times of the packaging plant. The comparison of stability with the hydrogen peroxide specialities used at present for the "slower"-running machines serves as the variable for measuring this.

Surprisingly, it was discovered that hydrogen peroxide can be stabilised so efficiently and effectively by the addition of small amounts of phosphonic acids permitted under food regulations, preferably aminotris(methylene) phosphonic acid, that a substantially lesser reduction in concentration is observed even at temperatures of 85°C compared with the special hydrogen peroxide types nowadays used in dip bath technology.

This improvement in the stability behaviour is not restricted only to hydrogen peroxide which has not yet been used in the process and accordingly has not picked up any contamination from the packaging material. Also hydrogen peroxide which as a result of the process exhibits enrichment of packaging material residues, which results in heterogeneous decomposition, behaves substantially more

stably even at higher temperatures compared with standard hydrogen peroxide qualities.

The amount of stabiliser necessary for the stabilisation of hydrogen peroxide is 200 to 500 ppm aminotrismethylene phosphonic acid in the form of a 50%-strength aqueous solution relative to 1 l hydrogen peroxide.

One further surprising advantage of the hydrogen peroxide stabilised with aminotrismethylene phosphonic acid is that upon the removal of residual hydrogen peroxide following the dip bath process even with a continuous process no hard residues are built up on the scraper rolls.

One further advantage is the preparation of the hydrogen peroxide stabilised with aminotrismethylene phosphonic acid. The necessary amount of stabiliser is mixed into a hydrogen peroxide distillate; the addition of further stabilisers can be omitted.

The following examples are intended to explain the invention, without limiting it.

1. 250, 500 and 1000 μ l of an aqueous 50%-strength solution of aminotrismethylene phosphonic acid, trade name Cublen AP1 (manufacturer ZSCIMMER & SCHWARZ, MOHSDORF GmbH & Co KG, Mohsdorf) was dissolved in commercially available hydrogen peroxide of the type D0032 from Solvay Interlox. The stability values of these mixtures are reproduced in Table 1.
2. Analogously to Example 1, 250, 500 and 1000 μ l/l H_2O_2 of an aqueous 50%-strength solution of aminotrismethylene phosphonic acid, trade name Cublen AP1 (manufacturer

ZSCIMMER & SCHWARZ, MOHSDORF GmbH & Co KG, Mohsdorf) was dissolved in commercially available hydrogen peroxide of the type D0035, which has been passed by the apparatus manufacturer for dip bath technology. The stability values of these mixtures are reproduced in Table 2.

3. To measure the stability, during determination a defined number of packaging material chips with a surface area of 55 - 60 mm²/chip are added to the samples from the Examples listed above. To measure the stability, approximately 50 ml of the sample solution, with known concentration (W_a) was stored at a storage temperature of 70°C or 85°C over a period of 960 min. in a glass flask. Then after the necessary correction of volume, caused by evaporated water, the hydrogen peroxide content was again determined by conventional methods for this purpose (W_e). The stability loss is calculated by: $(W_a - W_e)/W_a \times 100$.

W_a = initial concentration of the hydrogen peroxide used.

W_e = final concentration of the hydrogen peroxide after 16 h test at the respective test temperature.

Table 1:

	H ₂ O ₂ type D0032	H ₂ O ₂ type D0035
Addition of stabiliser (µl/l H ₂ O ₂)	Stability loss (%)	Stability loss (%)
0	38	23
250	12	15
500	5	11
1000	6	3
Stabiliser: Cublen AP1 (50%-strength solution) Test temperature: T = 85°C Testing time: t = 960 min Packaging material chips: n = 50		

Table 2:

	H ₂ O ₂ type D0035
Addition of stabiliser (µl/l H ₂ O ₂)	Stability loss (%)
0	6
250	
500	2
1000	1
Stabiliser: Cublen AP1 (50%-strength solution) Test temperature: T = 70°C Testing time: t = 960 min Packaging material chips: n = 50	

Table 3:

Temperature (°C)	Number of chips	Stability loss (%)
70	0	1
	25	1
	50	6
85	0	1
	25	
	50	23
96	0	1
	25	
	50	50
Hydrogen peroxide type D0035		
Testing time: t = 960 min		

Claims

1. Stabilised hydrogen peroxide, characterised in that it is stabilised with 1 to 1,000 ppm foodstuff-compatible phosphonic acids.

2. Stabilised hydrogen peroxide according to Claim 1, characterised in that it is stabilised with 200 to 500 ppm foodstuff-compatible phosphonic acids.

3. Stabilised hydrogen peroxide according to Claims 1 and 2, characterised in that the hydrogen peroxide is stabilised with aminotrismethylene phosphonic acid.

4. The use of hydrogen peroxide stabilised with foodstuff-compatible phosphonic acids in accordance with Claims 1 to 3 as dip bath liquid for the chemical sterilisation of packaging materials in high-speed aseptic packaging plants.

5. The use of stabilised hydrogen peroxide as dip bath liquid according to Claim 4, characterised in that the dip bath liquid is at a temperature of 80 to 85°C.