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(54) Title: FOOD PACKAGE FOR AMINES CONTROL OR REMOVAL

(57) Abstract: A food package suitable for manufacturing as a closed packaging system contains an amine-absorbent element comprising ammonium- exchanged mordenite (MOR) type zeolites and optionally further comprises ZnO-doped Faujasite (FAU) type zeolites and/or CuO-doped ZSM-5 type zeolites.

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FOOD PACKAGE FOR AMINES CONTROL OR REMOVAL

The present invention relates to a food package for amines control or removal containing an amine-absorbent element comprising ammonium-exchanged mordenite (MOR) type zeolites.

Amines are organic derivatives of ammonia in which one, two or all three of the ammonia hydrogens are replaced by organic groups such as alkyl or aryl groups. This class of compounds have a typical nucleophilic behavior and, for this reason, they usually react through very fast kinetics with acyl compounds derived from carboxylic acids.

Amine moiety is ubiquitous in biology and, considering the application field of the present invention, one of the most interesting biological process is the amine release derived from the breakdown of amino acids. Specifically, processes like this are involved in fish decaying, and some compounds such as trimethylamine (TMA), dimethylamine (DMA) and ammonia are typically frequently associated with the spoilage of marine fish stored under ice. TMA in particular is one of the most characteristic spoilage metabolites of marine fish and, due to its intense ammonia-like and fishy off-odors, it is typically able to dominate other odors even at low concentrations. The impact of TMA on food spoilage depends on the animal species, on the applied atmosphere and on the storage temperature.

Despite amines detection can be easily managed, it is important to underline that this cannot represent an effective marker to determine the product quality deterioration. At the same time, these molecules smell bad and their accumulation in closed food packages can lead to consumer rejection of fresh food. In this regards, many efforts have been done to remove the produced amines to allow a reduction of the number of rejects but, so far, no efficient solution has been identified.

One possibility to solve the problem, as reported in WO 2014/052055, consists in the removal of the biogenic amines through the use of an acid reactant, generally a carboxylic acid, absorbed onto a carrier: the amines react with acids to form ammonium salts and consequently reducing the food odor. Another possible approach, disclosed by the same applicant in WO 2014/052053, describes a package for protein-containing foods

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comprising an oxidizer, typically hydrogen peroxide or sodium chlorite, absorbed onto a carrier. Also in this application, the aim of odor control is reached through the reaction of the active species with amines.

5 Therefore, it is clear that both methods described in the cited prior art do not use an absorbing approach to solve the odor problem related to protein rich foods but a converting approach, i.e. resulting in the formation of some reaction products. Zeolites are cited together with activated carbon, silica gel, cellulose paper and generic "absorbent polymers" just as potential carriers for the active species, but it is important to point out that the claimed processes may be too strong for the use of zeolites which, both in acid
10 and oxidizing environment, would be destroyed.

Moreover, WO 2014/052053 discloses embodiments related to a releasable system as activated carbon and silica gel; specifically, the absorbed biogenic amine is released into the closed package and the oxidizer system reacts with the released amine to irreversibly retain it. It is therefore clear that the absorbing mechanism requires the
15 coupling with other retaining systems, i.e. systems able to block the reaction products.

In the prior art, different documents describe the use of zeolites as odor-controlling adsorbent materials in various fields such as detergent compositions and cleansing bar compositions. US patents 4795482 and 4826497 disclose zeolites having "high" silicate/aluminate ratios with a Si/Al ratio in the range 100-250; similarly, US 5211870
20 reports to zeolites characterized by a Si/Al ratio between 100 and 250.

Other documents describe the use of zeolites as inorganic antimicrobial agents for items that come into contact with foods, such as a food tray in US 2002/012760 or a closure for a container for liquids in WO 00/26100. Another application of zeolites disclosed in the prior art is as components for compositions that can be used as a material
25 for food packaging materials, such as in a method for producing 2,6-dialkylnaphthalene in JP H06/40958 or a propylene- α -olefin block copolymer composition in JP H10/7875.

It is an object of the present invention to provide a food package, manufactured as a closed packaging system, for amines odor control or removal in its enclosed volume, said food package containing an amine-absorbent element comprising ammonium-

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exchanged mordenite (MOR) type zeolites with a Si/Al atomic ratio comprised between 5 and 20.

The described composition is therefore characterized by a lower Si/Al ratio compared to the known ratios reported above, which brings to an increasing of total acidity improving both activity and selectivity of zeolites, and a strong affinity to amines.

In a preferred embodiment, said Si/Al ratio is comprised between 8 and 20.

MOR zeolites, suitable to be used in the present invention, are present in an amount comprised between 2 μ g and 50 μ g per gram of weight of an amines-releasing fresh food.

In some alternative embodiments of the present invention, the above cited MOR zeolites can be used in combination with other kind of zeolites suitable to remove amines.

For example, in order to increase the sorption capacity of the system while keeping high reversibility at low temperature (i.e. a temperature lower than 100°C) it is possible to further add ZnO-doped Faujasite (FAU) type zeolites with a Si/Al atomic ratio comprised between 2 and 30. Indeed, according to TMA tests realized with the Temperature Program Desorption (TPD) technique on ZnO-doped zeolites, this metal oxide presence leads to an increase of the intensity of the first release peak at lower temperature and to a decrease of the temperature of the second release peak that occurs at higher temperature, that correspond to an overall increase of the sorption performance in the 25-100°C range.

Said FAU zeolites are preferably present in an amount comprised between 1 μ g and 40 μ g per gram of weight of an amines-releasing fresh food.

Moreover ZSM-5, CuO-doped zeolites show a relevant component related to high energy acid sites. Thus, in order to obtain highest sorption capacity in the range comprised between 150-270°C, the amines-absorbent element of the herein disclosed food package can further comprise CuO-doped ZSM-5 type zeolites with a Si/Al atomic ratio comprised between 10 and 50 in an amount comprised between 1.5 μ g and 40 μ g per gram of weight of an amines-releasing fresh food.

According to the present invention, the zeolites are in the form of powders with an average size characterized by an X_{90} between 0.2 μ m and 10 μ m where X_{90} indicates the

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spherical diameter at which 90% of the particles in the sample are comprised in the given range on a volume basis. In some embodiments, the above-described zeolite powders are contained in a bag realized with a material selected in the group consisting of low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), ethylene-
5 vinyl acetate (EVA), polystyrene (PS), styrene-ethylene-butylene-styrene (SEBS), polylactic acid (PLA), polyesters and biopolyesters.

Those bags can be placed in the internal volume of the package, preferably in the head space.

In other possible embodiments, said zeolite powders are dispersed in a polymeric
10 matrix selected among acrylics, siloxanes and polysiloxanes, acrylics-styrene, -vinyl and alkyd copolymer, urethane-acrylics, aliphatic-urethanes, urethanes, polyesters, biopolyesters, epoxies, polyurethanes, polystyrene, phenolic resin, ethylene-vinyl alcohol (EVOH), polyvinyl alcohol (PVA) and waterborne or water reducible latex.

Said polymeric matrix can be realized in the form of a layer characterized by a
15 thickness comprised between 0.5 and 50 μm and the possibility to be coated on a polymer or a cellulose paper substrate, or paper substrates deriving from agriculture and food waste.

The packaging system according to the present invention can be used for hermetically sealing foods which typically release amines during their spoilage. Thus, in
20 a preferred embodiment said packaging system is a sealed bag or alternatively a film suitable for wrapping and closing a food container. Hereinafter, the invention will be explained in more detail with reference to the following examples.

Example

25 MOR (NH₄) is selected as sample S1, according to the present invention, and has an average size comprised between 2 μm and 10 μm and a Si/Al ratio of 10 as summarized in Table 1.

Similarly, samples S2-S5 have been prepared by mixing MOR zeolites with FAU and ZSM-5 ion-exchanged zeolites as reported in Table 1.

Comparative sample 1 (C1) MOR (H) zeolites are prepared by thermal treatment at 500°C for 5 hours in air, from the same samples identical to the above S1. This thermal treatment allows to remove ammonium ions from the zeolite framework resulting in un-exchanged MOR (H) zeolites having an average size comprised between 2 µm and 10 µm and a Si/Al ratio of 10.

Comparative sample 2 (C2) ZnO-doped MOR (H) zeolites were prepared, first, by thermal treatment, at 500°C for 5 hours in air, of the sample MOR (NH4) and then, by ion exchange process. MOR (H) zeolites have an X₉₀ comprised between 0.2 µm and 10 µm. 10g of zeolites were dispersed in a solution of zinc salt (e.g. nitrate salt or acetate salt) then filtered on a filter paper and thermally treated to promote the solvent evaporation.

Resulting zinc-exchanged amount is about 2.4%wt over MOR zeolites weight, as evaluated by ICP Mass Spectrometry.

Sample ID	1 st zeolite	1 st zeolite Si/Al atomic ratio	1 st zeolite cation exchanged	2 nd zeolite	2 nd zeolite Si/Al atomic ratio	2 nd zeolite cation exchanged	1 st /2 nd zeolite ratio
S1	MOR (NH4)	~ 10	NH4	-	-	-	-
C1	MOR (H)	~ 10	H+	-	-	-	-
C2	MOR (H)	~ 10	Zn	-	-	-	-
S2	MOR	10	NH4	FAU	15	Zn	1
S3	MOR	10	NH4	ZSM5	11.5	Cu	1
S4	MOR	10	NH4	FAU	15	Zn	0.43
S5	MOR	10	NH4	ZSM5	11.5	Cu	0.43

Table 1 – Samples description

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Zeolites reported in Table 1 are tested under Temperature Program Desorption (TPD) technique to determine the kinetic and thermodynamic parameters of desorption process. Each sample is heated with a temperature program and the partial pressures of atoms and molecules evolving from the sample are detected.

The reactor is saturated under static conditions by injecting 10 cm³ of gaseous TMA left for 10 min at 30°C. After saturation, the reactor is connected on-line with the carrier flow, recording the release of TMA at the saturation temperature (dead volume). TPD is finally carried out up to 500°C.

The results are reported in the following table 2 in order to provide an overall picture for the tested zeolites. The zeolite characteristics and the correlation between results and zeolites characteristics are discussed below.

Sample	desorbed TMA (mmol/g _{zeo})	TMA sorption capacity (%wt)
S1	1.33	7.86
C1	0.78	4.61
C2	0.67	3.96
S2	1.05	6.20
S3	1.02	6.00
S4	1.25	7.40
S5	1.32	7.78

Table 2 – Sample results

Considering the characterization results, all MOR zeolites exhibit larger acid sites (i.e. higher overall amine sorption amount) than other commercially available zeolites but sample S1 with ammonium-exchanged MOR zeolites ensures a higher amount of sorbed

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TMA if compared to comparative sample C1 with un-exchanged MOR. Sample C2, i.e. zinc oxide doped MOR zeolites, confirmed a lower overall TMA sorption capacity.

5 Furthermore, Samples S2 – S5 have been prepared as mixture of MOR zeolites with FAU and ZSM-5 ion-exchanged zeolites, with the aim of proving the maintenance of high levels of TMA absorption, while improving the possible package applications. In fact, the addition of ZnO-doped Faujasite (FAU) type zeolites increases the sorption capacity of the system while keeping high reversibility at temperature lower than 100°C, or the use of CuO-doped ZSM-5 type zeolites, improves the sorption capacity in the range comprised between 150-270°C).

CLAIMS

1. A food package manufactured as a closed packaging system, for amines control or removal, containing an amine-absorbent element comprising ammonium-exchanged mordenite (MOR) type zeolites with a Si/Al atomic ratio comprised between 5 and 20.
2. A food package according to claim 1, wherein said Si/Al atomic ratio is comprised between 8 and 20.
3. A food package according to any of the previous claims, wherein said MOR zeolites are present in an amount comprised between 2 μg and 50 μg per gram of weight of an amines-releasing fresh food.
4. A food package according to any of the previous claims, wherein the amine-absorbent element further comprises ZnO-doped Faujasite (FAU) type zeolites with a Si/Al atomic ratio comprised between 2 and 30.
5. A food package according to claim 4, wherein said FAU zeolites are present in an amount comprised between 1 μg and 40 μg per gram of weight of an amines-releasing fresh food.
6. A food package according to any of the previous claims, wherein the amine-absorbent element further comprises CuO-doped ZSM-5 type zeolites with a Si/Al atomic ratio comprised between 10 and 50.
7. A food package according to claim 6, wherein said CuO-doped ZSM-5 zeolites are present in an amount comprised between 1.5 μg and 40 μg per gram of weight of an amines-releasing fresh food.
8. A food package according to any of the previous claims, wherein the zeolites are in the form of powders with X_{90} comprised between 0.2 and 10 μm .
9. A food package according to claim 8, wherein said powders are contained in a bag.
10. A food package according to claim 9, wherein the bag is composed of a material selected in a group consisting of low density polyethylene (LDPE), high density

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polyethylene (HDPE), polypropylene (PP), ethylene-vinyl acetate (EVA), polystyrene (PS), styrene-ethylene-butylene-styrene (SEBS), polylactic acid (PLA), polyesters and biopolyesters.

11. A food package according to claim 10, wherein the bag is placed in the
5 internal volume of the package.

12. A food package according to claim 11, wherein the bag is placed in the head space of the package.

13. A food package according to claim 8, wherein said powders are dispersed in a polymeric matrix.

10 14. A food package according to claim 13, wherein the polymeric matrix is selected in a group consisting of acrylics, acrylics-styrene, -vinyl and alkyd copolymer, urethane-acrylics, aliphatic-urethanes, urethanes, polyesters, biopolyesters, epoxies, siloxanes and polysiloxanes, polyurethanes, polystyrene, phenolic resin, ethylene-vinyl alcohol (EVOH), polyvinyl alcohol (PVA) and waterborne or water reducible latex.

15 15. A food package according to claim 13 or 14, wherein said polymeric matrix is in the form of a layer with a thickness comprised between 0.5 and 50 μm .

16. A food package according to claim 15, wherein said layer is coated on a polymer or a cellulose paper substrate, or paper substrates deriving from agriculture and food waste.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2020/083094

A. CLASSIFICATION OF SUBJECT MATTER

INV. B65D81/26

ADD. B01J20/18 B01J20/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B65D G01N B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP H04 255767 A (NICHIBAN KENKIYUUSHIYO KK) 10 September 1992 (1992-09-10) paragraphs [0001] - [0038] -----	1,2
X	US 2002/012760 A1 (BARRY JOHN E [US] ET AL) 31 January 2002 (2002-01-31) paragraphs [0005] - [0053] figures 1, 2 -----	1,2
X	WO 00/26100 A1 (HEALTHSHIELD TECHNOLOGIES L L [US]) 11 May 2000 (2000-05-11) pages 1-9 figures 1-3A -----	1,2
X	JP H10 7875 A (SHOWA DENKO KK) 13 January 1998 (1998-01-13) paragraphs [0001] - [0033] ----- -/-	1,2



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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INTERNATIONAL SEARCH REPORT

International application No PCT/EP2020/083094

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP H06 40958 A (NIPPON STEEL CHEMICAL CO) 15 February 1994 (1994-02-15) paragraphs [0001] - [0032] -----	1-3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2020/083094

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-3

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-3

A food package wherein the MOR zeolites are present in an amount comprised between 2 and 50 micrograms per gram of weight of an amines-releasing fresh food.

2. claims: 4, 5

A food package wherein the amine-absorbent element further comprises ZnO-doped Faujasite (FAU) type zeolites with a Si/Al atomic ratio comprised between 2 and 30.

3. claims: 6, 7

A food package wherein the amine-absorbent element further comprises CuO-doped ZSM-5 type zeolites with a Si/Al atomic ratio comprised between 10 and 50.

4. claims: 8-16

A food package wherein the zeolites are in the form of powders with X90 comprised between 0,2 and 10 micrometres.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/083094

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP H04255767	A	10-09-1992	NONE

US 2002012760	A1	31-01-2002	AU 3615400 A 21-09-2000
			US 2002012760 A1 31-01-2002
			WO 0052088 A1 08-09-2000

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			EP 1044139 A1 18-10-2000
			WO 0026100 A1 11-05-2000

JP H107875	A	13-01-1998	NONE

JP H0640958	A	15-02-1994	NONE
