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(54) **Title**: HEAT-EXPANDABLE MICROCAPSULES COMPRISING MAGNETIC METAL OXIDE PARTICLES

(57) **Abstract**: Microcapsule consisting of a capsule shell made of a thermoplastic resin and a dispersion enclosed by the capsule shell which comprises magnetic particles and one or more hydrocarbons with a boiling point of -15°C to 220°C, where the magnetic particles are magnetic metal oxide particles with a shell comprising silicon dioxide and the coated metal oxide particles have an average primary particle diameter of from 2 to 100 nm and where the average diameter of the microcapsule is 5 to 50 μm. The microcapsule can be obtained by subjecting a) an organic dispersion which comprises coated metal oxide particles having an average primary particle diameter of from 2 to 100 nm, the shell of which comprises amorphous silicon dioxide, b) an aqueous solution or water and c) one or more monomers, if appropriate in the presence of one or more polymerization catalysts, to a dispersion polymerization.

Heat-expandable microcapsules comprising magnetic metal oxide particles

The invention relates to heat-expandable microcapsules which comprise magnetic metal oxide particles enclosed by a shell, their production and use.

US 6106946 discloses heat-expandable microcapsules which comprise magnetic particles having an average particle diameter of from 5 to 200 nm. The microcapsules are a constituent of sound-absorbing and insulating materials, as are used in electrical devices, vehicles or building materials.

EP-A-1185594 discloses heat-expandable microcapsules which expand as a result of the introduction of heat and thereby weaken the cohesion of adhesives and the interfacial bonds. A disadvantage of this process is considered to be that the entire object warms up as a result of introducing the heat and not just the area where the bonds are to be broken. For articles which have heat-sensitive areas, such a process can only be used to a limited extent. Moreover, it is not very energy-efficient to heat large parts when it is only necessary to heat small areas in a targeted manner.

WO 2006/042782 discloses a process for recycling electrical or electronic components in which, in one process step, an adhesive connection between two elements of the component, formed by an adhesive mass, is broken by expandable particles located in the adhesive mass expanding as a result of supplying energy and thereby being able to force open the adhesive bond. The adhesive

mass here can comprise ferromagnetic, ferrimagnetic or superparamagnetic particles which permit inductive heating of the adhesive mass. Furthermore, the adhesive mass can comprise heat-expandable microcapsules which are ultimately intended to lead to breaking of the adhesive bond. The disadvantage of this process is that the magnetic particles and the microcapsules are spatially separate from one another, meaning that the advantages of inductive heating are only partly translated. Furthermore, the application of the magnetic particles involves difficulties in the form of an uneven distribution of the magnetic particles and/or an agglomeration of the magnetic particles. As a result of these effects too, the effectiveness of inductive heating is reduced.

It was therefore the object of the present invention to provide a subject matter which allows a more efficient heating of adhesive bonds than is known in the prior art.

The invention provides a microcapsule consisting of a capsule shell made of a thermoplastic resin and a dispersion enclosed by the capsule shell which comprises magnetic particles and one or more hydrocarbons with a boiling point of -15°C to 220°C, or consists thereof, where the magnetic particles are magnetic metal oxide particles with a shell comprising silicon dioxide, preferably a shell consisting of silicon dioxide, and the coated metal oxide particles have an average primary particle diameter of from 2 to 100 nm, preferably 10 to 80 nm and particularly preferably 20 to 70 nm, and where the average diameter of the microcapsules is 5 to 50 µm, preferably 10 to 30 µm.

In this connection, magnetic metal oxide particles are to be understood as meaning those which have ferromagnetic, ferrimagnetic and/or superparamagnetic properties. In the presence of electrical, magnetic or electromagnetic alternating fields, these particles lead to a heating of the dispersion located in the microcapsule and thus to an expansion of the microcapsule.

The coated metal oxide particles may be isolated individual particles or aggregated particles. The aggregated particles may be present here in a form in which metal oxide particles have become intergrown and the shell surrounds the intergrown metal oxide particles. Furthermore, there is the possibility that the coated metal oxide particles have become intergrown via their shell. Preferably, the microcapsule according to the invention can comprise, essentially or exclusively, such coated metal oxide particles, in which the metal oxide particles have become intergrown and the shell surrounds the intergrown metal oxide particles.

The average diameter of the microcapsules according to the invention can increase upon heating to 80 to 220°C by a hundred times, preferably by 40 to 80 times, the original average diameter without leading to destruction of the microcapsule.

The thickness of the microcapsule according to the invention is preferably 1 to 10 mm, particularly preferably 4 to 8 mm.

Furthermore, preference is given to an embodiment in which the fraction of the coated metal oxide particles is 0.001 to 5% by weight, based on the microcapsule. As a rule, a

fraction of from 0.01 to 1% by weight is adequate for an expansion of the microcapsule by a factor of 40 to 80 in the presence of electromagnetic alternating fields.

In this connection, the fraction of the coated metal oxide particles, based on the dispersion, can be 0.1 to 10% by weight, preferably 0.5 to 5.

The metal oxide particles present in the microcapsule according to the invention are preferably selected from the group consisting of the oxides of cobalt, chromium, dysprosium, iron, erbium, gadolinium, holmium, nickel and terbium. Within the context of the invention, ferrites are also considered to be metal oxides. These may be for example ferrites of the general formula MFe_2O_4, where M = Ca, Cd, Co, Cu, Mg, Ni or Zn. Preferably, the metal oxides are iron oxides, such as haematite, magnetite and maghemite. These may be present individually or in the form of a mixture.

In particular, preference is given to a microcapsule in which the coated metal oxide particles have

a) a BET surface area of from 10 to 80 m^2/g,

b) a thickness of the shell of from 2 to 30 nm and

c) a content of iron oxide of from 60 to 90% by weight and of silicon dioxide of from 10 to 40% by weight, in each case based on the coated metal oxide particles.

Furthermore, metal oxide particles may also be present, the shell of which has been surface-modified. These can be obtained by treating the coated metal oxide particles with a surface-modifying agent, in particular one with which a

hydrophobicization of the surface results. By virtue of this measure, the stability of the dispersion in the inside of the microcapsule can be improved.

Preferred surface-modifying agents may be in particular the following silanes:

Organosilanes $(RO)_3Si(C_nH_{2n+1})$ and $(RO)_3 Si(C_nH_{2n-1})$ where R = alkyl, such as methyl, ethyl, n-propyl, isopropyl, butyl and n = 1-20.

Organosilanes $R'_x(RO)_ySi(C_nH_{2n+1})$ and $R'_x(RO)_ySi(C_nH_{2n-1})$ where R = alkyl, such as methyl, ethyl, n-propyl, isopropyl, butyl; R' = alkyl, such as methyl, ethyl, n-propyl, isopropyl, butyl; R' = cycloalkyl; n = 1-20; x + y = 3, x = 1, 2; y = 1, 2.

Haloorganosilanes $X_3Si(C_nH_{2n+1})$ and $X_3Si(C_nH_{2n-1})$ where X = Cl, Br; n = 1-20.

Haloorganosilanes $X_2(R')Si(C_nH_{2n+1})$ and $X_2(R')Si(C_nH_{2n-1})$ where X = Cl, Br, R' = alkyl, such as methyl, ethyl, n-propyl, isopropyl, butyl;

R' = cycloalkyl; n = 1-20.

Haloorganosilanes $X(R')_2Si(C_nH_{2n+1})$ and $X(R')_2Si(C_nH_{2n-1})$ where X = Cl, Br; R' = alkyl, such as methyl, ethyl, n-propyl, isopropyl, butyl; R' = cycloalkyl;

n = 1-20.

Organosilanes $(RO)_3Si(CH_2)_m$-R' where R = alkyl, such as methyl, ethyl, propyl; m = 0, 1-20; R' = methyl, aryl such as $-C_6H_5$, substituted phenyl radicals, C_4F_9, OCF_2-CHF-CF_3, C_6F_{13}, OCF_2CHF_2, S_x-$(CH_2)_3Si(OR)_3$;

Organosilanes $(R")_x(RO)_ySi(CH_2)_m-R'$ where R" = alkyl, x + y = 3; cycloalkyl,
x = 1, 2, y = 1, 2; m =0, 1 to 20; R' = methyl, aryl, such as C_6H_5, substituted phenyl radicals, C_4F_9, $OCF_2-CHF-CF_3$, C_6F_{13}, OCF_2CHF_2, $S_x-(CH_2)_3Si(OR)_3$, SH, NR'R''R''' where R' = alkyl, aryl; R'' = H, alkyl, aryl; R''' = H, alkyl, aryl, benzyl, C_2H_4NR'''' R''''' where R'''' = H, alkyl and R''''' = H, alkyl.

Haloorganosilanes $X_3Si(CH_2)_m-R'$ X = Cl, Br; m = 0, 1-20; R' = methyl, aryl such as C_6H_5, substituted phenyl radicals, C_4F_9, $OCF_2-CHF-CF_3$, C_6F_{13}, $O-CF_2-CHF_2$, $S_x-(CH_2)_3Si(OR)_3$, where R = methyl, ethyl, propyl, butyl and x = 1 or 2, SH.

Haloorganosilanes $RX_2Si(CH_2)_mR'$ where X = Cl, Br; m = 0, 1-20; R' = methyl, aryl such as C_6H_5, substituted phenyl radicals, C_4F_9, $OCF_2-CHF-CF_3$, C_6F_{13}, $O-CF_2-CHF_2$, $-OOC(CH_3)C=CH_2$, $-S_x-(CH_2)_3Si(OR)_3$, where R = methyl, ethyl, propyl, butyl and x = 1 or 2, SH.

Haloorganosilanes $R_2XSi(CH_2)_mR'$ where X = Cl, Br; m = 0, 1-20; R' = methyl, aryl such as C_6H_5, substituted phenyl radicals, C_4F_9, $OCF_2-CHF-CF_3$, C_6F_{13}, $O-CF_2-CHF_2$, $-S_x-(CH_2)_3Si(OR)_3$, where R = methyl, ethyl, propyl, butyl and x = 1 or 2, SH.

Furthermore, silazanes of the general formula $R'R_2SiNHSiR_2R'$ where R,R' = alkyl, vinyl, aryl, can be used as surface-modifying agents.

The cyclic polysiloxanes D3, D4, D5 and also polysiloxanes and silicone oils can also be used. In this connection, D3, D4 and D5 are to be understood as meaning cyclic

polysiloxanes having 3, 4 or 5 units of the type $-O-Si(CH_3)_2$.

The following substances can preferably be used as surface-modifying agents: octyltrimethoxysilane, octyltriethoxysilane.

Hexamethyldisilazane, octyltriethoxysilane and dimethylpolysiloxanes can be used particularly preferably.

Besides the coated metal oxide particles, the dispersion in the inside of the microcapsule also comprises one or more hydrocarbons having a boiling point of from -15°C to 220°C. Within the context of the invention, hydrocarbon is also intended to include a halogenated hydrocarbon. Examples which may be mentioned are isobutane, n-butane, n-pentane, isopentane, n-hexane, cyclohexane, n-heptane, petroleum ether, neopentane, propane, propene, butene, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, $CClF_2$-$CClF_2$, CH_2FCF_3, CH_3CHF_2 and CHF_2CF_3.

The capsule shell of the microcapsule according to the invention is a thermoplastic resin. It can be obtained from one or more polymerizable monomers, the monomers being selected from the group consisting of acrylamide, acrylonitrile, acrylic acid, benzyl methacrylate, cyclohexyl methacrylate, methacrylamide, methacrylonitrile, methacrylic acid, methyl methacrylate, N,N-dimethylacrylamide, N,N-dimethylmethacrylamide, tert-butyl methacrylate and N-vinylpyrrolidone.

In addition, one or more polymerizable crosslinking monomers having two or more polymerizable double bonds may

be present. Examples thereof are ethylene glycol di(meth)acrylate, propylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, glycerol di(meth)acrylate, triethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylates, 1,3-butanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, pentaerythritol hexa(meth)acrylate, 3-acryloyloxyglycerol monoacrylate, dimethyloltricyclodecane di(meth)acrylate and triarylformal tri(meth)acrylate.

The invention further provides a process for producing the microcapsule according to the invention, in which

a) an organic dispersion which comprises coated metal oxide particles having an average primary particle diameter of from 2 to 100 nm, the shell of which comprises amorphous silicon dioxide,

b) an aqueous solution or water

c) and one or more monomers, if appropriate in the presence of one or more polymerization catalysts,

are subjected to a dispersion polymerization.

Of suitability as polymerization catalyst in both variants are, for example, peroxides, such as benzoyl peroxide, tert-butyl perbenzoate, cumyl hydroperoxides, tert-butyl peracetate, lauryl peroxide and diisopropyl peroxydicarbonate, azonitriles, such as azobisdimethylvaleronitrile and azobisisobutyronitrile,

and also azo compounds such as azoamide compounds and alkylazo compounds.

The dispersion polymerization preferably takes place at temperatures of from 40 to 80°C.

Preference is likewise given to an embodiment in which the dispersion polymerization is carried out under shearing conditions at an energy density of at least 1000 KJ/m^3.

The invention further provides the use of the microcapsules in the presence of electromagnetic alternating fields for the breaking ("debonding") of adhesive bonds, such as fixed glazings or boards, as a constituent of coating compositions, such as paints or inks, for the filling of cracks, in the processing of thermoplasts, as a constituent of thermosets, as a constituent of paper products and in technical textile fabrics.

Patent claims

1. Microcapsule consisting of a capsule shell made of a thermoplastic resin and a dispersion enclosed by the capsule shell which comprises magnetic particles and one or more hydrocarbons with a boiling point of -15°C to 220°C, characterized in that the magnetic particles are magnetic metal oxide particles with a shell comprising silicon dioxide and the coated metal oxide particles have an average primary particle diameter of from 2 to 100 nm and where the average diameter of the microcapsule is 5 to 50 µm.

2. Microcapsule according to Claim 1, characterized in that its thickness is 1 to 10 mm.

3. Microcapsule according to Claims 1 or 2, characterized in that the fraction of the coated metal oxide particles is from 0.001 to 5% by weight, based on the microcapsule.

4. Microcapsule according to Claims 1 to 3, characterized in that the fraction of the coated metal oxide particles, based on the dispersion, is 0.1 to 10% by weight.

5. Microcapsule according to Claims 1 to 4, characterized in that the core of the coated metal oxide particles consists of one or more iron oxides comprising haematite, magnetite and maghemite.

6. Microcapsule according to Claims 1 to 5, characterized in that the coated metal oxide particles have

a) a BET surface area of from 10 to 80 m^2/g,

b) a thickness of the shell of from 2 to 30 nm and

c) a content of iron oxide of from 60 to 90% by weight and of silicon dioxide of from 10 to 40% by weight, in each case based on the core/shell particles.

7. Microcapsule according to Claims 1 to 6, characterized in that the shell of the metal oxide particles is surface-modified.

8. Microcapsule according to Claims 1 to 7, characterized in that the hydrocarbon is selected from the group consisting of isobutane, n-butane, n-pentane, isopentane, n-hexane, cyclohexane, n-heptane, petroleum ether, neopentane, propane, propene, butene, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, $CClF_2$-$CClF_2$, CH_2FCF_3, CH_3CHF_2 and CHF_2CF_3 C.

9. Microcapsule according to Claims 1 to 8, characterized in that the capsule shell is obtained from one or more polymerizable monomers, where the monomers are selected from the group consisting of acrylamide, acrylonitrile, acrylic acid, benzyl methacrylate, cyclohexyl methacrylate, methacrylamide, methacrylonitrile, methacrylic acid, methyl methacrylate, N,N-dimethylacrylamide, N,N-dimethylmethacrylamide, tert-butyl methacrylate and N-vinylpyrrolidone.

10. Microcapsule according to Claim 9, characterized in that the capsule shell is additionally obtained from one or more polymerizable crosslinking monomers having two or more polymerizable double bonds.

11. Process for producing the microcapsule according to Claims 1 to 10, characterized in that

a) an organic dispersion which comprises coated metal oxide particles having an average primary particle diameter of from 2 to 100 nm, the shell of which comprises amorphous silicon dioxide,

b) an aqueous solution or water and

c) one or more monomers, if appropriate in the presence of one or more polymerization catalysts,

are subjected to a dispersion polymerization.

12. Process according to Claim 11, characterized in that the dispersion polymerization is carried out at temperatures of from 40 to 80°C.

13. Process according to Claims 11 or 12, characterized in that the polymerization is carried out under shearing conditions at an energy density of at least 1000 KJ/m^3.

14. Use of the microcapsules according to Claims 1 to 10 in the presence of electromagnetic alternating fields for the breaking of adhesive bonds such as fixed glazings or boards, as a constituent of coating compositions, for the filling of cracks, in the processing of thermoplasts, as a constituent of thermosets, as a constituent of paper products and in technical textile fabrics.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J9/32 C08K7/22 B01J13/14
ADD.

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)
B01J C08K C09C C08J C09J

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 practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/249037 A1 (KOLBE JANA [DE] ET AL KOLBE JANA [DE] ET AL) 9 December 2004 (2004-12-09) figure 1 paragraph [0048] - paragraph [0052] claims	1-14
X	US 6 106 946 A (TANAKA KOJI [JP] ET AL) 22 August 2000 (2000-08-22) cited in the application column 6, line 1 - line 28 examples 2-4; table 1 examples 5-12; tables 2,3 claims 2,6,7	1-14

☐ 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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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