

(19)



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European Patent Office
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(11) Publication number:

0 546 237 A1

(12)

EUROPEAN PATENT APPLICATION(21) Application number: **92103933.5**(22) Date of filing: **07.03.92**

(51) Int. Cl.⁵: **C10M 169/04**, B27K 7/00,
/(C10M169/04,107:50,109:00,
125:10,125:26,129:16,129:40,
129:76,147:02),C10N40:00

(30) Priority: **12.12.91 IT GE910166**

(43) Date of publication of application:
16.06.93 Bulletin 93/24

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR LI NL PT SE

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(54) **Method for lubrication and sealing of cork stoppers with silico-paraffin and plasto-silico-paraffin compounds.**

(57) This method for lubrication and sealing of cork stoppers is based on a well balanced synergic association of non toxic chemically inert products suitable for foodstuffs, consisting of a silicone based fluid, paraffin, a paraffin oxy-stabilizer, amorphous colloidal silica gel to stabilize the silicone-paraffin compound, a metal salt stearate having an antistick-slip action, to which pigments and plasticizers may be added. This association can be obtained by hot or cold process to form a cream to be cold applied to the cork stoppers.

EP 0 546 237 A1

This invention covers a method for lubrication and sealing of cork stoppers and for the organoleptic preservation of the contents of these containers.

Some time ago, cork stoppers were coated with hydrocarbon based lubricating agents such as paraffin and vaselin to facilitate stoppering and later removal of the corks and to guarantee perfect sealing and organoleptic preservation of the product.

Furthermore, in the past, product fermentation (e.g. of sweet wine) was prevented by anti-fermentation agents. Paraffins and vaselins were suitable for these lubrication and sealing purposes.

At present, product fermentation is no longer blocked by anti-fermentation agents but by pasteurization in the 50°-100° temperature range, according to the product type. This means that paraffin and vaselin can no longer be used as cork sealants and lubricants since their melting point is ranging between 40° and 50° C. During pasteurization they would melt and seep into the bottle with unpleasant consequences for its contents from aesthetic and organoleptic viewpoint.

An attempt was made to obviate this drawback by coating the stoppers with pure silicone oil which is perfectly harmless and remains unaltered during pasteurization. But this solution was not very successful since pure fluid silicone impregnates the stopper, seeps into the bottles during bottling and tends to penetrate into the cork after the bottle is sealed, thus causing insufficient lubrication and sealing. The cork is also difficult to remove.

A further attempt was therefore made, according to the European Patent EP-A-0277603, to improve cork lubrication and sealing by using a silicone based grease, i.e. an emulsion of pure fluid silicone with a chemically inert and non toxic thickener such as silica gel or a metal stearate to obtain a liquid or paste having a higher density than pure silicone oil, in order to eliminate the above mentioned drawbacks.

Another procedure, based upon the EP-A-91109251.8 is also known for cork stopper lubrication, according to which a plasticizing compound like tetrafluorethylene is added to the silicone grease, thus achieving at the same time lubrication and plasticization of the cork stoppers through a simple and fast procedure.

After having thus defined known stopper lubrication techniques, this invention has the aim further to improve on known techniques by a new method based upon a peculiar association of products and their preparation.

As explained above, paraffins were used for cork stopper lubrication, but these paraffins cannot be used for pasteurization purposes because of their low melting point.

On the other hand, paraffins have proved to be excellent and harmless lubricants and sealants for cork stoppers, so that this invention has the aim to ensure their re-utilization by batching them with suitable other products in order to create a thermostable product having good lubrication and sealing characteristics.

This objective is achieved by this invention using a compound in which the following synergically balanced constituents are associated:

- a chemically inert and non toxic silicone fluid, such as dimethylsilicone;
- a food grade F.U.Paraffin in scales or powder
- a paraffin oxystabilizer
- a food grade colloidal amorphous silica gel
- a non toxic and chemically inert metal salt stearate
- food grade pigments
- if necessary, food grade plastizing agents

The product thus obtained is water repellent, tixotropic, odourless, tasteless and without any solvents.

Stabilization of the two main constituents in the batch i.e. silicone fluid and paraffin, which are chemically incompatible since they are mutually insoluble, non emulsifiable in absence of solvents and are having completely different melting points, is achieved by adding pyrolitic silica gel acting as a thickener of the silicone fluid and a mix of finely homogenized, thermal and physically stable constituents.

The paraffin is oxystabilized, for instance, by adding butyloxyanisole or a synergic mixture of butyloxyanisole and dodecylgallate.

Metal stearates like lithium, magnesium, sodium, calcium etc. will also be added as anti stick-slip agents to ensure dynamic and static balancing of the friction coefficient of the cork stopper at a rational average value.

The dynamic component has indeed the aim to provide for smooth stoppering and unstoppering of the bottles, whereas the static component shall provide for a perfect seal and prevent the liquid from seeping along the cork surface into the bottle when no proper steps are taken to keep the bottles in upright position for at least 24 hours after stoppering to allow for re-expansion of the cork stoppers. Furthermore, pigments such as titanium bioxide and iron oxides may be added, to dye the processed corks in various shades, according to specific requirements.

Finally, to improve upon the protection provided by the blend, plastic polymers like tetrafluoroethylene (TFE) suitable for foodstuffs may also be added.

This compound offers the following advantages:

- the synergic combination between silicone and paraffin increases the weep point of the resulting batch, as determined according to the ASTM D 566-64 method, to 120 °C which is much higher than obtainable with even the best paraffins, the weep point of which never exceeds 38 ° - 56 ° C;
- the compound can therefore safely be used to coat cork stoppers for products which have to be pasteurized, without any risk of its seeping or dripping into the bottles;
- the compound can be cold applied, without need for heating sources;
- after coating, the corks can be kept at very low temperatures or can be stored for long periods without crystal or scale formation as would happen when using even the best paraffins;
- the coated cork stoppers will be smoothly sliding and easy to introduce or remove from the bottle;
- the coated corks have a brighter appearance and any fire or ink markings will stand better out;
- protection from direct contact with the bottled liquids is rationally safeguarded, while migration values are much lower than the 60 ppm provided by Law;
- antioxidase stabilization of the paraffin constituent is achieved by adding a synergic mix for foodstuffs; usually this mixture is consisting of butyloxyanisole and dodecyl gallate.

Preparation of the compound subject matter of this invention can be by hot or cold processing.

The hot process is sequenced as follows:

- the silicone fluid, to which the dye pigments and plasticizers may have been added, is heated to about 100 ° C in a stainless steel autoclave.
- at this point, a variable percentage of F.U. type solid paraffin is added;
- when the paraffin is completely dissolved, the oxystabilizer 6 and colloidal silica gel are added to stabilize the mixture which otherwise would break up into its two main constituents;
- the heating is turned off when all constituents are perfectly homogenized, but stirring and filtering shall continue until the mixture has cooled down to about 60 ° C;
- at 60 ° C, anti stick-slip agents are added;
- The process is now completed and when the batch has cooled down to 50 ° C, it can be filtered and directly poured into the containers earmarked for end users where it will take on the appearance of a more or less thick cream having tixotropic characteristics, based upon the viscosity of the selected silicone fluids.

EXAMPLE N°1 OF HOT PROCESSING (without plasticizer)

- 1) - Pour 62 kg of dimethylxyloxane silicone and 2 kg of titanium bioxyde or titanium rutile or anatase dye in the autoclave;
- 2) - Heat the mixture to 100 ° C while stirring with a tangential agitator and a recycling pump in operation;
- 3) - at 100 ° C, add 30 kg F.U. grade paraffin, which may be in flakes, having an polycyclic aromatic hydrocarbon content not exceeding 0.67 ppm and wait until the paraffin is completely dissolved.
- 4) - with the agitator and recycling pump running, add the oxystabilizing mixture consisting of 0.02 kg of butyloxyanisole and 0.005 kg of dodecyl gallate to the completely dissolved paraffin;
- 5) - Keep the temperature stable and very slowly add 4 kg of colloidal silica gel while strongly agitating the mixture;
- 6) - Stop heating but continue stirring and recycling until the batch has spontaneously cooled down to 60 ° C; then add 2 kg of lithium stearate.
- 7) - Stirring shall continue for at least two hours while keeping the temperature thermostat controlled at about 50 ° C to ensure complete homogenization of all constituents.
- 8) - While hot filtering, pour the mixture into the containers for distribution to users, where the preparation will reach its final consistency.

EXAMPLE N° 2 OF HOT PROCESSING (with plasticizer)

- 1 - Pour 52 kg of fluid dimethylxyloxane silicone, 10 kg of a plasticizing agent such as tetrafluoroethylene and 2 kg of titanium bioxyde or titanium rutile or anatase dye into the autoclave;
- 2) - Heat the mixture to 100 ° C while stirring with a tangential agitator and a recycling pump in operation;
- 3) - at 100 ° C, add 30 kg of F.U. grade paraffin, which may be in flakes, having an polycyclic aromatic hydrocarbon content not exceeding 0.67 ppm and wait until the paraffin is completely dissolved.

4) - with the agitator and recycling pump running, add the oxystabilizing mixture consisting of 0.02 kg of butyloxyanisole and 0.005 kg of dodecyl gallate to the completely dissolved paraffin;

5) - Keep the temperature stable and very slowly add 4 kg of colloidal silica gel while strongly agitating the mixture;

6) continue mixing for at least four hours to ensure homogenization of the constituents.

7) - Turn off the heating system but continue stirring and recycling until the batch has spontaneously cooled down to 60 °C;

8) - Now add 2 kg of lithium stearate and continue stirring for at least two hours while keeping the temperature thermostat controlled at about 50 °C.

9) - While hot filtering, pour the mixture into the containers where the preparation will reach its final consistency, ready for distribution to users. Subject to utilization of the above mentioned constituents, a similar result may be achieved by adopting the cold process, except for the following precautionary measures:

EXAMPLE N°3 FOR COLD PROCESSING (without plasticizer)

1 - As a preliminary measure, pulverize the solid paraffin in a mill equipped with water cooling system;

2 - For blending, use reciprocating vertical screw mixers in stainless steel vessels equipped with a recycling pump and filtering elements.

3 - All constituents shall be introduced as explained in the examples n°1 and n°2, while stirring continuously and keeping the filter pump running.

4 - Processing shall continue for at least 8 hours during which any clogged filter elements shall be immediately replaced.

5 - The resulting compound will have the appearance of a less homogeneous batch than can be obtained by hot processing, but which will cause no trouble for practical utilization purposes.

With reference to the processing example n°3, please note that paraffin may be substituted by F.U. viscous Vaseline or soft white vaseline which requires no powdering.

Claims

1. Method for lubrication and sealing of cork stoppers with the utilization of known silicone and hydrocarbon based products, such as fluid silicone and paraffin, **characterized** by the fact that a well balanced synergic combination is formed of the following constituents:

- chemically inert and non toxic silicone fluid, such as dimethylsilicone;
- F.U. food grade paraffin
- a food grade oxystabilizer for paraffin such as butyloxyanisole or a mixture of butyloxyanisole and dodecyl gallate;
- colloidal amorphous silica gel suitable for foodstuffs to ensure thermal and physical stabilization of the fluid silicone/paraffin batch;
- a food grade metal salt stearate having an anti stick-slip action;
- food grade pigments such as titanium dioxide or iron oxide,
- food grade plasticizers, if required, e.g. tetrafluoroethylene to plastolubricate the cork stoppers;

in order to obtain a chemically inert, non toxic waterrepellent, tixotropic, odourless and tasteless and solventless compound.

2. Method as described in claim 1, **characterized** by the fact that the batch, without plasticizers, has approximately the following composition in weight:

- silicone fluid	approx. 62%
- paraffin	approx. 30%
- paraffin oxystabilizer	approx. 0.025%
- silica gel	approx. 4%
- metal salt stearate	approx. 2%
- pigments	approx. 2%

3. Method as described in claim 2, **characterized** by the fact that the approximate composition of the batch containing plasticizers requires replacement of about 10% in weight of the fluid silicone, which is lowered to about 52%, by 10% in weight of plastifying agents.

5 4. Method as described in Claim 1, **characterized** by the fact that homogeneous and stable batching of the constituents with or without plasticizers can be achieved by hot or cold processing.

5. Method as described in Claim 4, **characterized** by the fact that hot processing is sequenced in the following steps:

- 10 - the silicone fluid to which any necessary pigments and plasticizers have already been added, is heated to about 100 °C in an autoclave and stirred with a tangential agitator and recycling pump with builtin filter unit;
- solid paraffin, possibly in flakes, is added and thoroughly stirred until the paraffin is completely dissolved in the silicone fluid;
- 15 - the oxystabilizer and silica gel are added to achieve thermal and physical stabilization of the silicone-paraffin mix which is batched until complete homogenization;
- the heat is turned off but stirring continues until the batch has reached a temperature of about 60 °C;
- anti stick-slip metal stearates are added and homogenized by stirring;
- 20 - when cooled down to about 50 °C, the still fluid batch is discharged and poured into containers for complete cooling to a creamy substance to be distributed to end users.

6. Method as described in claim 1, **characterized** by the fact that a vertical screw mixer is used for cold processing and that the paraffin is previously pulverised in a water cooled mill.

25 7. Method as described in claim 6, **characterized** by the fact that the pulverized paraffin may be substituted by food grade viscous vaselin.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 10 3933

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,P, A	EP-A-0 465 830 (LA TECNOCHIMICA) * Whole document * ---	1-4	C10M169/04 B27K7/00 //(C10M169/04, 107:50,109:00, 125:10,125:26, 129:16,129:40, 129:76,147:02) (C10N40:00)
A	EP-A-0 351 503 (LA TECNOCHIMICA S.A.S DI UGO MESTRALLET) * column 2, line 22 - line 24 * * claims 1,2 * ---	1,2	
D,A	EP-A-0 277 603 (LA TECNOCHIMICA S.A.S DI UGO MESTRALLET) * claims 1-3 * ---	1,2	
A	DE-A-2 336 841 (RENATE WÖRZ) * page 3, line 12 - line 16 * ---	1,2	
A	DATABASE WPI Week 7551, Derwent Publications Ltd., London, GB; AN 75-83340W [51] & DE-A-2 424 451 (FA STAEDLER) 11 December 1975 * abstract * ---	1	
A	EP-A-0 167 202 (PROCTER & GAMBLE) * page 10, line 3 - line 22 * -----	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15 MARCH 1993	Examiner HILGENGA K.J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			