Candidate's answer

Artificial Snow

The present invention relates to artificial snow. Further, the invention relates to artificial snow granules for making such snow and to a method of their production.

Snowfall is *becoming more and more irregular, probably because of climate change. In order to make sure that ski season would remain as long as possible,* the present inventors have conducted *chemical research into making artificial snow.*

There are three properties of snow that are very important for skiing. The first one is its density. New snowfall typically has a density of 0.07 to 0.12g/cm³. Exposure to wind often increases the density to 0.2 to 0.3 g/cm³. The density of snow will increase over time due to snow settlement. Old snow can reach densities of 0.4 to 0.5 g/cm³. Snow with the highest density is snow that has survived a whole year. This type of snow has a density of around 0.6 g/cm³. The ideal snow for skiing has a density of 0.2 to 0.4 g/cm³, preferably around 0.3 g/cm³.

The hardness of the snow on the ski slopes is a parameter that is related to the density of the snow. The snow should not be too hard, neither should it be too soft. The hardness of the snow is expressed in kg/cm² and is measured using a Densosnow® by a procedure well-known in the prior art. The hardness of snow for skiing is preferably 3 to 5 kg/cm².

The kinematic friction factor (µk) is a parameter that can be used to define the gliding properties of snow. Natural powdery snow has a kinematic friction factor of 0.03 to 0.05. The lower the kinematic friction factor, the better are the gliding properties of the snow. Values below those of natural snow (i.e. below 0.03) would provide an extremely good skiing experience. There is probably also a minimum value for the kinematic friction factor at which the snow becomes uncomfortably slippery, but such snow has not been made available until now. Such value would probably lie below 0.01, but this is not known, since such low values have never been achieved.

Snow machines are used in many ski resorts to prolong the skiing season. Snow machines fall into two groups: a cannon type and a fan type. A method of making artificial snow by snow machines comprises atomising water under pressure into air at a temperature below 0°C to make fine ice particles. The artificial snow thus produced contains 10 wt. % or more of water, has a density of 0.3 to 0.4 g/cm³, and a hardness of less than 1 kg/cm². Such artificial snow changes more quickly than natural snow, and, in certain cases, within a few days it forms corn snow having particles with an average outer diameter of about 1 to 5 mm. Corn snow is troublesome for skiers.

D1 describes artificial snow based on water–absorbing chemical polymers. Skiing on the artificial snow is said to feel like skiing on real snow, sometimes even better.

The artificial snow is stated to have a density of around 0.3 g/cm³, a hardness of around 4 kg/cm² and a kinematic friction factor of 0.03 to 0.05 or less.

D1 gives no details regarding the composition of the artificial snow.

The present inventors have approached the publishers of D1 to get further information, but to no avail.

However, a tiny sample from the village SNOWY (as mentioned in D1) has been sent to a laboratory for chemical analysis. The laboratory was not very specialised, but they were able to determine that the sample did not contain any silicon or fluorine.

D2 describes commercially available superabsorbing polymers selected from *Cellulose or starch-acrylonitrile graft polymers, Cross-linked polyacrylates and polyacrylamides and Cross-linked maleic anhydride copolymers* and their uses, e.g. as granules for artificial snow. D2 also describes a method for making cross-linked polyacrylates and polyacrylamides. This method involves reverse–phase polymerisation.

D2 does not make any mention of coating the particles or of coated superabsorbent polymer granules for use as artificial snow. Nor does it mention snow made from such particles.

The present invention seeks to provide an alternative to the artificial snow in D1 and to a method for making it.

In their *small laboratory,* the inventors *have now developed a new type of artificial snow that has very similar skiing properties to natural snow. In fact,* they *found that under most circumstances it is nicer to ski on* the *artificial snow* disclosed herein *than on natural snow.*

The inventors *have found a way to provide artificial snow that has a kinematic friction factor (µk) similar to that of natural powdery snow and good properties for gliding over on skis, as well as artificial snow granules for making such snow. A snow granule is a spherical particle made of superabsorbing polymer that is able to absorb a large amount of water. The snow granule retains its original spherical form after absorption of the water. The snow granules also do not stick to each other.*

The superabsorbing polymers include homopolymers or copolymers of acrylic acid, methacrylic acid, acrylic acid salts or methacrylic acid salts. Copolymers of acrylic acid and methacrylic acid are preferred. Copolymers are polymers in which the polymer is built out of a combination of two different monomers which are polymerised together, thus resulting in a polymer in which the different monomer units are mixed. The polymers are in the shape of spherical granules.

Such spherical granules are made by reverse-phase polymerisation in which the polymerisation takes place in a two-phase system containing as aqueous phase and a phase comprising an organic solvent. In such a reverse-phase polymerisation, a hydrophilic monomer is dissolved in water. This solution is then emulsified in a continuous hydrophobic oil phase. The polymerisation is helped by using a water-soluble initiator such as a water-soluble persulphate (like potassium persulphate or ammonium persulphate) or hydrogen peroxide. The presence of such an initiator is essential. The amount has to be within the range of 0.1 to 2.0 wt. %, preferably 0.2 to 1.0 wt. %, based on the amount of monomer used.

The concentration of the monomers (acrylic acid, methacrylic acid or salts thereof) in the aqueous solution is preferably 35 to 75 wt. %, more preferably 40 to 70 wt. %. Of course, a mixture of the different acids or salts is used when a copolymer is to be produced.

The second phase for the reverse-phase polymerisation is provided by an aliphatic organic solvent. Solvents suitable for use in the reverse-phase polymerisation include aliphatic hydrocarbons such as n-pentane, n-hexane, n-heptane, and n-octane or alicyclic hydrocarbons such as cyclohexane, methyl cyclohexane and decalin. The preferred solvent is n-hexane, n-heptane or cyclohexane.

It is essential that the resulting polymer is cross-linked using a cross-linking agent in order to obtain superabsorbing polymers. Cross-links are covalent bonds linking one polymer chain to another. For producing our snow granules, the cross-linking agent needs two hydroxyl groups capable of reacting with carboxyl groups or carboxylate groups of the polymer. The cross-linking agents which must be used are linear alkane diols with 2 to 5 carbon atoms. Butanediol has turned out to be a very good cross-linking agent.

The amount of cross-linking agent must be within the range of 0.05 to 2 wt. % based on the amount of polymer, depending on the particular cross-linking agent employed. When the amount is less than 0.05 wt. %, the mechanical strength of the water-swollen granules becomes poor. When the amount is more that 2 wt. %, the cross-linking density becomes too high, resulting in a marked decrease in water-absorbing power. The extent of cross-linking is very important for the shape of the granules.

The cross-linking can be carried out in the presence of a solid inorganic substance like graphite, talc, hydrotalcite or pulverised silica. The presence of these inorganic compounds increases the fluidity of the resulting granules. Preferred inorganic materials are graphite and hydrotalcite because of their layered structure. Such inorganic materials are preferably present in an amount of 0.5 to 1.0 wt. % with respect to the reaction mixture.

Superabsorbing polymers as described above are well-known in the art. Two of such superabsorbing polymers are available commercially under the trademarks Sorbeau® and Wassersorb®. The process for making them is also known, as can be seen from document D2.

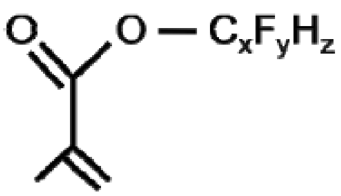
The superabsorbing polymers described above are as such suitable for use as artificial snow, but they do not give a product that resembles real snow in any way. In order to get the properties that we have mentioned above, the granules of the superabsorbing polymer have to be coated with a fluorine-containing polymer or a silicone oil. This coating ensures that the individual granules do not stick together. The coating also improves the gliding properties of the snow. The surface coating is applied after the reverse-phase polymerisation process by contacting the granules with an aliphatic hydrocarbon solution in which the fluorine-containing polymer or silicone oil is dissolved. Other superabsorbing polymers are not compatible with this coating.

The amount of fluorine-containing polymer or silicone oil is within the range of 0.1 to 10 wt. %, preferably 0.5 to 3 wt. %, on the basis of the total amount of superabsorbing polymer. When the amount is less than 0.1 wt. %, no improvement of the gliding properties on skis can be seen. On the other hand, when the amount is more that 10 wt. %, no further improvement on the gliding properties can be measured.

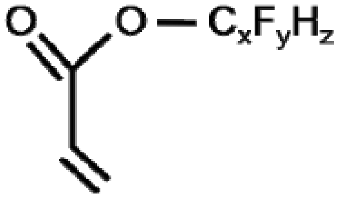
Thus, from a first aspect, the invention provides <repeat claim 1>, preferably <repeat claim 2>.

In a preferred embodiment, the invention provides <repeat claim 3>.

Suitable fluorine-containing polymers are fluoroalkyl(meth)acrylate-based polymers and copolymers obtained by polymerisation of a fluorine-containing(meth)acrylate as a monomer. The fluoroalkyl group has 1 to 5 carbon atoms and at least 2 fluorine atoms. The polymers are polymerised to a molecular weight of between 500 and 5 000 so that they have the consistency of a viscous liquid. The monomers used to have the following general formulae:
(formula (i) = methacrylate and formula (ii) = acrylate):



(i)



(ii)

in which $x = 1$ *to 5,* $y \geq 2$, $y + z = 2x + 1$*:*

The preferred fluorine-containing polymer is an acrylic (co)polymer obtained from a fluoroalkyl(meth)acrylate in which the fluoroalkyl group has 3 fluorine atoms and 2 to 4 carbon atoms. The monomers and polymers are available from Halopol Inc. We believe that all fluorine-containing polymers can be used instead of fluoroalky(meth)acrylate-based polymers and copolymers.

As motioned above, instead of the fluorine-containing polymer, a silicone oil can be used. Silicone oils with viscosity of 100 to 1000 mm²/s at 25°C are preferred. Typical examples are methyl silicone oils, fluoromethyl silicone oils and phenylmethyl silicone oils. Surprisingly good results have been obtained by using a combination of a silicone oil and a fluorine-containing polymer. Such a mixture is sold as an additive for motor oils.

Thus, the invention provides <repeat claim 4>.

The invention also provides <repeat claim 5>.

The superabsorbing polymer is granular. The average size of the superabsorbing polymer granules usually lies within the range of 20 to 500 µm before absorption of water, and lies within the range of 0.05 to 2 mm after absorption of water. When the granule size before absorption of water is less than 20 µm, very hard snow is obtained because the granules are too fine. When the granule size is more that 500 µm, artificial snow in the form of corn snow is obtained. The disadvantages of this type of snow have been mentioned before. The polymers keep the same shape after absorption of water.

For optimum performance it is important that the granules are as spherical as possible. The sphericity coefficient is a well-known parameter that is often used to describe the shape of granules. A perfect sphere has a sphericity coefficient of 1.

The granules must have a spericity coefficient of at least 0.8, preferably more than 0.9. Above 0.95, the skiing properties of the artificial snow will be better than those of natural snow.

<Thus claim 10>.

Spherical granules of a superabsorbing polymer are preferred for the following reasons:

i) they are easy to handle,
ii) they lead to spherical artificial snow granules which provide good gliding properties and
iii) they can be easily blended with natural snow.

The granules are transformed into artificial snow by absorbing water. At least 5 times the weight of water based on the weight of the granules needs to be absorbed to obtain artificial snow. The water is preferably absorbed near the place where the granules will be used because the dry granules are much cheaper to transport. The absorption of water preferably takes place at a temperature above 10°C, because, at above 10°C, the kinetics of absorption are better. After absorption of water, the granules need to be refrigerated. This can be done by any known refrigerating method. Preferably, the refrigeration is performed using liquid coolants like liquid nitrogen or liquid air because these liquids are easily mixed with the granules, thereby obtaining rapid refrigeration.

Thus, the invention provides <repeat claim 6>, preferably <repeat claim 7>, <claim 8>.

After this refrigeration, the granules can be stored or applied immediately on the ski slopes, preferably using a snow cannon.

The invention also provides <repeat claim 9>.

Examples

Several experiments were performed to show the advantages of our new artificial snow.

Example 1:

In this example, the effect of coating polymer granules with fluorine-containing materials or with a silicone oil was studied. All samples contained 1 wt. % of butanediol cross-linking agent and had a sphericity coefficient of 0.90.

The following superabsorbing polymers were used:
A: Polyacrylate, molecular weight 100 000
B: Polymethacrylate, molecular weight 98 000
C: Copolymer of acrylic acid and methacrylic acid, molecular weight 101 000.

All polymers were synthesised using the reverse-phase polymerisation process described above. Cyclohexane was used as solvent.

Granules obtained from these polymers were coated with two different fluorine-containing polymers or one silicone oil using hexane as a solvent, as follows:
X: polymer or tifluoroethyl acrylate (molecular weight 1 500)
Y: polymer of difluoromethyl methacrylate (molecular weight 1 500)
Z: silicone oil having viscosity of 500 mm^2/s at 25°C.
The amount of either fluorine-containing polymer or silicone oil was 2 wt. % on the basis of the total amount of polymer granules in all cases.
For example, in table 1, A+X means that granules made of polymer A are coated with coating agent X. In the comparative examples granules made of polymers A, B and C are used without a coating.

Table 1: *Effect of type of polymers used*

	Snow density on slope (g/cm³)	*Snow hardness on slope (kg/cm²)*	*Kinematic friction factor (µk)*
A+X	*0.35*	*3 – 4*	*0.035*
A+Y	*0.34*	*3.5 – 4.5*	*0.032*
A+Z	*0.37*	*3 – 5*	*0.041*
A (comparative)	*0.40*	*2 – 4*	*0.082*
B+X	*0.33*	*3.5 – 4*	*0.037*
B+Y	*0.35*	*3 – 4*	*0.036*
B+Z	*0.39*	*4 – 5*	*0.042*
B (comparative)	*0.42*	*2 – 4*	*0.089*
C+X	*0.29*	*3 – 4*	*0.029*
C+Y	*0.30*	*3 – 3.5*	*0.031*
C+Z	*0.35*	*4 – 5*	*0.039*
C (comparative)	*0.39*	*3 – 5*	*0.068*

Example 2:

In this example, the effect of coating the polymer granules with a mixture of a silicone oil and a fluorine containing polymer was studied. Again, the samples contained 1 wt. % of cross-linking agent and had a sphericity coefficient of 0.90. The components A, X, Y and Z were the same as identified in example 1. As for example 1, the amount of either fluorine-containing polymer or silicone oil was 2 wt. % on the basis of the total amount of polymer granules. When two compounds were used, the combined amount was 2 wt. % on the basis of the total amount of polymer granules.

Table 2: *Effect of mixing silicone oil with fluorine-containing polymers*

	Kinematic friction factor (µk)
A+X+Z	*0.029*
A+Y+Z	*0.027*
A+X	*0.035*
A+Y	*0.032*
A+Z	*0.041*

Example 3:

In this example, the effect of the sphericity coefficient of the granules was examined. The sphericity coefficient was affected by changing the amount of cross-linking agent during the reverse-phase polymerisation reaction. The correct amount of cross-linking agent for a certain sphericity coefficient was easily determined. From table 3 it is clear that granules having a sphericity coefficient below 0.8 had inferior properties. These granules are not suitable for the use as artificial snow. Table 3 further shows the extremely good properties of granules having a sphericity above 0.95.

Table 3: *Effect of the sphericity coefficient on the properties of the artificial snow.*

Sphericity Coefficient	*Kinematic Friction Factor (µk)*
0.71	*0.061*
0.80	*0.031*
0.90	*0.029*
0.96	*0.020*

Claims

1. Spherical superabsorbing polymer granules which are cross-linked mopolymers or copolymers of acrylic acid, methacrylic acid, acrylic acid salts, methacrylic acid salt or mixtures thereof containing from 0.05 to 2wt. % of a cross-linking agent which is a linear alkane diol with 2 to 5 carbon atoms based on the amount of polymer and which are coated with at least 0.1 wt. % of a fluorine–containing polymer and/or silicone oil based on the total amount of superabsorbing polymer, wherein said granules have a sphericity efficient of at least 0.8.

2. The granules of claim 1, which are copolymers of acrylic acid and methacrylic acid.

3. The granules of claim 1 or claim 2, wherein the mount of fluorine-containing polymer and/or silicone oil is within the range of 0.1 to 10 wt. %.

4. The granules of any one of the preceding claims, wherein the granules are coated with a combination of silicone oil and a fluorine-containing polymer.

5. Method for making the spherical superabsorbing polymer granules of claim 1 comprising the following steps:

   i) dissolving a hydrophilic monomer selected from acrylic acid, methacrylic acid, acrylic acid salts, methacrylic acid salts and mixtures thereof in water to form an aqueous phase

   ii) polymerisating the aqueous phase by emulsifying in an aliphatic organic solvent using a water-soluble initiator in an amount within the range of 0.1 to 2.0 wt% based on the amount of monomer used;

   iii) cross-linking the resulting polymer using a linear alkane diol with 2 to 5 carbon atoms in an amount from 0.05 to 2 wt. % based on the amount of polymer;

   iv) coating the granules with a fluorine-containing polymer or a silicone oil by contacting the granules with an aliphatic hydrocarbon solution in which the fluorine-containing polymer or silicone oil is dissolved, wherein the amount of fluorine-containing polymer or silicone oil is at least 0.1 wt. % on the basis of the total amount of superabsorbing polymer.

6. Method of making artificial snow comprising the absorption of water by the granules of any one of claims 1 to 4 wherein at least 5 times the weight of water based on the weight of the granules is absorbed, followed by refrigeration of the granules, wherein the size of the granules after absorption of water lies within the range of 0.05 to 2 mm.

7. The method of claim 6, wherein the water is absorbed at a temperature above 10°C.

8. The method of claim 6 or claim 7, wherein the refrigeration is performed using a liquid coolant which is easily mixed with the granules.

9. Artificial snow obtainable by the method of any one of claims 6 to 8.

10. The granules of any one of claims 1 to 4, wherein the sphericity coefficient is more than 0.90, preferably more than 0.95.

EXAMINATION COMMITTEE I

Candidate No.

Paper A (Chemistry) 2013 - Marking Sheet

Category		**Maximum possible**	**Marks awarded**	
			Marker	Marker
Independent claims	Granule	35	35	35
	Process	10	10	10
	Snow	10	10	10
	Method snow	10	8	8
	Use	5	0	0
Dependent claims		15	9	9
Description		15	11	11
Total		100	83	83

Examination Committee I agrees on 83 marks and recommends the following grade to the Examination Board:

☒ PASS (50-100)

☐ COMPENSABLE FAIL (45-49)

☐ FAIL (0-44)

27 June 2013

Chairman of Examination Committee I