

(19) **DANMARK**

(10) **DK/EP 2723695 T3**



(12) **Oversættelse af  
europæisk patentskrift**

Patent- og  
Varemærkestyrelsen

- 
- (51) Int.Cl.: **C 04 B 24/10 (2006.01)**                      **C 04 B 28/02 (2006.01)**                      **C 04 B 40/00 (2006.01)**  
**C 04 B 103/52 (2006.01)**
- (45) Oversættelsen bekendtgjort den: **2017-04-03**
- (80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2017-01-04**
- (86) Europæisk ansøgning nr.: **12732587.6**
- (86) Europæisk indleveringsdag: **2012-06-21**
- (87) Den europæiske ansøgnings publiceringsdag: **2014-04-30**
- (86) International ansøgning nr.: **EP2012061907**
- (87) Internationalt publikationsnr.: **WO2012175583**
- (30) Prioritet: **2011-06-24 US 201161500882 P**
- (84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**
- (73) Patenthaver: **Construction Research & Technology GmbH, Dr.-Albert-Frank-Str. 32, 83308 Trostberg, Tyskland**
- (72) Opfinder: **FARRINGTON, Stephen A., 2575 Laurelhurst Drive, University Heights, OHIO 44118, USA**  
**STEFAN, Madalina Andrea, Dr.-Albert-Frank-Strasse 32, 83308 Trostberg, Tyskland**
- (74) Fuldmægtig i Danmark: **RWS Group, Europa House, Chiltern Park, Chiltern Hill, Chalfont St Peter, Bucks SL9 9FG, Storbritannien**
- (54) Benævnelse: **CEMENTADDITIV**
- (56) Fremdragne publikationer:  
**WO-A1-2010/062484**  
**CN-A- 1 089 245**  
**CN-A- 102 115 316**  
**GB-A- 191 210 424**  
**US-A- 2 311 290**  
**US-A- 3 857 715**  
**US-B1- 6 641 661**



## DESCRIPTION

**[0001]** Cement additives typically include materials which are utilized during manufacture and/or processing of cement to increase the efficiency of the manufacturing process and/or increase the quality of the resulting cement. The term "cement" may be broadly defined to designate many different kinds of substances that are used as binders and/or adhesives. Hydraulic cements set, harden and gain strength in the presence of water and do not degrade or lose strength in the presence of moisture. Portland cement, one type of hydraulic cement, is prepared by grinding, then pyroprocessing a mixture of components including calcium carbonate (typically as limestone), aluminosilicate (typically as clay or shale), silicon dioxide (typically as sand) and miscellaneous iron oxides. During pyroprocessing, such as calcining and sintering, or clinkering, chemical reactions take place whereby hardened nodules, commonly referred to as cement clinker, are formed.

**[0002]** After the clinker has cooled, it is pulverized or ground, typically together with a small amount of gypsum and/or limestone, in a finish grinding mill to provide a fine, homogenous powdery product. Due to the extreme hardness of clinker, a large amount of energy is required to properly mill the clinker into the desired powder form. Grinding aids, one type of cement additive, may be used to reduce the energy required to grind the clinker. In addition to reducing grinding energy, commonly used grinding aids are frequently used to improve the ability of the powder to flow easily and reduce its tendency to form lumps during storage. Conventional grinding aids include glycols, alkanolamines, amine acetates, and aromatic acetates.

**[0003]** Grinding aids function, at least in part, by compensating for the charges on freshly broken surfaces. Through adsorption of the molecules of the grinding aid material to the surfaces of the ground particles, the surface energy requirements are satisfied. This minimizes particle agglomeration and prevents caking of the mill interior wall and coating of the grinding media. Mill efficiency and throughput are increased as a result.

**[0004]** Performance enhancers, another type of cement additive, function, at least in part, by increasing the reactivity of the cement. They may be added to improve the early-age or late-age strength of hydrated cementitious materials.

**[0005]** The use of standard molasses as clinker grinding agent is known from US2311290 and CN1089245. In WO2010062484 spent molasses concentrate (SMC) is used as grinding agent for cement.

**[0006]** The cementitious composition industry is constantly searching for new additives which will increase the efficiency of cement manufacturing processes and/or produce improved cement materials.

**[0007]** Provided is a cement additive and/or cementitious composition comprising at least one desugared molasses. Also provided is a method of manufacturing a cementitious material comprising adding, after pyroprocessing, at least one desugared molasses to at least one cementitious and/or pozzolanic material during manufacture of the at least one cementitious and/or pozzolanic material.

**[0008]** As used herein, the term "desugared molasses" is defined as at least one of: (i) a molasses which has undergone a process to remove sugar from the molasses; or (ii) a molasses with a total sugar content less than or equal to about 45% by weight of the molasses, based on the dry weight of the molasses. In certain embodiments, a "desugared molasses" may have a sucrose content less than or equal to about 40% by weight of the molasses, based on the dry weight of the molasses. In certain embodiments, a "desugared molasses" may have a sucrose content less than or equal to about 35% by weight of the molasses, based on the dry weight of the molasses. In certain embodiments, a "desugared molasses" may have a sucrose content less than 30% by weight of the molasses, based on the dry weight of the molasses. In certain embodiments, a "desugared molasses" may have a total water content of less than about 40% by weight as manufactured, excluding any water added to the desugared molasses product after manufacturing, based on the total weight of the desugared molasses. In certain embodiments, a "desugared molasses" may exclude by-products of molasses fermentation processes.

**[0009]** Desugared molasses is available commercially from a number of sources, such as MidWest Agri-Commodities, San Rafael, California, American Crystal Sugar Company, Hillsboro, North Dakota and Western Sugar Cooperative, Denver, Colorado. As used herein, the term "desugared", when not used in the exact term "desugared molasses", refers to the result of a process to remove sugar from a material. The term "dry weight" refers to the total weight of a material or mixture, excluding the weight of any water present in the material or mixture.

**[0010]** Molasses is a byproduct of many sugar refining processes, and includes the material which is left over after sugar is extracted from a raw material, such as sugar beets or sugar cane. Molasses may contain high amounts of residual sugars, and for that reason molasses may be processed to extract additional sugar therefrom in order to maximize the sugar yield of a sugar

refining process. The material left over after molasses has been processed is sometimes referred to generally as desugared molasses. However, the definition of the term "desugared molasses" provided above extends beyond byproducts of processes utilized to extract sugar from molasses.

**[0011]** A non-limiting example of a process to remove sugar from sugar beet molasses is molasses desugaring by chromatography ("MDC"), described in Chapter 8 of Beet Sugar Handbook by Mosen Asaid, PhD (Wiley Interscience, 2007, pp. 517-545). The MDC process may be based on ion-exclusion chromatography technology. The MDC process works based on the exclusion or rejection of ionic compounds and the inclusion or absorption of nonionic compounds. The MDC process is a multi-component process separating not only the sucrose fraction (or extract) from the nonsucrose fraction (raffinate), but also recovering other valuable components of molasses, such as betaine.

**[0012]** Briefly outlined, the steps of the MDC process include: (1) diluting the molasses to 60% to 70% dry solids with water; (2) filtering the diluted molasses to remove suspended solids; (3) heating the filtered dilute molasses; (4) deaerating the dilute molasses; (5) feeding the deaerated dilute molasses through a distributor to a separator containing packed resin in sodium or potassium form; and (6) eluting the separator to remove the products trapped by the resin. As the feed passes through the resin, the nonionic substances (mainly sucrose) attach to the resin, and the ionic substances (mainly nonsucroses) continue moving through the resin bed. The ionic compounds fraction (raffinate) is collected first, and after additional processing becomes a desugared molasses. The elution water then removes sucrose and other nonionic components from the resin in order to produce additional sugar.

**[0013]** A non-limiting example of a process to remove sugar from sugar cane molasses is simulated moving bed chromatography ("SMB chromatography"), described in "Enhancement of Sugar Production Part 2: Chromatographic Separation of Sugarcane Molasses" by H.N.P. Stolz and P.I. Bekker (Proc S Afr Sug Technol Ass (2001) 75, pp. 351-357 ). The SMB chromatography process is similar to the MDC process describe above, with additional measures taken to ensure efficient separation of sugar cane molasses.

**[0014]** Those materials which fall into the definition of desugared molasses provided above are typically (but need not be) waste products of sugar or other agricultural refining processes. For this reason, desugared molasses may be less costly to procure than other additives for cementitious compositions. Surprisingly, the subject desugared molasses provides benefits to cementitious compositions that meet or exceed those benefits provided by conventional additives, while reducing the potentially negative effects of such conventional additives as molasses.

**[0015]** In certain embodiments, a cementitious material is provided which is manufactured by a process comprising adding, after pyroprocessing, at least one desugared molasses to at least one cementitious and/or pozzolanic material during manufacture of the at least one cementitious and/or pozzolanic material.

**[0016]** In certain embodiments, provided is a method of manufacturing a cementitious material comprising adding, after pyroprocessing, at least one desugared molasses to at least one cementitious and/or pozzolanic material during manufacture of the at least one cementitious and/or pozzolanic material.

**[0017]** The at least one desugared molasses may be added to the at least one cementitious and/or pozzolanic material prior to and/or during grinding of the at least one cementitious and/or pozzolanic material.

**[0018]** The cementitious and/or pozzolanic material may comprise at least one of cement, fly ash, slag, such as blast furnace slag, silica fume or metakaolin. The cement may be a portland cement, a calcium aluminate cement, a magnesium phosphate cement, a magnesium potassium phosphate cement, a calcium sulfoaluminate cement, a gypsum-based cement, or any other suitable hydraulic binder.

**[0019]** In certain embodiments, the at least one desugared molasses may comprise at least one of desugared sugar beet molasses, desugared sugar cane molasses, or soy molasses (which may or may not be desugared). The subject desugared molasses may act as a grinding aid or performance enhancer in the manufacture of cementitious materials.

**[0020]** Desugared molasses is typically available as a liquid material, but it may be dried for use according to the present compositions and method. In certain embodiments, the at least one desugared molasses may contain an effective amount of from greater than 0% to about 45% sugars by weight, based on the dry weight of the at least one desugared molasses. In further embodiments, the at least one desugared molasses may contain an effective amount of from greater than 0% to about 40% sucrose by weight, based on the dry weight of the at least one desugared molasses.

[0021] Desugared sugar beet molasses is a desirable product for use in the subject cementitious composition, additive and method because it is not fit for human consumption, which reduces the value of the material. Samples of commercially available desugared sugar beet molasses were analyzed and determined to have the following composition (percentages are by weight based on total weight of the sample):

Table A

Total Water - Karl-Fischer Method	36-40%
Total Dry Matter Content	60-64%
Protein	6.3-6.9%
NPN Equivalent to Protein	0.1-0.2%
Calcium	0.05-0.3%
Phosphorous	<0.1%
Potassium	6.7-8.1%
Sodium	1.6-1.9%
Chloride	0.4-0.5%
Sulfates	0.6-1.5
Reducing Sugars	1.2-1.9%
Fructose	<0.1%
Glucose	<0.1%
Lactose	0-1.2%
Maltose	0-1.9%
Sucrose	12-22%

The analyzed desugared sugar beet molasses should not be construed to limit in any way the scope of the present subject matter. Desugared sugar beet molasses is merely one example of possible desugared molasses which may be utilized according to the present compositions and method. Further, the composition of desugared sugar beet molasses may vary widely, and some desugared sugar beet molasses may not contain components which fall within the ranges presented in Table A. Table A is provided for illustrative purposes only.

[0022] The subject desugared molasses may be combined with any of a number of conventional additives for cementitious compositions which act as grinding aids or performance enhancers, and which include, but are not limited to glycols, alkanolamines, organic or inorganic salts, and organic polymers.

[0023] A pozzolan is a siliceous or aluminosiliceous material that possesses little or no cementitious value but will, in the presence of water and in finely divided form, chemically react with the calcium hydroxide produced during the hydration of portland cement to form materials with cementitious properties. Diatomaceous earth, opaline cherts, clays, shales, fly ash, slag, such as blast furnace slag, silica fume, metakaolin, volcanic tuffs and pumicites are some of the known pozzolans. Certain ground granulated blast-furnace slags and high calcium fly ashes possess both pozzolanic and cementitious properties. Natural pozzolan is a term of art used to define the pozzolans that occur in nature, such as volcanic tuffs, pumices, trasses, diatomaceous earths, opaline cherts, and some shales. Fly ash is defined in ASTM C618.

[0024] If used, silica fume can be uncompacted or can be partially compacted or added as a slurry. Silica fume additionally reacts with the hydration byproducts of the cement binder, which may provide for increased strength of the finished articles and may decrease the permeability of the finished articles.

[0025] In certain embodiments, the at least one desugared molasses may be added to the at least one cementitious and/or pozzolanic material in an amount of from about 0.01 to about 0.3 dry weight percent, based on the weight of cementitious material. In certain embodiments, the at least one desugared molasses may be added to the at least one cementitious and/or pozzolanic material in an amount of from about 0.01 to about 0.1 dry weight percent, based on the weight of cementitious material. As used herein, "based on the weight of cementitious material" refers to the total dry weight of all cementitious and/or pozzolanic materials present in a cementitious composition.

[0026] In certain embodiments, the method and/or process may further comprise adding to the at least one cementitious and/or pozzolanic material at least one grinding aid and/or performance enhancer in addition to the desugared molasses, optionally in formulation with the at least one desugared molasses. The at least one grinding aid and/or performance enhancer may be added

to the cementitious and/or pozzolanic material in an amount of from about 0.005 to about 0.2 weight percent, based on the weight of cementitious material.

[0027] The following examples are set forth merely to further illustrate the subject cementitious composition and/or admixture. The illustrative examples should not be construed as limiting the cementitious composition and/or admixture in any manner.

[0028] In the following samples, various additives were incorporated into cement clinker in order to attempt to improve the grinding process. The additives were added to the cement clinker in a 46% aqueous solution, by weight of the total additive/water mixture. The cement clinker was ground until a Blaine value of  $3800 \pm 200 \text{ cm}^2/\text{g}$  was achieved. The results are reported in Table 1. Dosages reported in Table 1 are based on total dry weight of cement clinker.

Table 1

Grinding Aid	Dose (wt%)	Time (min)	Final Blaine value (cm <sup>2</sup> /g)
Glycerol-based	0.03	118	3900
Glycerol-based	0.06	110	3920
Amine acetate-based	0.03	105	3910
Amine acetate-based	0.06	105	4000
Desugared Molasses	0.03	100	3760
Desugared Molasses	0.06	122	3890

[0029] In the following samples, various mortars were tested to determine the compressive strength of mortars made with cements with various grinding aids added, as compared to a mortar prepared from a cement produced with no grinding aid added. All of the mortar samples had a water to cement weight ratio of 0.5 and a sand to cement weight ratio of 3. The spread at 0 minutes and 30 minutes after preparation, as well as the air content of each sample, were also determined. Results are reported in Table 2. Dosages reported in Table 2 are based on total dry weight of cement clinker.

Table 2

Grinding Aid	Dose (wt%)	Spread (cm)		Air (%)	Compressive Strength (MPa)			
		0	30		1 day	2 day	7 day	28 day
None		20.1	19.3	5.1	18.2	29.4	46.0	57.4
Diethylene Glycol	0.02	19.8	19.2	5.3	18.8	30.6	46.0	57.4
Diethylene Glycol	0.08	19.2	19.1	5.9	18.8	28.8	43.1	52.7
Molasses	0.02	20.3	19.2	5.1	18.0	29.7	47.6	60.1
Molasses	0.08	20.4	19.4	5.6	17.0	29.9	48.7	60.7
Desugared Molasses	0.02	19.5	18.9	5.1	20.1	30.2	50.5	60.6
Desugared Molasses	0.08	20.3	19.2	5.4	16.6	28.9	47.2	60.0

[0030] In a first embodiment, a cementitious material may be manufactured by a process comprising adding, after pyroprocessing, at least one desugared molasses to at least one cementitious and/or pozzolanic material during manufacture of the at least one cementitious and/or pozzolanic material.

[0031] The cementitious material of the first embodiment may include that the at least one desugared molasses is added to the at least one cementitious and/or pozzolanic material prior to and/or during grinding of the at least one cementitious and/or pozzolanic material.

[0032] The cementitious composition of either or both of the first or subsequent embodiments may include that the at least one cementitious and/or pozzolanic material comprises at least one of cement, fly ash, slag, silica fume or metakaolin.

[0033] The cementitious composition of any of the first or subsequent embodiments may further include that the at least one desugared molasses comprises at least one of desugared sugar beet molasses, desugared sugar cane molasses or soy molasses.

**[0034]** The cementitious composition of any of the first or subsequent embodiments may further include that the at least one desugared molasses contains an effective amount of from greater than 0% to about 45% sugars by weight, based on the dry weight of the at least one desugared molasses.

**[0035]** The cementitious composition of any of the first or subsequent embodiments may further include that the at least one desugared molasses contains an effective amount of from greater than 0% to about 40% sucrose by weight, based on the dry weight of the at least one desugared molasses.

**[0036]** The cementitious composition of any of the first or subsequent embodiments may further include that the at least one desugared molasses has a total water content of less than about 40% by weight as manufactured, excluding any water added to the desugared molasses product after manufacturing, based on the total weight of the desugared molasses.

**[0037]** The cementitious composition of any of the first or subsequent embodiments may further include that the at least one desugared molasses is added to the at least one cementitious and/or pozzolanic material in an amount of from about 0.01 to about 0.3 dry weight percent, based on the weight of cementitious material. The at least one desugared molasses may be added to the at least one cementitious and/or pozzolanic material in an amount of from about 0.01 to about 0.1 dry weight percent, based on the weight of cementitious material.

**[0038]** The cementitious composition of any of the first or subsequent embodiments may further comprise at least one grinding aid and/or performance enhancer in addition to the desugared molasses, added to the at least one cementitious and/or pozzolanic material, optionally in formulation with the at least one desugared molasses. The at least one grinding aid and/or performance enhancer may be added to the at least one cementitious and/or pozzolanic material in an amount of from about 0.005 to about 0.2 weight percent, based on the weight of cementitious material.

**[0039]** In a second embodiment, a method of manufacturing a cementitious material may comprise adding, after pyroprocessing, at least one desugared molasses to at least one cementitious and/or pozzolanic material during manufacture of the at least one cementitious and/or pozzolanic material.

**[0040]** The method of the second embodiment may include that the at least one desugared molasses is added to the at least one cementitious and/or pozzolanic material prior to grinding the at least one cementitious and/or pozzolanic material.

**[0041]** The method of either or both of the second or subsequent embodiments may further include that the at least one cementitious and/or pozzolanic material comprises at least one of cement, fly ash, slag, silica fume or metakaolin.

**[0042]** The method of any of the second or subsequent embodiments may further include that the at least one desugared molasses comprises at least one of desugared sugar beet molasses, desugared sugar cane molasses or soy molasses.

**[0043]** The method of any of the second or subsequent embodiments may further include that the at least one desugared molasses contains an effective amount of from greater than 0% to about 45% sugars by weight, based on the dry weight of the at least one desugared molasses.

**[0044]** The method of any of the second or subsequent embodiments may further include that the at least one desugared molasses contains an effective amount of from greater than 0% to about 40% sucrose by weight, based on the dry weight of the at least one desugared molasses.

**[0045]** The method of any of the second or subsequent embodiments may further include that the at least one desugared molasses has a total water content of less than about 40% by weight as manufactured, excluding any water added to the desugared molasses product after manufacturing, based on the total weight of the desugared molasses.

**[0046]** The method of any of the second or subsequent embodiments may further include that the at least one desugared molasses is added to the at least one cementitious and/or pozzolanic material in an amount of from about 0.01 to about 0.3 dry weight percent, based on the weight of cementitious material. The at least one desugared molasses may be added to the at least one cementitious and/or pozzolanic material in an amount of from about 0.01 to about 0.1 dry weight percent, based on the weight of cementitious material.

**[0047]** The method of any of the second or subsequent embodiments may further comprise adding at least one grinding aid and/or performance enhancer in addition to the at least one desugared molasses, optionally in formulation with the at least one desugared molasses. The at least one grinding aid and/or performance enhancer may be added to the at least one cementitious

and/or pozzolanic material in an amount of from about 0.005 to about 0.2 weight percent, based on the weight of cementitious material.

## **REFERENCES CITED IN THE DESCRIPTION**

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

### **Patent documents cited in the description**

- [US2311290A \[0005\]](#)
- [CN1089245 \[0005\]](#)
- [WO2010062484A \[0005\]](#)

### **Non-patent literature cited in the description**

- Beet Sugar Handbook **MOSEN ASAD** PhD Wiley Interscience 20070000517-545 [\[0011\]](#)
- **H.N.P. STOLZ** P.I. **BEKKER** Enhancement of Sugar Production Part 2: Chromatographic Separation of Sugarcane Molasses Proc S Afr Sug Technol Ass, 2001, vol. 75, 351-357 [\[0013\]](#)

## Patentkrav

1. Fremgangsmåde til fremstilling af et cementholdigt materiale, der efter pyroprocessering omfatter tilsætning af  
5 mindst én afsukret melasse til mindst ét cementholdigt materiale og/eller puzzolanmateriale under fremstilling af det mindst ene cementholdige materiale og/eller puzzolanmateriale.
2. Fremgangsmåde ifølge krav 1, hvor den mindst ene  
10 afsukrede melasse tilsættes til det mindst ene cementholdige materiale og/eller puzzolanmateriale før og/eller under formalingen af det mindst ene cementholdige materiale og/eller puzzolanmateriale.
- 15 3. Fremgangsmåde ifølge enten krav 1 eller krav 2, hvor det mindst ene cementholdige materiale og/eller puzzolanmateriale omfatter mindst én af cement, flyveaske, slagge, mikrosilica eller metakaolin.
- 20 4. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 3, hvor den mindst ene afsukrede melasse omfatter mindst én af afsukret sukkerroemelasse, afsukret sukkerrørmelasse eller sojamelasse.
- 25 5. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 4, hvor den mindst ene afsukrede melasse indeholder en effektiv mængde af fra mere end 0 til ca. 45 vægt-% sukrebaseret på tørvægten af den mindst ene afsukrede melasse.
- 30 6. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 4, hvor den mindst ene afsukrede melasse indeholder en effektiv mængde af fra mere end 0 til ca. 40 vægt-% sukrebaseret på tørvægten af den mindst ene afsukrede melasse.
- 35 7. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 6, hvor den mindst ene afsukrede melasse har et samlet vandindhold på mindre end ca. 40 vægt-% ved fremstilling eksklusive eventuelt vand, der tilsættes til det afsukrede

melasseprodukt efter fremstilling, baseret på den samlede vægt af den afsukrede melasse.

8. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 7, hvor den mindst ene afsukrede melasse tilsættes til det mindst ene cementholdige materiale og/eller puzzolanmateriale i en mængde fra ca. 0,01 til ca. 0,3 tørvægt-% baseret på vægten af cementholdigt materiale.
9. Fremgangsmåde ifølge krav 8, hvor den mindst ene afsukrede melasse tilsættes til det mindst ene cementholdige materiale og/eller puzzolanmateriale i en mængde fra ca. 0,01 til ca. 0,1 tørvægt-% baseret på vægten af cementholdigt materiale.
10. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 9, der yderligere omfatter tilsætning til det mindst ene cementholdige materiale og/eller puzzolanmateriale af mindst ét formalingshjælpemiddel foruden den mindst ene afsukrede melasse, eventuelt i formulering med den afsukrede melasse.
11. Fremgangsmåde ifølge krav 10, hvor det/den mindst ene formalingshjælpemiddel og/eller produktionsfremmer tilsættes til det mindst ene cementholdige materiale og/eller puzzolanmateriale i en mængde fra ca. 0,005 til ca. 0,2 vægt-% baseret på vægten af cementholdigt material.
12. Cementholdigt materiale fremstillet ved hjælp af fremgangsmåden ifølge et hvilket som helst af kravene 1 til 11.