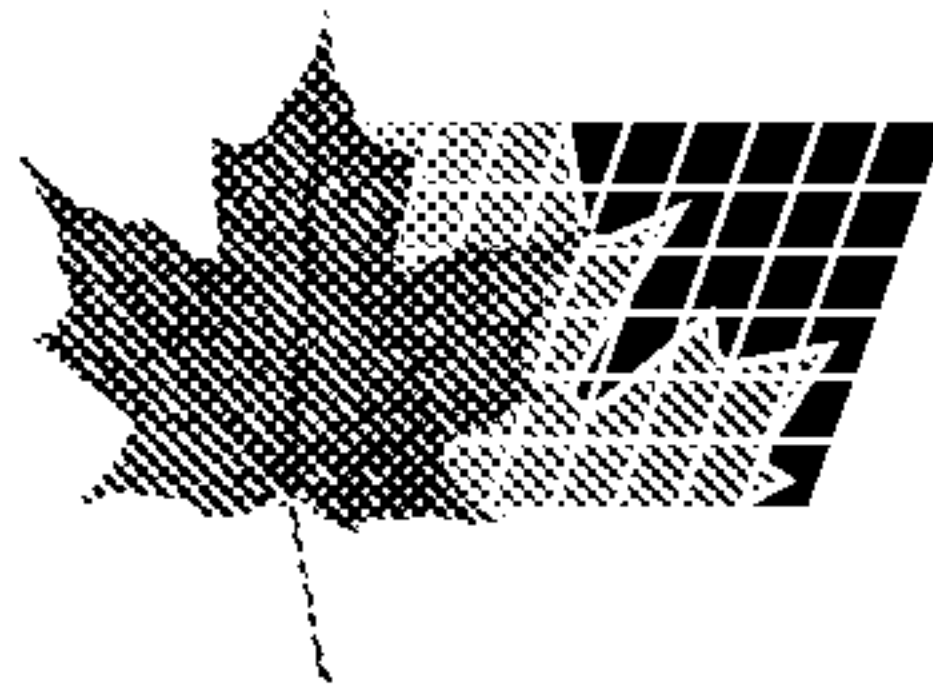




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(54) **PROCEDE DE PREPARATION DE PRODUITS ABSORBANT
L'EAU PAR INTERMOLECULARITE**

(54) **METHOD OF PREPARATION OF PRODUCTS WHICH ABSORB
WATER INTERMOLECULARLY**

(57) L'invention porte sur un procédé de réticulation de polymères et copolymères de polystyrène en vue de la formation de matériaux macroplegmatisés d'un Mc allant de 30 000 à 50 000. Lesdits matériaux se présentent sous forme de gel insoluble extrudé en morceaux de 3 à 5 cm soumis à une sulfonation: par de l'acide sulfurique dense, par de l'acide oléosulfurique, par du trioxyde de soufre, et par de l'acide chlorosulfonique, puis à l'introduction de groupes sulfoniques à haute densité, à l'introduction d'un groupe nitrique, et à l'introduction d'un groupe carboxylique avec le copolymère de styrène-acrylonitrile. Le groupe chlorosulfonique favorise la sulfonation et la réticulation avec formation de liaisons avec le groupe sulfone lequel est contrôlé par une adjonction de 10 à 20 % d'acide acétique comme régulateur. On obtient ainsi un volume insoluble de gel qui après élimination du solvant et mûrissement pendant 4 à 7 heures est traité à l'éthanol ou au propanol pour en extraire l'acide chlorosulfonique n'ayant pas réagi qui est neutralisé par de la soude ou de la potasse, ledit gel étant alors extrudé en morceaux de 3 à 5 cm. Après neutralisation et réduction de la teneur en eau à 10 %, les produits sont désodorisés à 160 °C sous vide, ce qui donne des matériaux dont les molécules absorbent l'eau jusqu'à 300 fois leur poids. En raison de leur teneur de 72, 75 % en substances minérales, ils présentent une grande stabilité dans les sols, ne se dégradent pas, et peuvent resservir indéfiniment pour l'absorption/libération d'eau. Ils constituent donc des promoteurs de fertilité pour tout type de sol où ils favorisent la croissance de l'herbe, la croissance des arbres et des forêts, et la maturation précoce des plantes alimentaires.

(57) A method of crosslinking polystyrene polymers and co-polymers for the formation of macroplegmatic materials of an Mc 30,000 to 50,000 is described. The materials forming an insoluble gel which is shaped in an extruder to 3 to 5 cm pieces and is subject to sulphonation with dense sulphuric acid, with oleum sulphuric acid with sulphur trioxide and with chlorosulphonic acid, and the introduction of sulphonic groups to a high density and with the introduction of nitric group and with the introduction of carboxylic group with the copolymer styrene-acrylonitrile. The chlorosulfonic group promotes sulphonation and crosslinking with the formation of bridges with the sulfone group which is controlled with a 10-20 % of acetic acid present as regulator and an insoluble volume of gel is formed which following drainage of the solvent and after remaining to ripen for 4-7 hours it is treated with ethanol or propanol to extract the unreacted chlorosulphonic acid then is neutralised with sodium or potassium hydroxide subjected to an extruder for the preparation of 3-5 cm products. Following neutralisation and shrinkage to a 10 % water content and the products produced are deodorised at a temperature of 160 °C under vacuum and are converted to materials which absorb water inside their molecules up to 300 times their weight; having an inorganic content of 72-75 % they exhibit a high degree of stability in the ground, they do not degrade and can be used indefinitely for water absorption-release so that they operate as fertility promoters to any type of soil leading to an increase of green growth, and to the planting of trees and forests and to advance food production.



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(54) Title: METHOD OF PREPARATION OF PRODUCTS WHICH ABSORB WATER INTERMOLECULARLY (57) Abstract A method of crosslinking polystyrene polymers and co-polymers for the formation of macroplegmatic materials of an Mc 30,000 to 50,000 is described. The materials forming an insoluble gel which is shaped in an extruder to 3 to 5 cm pieces and is subject to sulphonation with dense sulphuric acid, with oleum sulphuric acid with sulphur trioxide and with chlorosulphonic acid, and the introduction of sulphonic groups to a high density and with the introduction of nitric group and with the introduction of carboxylic group with the copolymer styrene-acrylonitrile. The chlorosulfonic group promotes sulphonation and crosslinking with the formation of bridges with the sulfone group which is controlled with a 10-20 % of acetic acid present as regulator and an insoluble volume of gel is formed which following drainage of the solvent and after remaining to ripen for 4-7 hours it is treated with ethanol or propanol to extract the unreacted chlorosulphonic acid then is neutralised with sodium or potassium hydroxide subjected to an extruder for the preparation of 3-5 cm products. Following neutralisation and shrinkage to a 10 % water content and the products produced are deodorised at a temperature of 160 °C under vacuum and are converted to materials which absorb water inside their molecules up to 300 times their weight; having an inorganic content of 72-75 % they exhibit a high degree of stability in the ground, they do not degrade and can be used indefinitely for water absorption-release so that they operate as fertility promoters to any type of soil leading to an increase of green growth, and to the planting of trees and forests and to advance food production.		

METHOD OF PREPARATION OF PRODUCTS WHICH ABSORB WATER INTERMOLECULARLY

Subject of the Invention

The invention refers to a method for the preparation of products which are
5 defined by a polymer of a macroplegmatic structure which includes ionic
groups at a large density and from which products are derived which absorb
intermolecularly, i.e inside their molecules , large quantities of water, up to
300 times their weight and which exhibit a high ability in the ground to
promote soil fertility and cover water consumption needs, offering a
10 reduction of water consumption of up to 12 times.

Objective of the Invention

Saving in water consumption is at present a principal subject of global
importance , whereas the phenomenon of desertification that has arisen in
several areas of the planet constitutes a primary source of global concern
15 associated with the survival of the planet. Agriculture production in
synchronisation with the needs of the over-populated planet in what
concerns the satisfaction of food demand , whereas the so-called green
revolution has several weaknesses, leads to enforcement of nature and to
soil erosion. The principal cause for all that is covering the needs of water ,
20 in a manner that serves but does not erode nature.

This problem is severely aggravated at present, as the water balance is
broken , the sea starts covering large areas of shores reducing the
availability of fertile land and leading to a new geographical status of
equilibrium between the sea and the land. It is hence a primary need to
25 introduce new principles in water usage leading to saving associated both
with human consumption as well as with the use of water for agricultural
needs, where solutions which offer maximum economy in water usage must
be introduced.

Development of the Invention

5 The invention describes products which cover the needs of soil in water leading to water saving in the Earth, the Nature and the Agriculture , thus the invention provides concern of water economy in these uses.

10 The products which absorb water inside their molecules which are subject of this invention, are produced following a special crosslinking processing of polymers towards a stable macroplegmatic structure; such polymers contain active aromatic rings such as polystyrene ,hydrogenated SBR, styrene-acrylonitrile and all their co-polymers. As crosslinking agents the dibenzo-X-dimethylbenzene and the sulphonic -SO₂ ,radical, are used. The processing is promoted in solutions of the polymer on chlorinated hydrocarbon solvents , and in molten phases of the polymers at high temperatures.

15 The macroplegmatic polymers as produced in the form of a gel are practically insoluble and must be subject to processing for the introduction of the ionic groups and for this reason , the macroplegmatic polymers are subject to a suitable shaping in the special cutting equipment where the gel formed is entered in an array of tubes of a length of one meter and of
20 diameter of two to four centimetres where the gel is cut longitudinally and at its end transversely in three to four centimetre pieces so that discrete particles of dimensions of three by four centimetres are produced. In this form ,the material prepared suspended in the solvent is subsequently subject to a sulfonation for the introduction of high density sulfonic groups

25 Strong agents of sulphonation are utilised for the introduction of sulfonic groups to the suspension of the polymer , such as chlorosulphonic acid in a quantity of 1,5-2 Moll to the aromatic rings or sulphur trioxide in a similar quantity or oleum sulphuric acid according to the sulphur trioxide contained .Sulphonation is fast and efficient as also is the introduction of nitric groups

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and the introduction of carboxylic groups with the use of the co-polymer styrene-acrylonitrile as hydrolysis of the -CN group contained occurs , with a final shaping of spherical products suspended in the solvent of the sulphonation process .The product is then removed the solvent is decanted
5 and it is washed with ethyl or propyl alcohol to collect the unreacted chlorosulphonic acid , then is neutralised in 30% sodium or potassium hydroxide in a recalculated quantity and having adsorbed water to a degree of 30-50 times its weight ,it is then introduced to a tank which contains a 15-25% sodium chloride solution where the polymer shrinks in terms of water
10 content to about 10%.The product can be also dehydrated by passing through a 20V electrical field .Finally ,the product is heated under vacuum up to 160oC degrees and is fully dehydrated and freed from the solvent ,so that it becomes a marketable product able to absorb water up to 150-300 times its weight. It has the form of small spheres or leaves depending on the
15 cutting process in the extruder

In a different preparation process to the 10-30% solution of polymer chlorosulfonic acid is added as a 30% solution in a quantity of 2-2,2 Mol to the benzene rings .The solution contains 12% acetic acid as an inhibitor of the control of introduction of crosslinking with sulphone groups. As the
20 sulphonation reaction progresses, as measured by the release of hydrogen chloride, an insoluble gel is formed by the macroplegmatic evolution of the polymer with the formation of sulphone bridges. The gel as it being formed which lasts 4-6 hrs ,it is removed the solvent which constitutes its own layer and is removed by draining ; the gel is then washed with ethanol or propanol
25 to react the unreacted chlorosulfonic acid and the solution is drained ; finally the pure gel which is into a non stirrable volume is neutralised with calculated amounts of sodium or potasium hydroxide. Then it is strained and passed to an extruder where it is cut to the desired size and shape of particles and is then subject to complete neutralisation to size reduction and
30 to deodorisation and becomes a marketable product as previously described.

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As already mentioned, hydrogen chloride is formed during the sulphonation reaction with chlorosulphonic acid. This is absorbed in a sulphur trioxide solution in chlorinated solvents with the formation of chlorosulphonic acid and the procedure mentioned is combined with the preparation of
5 chlorosulphonic acid with delivery of sulphur trioxide to a solution.

Furthermore, a process has been developed involving phase dispersion conditions during crosslinking of the polymer with the 1,4-dichloromethyl-2,5-dimethylbenzene between the solvent 1,2 dichloroethane and an equal volume of dense sulphuric acid in a constant temperature around 50°C
10 during which small spheres are formed. In the sequel sulphuric acid is added to the spheres formed with sulphonation promotion with temperature rise up to 80°C, or 1,5-2.0 Mol of chlorosulphonic acid added at a normal temperature along with a 12% acetic acid solution to the solvent used and, following three hours of stirring the sulphonation is complete and the product
15 is collected, strained and neutralised, shrunk and deodorised. Finally a high specification product is received regarding the colour and spherical shape. With the above process involving processing sulphuric acid and chlorosulphonic acid, straining gives a mixture of solvent and sulphuric acid of a volume about four cubic meters per ton of product which must be
20 distilled for the collection of solvent and to dispose or use of sulphuric acid in a pure quality for recycling.

The inventor has also invented and developed products that absorb intermolecularly water following simple immersion of inflated polystyrene into oleum sulphuric acid of a content of trioxide 20, 30 and 65% with which the
25 polymer is decayed by the sulphur trioxide and large spheres of great uniformity are formed. They exhibit a degree of inflation of 40 to 70 which depends on the degree of inflation of polystyrene. These materials, following 12 hours maturing, are collected and washed with water. This product is not neutralised but delivered in acidic form and constitutes a product which
30 promotes in the soil water economy and fertility.

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In all the above the process of our invention is described in the form of materials which absorb water intermolecularly and promote fertility to the ground. These products have been studied in terms of activity and the following have been observed:

5

a) With the addition of these products to the soil, the growth of trees and forests is possible with full survival and acceleration of growth as water economy in the order of 12 is achieved sufficient for 120 days of biological activity

10 b) The growth of fruit bearing trees is promoted with an acceleration of growth in the order of 30 to 40%, a biomass production increase of 30 to 50% and a doubling of fruit production

15 c) Soil fertility is promoted in problematic, sterile and mountain areas as these materials offer water economy to the ground, and help the growth of green and the development of soil biological activity

These materials which contain water intermolecularly which does not evaporate nor is leaked in the ground but kept as in a tank for covering the water needs of plants and of trees, consist of inorganic material to the extent of 72 to 75% where the polymer is only the shell and accounts for only 25-
20 28% by weight. Thus, these materials have maximum stability in soil where they not degrade biologically nor are they altered in terms of composition. Thus the products of the invention can operate for indefinite long period of time by absorbing/delivering water in the soil.

25 As a consequence, the products of the invention analysed and described above constitute means of the highest value and utility in maintaining the natural operation, the promotion of natural growth and the production of food production in a sustained manner as they promote soil fertility independently of the quality of the soil and in every soil under any conditions.

Example No 1

a. Preparation of the crosslinking agent

The mixture of reactants for the preparation of the crosslinking agent 2,5-dichloromethyl -1,4-dimethylbenzene , are : 246.2 ml of o-xylene , 2370 ml
5 of a 37% formaldehyde solution in a 5 litres of hydrochloric acid solution 35%
(Molar ratio 1:6;12).The mixture is brought to a 10 litres glass reactor
heated to 95oC and stirred for 5 hours ; it then remains at normal
temperature for 12 hours forming crystals of the crosslinking agent which is
collected by filtration (205 grams) Furthermore 400 ml of hydrogen chloride
10 are added to the solution. Following heating under stirring for 5 hours and
then cooling a new quantity of the crosslinking agent settles(152 grams)with
91% yield

The product is then recrystallised in alcohol and form a pure product with a
melting point of 125oC

15

b. Preparation of the macroplegmatic gel

In a pilot unit featuring a 200 litres dissolution tank a 2 k.m. sulphonation
reactor and other parts which will be described in the following , 30 kg of
polystyrene solution in 100 litres of chlorinated solvent is formed : 300 gram
20 of crosslinking agent are added to the solution under stirring conditions .
followed by a dense sulphuric acid catalyst until a grit is formed (5 cm of
catalyst 20 minutes resistance time) the macroplegmatic gel formed is
extracted and cut into 4-5 cm pieces

Example No 2

25 In the pilot plant of example No 1 , 20kgs of polystyrene solution is formed in
100 litres of solvent ; to this 200 grams of crosslinking agent are added and
then sulphuric acid as catalyst until a grit is formed (6 ml, 24 minutes) The
mixture is transferred to the extruder before the formation of the gel ,the

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extruder being defined by a system of 3 cm 1 meter long tubes featuring a space for the draining of the mixture. The solution is converted to macroplegmatic and then compressed in the tube system towards the outlet where a cutting system operates for forming 3-5 cm particles

- 5 The small particles and the solvent are brought to the sulphonation reactor where 65% oleum sulphuric acid is added as a 30% solution in the chlorinated solvent at quantity so that the sulphur trioxide to contain 2.2 Moles/Mole of benzene units. The stirring lasts for 2 hours following the end of sulphonation and in the sequel ,the product is extracted and brought to a
- 10 perforated container for staining of the solvent .In the sequel it is passed with the perforated container to be washed with propanol to extract the unreacted chlorosulphonic acid and then is brought to a neutralisation tank with 30% potassium hydroxide; then is immersed in 20 % sodium chloride for shrinkage and it is passed with water content of 12% to a container for
- 15 heating to 160oC with stirring and under vacuum , following which 80 kgs of product are received in the form of irregular small spheres ; in technical terms it is a light product with a degree of inflation in water in the order of 225 and with a composition of 75% inorganic and 25% organic , with a practical yield of 100%

20

Example No 3

- A 200 litres 30% polystyrene solution in 1,2 dichloroethane as solvent which contain 12% acetic acid is brought to the sulphonation reactor where chlorosulphonic acid is added 2-2,2 Moles/Mole of benzene units with
- 25 stirring as a 25% solution The reaction of sulphonation and formation of grosslinks with sulphone radicals advance rapidly and this is measured by the release of hydrogen chloride and the gradual release of the solvent Finally a gel is formed which is insoluble and after 4 hrs of ripening the solvent is decanted ;then to the gel is added propanol to extract the
- 30 unreacted chlorosulphonic acid , then it is subjected to partial neutralisation

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with 30% potassium hydroxide. It is taking to the extruder and cut to pieces of 3 to 5 cm is completely neutralised and then after shrinkage treatment by passing through an electrical field of 20V .Finally is taking for deodorisation by heating at 160oC under vacuum and stirring and the product obtained is
 5 of brilland colour with a degree of inflation 258 and with a composition 23% organic, 77% inorganic

The hydrogen chloride released is passed to a sulphur trioxide solution in 1,2 dichroloethane where it is absorbed to form chlorosulphonic acid The exploitation of the hydrogen chloride produced simplifies the transfer of the
 10 reactants by passing to a sulphur trioxide solution and formation of chlorosulphonic acid during the reaction with continuous recycling

Example No 4

20 gr. of the 50-50% styrenbe -acrylonitrile copolymer are dissolved in the solution reactor in 100 litres of pure 1,2 dichloroethane .!00 grans of the
 15 crosslinking agent are added to the solution and then sulphuric acid is also added until a grit is formed. The mixture is brought to an extruder where .a gel is formed and with the exertion of pressure it is promoted to the tubes so that the material is cut into 4 to 5 centimetres pieces.

The pieces and the solvent are brought to the sulphonation reactor where
 20 65% of oleum sulphuric acid as a 25% solution and at quantity of 2 Moles/Mole of benzene nuclei Following a reaction and stirring for 5 hours the product is removal .strained neutralised and passed to a 20 V electric field and finally ,with a 5% water content it is heated at 160°C with stirring and with the application of vacuum and is converted into a high specification
 25 product with a degree of inflation in water of 185 .This product has two ionic groups , a sulphonic one and a carboxylic one from the hydrolysis of acrylonitrile

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20 gr. of fully hydrogenated SBR (styrene 40%) are brought to a reactor in 100 litres of 1,2 dichloroethane. Following dissolution, 80 gr. of crosslinking agent are added and with the addition of sulphuric acid as a catalyst, the mixture is passed to the extruder where it is transformed to a

5 macroplegmatic material. The 4 to 5 centimetres pieces finally produced and the solvent are brought to the sulphonation reactor where 65% oleum sulphuric acid is added as a 25% solution in a quantity of 2 Mole SO₃ per Mol of benzene nuclei. Following reaction and stirring for four hours, the product is removed, trained, strained, neutralised and shrunk in a 20 V

10 electric field and following heating at 160 °C under stirring and vacuum a high specification product is received with an inflatability ratio of 120

Example No 6

Inflated polystyrene is brought to 65% oleum sulphuric acid and left to be eroded by the acid. Sulphonated products are formed in the form of sizeable

15 spheres in a normal shape and in order. These, following a residence time of 12 hours are collected, washed with water and form a high added value and usability products. They adsorb water up to 40-70 times their weight, depending on the degree of inflation of the polystyrene and are offered as products for agricultural use in the acidic form

CLAIMS

1. Method for the preparation of a particulate, stable macroplegmatic polymer product with MC 30 000 to 50 000, capable of intermolecularly absorbing about 100 to 300 times its weight of water, said method comprising the steps of:
 - (i) subjecting a polymer having aromatic groups, in a form of a 10-30% solution in chlorinated solvent(s), to a crosslinking reaction with 2,5-dichloromethyl-1,4-dimethylbenzene, to obtain an insoluble macroplegmatic gel;
 - (ii) extruding and cutting said insoluble macroplegmatic gel to obtain discrete macroplegmatic gel particles of a main dimension of 3 to 5 centimeters;
 - (iii) reacting said macroplegmatic gel particles, suspended in chlorinated solvent(s), with strong acidic agent(s) to introduce anionic groups in a high density and obtain highly anionic macroplegmatic gel particles;
 - (iv) subjecting said highly anionic macroplegmatic gel particles to a work-up procedure comprising removing solvent(s) by vacuum distillation, washing with methanol or ethanol to remove / react excess acidic agent, neutralizing in about 30% aqueous sodium or potassium hydroxide, shrinking/dehydrating in 15-25% aqueous sodium chloride to a water content of about 5-15%, and deodorizing by heating under vacuum in a temperature up to about 160°C to essentially remove all remaining alcohol and alcohol products and traces of solvent(s).
2. Method according to claim 1, wherein said polymer having aromatic groups is selected from the group comprising polystyrene, hydrogenated styrene butadiene rubber (SBR), styrene-acrylonitrile copolymers and mixtures and/or copolymers thereof.
3. Method according to claim 1, wherein said crosslinking reaction in (i) is carried out in a melt of said polymer.
4. Method according to claim 1, wherein said reaction in (i) is carried out in a temperature ranging from room temperature to about 50°C and optionally using, as further catalysts, SbCl_5 and/or TiCl_4 , in catalytic amounts.
5. Method according to claim 1, wherein said strong acidic agent(s) in (iii) comprise sulfonating agent(s) for the introduction of sulfonic groups, said sulfonating agent(s) being selected from chlorosulfonic groups, suflur trioxide or oleum sulfuric acid, each in a molar ratio of equivalent suflur trioxide of 1,5-2,2 mol per mol of aromatic groups contained in said

insoluble macroplegmatic gel particles and/or a nitration acid for the introduction of nitric groups.

6. Method according to claim 5, wherein said reaction with sulfonating agent(s) produces further crosslinking of said macroplegmatic gel particles, through the formation of sulphone bridges, said further crosslinking being controlled with the addition of acetic acid or acetic anhydride as a crosslinking inhibitor in a proportion of 10-20% on the polymer used.
7. Method according to claims 2 and 5, wherein in the case that said polymer having aromatic groups comprises styrene-acrylonitrile copolymer(s), then carboxylic groups are formed as additional anionic groups, from the hydrolysis of cyano groups in the sulfonation reaction conditions.
8. Method according to claim 1 wherein said extrusion is carried out by pressing said macroplegmatic gel through an extruder comprising an array of parallel tubes of length of about 1 meter and diameter of about 3 to 4 centimeters and a cutting system at one end of the tubes, to form said particles.
9. Method according to claim 8, wherein said insoluble macroplegmatic gel is formed while the reaction mixture moves through said extruder.
10. Method according to claim 1 wherein said shrinking/dehydration in (iv) is carried out by subjecting said highly anionic macroplegmatic gel particles to an electric field of 20V.
11. Method according to claim 1, comprising the steps of:
 - (i) crosslinking of said polymer having aromatic groups with 2,5-dichloromethyl-1,4-dichlorobenzene and sulfuric acid as the catalyst, under phase dispersion conditions in a two phase system consisting of equal volumes of chlorinated solvent(s) and concentrated sulfuric acid, at a temperature of about 50°C, to obtain small spheres of macroplegmatic gel;
 - (ii) sulfonating said spheres with the addition of:
 - sulfuric acid at about 80°C or
 - chlorosulfonic acid at room temperature in a molar excess of about 1,5-2,0 of the mols of aromatic rings present in said polymer having aromatic groups,
 in the presence of acetic acid as a crosslinking inhibitor, to obtain sulfonated macroplegmatic gel spheres; and
 - (iii) removing said sulfonated macroplegmatic gel spheres by filtration, and shrinking/dehydrating and deodorizing same;
 wherein the solvent system is recovered after the reaction, purified through distillation and recycled in the process.

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12. Method according to claim 1 comprising the steps of:

- (i) sulfonating a 10-30% solution of said polymer having aromatic groups in chlorinated solvent(s) with a sulfonating agent comprising chlorosulfonic acid, whereby the formation of sulfone crosslinks is also promoted and regulated through the presence of about 10-20% of the polymer used of acetic acid as a crosslinking inhibitor, to obtain insoluble sulfonated/crosslinked macroplegmatic gel;
- (ii) distilling off the solvent by vacuum distillation with the acetic acid in it for recycling
- (iii) washing said insoluble sulfonated/crosslinked macroplegmatic gel with methanol or ethanol to react and remove the unreacted chlorosulfonic acid and subsequently partly neutralizing the same in concentrated sodium or potassium hydroxide, to obtain the pure product
- (iv) shaping the product obtained of the neutralized sulfonated macroplegmatic structure in an extruder to obtain particles of the product of main dimension of about 3-5 centimeters;
- (v) subjecting said particles of the product to full neutralization as in (ii) above, shrinking/dehydration of the product if needed and deodorization by heating under vacuum in a temperature up to about 160°C to essentially remove all remaining water and traces of solvent(s).

13. Method according to claim 11 or 12, wherein said polymer having aromatic groups is selected from the group comprising polystyrene, hydrogenated styrene butadiene rubber (SBR), styrene-acrylonitrile copolymers and mixtures and/or copolymers thereof.

14. Method according to claims 11 or 12 and 13, wherein in the case that said polymer having aromatic groups comprises styrene-acrylonitrile copolymer(s), then carboxylic groups are formed as additional anionic groups, from the hydrolysis of cyano groups in the reaction conditions.

15. Method according to claim 12 wherein said extrusion is carried out by pressing said macroplegmatic polymer product through an extruder comprising an array of parallel tubes of length of about 1 meter and diameter of about 3 to 4 centimeters and a cutting system at one end of the tubes, to form said particles of product.

16. Method according to claim 11 or 12 wherein said shrinking/dehydration is carried out by subjecting said particles to an electric field of 20V.

17. Method for the preparation of sulfonated polystyrene spheres capable of intermolecularly absorbing about 40 to 70 times their weight of water and being in an acidic form, said method comprising:

- (i) sulfonation of inflated polystyrene by simple immersion in oleum sulfuric acid, to produce regularly shaped sulfonated polystyrene spheres;
- (ii) filtration of said sulfonated polystyrene spheres and washing of same with water;

wherein the water absorption capacity depends on the degree of inflation of said inflated polystyrene.

18. A stable product obtained according to any of the preceding claims, which is mixed with a soil to act constantly as humidity regulator and fertility promoter thereof.