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Chemistry

This paper comprises:

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LETTER FROM THE APPLICANT

Let-It-Snow AG
Bergstrasse 123
Bergen
Switzerland

Dear Sirs,

[001] We are a small company in the Swiss Alps that manages ski resorts. A few years ago, we realised that snowfall was becoming more and more irregular, probably because of climate change. In order to make sure that our ski season would remain as long as possible, we started doing some chemical research into making artificial snow. We now believe we have invented something worth patenting and would like you to draft a patent application for it. The procedure is rather costly for a small company like ours, it is therefore our company policy not to pay claims fees.

[002] 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 0.12 g/cm^3. Exposure to wind often increases the density to 0.2 to 0.3 g/cm^3. The density of snow will increase over time due to snow settlement. Old snow can reach densities of 0.4 to 0.5 g/cm^3. 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/cm^3. The ideal snow for skiing has a density of 0.2 to 0.4 g/cm^3, preferably around 0.3 g/cm^3.

[003] 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/cm^2 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/cm^2.

[004] The kinematic friction factor (μk) is a parameter that can be used to define th gliding properties of snow. Natural powdery snow has a kinematic friction factor of 0.0 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.

[005] 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/cm^3, and a hardness of less than 1 kg/cm^2. 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.

[006] SNOWY, a company from a neighbouring village, has recently advertised in the local newspaper that they guarantee snow. They achieve this using a type of artificial snow. I enclose a copy of this advertisement in the form of document D1. We have tried to get information about the composition of the snow used by SNOWY. However, there has always been a huge rivalry between our villages and the employees from SNOWY were not willing to tell us. One of our employees has now taken a tiny sample which we have 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. As far as we are aware, SNOWY has not published anything else about their artificial snow.

[007] In our small laboratory, we have now developed a new type of artificial snow has very similar skiing properties to natural snow. In fact, we found that under most circumstances it is nicer to ski on our artificial snow than on natural snow.

[008] We 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.

[009] 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. As you probably know, 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 preferably 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 an 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.

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

[011] 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.

[012] 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.

[013] 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 than 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.

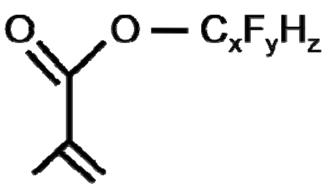
[014] The cross-linking can be carried out in the presence of a solid inorganic substance like graphite, talc, hydrotalcite or pulverised silica. The presence of these inorganic compounds increases the fluidity of the resulting granules. Preferred inorganic materials are graphite and hydrotalcite because 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.

[015] Superabsorbing polymers as described above are well-known in the art. Tw 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.

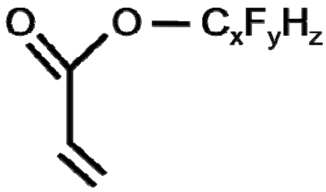
[016] The superabsorbing polymers described above are as such suitable for use as artificial snow, but they do not give a product that resembles real snow in any way. In order to get the properties that we have mentioned above, the granules of the superabsorbing polymer have to be coated with a fluorine-containing 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.

[017] 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 than 10 wt. %, no further improvement on the gliding properties can be measured.

[018] 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 have the following general formulae:
(formula (i) = methacrylate and formula (ii) = acrylate):



(i)



(ii)

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

[019] 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 fluoroalkyl(meth)acrylate-based polymers and copolymers.

[020] As mentioned above, instead of the fluorine-containing polymer, a silicone oil can be used. Silicone oils with a viscosity of 100 to 1000 mm^2/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.

[021] The superabsorbing polymer is granular. The average size of the superabso 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 than 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.

[022] 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.

[023] The granules must have a sphericity 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.

[024] 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.

[025] The granules are transformed into artificial snow by absorbing water. At leas times the weight of water based on the weight of the granules needs to be absorbed t 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 10ºC, because, at above 10ºC, 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.

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

Examples

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

Example 1:

[028] 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.

[029] 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.

[030] All polymers were synthesised using the reverse-phase polymerisation proc described above. Cyclohexane was used as solvent.

[031] 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 of trifluoroethyl 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/cm^3)	Snow hardness on slope (kg/cm^2)	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:

[032] 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:

[033] 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 coefficient 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

Yours sincerely,

S. Nowman

Document D1

SNOWY AG

Guaranteed snow, throughout the season!

[001] Don’t you hate it when you arrive at your skiing destination and find there is hardly any snow?

[002] Our ski slopes in the Swiss Alps have been well-known for their good snow and interesting skiing possibilities. However, as you know, recently more and more days of the ski season go by without any proper snow on the slopes.

[003] We have invested a lot of time to overcome this problem and to provide you with snow all through the season. And now it is finally happening! As the only ski resort in Switzerland (and probably even in the world) we provide you with guaranteed snow on the slopes!

[004] On days when there is no natural snow, we provide artificial snow by our new technology based on water-absorbing chemical polymers. We don’t want to tire you with details of the chemistry, but you can believe us: skiing on our slopes of artificial snow is like skiing on real snow!

[005] Technically interested people may like to know that we make artificial snow that has a density of around 0.3 g/cm^3, a hardness of around 4 kg/cm^2 and a kinematic friction factor of 0.03 to 0.05 or less. Sometimes our artificial snow even feels better than real snow!

[006] Book now and try it out this season!

Document D2

Superabsorbing polymers and their uses

[001] Superabsorbing polymers are water-insoluble hydrophilic polymers that are able to swell and absorb amounts of water or saline solutions, sometimes as high as 10 to 1000 times their own weight. The possibility to absorb saline solutions, like urine, is very important because the main application for these polymers is in personal care and hygienic products, for example disposable diapers, sanitary napkins, towels, sponges etc. However, several other applications are also being developed for these polymers. For example, superabsorbing polymers are used for dehydrating oils and fuels, as thickening agents and as release agents for pharmaceuticals or agrochemicals. Very recently it has been published that granules made of these polymers could be suitable as artificial snow. Currently tests are being performed in a ski resort in Switzerland.

[002] A lot of research has been performed on this type of polymer, especially because personal care and hygienic products represent a huge global market.

[003] There are many different kinds of superabsorbing polymers. However, the most important superabsorbing polymers currently used can be grouped into three main classes:

1. Cellulose- or starch-acrylonitrile graft polymers,
2. Cross-linked polyacrylates and polyacrylamides,
3. Cross-linked maleic anhydride copolymers.

All of these polymers are available commercially.

[004] The most interesting superabsorbing polymers are cross-linked polyacrylates and polyacrylamides. These polymers are prepared by well-known polymerisation techniques.

[005] These polymers are usually prepared by reverse-phase polymerisation. In a reverse-phase polymerisation process the polymerisation takes place in a two-phase system, an aqueous phase and a phase comprising an aliphatic organic solvent. 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 important. The amount must 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.

[006] The concentrations of monomer in the aqueous solution are generally in the range of 35 to 75 wt. %.

[007] The second phase for the reverse-phase polymerisation is provided by an aliphatic organic solvent. Examples of such 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.

[008] In order that the polymers absorb water, they need to be cross-linked. Any compound having two or more of the functional groups capable of reacting with a carboxyl group or a carboxylate group of the polymer may be used as the cross-linking agent. The amount of cross-linking agent is usually about 1 wt. % based on the amount of polymer. A very good cross-linking agent is butanediol.

[009] The cross-linking can be carried out in the presence of a solid inorganic substance like graphite, talc, hydrotalcite or pulverised silica.

[010] The granules obtained from these polymers have good absorption properties.