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#### **Description**

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#### Field of the invention

The present invention relates to heavy-duty detergents in which the activation of the washing-active substances is temperature-dependent, as well as a method for their preparation.

## Background of the invention and prior art

Since the beginning of humanity, there has been the pursuit of hygiene. After all, hygiene in everyday life is an important component for humans. The hygiene concept of humans consists primarily in the maintenance of health. In addition to the thorough cleansing effects, there was further development of possibilities in the area of fragrance as well as the improvement of the cleaning performance by the raw material mixtures used. The optimization of the cleaning performance is characterized, in particular, by the possibility of extending a hygienically clean condition and an improvement in the degree of purification.

Today, hygiene may be divided into the areas of body, surface and textile hygiene. The latter is differentiated according to the material and color of the textile. At the latest in the 1990s, ecological cleaning also entered the consciousness of consumers. On the one hand, it is desirable to obtain the already achieved advantages of a detergent, and, on the other hand, to invent further innovative and ecologically sensible product solutions.

In the initial industrial production of detergents, they were supplied as a powder. A detergent powder is still a mixture of different washing-active substances.

With progress in the development of detergents, enzymes and other new surfactant compounds found their way into this market segment. In addition to the substances required for cleaning, large quantities of filler are added nowadays. This means that a change in the dosage behavior of the consumer was not required. Initial attempts to dispense with the fillers led to overdosing of the surfactants due to the usual use by consumers.

This was followed by the introduction of liquid detergents, which are metered residue-free and represent a physical alternative to the solid mixture of detergents. However, in their cleaning properties, liquid detergents could not achieve the level of cleaning of a heavy-duty detergent (i.e. a solid mixture) until today. This is based on the limitation in the case of liquid detergents with respect to liquid or water-soluble components. The key missing substance in a liquid detergent is the group of zeolites. These support the dirt adsorption, as well as brightness formation/color fastness during use.

Another important factor for optimal cleaning using a commercial washing machine is the timely dosing of washing-active substances within the washing method. With conventional detergents (powder detergents and liquid detergents), this is effected through the washing program. The metering chambers allow a temporal differentiation in the addition of fabric softener and detergent in the prewash and main wash.

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A current product trend is the way in which the detergent is portioned. This may be done by packing a liquid detergent in small polymer bags. In this case, all the washing-active substances are released at the time of dissolution of the polymer bag.

Another physical modification of the detergent is to mix a detergent with a fatty alcohol so that desired shapes may be obtained. In this case, the release of the washing-active substances takes place via the dissolution of the structure of the detergent/fatty alcohol mixture.

As already disclosed in DE 10 2010 060 126 A1, a multiphase product may also be described. The laundry detergent sheet disclosed therein is characterized by the combination of a carrier substrate with a liquid impregnation solution (two-phase product). Because of the preferred use of hydrophilic carrier substrates and impregnation solutions, there is a washing-out process which is comparable to the dissolution of the polymer bags mentioned above in connection with the liquid detergents packaged in small polymer bags. The only difference being that the activation could be effected earlier.

DE 102013014015 discloses a further optimized product in which a dispersion was applied to a solid carrier substrate at room temperature. By using a dispersion initially, it was possible to effect a cleaning performance with the characteristics of a detergent powder (for example zeolites, phyllosilicates, etc.). In this case, hydrophobic carrier substrates were primarily used, since the detergent dispersion also has a hydrophobic property due to the higher proportion of detergent substances in relation to the two-phase system. As a result, an activation of the washing-active substances (phase-exit diffusion) could be observed over a longer period of time. Enzymes play an important role in cleaning. Upon cleaning, they serve the purpose of removing stains in the dirt groups of starch, egg yolk, protein, blood, fat, butter, oil, etc. Equivalent dirt removal in these categories can not be achieved by the sole use of surfactants which merely result in the binding and removal of these contaminants from the respective textile surface. Although bleaching agents (oxygen donors and their activators) and enzymes within a formulation may also be used in powder detergents, since these starting materials, despite their chemical

incompatibility, are in the physical form of a solid powder and thus, initially, a passive form. By dissolving these components, however, an interaction is created that causes the bleaching agents to decompose the enzymes and thus deactivate them. Liquid detergents, in turn, allow either the addition of enzymes or bleaches (oxygen donors and their activators) in the commercial form, but no combination of these two classes of substances.

DE 103 61 170 A1 discloses a method for the preparation of a multilayer capsule system loaded with at least one organic peroxycarboxylic acid, in particular imidoperoxycarboxylic acid, in which at least two mutually different shell layers are applied in succession to an organic peroxycarboxylic acid that is present in the form of solid particles, in particular imidoperoxycarboxylic acid based on at least one polyelectrolyte and/or ionic surfactant, so that a capsule system results which comprises at least one organic peroxycarboxylic acid, in particular imidoperoxycarboxylic acid, in a multi-layered capsule shell comprising at least two shell layers. US 6,673,763 B1 discloses a solid component liquid composition comprising a solid wax matrix in which an active ingredient is dispersed.

DE 2009 028 002 A1 discloses a washing aid comprising a water-insoluble textile substrate and a bleach-containing washing aid in the form of a composition which is solidified on the substrate, wherein the washing aid composition comprises a film-forming polymer for fixing the bleach particles. The object of the present invention is, therefore, the preparation of a detergent in which bleaching agents (oxygen donors and their activators) and enzymes may be used without affecting their mutual incompatibility.

#### **Summary of the invention**

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It is an object of the present invention to provide a washing detergent in which the incompatible substance classes, enzymes on the one hand, and bleach (oxygen donors and their activators), on the other hand, are activated at different times of the washing process.

This object has been achieved by a method for producing a heavy-duty sheet according to claim 1, characterized by the steps of: (a) incorporating oxygen donors and their activators in a wax matrix surrounded by an ionic polymer layer to obtain a capsule system, (b) incorporating the capsule system into a dispersion consisting of a liquid detergent and a water-insoluble functional additive, (c) applying the capsule-system-dispersed dispersion to a carrier that is solid at room temperature.

This object has also been achieved by a method for making a heavy duty sheet according to claim 2, characterized by the steps of: (a) incorporating oxygen donors and their activators in a wax matrix surrounded by an ionic polymer layer to form a capsule system, (b) incorporating the capsule system into a support medium that is solid at room temperature, (c) applying a dispersion consisting of a liquid detergent and a water-insoluble functional additive to the support substrate provided with the capsule system.

This object has also been achieved by a heavy-duty washing sheet according to claim 3, comprising a carrier substrate that is solid at room temperature and is applied to the carrier substrate, wherein it consists of a liquid detergent and a water-insoluble functional additive dispersion and which is characterized in that a heavy-duty washing sheet further comprises a capsule system incorporated into the dispersion, or incorporated directly into the carrier material, and which contains oxygen donors and their activators introduced into a wax matrix surrounded by an ionic polymer layer.

Advantageous embodiments of the invention heavy-duty washing sheet and its manufacturing process emerge from the dependent claims.

#### **Description of the preferred embodiments**

Common bleaching agents used in detergents (oxygen donors and their activators) are:

• perborate

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- hydrogen peroxide
- 20 phthalimido peroxo-caproic acid
  - hypochlorites
  - TAED (tetraacetic ethylenediamine)
  - chlorates
  - permanganate
- percarbonates

Common enzymes used in detergents are:

- protelase
- cellulase
- 30 lipase
  - amylase

Fig. 1 shows, *inter alia*, the non-regulatable temporal release of the washing-active substances of ready-to-use dosed detergents according to the prior art: wherein (1) is the curve for liquid detergents filled in small polymer bags, (2) is the curve for detergents blended with fatty alcohols, and (3) is the curve for the washing detergent according to DE 10 2010 060 126 A1. As mentioned above, incompatible substances such as enzymes and bleaching agents (oxygen donors and their activators) can not be combined with one another in conventional detergents.

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Surprisingly, this problem was solved according to the invention by the incorporation of a bleaching agent (oxygen donors and their activators) in a wax matrix surrounded by an ionic polymer layer, so that the oxygen donors and their activators of the wax matrix and the polymer layer is encapsulated as shown in Fig. 2. This capsule system is then incorporated into a liquid detergent, e.g. by stirring.

In the case of a heavy-duty washing sheet according to the invention, the liquid detergent provided with the capsule system is used in a dispersion which (as disclosed in DE 10 2013 014 015) is applied to the carrier substrate, so that the incorporation of the capsule system in the liquid detergent or in the dispersion takes place upon application of the dispersion to the carrier substrate. In addition, it is also possible to apply the capsule system in the context of a pretreatment of the carrier substrate (i.e. before the application of the dispersion) directly onto it, which may, for example, be done using a dip tank or by spraying.

The wax matrix has a particle size of up to max.  $100 \, \mu m$ , wherein this particle size is proportional to the duration of the emission phase of the active oxygen donors and their activators (melting process). The activation of the oxygen donors and their activators may be controlled by the choice of the matrix material. By using the outer ionic polymer structure, the adhesion or cohesion of the wax matrix to the surface of the carrier substrate may be adjusted.

In this way, for the first time, a detergent application form has been successfully created that allows the effective use of enzymes and bleaches (oxygen donors and their activators). At the beginning of a washing cycle, the enzymes are first released directly, wherein they demonstrably release their power from about 30°C and are thus available at the beginning of the washing cycle or cleaning process. Using a washing program of at least 40°C, the outer polymer layer of the washing matrix is dissolved or melted during the further heating, and the oxygen donors and their activators are thus activated at this later time after the enzymes have already shown their effectiveness, and by washing-active degradation or program-related pumping out (e.g. after the

pre-wash cycle), they possibly already no longer exist. This time course is shown as curve (4) in Fig. 1. The temporal mode of operation of the temperature-dependent activation of the washing-active substances (in this case, in particular of the enzymes and bleaching agents or oxygen donors and their activators) of a detergent or heavy-duty detergent is thus given by the following steps:

- a) Release and activation of the enzymes by dissolution in water from about 30°C
- b) Dissolution of the polymer layer and wax matrix as a function of the selected educts from 40°C
- c) Activation of the oxygen donors and their activators
- 10 For the wax matrix, the following are, in particular, suitable:
  - beeswax

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- shea butter
- rice bran
- corn starch
- potato starch
  - fatty alcohols of medium chain length

For the preparation of the polymer layer of the wax matrix, in particular:

- linoleic acid
- hydroxyethyl behenamidopropyl diamonium chloride
- hydroxypropylgahydroxypropyl triammonium chloride
- hydrolysed starch
- methyl lactates
- methyldisopropylpropionamide
- cyclohexaneecarboxamide
- hydrolized starch octenylsuccinate
- PVM/MA copolymer acrylates/C12-22 alkyl methacrylate copolymers

By means of the controlled temperature-dependent dissolution of the ionic polymer layer and wax matrix of oxygen donors and their activators, for the first time a time-dependent control of the activation of both classes of compounds may be achieved within a washing process. For the fields of application, based on the present invention, the following basic formulations for a heavy-duty laundry sheet apply:

# Heavy duty detergent sheet (universal):

Anionic surfactants
Nonionic surfactants
Phosphonates/complexing agent
C10-C18 fatty acid salts
Optical brighteners
Enzymes
Builder (polycarboxylates, zeolites, phyllosilicates)
Stabilizers (propylene glycol, glycerol, borax, inulin)
Fragrances
Preservatives
Dirt-release polymer
pH regulators

# Color detergent sheet (color):

Anionic surfactants
Nonionic surfactants
Phosphonates/complexing agent
C10-C18 fatty acid salts
Dyes
Color fastness protection
Hydrotrope (sodium cumene sulfonate)
Enzymes
Builder (polycarboxylates, zeolites, phyllosilicates)
Stabilizers (propylene glycol, glycerol, borax, inulin)
Fragrances
Preservatives
Dirt-release polymer
pH regulators

# Black detergent sheet (black):

Anionic surfactants
Nonionic surfactants
Phosphonates/complexing agent
C10-C18 fatty acid salts
Dyes
Color fastness protection
Enzymes
Builder (polycarboxylates, zeolites, phyllosilicates)
Stabilizers (propylene glycol, glycerol, borax, inulin)
Opacifiers
Fragrances
Preservatives
pH regulators

# White detergent sheet (white):

Anionic surfactants
Nonionic surfactants
C10-C18 fatty acid salts
Optical brighteners
Soil release polymer
Color fastness protection
Enzymes
Builder (polycarboxylates, zeolites, phyllosilicates)
Stabilizers (propylene glycol, glycerol, borax, inulin)
Dyes
Opacifiers
Fragrances
Preservatives
pH regulators

### Fine detergent sheet:

Anionic surfactants
Nonionic surfactants
C10-C18 fatty acid salts
Phosphonates/complexing agent
Color fastness protection
Enzymes
Builder (polycarboxylates, zeolites, phyllosilicates)
Stabilizers (propylene glycol, glycerol, borax, inulin)
Fragrances
Defoamers
Preservative
pH regulators

## Wool detergent sheet:

Anionic surfactants
Nonionic surfactants
Amphoteric surfactants
C10-C18 fatty acid salts
Phosphonates/complexing agent
Color fastness protection
Builder (polycarboxylates, zeolites, phyllosilicates)
Fragrances
Preservatives
Opacifiers
Conditioners
pH regulators

The water-insoluble functional additive of the heavy-duty detergent dispersion may comprise a zeolite and/or layered silicate. The liquid detergent of the dispersion may have a viscosity greater than 500 mPas. The dispersion is randomly fixed on the carrier substrate.

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#### **Patentkrav**

- 5 1. Fremgangsmåde til fremstilling af et kogevaskemiddelstof, **kendetegnet ved** følgende trin:
  - (a) indarbejdelse af oxygendonatorer og disses aktivatorer i en voksmatriks, omgivet af et ionisk polymerlag, for at opnå et kapselsystem,
  - (b) indarbejdelse af kapselsystemet i en dispersion, der består af et flydende vaskemiddel og et vanduopløseligt funktionelt additiv,
- 10 (c) påføring af dispersionen, som er forsynet med kapselsystemet, på et bæresubstrat, som er fast ved stuetemperatur.
  - 2. Fremgangsmåde til fremstilling af et kogevaskemiddelstof, kendetegnet ved følgende trin:
  - (a) indarbejdelse af oxygendonatorer og disses aktivatorer i en voksmatriks, omgivet af et ionisk polymerlag, for at opnå et kapselsystem,
    - (b) indarbejdelse af kapselsystemet i et bæresubstrat, som er fast ved stuetemperatur,
    - (c) påføring af en dispersion, som består af et flydende vaskemiddel og et vanduopløseligt funktionelt additiv, på bæresubstratet, forsynet med kapselsystemet.

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- 3. Kogevaskemiddelstof, der omfatter et bæresubstrat, som er fast ved stuetemperatur, og en dispersion, som er påført bæresubstratet og består af et flydende vaskemiddel og et vanduopløseligt funktionelt additiv, **kendetegnet ved, at** kogevaskemiddelstoffet desuden omfatter et i dispersionen eller direkte i bærematerialet indarbejdet kapselsystem, som indeholder en voksmatriks, omgivet af et ionisk polymerlag, hvori der er indført oxygendonatorer og disses aktivatorer.
- **4.** Kogevaskemiddelstof ifølge krav 3, **kendetegnet ved, at** dispersionens vanduopløselige funktionelle additiv omfatter en zeolith og/eller et lagsilikat.
  - **5.** Kogevaskemiddelstof ifølge krav 3 eller 4, **kendetegnet ved, at** dispersionens flydende vaskemiddel har en viskositet over 500 mPas.

**6.** Kogevaskemiddelstof ifølge et af kravene 3-5, **kendetegnet ved, at** dispersionen statistisk er fikseret til bæresubstratet.

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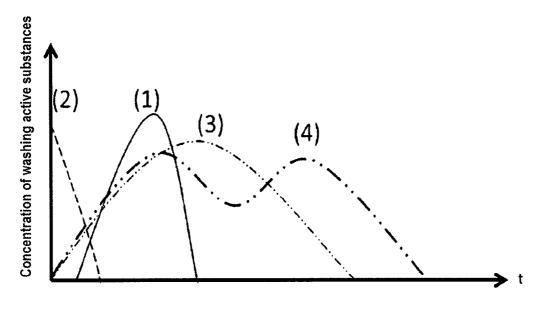


Fig. 1

