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(54) **Process for preparing granules containing silicone-based anti-foam.**

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EP-A- 0 008 829
EP-A- 0 040 091
EP-A- 0 054 436
EP-A- 0 071 481
EP-A- 0 075 433
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Description

This invention relates to granules containing a silicone-based antifoam and to a process for manufacturing them, as well as to a detergent powder containing the granules.

Granules containing a silicone-based antifoam are known. Certain granules of this type are described in British patent No. 1492939 and others in French patent No. 2 462 184.

Suds-suppressing granules containing both silicone oil and wax, for use in detergent compositions, and a process for the manufacture of such granules is described in EP-A-0 040 091. In this process, an absorbent is first impregnated with silicone oil usually as a solution or dispersion in an organic solvent, and then optionally, a solution of a paraffin wax, preferably in a different solvent is sprayed on to the absorbent and the second solvent is evaporated to provide a final protective envelope to protect the silicone oil already applied to the absorbent.

Foam regulators can also be formed as described in FR-A-2 194 771 by melting silicone together with a water-soluble or water-dispersible meltable vehicle. Carbowax (polyethylene glycol) is one such example of a meltable vehicle. Water-insoluble waxes are not suggested in this role.

European patent application No. 0 071 481 also relates to granules containing a silicone-based antifoam. The process which is described in the specification of that application involves granulating gelatinised starch whilst spraying on a mixture of a silicone oil and a hydrophobic silica. A solution of paraffin wax in chloroform is then sprayed onto the granules and the solvent is evaporated.

In a factory environment the use of volatile organic solvents is undesirable, because many of them are either inflammable or toxic, and so we have developed a new process for manufacturing granules containing a silicone-based anti-foam which does not involve the use of an organic solvent.

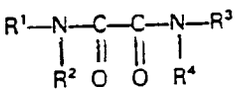
Accordingly, the present invention provides a process for the manufacture of granules containing from 5 to 40% by weight of a silicone antifoam, from 5 to 30% of a water-insoluble paraffin or petroleum wax having a melting point within the range of from 35 to 70°C, from 20 to 80% by weight of a granular absorbent and optionally up to 10% by weight of a nonionic surfactant, the process being characterised by the steps of:

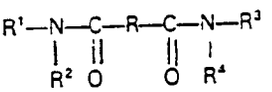
(a) forming a liquefied mixture of the silicone antifoam, the paraffin or petroleum wax and the optional nonionic surfactant, the mixture being free of organic solvent,

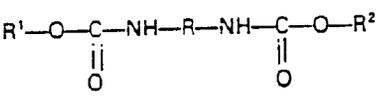
(b) spraying the solvent-free liquefied mixture onto an agitated bed of the granular absorbent,

the granular absorbent being gelatinised starch.

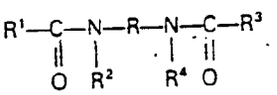
Preferably the silicone comprises a mixture of a liquid or liquifiable polysiloxane with particles of a hydrophobic material, and the hydrophobic material is preferably a hydrophobed silica, a water-insoluble salt of an alkyl phosphoric acid, or a compound of one of the following general formulae:

(i) 

(ii) 

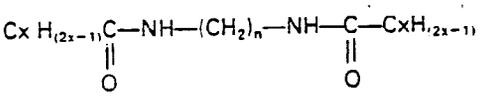
(iii) 

or

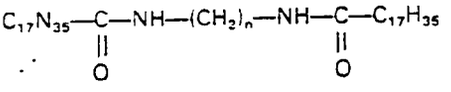
(iv) 

where R^1 and R^3 represent aliphatic hydrocarbon residues containing 14-22 carbon atoms, R^2 and R^4 represent hydrogen atoms or aliphatic hydrocarbon residues containing 1-22 carbon atoms, and R represents an aliphatic residue containing 1-9 carbon atoms.

Mixtures of silicone oils and hydrophobed silicas are sold by the Dow Chemical Company under the trade mark DB100, and this is the preferred material for use in the process of the invention. Amongst the various nitrogen compounds which are specified above, alkylene-bis-amides and in particular ethylene and methylene-bis-stearimide are the preferred compounds, that is to say compounds of the general formula:



where x is an integer from 5 to 25 and n is 1 or 2 and in particular compounds of the formula.



Waxes of mineral origin, derived from petroleum, include microcrystalline and oxidised microcrystalline petroleum waxes. Whatever wax is used, its melting point is between 35° and 70°C so that it is readily liquifiable.

The apparatus in which the liquifiable mixture of silicone and wax is sprayed onto the absorbent can be any of the apparatus conventionally used for granulation or agglomeration. Examples are the Eirich (registered Trade Mark) pan, the Schugi (registered Trade Mark) mixer, or any one of the numerous fluidised bed apparatus which are available, such as the Anhydro (registered Trade Mark) fluidised bed.

A typical composition of the granules formed in the process of the invention is:

	% by weight
Gelatinised starch	50.0
Silicone/hydrophobic silica mixture	21.5
Paraffin wax	23.5
Nonionic surfactant	5.0

However, considerable variations can be made based on this composition, provided that the absorbent is present in amounts of from 20-80%, the silicone compound in amounts of from 5-40%, the paraffin wax in amounts of from 5-30% and the nonionic surfactant in amounts up to 10%, the percentages being expressed by weight.

The granules may be incorporated into spray-dried (powdered) detergent compositions or into liquid ones. In the case of powdered detergent compositions they will be dosed into the powder after spray-drying, along with other materials which are conventionally post-dosed such as sodium perborate and fillers. In the case of liquids which are structured (sometimes called false-body liquids) the granules can be added to the liquid in the final step of the manufacturing process. There are two basic types of structured liquids, one in which the structure is imparted by interaction between surfactants and electrolytes, and the other in which it is imparted by means of a colloid such as a clay. Both types are capable of suspending the granules of the invention.

Whether the composition is in powdered or in liquid form it will normally contain both an anionic and a nonionic surfactant but may also contain either alone or a soap as the major detergent-active species. The powdered compositions will contain a detergency builder and the liquid ones will normally do so, but need not necessarily. Other components which will normally be present are corrosion inhibitors, anti-redeposition agents, fluorescers, stabilisers and substantial proportions of water.

Typical anionic surfactants, which may be present in amounts of from about 2 to 35% by weight of the finished compositions are sodium alkylbenzene sulphonates, preferably the C_{10}-C_{14} alkyl compounds, sodium primary and secondary alkyl sulphates, preferably the C_{10}-C_{22} alkyl sulphates, sodium olefine sulphonates, preferably the C_{10}-C_{18} sulphonates and sodium alkane sulphonates. Soaps of fatty acids may also be present, preferably the sodium and potassium salts of C_{10}-C_{22} fatty acids, both saturated and unsaturated. Where soap is the sole anionic surfactant it may be present in an amount up to about 65% by weight of the finished com-

position, down to about ½% by weight when other anionic surfactants are present. Typical soaps which can be used are those formed from coconut oil, tallow and natural oils containing high proportions of oleic acid such as sunflower oil.

Typical nonionic surfactants, are ethoxylated primary and secondary alcohols of from 8 to 25 carbon atoms containing from 3 to 25 moles of ethylene oxide per mole of alcohol. These materials may generally be present in an amount of from 1 to 15% by weight, based on the weight of the finished composition.

Typical detergency builders which can be used are the water-soluble phosphates, carbonates, percarbonates and aluminosilicates, particularly the sodium and potassium salts of these compounds. Organic builders may also be used, examples being sodium carboxymethyloxysuccinate, sodium citrate, sodium polyacrylates and sodium nitrilotriacetate. Any of these compounds, or any other builder compound, in any suitable mixture, may be used in amounts of from 5 to 50% by weight of the finished composition.

The invention will be further illustrated by means of the following examples:-

Example 1

47.6 parts by weight of gelatinised starch (Amigel 30076 registered Trade Mark, manufactured and sold by Société des Produits du Mais, of Clarmart, France) was placed in the pan of an Eirich (registered Trade Mark) pan granulator. A mixture of 20.5 parts by weight of a silicone anti-foam (DB100 manufactured and sold by Dow Chemical Ltd.), 27.1 parts by weight of a paraffin wax having a melting point of 40°C were heated to 65°C with agitation to produce a homogeneous liquid. The resultant liquid was then sprayed onto the gelatinised starch in the pan granulator then, 4.8 parts of nonionic surfactant (C_{13-18} primary alcohol 8EO) where sprayed onto the granules.

Example 2

The anti-foam properties of the granules produced by the process described in Example 1 were tested as follows.

The following detergent composition was prepared by conventional spray-drying and dry-dosing techniques, the granules of Example 1 being added in the dry-dosing step.

		% by weight
Sodium linear alkyl benzene sulphonate		6.7
C13—15 Primary alcohol 11EO		2.5
Sodium tripolyphosphate		34.0
Sodium silicate		6.0
Sodium perborate		24.0
Granules of Example 1		1
Moisture and minor components	balance to	100.0

The powder obtained was divided into two batches. The first batch was immediately subjected to the foam assessment test described below. The other batch was stored in unlaminated, sealed cartons at 37°C and 60% relative humidity. The stored batches were then subjected to test after 2 weeks and 4 weeks of storage.

The suds assessment test is performed by washing a standard load of clean washing in a Brandt 433 (registered Trade Mark) washing machine. The washing machine was specially modified to provide a window and the window had an arbitrary scale on it from which suds height could be read. The reservoir holding the wash liquor is fitted with a thermometer.

In a series of experiments the height of suds which is developed by each powder at various temperatures is determined. The results are shown in Table 1 from which it can be seen that where there is some de-activation of foam control effectiveness on storage. Nevertheless, all granules provide satisfactory foam control in the formulation described at all temperatures.

TABLE 1

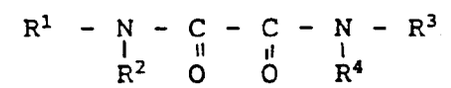
Foam heights (pan) \ Wash temp. °C	20°	30	40	50	60	70	80	90
Unstored powder	5	10	14	4	6	12	14	14
Powder stored for 2 weeks at 37°/60% RH	12	16	24	0	8	14	18	16
Powder stored for 4 weeks at 37°/60% RH	14	27	34	4	10	17	19	21

Claims

1. A process for the manufacture of granules containing from 5 to 40% by weight of a silicone antifoam, from 5 to 30% of a water-insoluble paraffin or petroleum wax having a melting point within the range of from 35 to 70°C, from 20 to 80% by weight of a granular absorbent and optionally up to 10% by weight of a nonionic surfactant, the process being characterised by the steps of:
   (a) forming a liquefied mixture of the silicone antifoam, the paraffin or petroleum wax and the optional nonionic surfactant, the mixture being free of organic solvent,
   (b) spraying the solvent-free liquefied mixture onto an agitated bed of the granular absorbent,
   the granular absorbent being gelatinised starch.

2. A process according to any preceding claim, characterised in the silicone comprises a mixture of a liquid or a liquefiable polysiloxane with particles of a hydrophobic material.

3. A process according to claim 2, characterised in that the hydrophobic material comprises a hydrophobed silica, a water-insoluble salt of an alkyl phosphoric acid or a compound of the general formula:

i)


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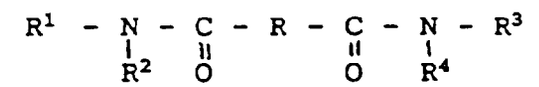

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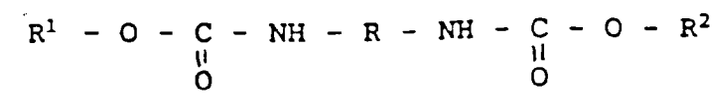
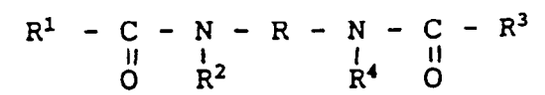
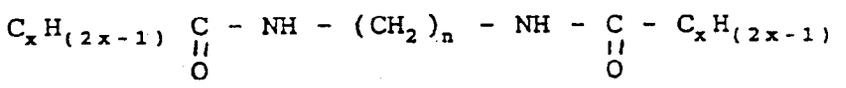


iv)


where R^1 and R^3 represent aliphatic hydrocarbon residues containing 14-22 carbon atoms, R^2 and R^4 represent hydrogen atoms or aliphatic hydrocarbon residues containing 1-22 carbon atoms, and R represents

an aliphatic residue containing 1-9 carbon atoms.

4. A process according to claim 3, characterised in that the hydrophobic material comprises a compound of the general formula:



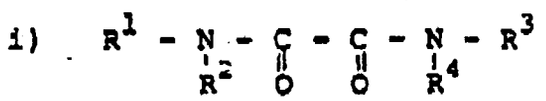
where x is an integer from 5 to 25 and n is 1 or 2.

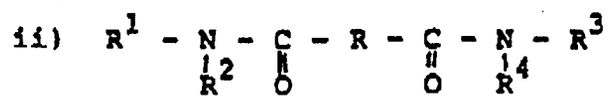
Patentansprüche

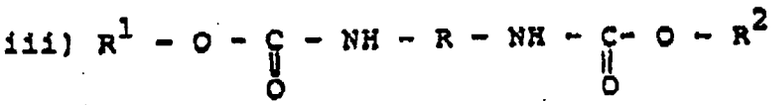
1. Verfahren zur Herstellung von Granulaten, die ein Antischaummittel auf Silikonbasis in einer Menge von 5 bis 40 Gew.-%, ein wasserunlösliches Paraffin- oder Erdölwachs mit einem Schmelzpunkt im Bereich von 35 bis 70°C in einer Menge von 5 bis 30 Gew.-%, ein granuliertes Absorbens in einer Menge von 20 bis 80 Gew.-% und fakultativ eine nichtionische, oberflächenaktive Substanz in einer Menge bis zu 10 Gew.-% enthalten, wobei das Verfahren durch folgende Schritte gekennzeichnet ist:
   (a) Bilden einer verflüssigten Mischung des Antischaummittels auf Silikonbasis, des Paraffin- oder Erdölwachses und der fakultativen, nichtionischen, oberflächenaktiven Substanz, wobei die Mischung frei von organischem Solvens ist,
   (b) Aufsprühen der solvensfreien, verflüssigten Mischung auf eine in Bewegung gehaltene Aufschüttung des granulierten Absorbens,
   wobei das granulierte Absorbens gelatinisierte Stärke ist.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Silikon eine Mischung eines flüssigen oder verflüssigbaren Polysiloxans mit Partikeln einer hydrophoben Substanz enthält.

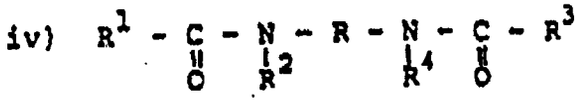
3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, daß die hydrophobe Substanz eine hydrophobierte Silica, ein wasserunlösliches Salz einer Alkylphosphorsäure oder eine Verbindung mit der allgemeinen Formel umfaßt:





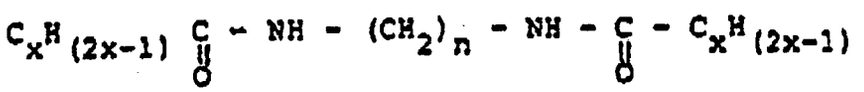


oder

iv) 

worin R^1 und R^3 für aliphatische Kohlenwasserstoffreste mit 14-22 Kohlenstoffatomen steht, R^2 und R^4 für Wasserstoffatome oder aliphatische Kohlenwasserstoffreste mit 1-22 Kohlenstoffatomen steht und R für einen aliphatischen Rest mit 1-9 Kohlenstoffatomen steht.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß die hydrophobe Substanz eine Verbindung mit der allgemeinen Formel



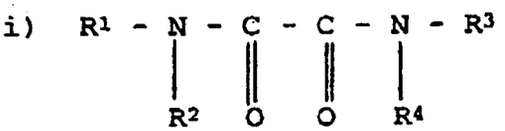
umfaßt, worin x eine ganze Zahl von 5 bis 25 ist und n 1 oder 2 ist.

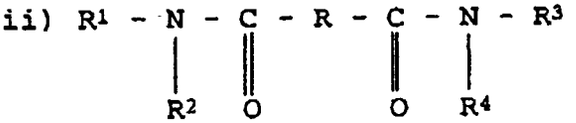
Revendications

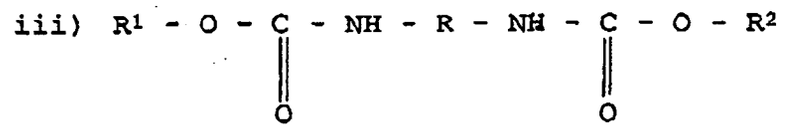
1. Procédé de préparation de granules contenant de 5 à 40 % en poids d'un silicone antimousse, de 5 à 30 % en poids d'une paraffine ou cire de pétrole insoluble dans l'eau ayant un point de fusion compris entre 35 et 70°C, de 20 à 80 % en poids d'un absorbant granulaire et facultativement jusqu'à 10 % en poids d'un agent tensio-actif non-ionique, le procédé se caractérisant par les étapes de :
   (a) formation d'un mélange liquéfié du silicone anti-mousse, de la paraffine ou cire de pétrole et de l'agent tensio-actif non-ionique facultatif, le mélange étant dépourvu de solvant organique,
   (b) pulvérisation du mélange liquéfié dépourvu de solvant sur un lit agité de l'absorbant granulaire, l'absorbant granulaite étant de l'amidon gélatinisé.

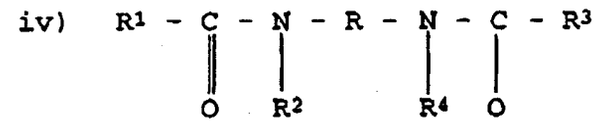
2. Procédé selon la revendication précédente, caractérisé en ce que le silicone comprend un mélange d'un polysiloxane liquide ou liquéfiable avec des particules de matière hydrophobe.

3. Procédé selon la revendication 2, caractérisé en ce que la matière hydrophobe comprend une silice rendue hydrophobe, un sel insoluble dans l'eau d'un acide alcoylphosphorique ou un composé de formule générale :

i) 

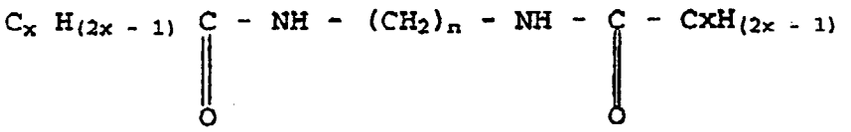
ii) 

iii) 

iv) 

où R^1 et R^3 représentent des résidus hydrocarbonés aliphatiques contenant de 14 à 22 atomes de carbone, R^2 et R^4 représentent des atomes d'hydrogène ou des résidus hydrocarbonés aliphatiques contenant de 1 à 22 atomes de carbone, et R représente un résidu aliphatique contenant de 1 à 9 atomes de carbone.

4. Procédé selon la revendication 3, caractérisé en ce que la matière hydrophobe comprend un composé de formule générale :



où x est un nombre entier allant de 5 à 25 et n vaut 1 ou 2.