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(54) Title: A RELEASE AGENT, THE PREPARATION AND USE THEREOF

(57) Abstract: The present invention provides a release agent, which comprises the following constituents: a hydrosilicone, a catalyst for dehydrogenation condensation, and a solvent. The release agent of the present invention is a semi-permanent release agent, in addition, it has the advantages of simple composition, rapid curing under low temperature, low transferring of release agent, less amount of wax accumulation, convenient application and low cost. Said release agent is especially suitable for the manufacturing of polyurethane foam article, representing a great breakthrough in the art, and the thus obtained article has a uniform open cell structure. The present invention further provides a process for preparing said release agent as well as a use in the manufacturing of polyurethane foam article, epoxy resin articles, glass fiber reinforced epoxy resin articles, rubber articles, unsaturated polyester articles and other polyurethane articles.



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A release agent, the preparation and use thereof

The present invention provides a release agent, which comprises the following constituents: a hydrosilicone, a catalyst for dehydrogenation condensation, and a solvent. The release agent of the present invention is a semi-permanent release agent, in addition, it has the advantages of simple composition, rapid curing under low temperature, low transferring of release agent, less amount of wax accumulation, convenient application and low cost. Said release agent is especially suitable for the manufacturing of polyurethane foam article, representing a great breakthrough in the art, and the thus obtained article has a uniform open cell structure. The present invention further provides a process for preparing said release agent as well as a use in the manufacturing of polyurethane foam article, epoxy resin articles, glass fiber reinforced epoxy resin articles, rubber articles, unsaturated polyester articles and other polyurethane articles.

Description

The present invention relates to a release agent, a process for the preparation thereof together with its uses. To be specific, the present invention especially relates to a release agent suitable for use in mold- releasing of polyurethane foam article, a process for the preparation thereof together with its uses.

In the fabrication of polymer material articles, usually molding processing is adopted: materials in melt or solution form are poured into a mold, after curing and shaping, the formed article is removed from the mold. In order to remove the article from the mold, release agent is usually pre-coated onto the mold so that an adhesion between the article and the surface of the mold will not be formed, and further good quality of the article can be ensured. Conventional release agent is mainly sacrificing release agent, and the so-called sacrificing release agent means when an article is formed in the mold, the release agent is used up or exhausted. The sacrificing release agent must be re-coated onto the surface of the mold before manufacturing other each article. Unfortunately,

the use of sacrificing release agent would lead to a number of questions: 1) with the repeated use of release agent, the release agent will accumulate on the surface of the mold, forming a scale, causing the fine characteristics of mold vague, so that the characteristic structure of the mold surface is unable to be duplicated onto the surface of polymer article, and thus the integrity of the article surface will be destroyed; 2) due to the existence of the scale, the mold needs to be cleaned periodically, causing an increase of manpower and expense, and further a decrease of output; in addition, during the cleaning of a mold, the mold will be destroyed more or less, causing the shortening of the life time of the mold; 3) due to the transferring of sacrificing release agent onto the surface of polymer material article, the subsequent processing for the article will be inevitably affected; 4) due to the need for re-coating of sacrificing release agent onto the surface of the mold before the fabricating of each article, the amount of release agent needed increases greatly, in the meantime, it will also increase the discharge of volatile organic chemicals (VOC, such as the solvents in the release agent), and thus further increasing the cost of production together with the pressure in terms of environmental protection.

Therefore, the development of a release agent which is removable from the mold repeatedly to some extent would overcome the above drawbacks to a great extent. For some polymer articles, such as epoxy resin articles, glass fiber reinforced epoxy resin articles and rubber articles, there have developed release agents which can be removed from a mold for several times.

However, for polyurethane foam article, the situation is quite different, since it is well known in the art that, it is much difficult to try to develop a semi-permanent release agent which can be conveniently used in polyurethane foam article.

Polyurethane foam system usually contains isocyanate radical (NCO), polyether polyol or polyester polyol segment, foaming agent, foam homogenizing agent, foam stabilizing agent, catalyst and etc. Due to the high reactivity of NCO radical, it can be reacted with various reactive groups, such as hydroxyl group, carboxyl group, amino group, and etc., as such, for a semi-permanent release agent used for polyurethane foam system, first, it is required that it does not react with NCO radical; second, the foam homogenizing agent and foam stabilizing agent are

surface active materials functioning as promoting fine and uniform polyurethane foams, thus it is certainly required for the release agent to not to change the composition of the surface active materials of the polyurethane foam system, thus avoiding defoaming of polyurethane foam surface. Furthermore, water and some solvents with low boiling points are usually used as a foaming agent or blowing agent in polyurethane foam materials, thus for the desired semi- permanent release agent, the composition of the foaming agent should not be changed, since the water remained in water-based release agent would not easily be evaporated in a short period of time (the molding temperature for polyurethane foam is relatively low, from room temperature to 80°C), thus it will affect the composition of the foaming agent. In addition, various polyurethane foam system would have different requirements for application times of release agent (the time from the start of coating of release agent to the injection of polyurethane raw materials), some of them may last as short as tens of seconds, and some of them are relatively longer, thus, based on the particular requirements for the curing of polyurethane foam, it is necessary to take some volatile solvent as a base material for the release agent.

Furthermore, the semi-permanent release agent used for manufacturing polyurethane foam article need meet the following requirements:

1) High reactivity of release agent

Since the mold temperature for manufacturing polyurethane foam article is relatively low (from room temperature to 80°C), whereas the curing time for a semi-permanent polyurethane release agent after coating is required to be short, rapid curing under low temperature must be met for semi-permanent polyurethane foam release agent. Thus, such a release agent should not be reactive with NCO radical, in the meantime, it should have high reactivity per se as well.

2) High inertness of release agent coating

Since polyurethane foam raw materials contain NCO groups which are reactive to most organic functional groups, including hydroxyl group, carboxyl group, amino group, and etc., thus in the release agent coatings, these reactive groups should be absent, the coating after the curing of release agent should be of high inertness, but these requirements usually cause the release agent unable to cure under low temperature.

3) High crosslinking degree of release agent coating

The surface open cell of polyurethane foam should be homogeneous, serious defects should be avoided. When free low-surface-energy substance remains in release agent, it will be easily adsorbed by the foams generated during the foaming of polyurethane foam through capillary action, thus changing the surface tension of the original foaming system, causing polyurethane article surface to skin or collapse. This requires an extremely high degree of crosslinking in the release agent coating, leaving almost no residues.

4) High strength of release agent coating

It is a fundamental requirement for the semi-permanent release agent to have a strong interaction with mold; in addition, since polyurethane foam article would form a large amount of micro-bubbles during manufacturing process, the capillary action would be great, thus the release agent coating is further required to have enough strength so as to not be destroyed.

Generally speaking, the release agents currently adopted for polyurethane foam article are based on solvent-based microcrystalline wax or mixture of solvent-based microcrystalline wax and silicones. These release agents could basically satisfy the requirements of polyurethane foam system curing, however, they all belong to sacrificing release agents.

JP 2004034464 discloses dispersing polyethylene wax in organic solvents for the purpose of defoaming polyurethane. Again, such as DE 102006026870.9 discloses melting polyethylene wax and microcrystalline wax and adding them into hydrocarbon solvents for the purpose of defoaming polyurethane.

On the other hand, it is also reported that solvent-based release agent composition has been used for polyurethane foam article, which comprises multiple component polysiloxanes as a release agent, and this release agent can be reused for multiple times. For example, US 4,761,443 discloses a release agent composition for highly elastic polyurethane foam material, which comprises two polydimethylsiloxane end-capped with hydroxyl groups and hydrosilicone oil crosslinker as a release agent, said release agent composition forms on the surface of the mold reusable rapid curing mold-releasing coating. However, the reactants of this composition contain multiple components, which need to be formulated prior to using, and the composition should be used

within a certain period of time, otherwise, the formulated mixture will lead to a reaction. That is, the storage and use of the release agent is inconvenient.

Thus, it would be a desirable breakthrough to obtain a semi-permanent release agent for polyurethane foam, which is simple in composition, stable in storage and easy to use. In addition, in usual cases, if a release agent could be used for polyurethane foam article mold-releasing for multiple times, it would be also applicable for other polymer articles, such as epoxy resin articles, glass fiber reinforced epoxy resin articles, rubber articles, unsaturated polyester articles and other polyurethane article, and etc.

The present invention provides a release agent, which comprises the following constituents: a hydrosilicone, a catalyst for dehydrogenation condensation, and a solvent.

The release agent according to the present invention is a semi-permanent release agent, that is, one-time of coating would be enough for achieving a plurality of times of mold-releasing, and, what is important is that the release agent of the present invention has the advantages of being simple in composition, rapid in curing under low temperature, having less transferring of release agent, having less accumulation of wax, being stable in storage and convenient in application. Said release agent represents a great breakthrough in the manufacturing of polyurethane foam article, and the polyurethane foam article obtained by using this release agent of the present invention has a homogeneous open cell.

The present invention further provides a process for manufacturing said release agent, including physical mixing constituents of the release agent with stirring, wherein the constituents comprises a hydrosilicone, a catalyst for dehydrogenation condensation, and a solvent.

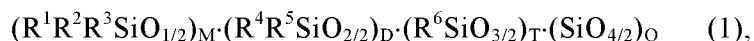
The present invention further provides use of said release agent in the manufacturing of polyurethane articles, epoxy resin articles, rubber articles and polyester articles, and etc.

In the present invention, the term “semi-permanent release agent” used herein means that the release agent will not be used up after one cycle of molding processing, that is, one-time coating of

the release agent, the mold-releasing operation can be last for a plurality of times.

In the hydrosilicone used in the release agent of the present invention, the Si-H bond is highly reactive, under the combined actions of catalyst and water molecule, it forms a Si-hydroxy radical, then it further reacts with the unreacted Si-H group to conduct a dehydro-reaction, forming a self-crosslinked coating, so as to obtain a semi-permanent coating of the release agent. Due to the use of the self-crosslinkable hydrosilicone, the amount of conventional crosslinkers, such as alkoxysilane, can be reduced or even be avoided.

Said hydrosilicone has an average compositional formula (I) as follows:



wherein R^1 to R^6 in each case are radicals independently selected from the group consisting of organic groups and a hydrogen atom, with the proviso that at least one of the radicals R^1 to R^6 is a hydrogen atom bonded directly to a silicon atom and thus forming a Si-H bond, and in the polysiloxane constituted by formula (I), there has at least two hydrogen atoms bonded directly to a silicon atom on average per molecule, and not all of R^1 to R^6 is a hydrogen atom; and M, T, and Q each represent a number ranging from 0 to less than 1, D represents a number greater than 0 and less than 1, $M+D+T+Q = 1$, and $T+Q > 0$.

In the above general formula (I), the content of the hydrogen atoms directly bonded to Si-atoms is preferably from 0.01 to 1.63 wt% on the basis of the total mass of the hydrosilicone, more preferably, the content of the hydrogen atoms directly bonded to Si-atoms is preferably from 0.1 to 1.6 wt% on the basis of the total mass of the hydrosilicone.

In the above general formula (I), the hydrosilicone has a weight-average molecular weight of 400-500,000 g/mol, more preferably 10,000-300,000 g/mol.

In the above general formula (I), the expression “in each case” indicates that every one of “ R^1 to R^6 ” and every existence of “ R^1 to R^6 ” are independent from each other, it may be the identical or different.

In a preferred embodiment, the organic groups for R^1 to R^6 are preferably selected from the group consisting of linear or branched alkyls having 1-20 carbon atoms, alkenyls having 2-20 carbon atoms, cycloalkyls having 5-25 carbon atoms, cycloalkenyls having 5-25 carbon atoms, aryls having 6-30 carbon atoms, arylalkyls having 7-30 carbon atoms, and halides of said alkyls, alkenyls, cycloalkyls, cycloalkenyls, aryls and arylalkyls.

In a more preferred embodiment, the organic groups for R^1 to R^6 are independently selected from the group consisting of linear or branched alkyls having 1-8 carbon atoms, alkenyls having 2-8 carbon atoms, cycloalkyls or cycloalkenyls having 5-10 carbon atoms, aryls having 6-10 carbon atoms, and arylalkyls having 7-30 carbon atoms.

In a more preferred embodiment, the organic groups for R^1 to R^6 in general formula (1) is independently methyl, ethyl, propyl, n-butyl, i-butyl, t-butyl, pentyl, i-pentyl, neopentyl, hexyl, i-hexyl, heptyl, i-heptyl, octyl, i-octyl, nonyl, decyl, vinyl, allyl, hexenyl, cyclopentyl, cyclohexyl, cyclooctyl, dicyclopentyl, cyclopentenyl, cyclohexenyl, phenyl, tolyl, ethyl phenyl, or halides of the above groups, more preferably methyl, ethyl, propyl, phenyl or vinyl, most preferably methyl, ethyl, propyl, or phenyl.

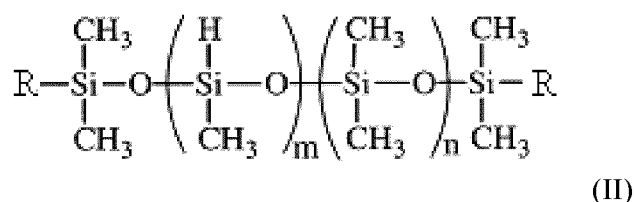
The term "halides" used in the present invention refers to mono- or multiple halogen-substituted groups, wherein the halogen is selected from fluoro-, chloro-, bromo- or iodo- radicals, preferably from fluoro-, chloro-, or bromo-.

In the above general formula (I), M, T, and Q each represent a number ranging from 0 to less than 1, D represents a number greater than 0 and less than 1, $M+D+T+Q = 1$, and $T+Q > 0$. In a preferred embodiment, M is from 0.01 to 0.5, D is from 0.1 to 0.8, T is from 0.1 to 0.7, Q is from 0 to 0.5, more preferably M is from 0.1 to 0.3, D is from 0.1 to 0.6, T is from 0.1 to 0.6, Q is from 0 to 0.3.

The content of said hydrosilicone is not particularly restricted; preferably it is from 0.1 to 80.0% of the total mass of release agent, more preferably from 1.0 to 50.0%, most preferably from 2.0 to 40.0%.

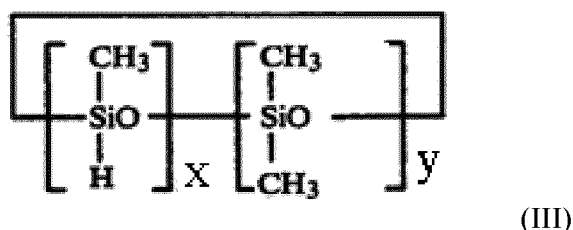
Said hydrosilicone can be liquid or solid, as long as it could be dispersed in a suitable solvent.

Said hydrosilicone is prepared as follows: dispersing at least one hydrosilicone oil, at least one hydroxyl silicone resin and at least one dehydrogenation catalyst in a solvent to form a dispersion, allowing the dispersion to react, then removing the solvent and the catalyst, and obtaining the desired hydrosilicone; wherein the hydrosilicone oil comprises a linear hydrosilicone oil of the following formula (II):



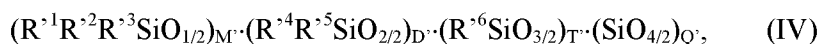
in which R is methyl or hydrogen, $m > 0$, $n \geq 0$, the number of Si-H groups per molecule is ≥ 3 , and the content of the hydrogen atoms directly bonded to Si-atoms is 0.1-1.6 % on the basis of the total mass of the hydrosilicone oil;

and/or a cyclic hydrosilicone oil of the following formula (III):



in which $x > 0$, $y \geq 0$, the number of Si-H groups per molecule is ≥ 3 , and the content of the hydrogen atoms directly bonded to Si-atoms is 0.1-1.6 % on the basis of the total mass of the hydrosilicone;

the hydroxyl silicone resin has an average compositional formula (IV):



in which R^1 to R^6 are identical or different radicals independently selected from the group consisting of organic groups and hydroxyl group, and at least one of R^1 to R^6 is a hydroxyl group;

M' , D' , T' and Q' each represent a number ranging from 0 to less than 1, $\text{M}'+\text{D}'+\text{T}'+\text{Q}' = 1$, and $\text{T}'+\text{Q}' > 0$, and the number of Si-OH groups per molecule of the hydroxyl silicone resin is ≥ 3 ;

with the proviso that the molar ratio of the Si-H groups in the hydrosilicone oil to the Si-OH groups in the hydroxyl silicone resin is from 1.0 to 100.0.

The catalyst according to the present invention is a commonly used catalyst derived from the dehydrogenation condensation of Si-H radical and Si-OH radical, it is not particularly restricted, and preferably includes amine catalyst and/or organometallic catalyst.

Preferably, said amine catalyst is one or more selected from the group consisting of:

triethylenediamine, bis(dimethylaminoethylether), dimethylcyclohexylamine, N-methyldicyclohexylamine, pentamethyldiethylenetriamine, pentamethyldipropylenetriamine, tetramethylethanediamine, tetramethylpropanediamine, tetramethylhexanediamine, N-methylmorpholine, N-ethylmorpholine, 2,2-bis(morpholino)diethyl ether, cocomorpholine, N-methylimidazole, 1,2-dimethylimidazole, 1,4-dimethylpiperazine, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,1,3,3-tetramethylguanidine, 2,4,6-tris(dimethylaminomethyl) phenol, 1,3,5-tris(dimethylaminopropyl)- 1,3,5-hexahydrotriazine, N,N-dimethylethanolamine, N,N-dimethylaminoethyl ethylene glycol, tri-methylethylolpropanediamine, N-methyl-N-(N,N-dimethylaminoethyl)ethanolamine, N,N-dimethylbenzylamine, tris(diaminopropyl)amine, triethylamine, N,N-dimethylcetylamine, vinyltris(methylethylketoximie)silane, and tetramethyliminodipropylamine; said organometallic catalysts are one or more preferably selected from: dibutyltin dilauryl, stannous octanoate, di(dodecylthio)dibutyltin, dibutyltin diacetate, potassium isooctanoate, potassium acetate, potassium oleate, lead isooctanoate, zinc isooctanoate, phenylmercuriacetate, tetrabutyl titanate, tetrakisopropyl titanate, platinum catalyst, and rhodium catalyst.

The catalyst according to the present invention is one or more catalysts preferably selected from of: triethylenediamine, stannous octanoate, 1,1,3,3-tetramethylguanidine, vinyltris(methylethylketoximie)silane, zinc isooctanoate, tetramethyliminodipropylamine, tetrabutyl titanate, triethylamine, and dibutyltin diacetate.

The platinum catalyst of the present invention is selected from platinum dioxide, chloroplatinic

acid, complex of chloroplatinic acid and diene, or platinum bis(acetylacetonate).

The contents of said catalyst is not particularly restricted, preferably it is from 0.01 to 5.0% of the total mass of the release agent, more preferably is from 0.1 to 2.0%, most preferably is from 0.1 to 1.0%.

The solvent of the present invention is chosen to allow said solvent to disperse the constituents of hydrosilicone, catalyst, and etc. uniformly, and it is volatile, and this solvent should be inert to reactants. Preferably the solvent is one or more selected from alcohols, alcohol ethers, ketones, esters, aliphatic hydrocarbons, cycloaliphatic hydrocarbons, aromatic hydrocarbons and ethers.

Preferably said alcohol solvents are one or more selected from ethanol, isopropanol, propylene glycol, butanol, 1,4-butanediol, 1,3-butanediol and glycerol; said alcohol ether solvents are preferably the following one or more: ethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monobutyl ether; said ketone solvents are preferably the following one or more: acetone, methylethyl ketone, methylisobutyl ketone and cyclohexanone; said ester solvents are preferably the following one or more: methyl acetate, ethyl acetate and butyl acetate; said aliphatic hydrocarbon solvents are preferably the following one or more: n-hexane, carbon tetrachloride, petroleum ether and isomeric alkane solvents (such as Isopar C, Isopar E, Isopar H); said cycloaliphatic hydrocarbon solvents are preferably the following one or more: cyclopentane and cyclohexane; said aromatic hydrocarbon solvents are preferably the following one or more: toluene and xylene; said ether solvents are preferably the following one or more: tetrahydrofuran, diisopropyl ether and dibutyl ether.

The content of said solvents preferably is from 10.0 to 99.85%, more preferably from 40.0 to 99.0%, most preferably from 50.0 to 98.0% of the total mass of the release agent.

The release agent of the present invention may further comprise other additives, as long as the use thereof does not significantly cause negative influences on the release agent of the present invention. Said other additives preferably include the following one or more: pigments, silanes,

level agents, anti-ageing agents, tackifier, release agent transferring indicators, and etc.

In the preparation of the release agent of the present invention, the constituents of the release agent, including hydrosilicone, catalyst for dehydrogenation condensation, and solvent, are physically mixed under stirring. Said physical mixing should be conducted at a temperature lower than the boiling point of the chosen solvent, and it is not particularly restricted. Preferably the temperature of mixing is from 0 to 100°C, more preferably from 0 to 70°C. The stirring speed of mixing is not particularly restricted as well, preferably it is from 10 to 1500rpm, more preferably from 100 to 1000rpm. The reaction time is not particularly restricted too, preferably it is from 1 to 500mins, more preferably 120mins.

One preferable process for the preparation of the release agent is conducted under a temperature of 0-100°C, a speed of 10-1500rpm stirring for 1-500min mixing. In a more preferred embodiment, the mixing temperature is from 0 to 70°C, stirring speed is from 100 to 1000rpm, and time of mixing is from 1 to 120mins.

The sequence for mixing is not particularly restricted, for example, hydrosilicone and solvent may mixed up first, that is, solvent is used to dilute the hydrosilicone, then catalyst is added; or each constituents are added simultaneously; or hydrosilicone and catalyst are added together, then solvent is added for dilution; preferably said physical mixing is conducted in a dry and sealed container.

The present invention further provides a use of said release agent in the manufacture of polymeric articles. The release agent of the present invention could preferably be used for the manufacturing of polyurethane articles, epoxy resin articles, glass fiber reinforced epoxy resin articles, rubber articles, saturated or unsaturated polyester articles, and etc.

The release agent used in the present invention is coated or sprayed on a mold of the molding process, said mold is generally made of metals, such as alumina, brass, and etc, and non-metallic materials may also be adopted, such as resin materials.

The release agent obtained in the present invention is a semi-permanent release agent, with one time of coating, multiple times (more than 5 times) mold-releasing operation could be achieved, so it is convenient to apply the release agent. This release agent has the advantages of simple composition and rapid curing under low temperature, thus reducing the amount of coating of the release agent as well as the discharge of VOC, reducing wax accumulation on the surface of the mold, shortening the duration for mold cleaning, and enhancing the using efficiency of the mold and production output. Due to the extremely low transferring amount of the release agent, the amount of the release agent remained on the surface of the article is extremely low, thus, post-processing for the article will not be negatively affected.

The release agent of the present invention is especially suitable for polyurethane foam material and polyurethane elastomer, which are polymer materials having special requirements for molding process. Of course, it will certainly be more suitable for the molding process of other common polymer articles, such as epoxy resin articles, glass fiber reinforced epoxy resin articles, rubber articles, saturated and or unsaturated polyester articles, and etc.

Examples

The present invention is further described by way of examples below, without any intention to limit the scope of the present invention by the examples.

Testing Method

In the present invention, the molecular weight of the hydrosilicone is determined by size exclusion chromatography (SEC), or specifically gel permeation chromatography (GPC) under the following conditions:

- eluent: THF (tetrahydrofuran)
- standard: Polystyrene
- temperature: 35°C (column and RI).

Further parameters are preferably:

- flow-rate: 0.8 ml/min

- detection: RI (refractive index)
- columns: 3 Plgel mixed-D columns in series
(Polymer laboratories, 7.5*300 mm)
- sample preparation: 2.5 mg/ml in THF
- injection volume: 100 µl.

The hydrosilicones used in the examples were:

SiH-1:

$((\text{CH}_3)_3\text{SiO}_{1/2})_{0.063}((\text{CH}_3)_2\text{SiO}_{2/2})_{0.155}(\text{HCH}_3\text{SiO}_{2/2})_{0.520}(\text{CH}_3\text{SiO}_{3/2})_{0.262}$, it has a weight average molecular weight of 87000, the content of the hydrogen atom in Si-H bond of the hydrosilicone is 0.79%.

SiH-2:

$((\text{CH}_3)_3\text{SiO}_{1/2})_{0.063}((\text{CH}_3)_2\text{SiO}_{2/2})_{0.153}(\text{HCH}_3\text{SiO}_{2/2})_{0.520}(\text{CH}_3\text{SiO}_{3/2})_{0.150}(\text{PhSiO}_{3/2})_{0.114}$, it has a weight average molecular weight of 50000, the content of the hydrogen atom in Si-H bond of the hydrosilicone is 0.72%.

SiH-3:

$((\text{CH}_3)_3\text{SiO}_{1/2})_{0.005}((\text{CH}_3)_2\text{SiO}_{2/2})_{0.230}(\text{HCH}_3\text{SiO}_{2/2})_{0.265}(\text{CH}_3\text{SiO}_{3/2})_{0.305}(\text{PhSiO}_{3/2})_{0.195}$, it has a weight average molecular weight of 210000, the content of the hydrogen atom in Si-H bond of the hydrosilicone is 0.33%

SiH-4:

$((\text{CH}_3)_3\text{SiO}_{1/2})_{0.006}((\text{CH}_3)_2\text{SiO}_{2/2})_{0.260}(\text{HCH}_3\text{SiO}_{2/2})_{0.334}(\text{CH}_3\text{SiO}_{3/2})_{0.244}(\text{PhSiO}_{3/2})_{0.156}$, it has a weight average molecular weight of 12000, the content of the hydrogen atom in Si-H bond of the hydrosilicone is 0.43%.

SiH-5:

$((\text{CH}_3)_3\text{SiO}_{1/2})_{0.050}((\text{CH}_3)_2\text{SiO}_{2/2})_{0.150}(\text{HCH}_3\text{SiO}_{2/2})_{0.330}(\text{PhSiO}_{3/2})_{0.370}(\text{SiO}_{4/2})_{0.100}$, it has a weight average

molecular weight of 94000, the content of the hydrogen atom in Si-H bond of the hydrosilicone is 0.36%.

SiH-6:

$((\text{CH}_3)_3\text{SiO}_{1/2})_{0.080}((\text{CH}_3)(\text{C}_3\text{H}_7)\text{SiO}_{2/2})_{0.350}(\text{HCH}_3\text{SiO}_{2/2})_{0.430}(\text{CH}_3\text{SiO}_{3/2})_{0.040}(\text{SiO}_{4/2})_{0.100}$, it has a weight average molecular weight of 73000, the content of the hydrogen atom in Si-H bond of the hydrosilicone is 0.56%.

SiH-7:

$((\text{CH}_3)_3\text{SiO}_{1/2})_{0.020}((\text{CH}_3)_2\text{SiO}_{2/2})_{0.430}(\text{HCH}_3\text{SiO}_{2/2})_{0.130}(\text{PhSiO}_{3/2})_{0.120}(\text{SiO}_{4/2})_{0.300}$, it has a weight average molecular weight of 320000, the content of the hydrogen atom in Si-H bond of the hydrosilicone is 0.17%.

SiH-8:

$((\text{CH}_3)_3\text{SiO}_{1/2})_{0.010}((\text{CH}_3)_2\text{SiO}_{2/2})_{0.250}(\text{HCH}_3\text{SiO}_{2/2})_{0.190}(\text{CH}_3\text{SiO}_{3/2})_{0.050}(\text{SiO}_{4/2})_{0.500}$, it has a weight average molecular weight of 18000, the content of the hydrogen atom in Si-H bond of the hydrosilicone is 0.30%.

Example 1

The formulation of the semi-permanent release agent is shown in table 1 below.

According to the amounts as showed in table 1, hydrosilicone was added to a dispersing kettle containing solvent therein, then catalyst was added with stirring at 100rpm; under a temperature of 20°C, the stirring was continued for 5 mins at 100rpm, thus obtaining a semi-permanent release agent.

Table 1

Example	Hydrosilicone	Catalyst	Solvent
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	Species	Amount (g)	Species	Amount (g)	Species	Amount (g)
1	SiH-1	5.0	triethylene diamine	0.2	ethylene glycol monobutyl ether	10.0
					acetone	84.8

Example 2

The formulation of the semi-permanent release agent is shown in table 2 below.

According to the amounts as showed in table 2, hydrosilicone was added to a dispersing kettle containing solvent therein, then catalyst was added with stirring at 200rpm; under a temperature of 25°C, the stirring was continued for 6 mins at 200rpm, thus obtaining a semi-permanent release agent.

Table 2

<u>Example</u>	Hydrosilicone		Catalyst		Solvent	
	Species	Amount (g)	Species	Amount (g)	Species	Amount (g)
2	SiH-2	6.6	stannous octanoate	0.4	cyclohexane	93.0

Example 3

The formulation of the semi-permanent release agent is shown in table 3 below.

According to the amounts as showed in table 3, hydrosilicone was added to a dispersing kettle containing solvent therein, then catalyst and silane were added with stirring at 250rpm; under a temperature of 30°C, the stirring was continued for 7 mins at 250rpm, thus obtaining a semi-permanent release agent.

Table 3

<u>Example</u>	hydrosilicone		catalyst		solvent	
	Species	Amount (g)	Species	Amount (g)	Species	Amount (g)
3	SiH-3	7.0	dibutyltin dilauryl	0.4	Isopar E	62.6
					butyl acetate	30.0

Example 4

The formulation of the semi-permanent release agent is shown in table 4 below.

According to the amounts as showed in table 4, hydrosilicone was added to a dispersing kettle containing solvent therein, then catalyst was added with stirring at 250rpm; under a temperature of 20°C, the stirring was continued for 3 mins at 250rpm, thus obtaining a semi-permanent release agent.

Table 4

<u>Example</u>	Hydrosilicone		Catalyst		Solvent	
	Species	Amount (g)	Species	Amount (g)	Species	Amount (g)
4	SiH-4	6.0	tetramethyl- guanidine	0.3	ethyl acetate	93.7

Example 5

The formulation of the semi-permanent release agent is shown in table 5 below.

According to the amounts as showed in table 5, hydrosilicone, solvent and catalyst were added to a dispersing kettle; under a temperature of 20°C, stirring was conducted for 8 mins at 300rpm, thus obtaining a semi-permanent release agent.

Table 5

<u>Example</u>	Hydrosilicone		Catalyst		Solvent	
	Species	Amount (g)	Species	Amount (g)	Species	Amount (g)
5	SiH-5	2.9	dibutyltin-dilauryl	0.1	xylene	87.0
					ethylene glycol monobutyl ether	10.0

Example 6

The formulation of the semi-permanent release agent is shown in table 6 below.

According to the amounts as showed in table 6, hydrosilicone was added to a dispersing kettle containing solvent therein, then catalyst was added with stirring at 300rpm; under a temperature of 20°C, the stirring was continued for 1 min at 300rpm, thus obtaining a semi-permanent release agent.

Table 6

<u>Example</u>	Hydrosilicone		Catalyst		Solvent	
	Species	Amount (g)	Species	Amount (g)	Species	Amount (g)
6	SiH-6	4.0	zinc iso-octanoate	0.2	methyl acetate	95.8

Example 7

The formulation of the semi-permanent release agent is shown in table 7 below.

According to the amounts as showed in table 7, hydrosilicone was added to a dispersing kettle containing solvent therein, then catalyst was added with stirring at 300rpm; under a temperature of 30°C, the stirring was continued for 1 min at 300rpm, thus obtaining a semi-permanent release agent.

Table 7

<u>Example</u>	Hydrosilicone		Catalyst		Solvent	
	Species	Amount (g)	Species	Amount (g)	Species	Amount (g)
7	SiH-7	6.0	tetramethylimino-dipropylamine	0.5	methyl acetate	11.0
					xylene	80.0

Example 8

The formulation of the semi-permanent release agent is shown in table 8 below.

According to the amounts as showed in table 8, hydrosilicone was added to a dispersing kettle containing solvent therein, then catalyst was added with stirring at 300rpm; under a temperature of 10°C, the stirring was continued for 5 mins at 300rpm, thus obtaining a semi-permanent release agent.

Table 8

<u>Example</u>	Hydrosilicone		Catalyst		Solvent	
	Species	Amount (g)	Species	Amount (g)	Species	Amount (g)
8	SiH-8	14.0	tetrabutyl titanate	0.6	xylene	79.4

Comparative Example 1

Sacrificing release agent for polyurethane flexible foam: KP-GHT (Xiamen KaPin chemical company).

The effective constituent for this release agent is linear aliphatic paraffin ($C_{20}H_{42}$ - $C_{36}H_{74}$), the content thereof is 1.5% by weight, the solvent is hydrocarbon solvent.

Effect Example

Effect testing of the release agent

A mold made of alumina was heated to 50-60°C, a 0.5mm nozzle was used to spray the release agents of examples 1-11 and comparative example 1 (at an amount of 5g/m²) onto the surface of the mold, after curing for 1-2mins, foamable polyurethane system was injected onto the surface of the alumina mold coated with the release agents, after 4mins foaming, the polyurethane foam was removed from the mold.

Table 12 Testing result of mold-releasing

Example of release agent	Evaluation of foam surface	Times of mold-releasing
1	fine open cell, dry	13
2	fine open cell, dry	20
3	fine open cell, dry	12
4	fine open cell, dry	13
5	fine open cell, dry	16
6	fine open cell, dry	12
7	fine open cell, dry	13
8	fine open cell, dry	15
Comparative example 1	fine open cell, dry	2

From table 12 it can be seen that, semi-permanent mold-releasing can be achieved by adopting the release agents through the formulation of the release agent per the present invention as well as the preparation process thereof, without the need to re-coat the release agent for each time, it is convenient for implement, thus reducing the coating amount of release agent and the accumulation of wax on the surface. The thus obtained article has a fine open cell, and is dry, which indicates that the amount of the remained release agent on the surface of the article surface is low, and the

transferring of the release agent is extremely less.

The release agent of the present invention was placed in a sealed bottle, and stored in an oven at a temperature of 60°C for 2 months; however, the mold-releasing effect was not negatively affected significantly, indicating the release agents are stable in storage.

The release agent of the present invention was placed in opened bottle, and stored at room temperature for 8 hours; the releasing effect is not negatively affected significantly as well, which could meet the operation requirements for release agent.

What is claimed is:

1. A release agent, comprising the following constituents: a hydrosilicone, a catalyst for dehydrogenation condensation, and a solvent.
2. The release agent as claimed in claim 1, wherein the hydrosilicone has an average compositional general formula (1):

$$(R^1R^2R^3SiO_{1/2})_M(R^4R^5SiO_{2/2})_D(R^6SiO_{3/2})_T(SiO_{4/2})_Q \quad (1),$$
 wherein R^1 to R^6 in each case are radicals independently selected from the group consisting of a hydrogen atom and organic groups, with the proviso that:

at least one of the radicals R^1 to R^6 is a hydrogen atom bonded directly to a silicon atom and thus forming a Si-H bond; and in the hydrosilicone represented by above formula (1), there is at least two Si-H bonds on average per molecule, and not all radicals R^1 to R^6 are hydrogen atom, and M, T, and Q each represent a number ranging from 0 to less than 1, D represents a number greater than 0 and less than 1, $M+D+T+Q = 1$, and $T+Q > 0$.
3. The release agent as claimed in claim 2, wherein the content of the hydrogen atoms directly bonded to Si-atoms is from 0.01 to 1.63%, preferably from 0.1 to 1.6%, on the basis of the total mass of the hydrosilicone.
4. The release agent as claimed in claim 2, wherein the hydrosilicone has a weight average molecular weight of 400-500,000 g/mol, preferably a weight average molecular weight of 10,000-300,000 g/mol.
5. The release agent as claimed in claim 2, wherein the organic groups are selected from the group consisting of linear or branched alkyls having 1-20 carbon atoms, alkenyls having 2-20 carbon atoms, cycloalkyls or cycloalkenyls having 5-25 carbon atoms, aryls having 6-30 carbon atoms, arylalkyls having 7-30 carbon atoms and halides thereof.
6. The release agent as claimed in claim 5, wherein the organic groups are selected from the group consisting of linear or branched alkyls having 1-8 carbon atoms, alkenyls having 2-8 carbon atoms, cycloalkyls or cycloalkenyls having 5-10 carbon atoms, aryls having 6-10 carbon atoms, arylalkyls having 7-30 carbon atoms.

7. The release agent as claimed in any one of claims 1-6, wherein the hydrosilicone is used in an amount of from 0.1 to 80.0%, preferably in an amount of from 1.0 to 50.0%, relative to the total mass of the release agent.
8. The release agent as claimed in any one of claims 1-6, wherein the catalyst for dehydrogenation condensation is an amine and/or an organometallic catalyst.
9. The release agent as claimed in claim 8, wherein the amine catalyst is one or more selected from the group consisting of triethylenediamine, bis(dimethylaminoethylether), dimethylcyclohexylamine, N-methyldicyclohexyl-amine, pentamethyldiethylenetriamine, pentamethyldipropylenetriamine, tetramethylethanediamine, tetramethylpropanediamine, tetramethyl- hexanediamine, N-methylmorpholine, N-ethylmorpholine, 2,2-bis(morpholino) diethyl ether, cocomorpholine, N-methylimidazole, 1,2-dimethylimidazole, 1,4-dimethylpiperazine, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,1,3,3-tetra- methylguanidine, 2,4,6-tris (dimethylaminomethyl)phenol, 1,3,5-tris (dimethylaminopropyl)-1,3,5- hexahydrotriazine, N,N-dimethylethanolamine, N,N-dimethylaminoethyl ethylene glycol, trimethylethylolpropanediamine, N-methyl-N-(N,N-dimethylaminoethyl)ethanolamine, N,N-dimethylbenzyl- amine, tris(diamino-propyl)amine, triethylamine, N,N-dimethylcetylamine, vinyltris(methylethyl-ketoximie)silane, and tetramethyliminodipropylamine; said organometallic catalyst is one or more selected from the group consisting of dibutyltin dilauryl, stannous octanoate, di(dodecylthio)dibutyltin, dibutyltin diacetate, potassium isooctanoate, potassium acetate, potassium oleate, lead isooctanoate, zinc isooctanoate, phenylmercuricacetate, tetrabutyl titanate, tetraisopropyl titanate, and platinum catalyst.
10. The release agent as claimed in claim 9, wherein the platinum catalyst is selected from the group consisting of platinum dioxide, chloroplatinic acid, complex of chloroplatinic acid and dienes, or platinum bis(acetylacetonate).

11. The release agent as claimed in claim 9, wherein the catalyst is one or more selected from the group consisting of triethylenediamine, stannous octanoate, 1,1,3,3-tetramethylguanidine, vinyltris(methylethylketoximie)- silane, zinc isooctanoate, tetramethyliminodipropylamine, tetrabutyl titanate, triethylamine, dibutyltin diacetate and platinum bis(acetylacetonate).
12. The release agent as claimed in any one of claims 1-6, wherein the catalyst is used in an amount of from 0.01 to 5%, preferably in an amount of 0.1-2.0%, relative to the total mass of the release agent.
13. The release agent as claimed in any one of claims 1-6, wherein the solvent is one or more selected from the group consisting of alcohols, alcohol ethers, ketones, esters, aliphatic hydrocarbons, cycloaliphatic hydrocarbons, , aromatic hydrocarbons and ethers.
14. The release agent as claimed in claim 13, wherein the alcohol solvents are one or more selected from the group consisting of ethanol, isopropanol, propylene glycol, butanol, 1,4-butanediol, 1,3-butanediol and glycerol; the alcohol ether solvents are one or more selected from the group consisting of ethyleneglycol monobutylether, propylene glycol monomethylether and propyleneglycol monobutylether; the ketone solvents are one or more selected from the group consisting of acetone, methylethyl ketone, methylisobutyl ketone and cyclohexanone; the ester solvents are one or more selected from the group consisting of methyl acetate, ethyl acetate and butyl acetate, the aliphatic hydrocarbon solvents are one or more selected from the group consisting of n-hexane, carbon tetrachloride, petroleum ether and isomeric alkane solvents; the cycloaliphatic hydrocarbon solvents are one or more selected from the group consisting of cyclopentane and cyclohexane; the aromatic hydrocarbon solvents are one or more selected from the group consisting of toluene and xylene; and the ether solvents are one or more selected from the group consisting of tetrahydrofuran, diisopropylether and dibutylether.
15. The release agent as claimed in claim 13 or 14, wherein the solvent is used in an amount of from 10.0 to 99.85%, preferably in an amount of from 40.0 to 99.0%, relative to the total mass of

the release agent.

16. The use of the release agent as claimed in any one of claims 1-15 in the manufacturing of polyurethane articles, epoxy resin articles, rubber articles and polyester articles to promote the mold-releasing of polymer materials.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/051681

A. CLASSIFICATION OF SUBJECT MATTER

INV. B29C33/64 C08G77/12 C08G77/58 C08G77/60 C08L83/04
ADD. C08L83/07

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)

B29C C08G C08L

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2003/065117 A1 (POREDDY NARSI REDDY [JP] ET AL) 3 April 2003 (2003-04-03) paragraphs [0001], [0002]; example 1 -----	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2003065117 A1	03-04-2003	JP 4247376 B2	02-04-2009
		US 2003065117 A1	03-04-2003
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