



(43) International Publication Date
30 May 2013 (30.05.2013)

(10) International Publication Number
WO 2013/076700 A1

(51) International Patent Classification:

C08F 6/10 (2006.01) *C08C 2/06* (2006.01)
C08C 2/00 (2006.01)

(21) International Application Number:

PCT/IB2012/056680

(22) International Filing Date:

23 November 2012 (23.11.2012)

(25) Filing Language:

Italian

(26) Publication Language:

English

(30) Priority Data:

MI2011A002156 25 November 2011 (25.11.2011) IT

(71) Applicant (for all designated States except US): **VER-SALIS S.P.A.** [IT/IT]; Piazza Boldrini 1, I-20097 San Donato Milanese (MI) (IT).

(72) Inventors; and

(71) Applicants (for US only): **PARISI, Maria** [IT/IT]; Via Vulcano 31, I-48124 Ravenna (IT). **MAESTRI, Piero** [IT/IT]; Via Mazzolini 7, I-47034 Forlimpopoli (Forli-Cesena) (IT).

(74) Agent: **MAIWALD PATENTANWALTS GMBH**; Elisabethstr. 3 / Elisenhof, 80335 Munich (DE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

— with international search report (Art. 21(3))
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: PROCESS FOR THE REMOVAL OF THE SOLVENT FROM A POLYMERIC SOLUTION

(57) Abstract: A process for the removal of the solvent from a polymeric solution including at least one elastomeric polymer, which comprises subjecting said polymeric solution to a stripping step by means of water vapour, in the presence of a dispersant system comprising: - from 0.005% by weight to 1% by weight, preferably from 0.008% by weight to 0.8% by weight, with respect to the total weight of the dry elastomeric polymer, of at least one lamellar material; - from 0.0005% by weight to 1% by weight, preferably from 0.0008% by weight to 0.8% by weight, with respect to the total weight of the dry elastomeric polymer, of at least one cationic surfactant.



WO 2013/076700 A1

PROCESS FOR THE REMOVAL OF THE SOLVENT FROM A POLYMERIC SOLUTION

The present invention relates to a process for the removal of the solvent from a polymeric solution.

5 More specifically, the present invention relates to a process for the removal of the solvent from a polymeric solution which includes at least one elastomeric polymer, comprising subjecting said polymeric solution to a stripping step by means of
10 water vapour, in the presence of a dispersant system including at least one lamellar material and at least one cationic surfactant.

As is known, the removal of the solvent from polymeric solutions in order to obtain polymers in
15 solid state, can be divided into two process types defined as "Traditional Technology" and "Direct Devolatilization" respectively.

The term "Traditional Technology" refers to a technology described, for example, in American patents
20 US 3,337,422, US 3,462,347 or US 4,278,506, whereas the term "Direct Devolatilization" refers to a technology which provides the evaporation of the solvent contained in the polymeric solution in specific machines that treat the polymer in continuous solid phase or in the
25 form of granules, as described, for example, in American patents US 4,909,989, US 5,283,021, US 5,478,509, US 6,150,498, or in American patent application US 2006/193197.

The "Traditional Technology" generally comprises a

first section ("steam stripping") and a second section (drying).

In the first section, the polymeric solution is fed to a stripper containing water (water bath) to which a stream of water vapour is also fed. An aliquot of the water vapour condenses providing the heat necessary for the evaporation of the solvent: a suspension of lumps of polymer in water is obtained, with a sufficiently low residual content of solvent. Furthermore, in said first section, the use is envisaged of a dispersant system, in order to avoid the cohesion of the polymer lumps and to maintain the suspension in a stable form which allows it to be pumped.

In the second section, the polymer lumps are dried (elimination of the water contained in the lumps) through mechanical removal (squeezing) followed by evaporation of the water. These two operations, i.e. mechanical removal and evaporation, are generally carried out in two different extruders. The first extruder compresses the lumps of polymer, allowing the outflow of water in liquid form, whereas the second extruder allows the evaporation of the residual water as, due to dissipation of mechanical energy, the temperature of the polymeric phase increases, allowing, in suitable degassing areas, the "flash" of water in the form of vapour.

In short, the "Traditional Technology" provides a first step in which the solvent is removed by evaporation through the use of water vapour, and a

second step, in which said water is removed in both liquid phase, by squeezing, and in vapour phase, through the energy provided by mechanical dissipation.

As mentioned above, the "Traditional Technology" therefore provides feeding the polymeric solution and vapour to a stripper containing water (water bath). The evaporation of the solvent, however, can cause the formation of lumps of polymer which still contain a certain amount of solvent. Consequently, in the "Traditional Technology" the polymer is discharged as "slurry", i.e. lumps suspended in water.

In order to prevent blockages and obstructions of the stripper and discharge lines, and also of the extruders used for the drying, it is therefore fundamental to guarantee the correct dimension of the polymer lumps and to avoid the possibility of their agglomeration. In order to avoid these phenomena, the "Traditional Technology" provides the addition of a dispersant system to the water contained in the stripper, which is aimed at reducing the possibility of agglomeration. In the case of styrene copolymers, such as styrene-butadiene (SB) copolymers or styrene-butadiene-styrene (SBS) copolymers, or polybutadiene (BR), for example, a dispersant system is generally used comprising an organic dispersant (e.g. Sopropo[®] T 36 of Rhone-Poulenc, Geropon[®] T/36 of Rodhia, Orotan[®] 731K of Rhom & Haas) and calcium chloride, whereas in the case of olefinic copolymers such as, for example, ethylene-propylene (EP) copolymers or ethylene-

propylene-diene (EPDM) copolymers, talc in dispersion is used.

The use of said dispersant systems, however, can cause various drawbacks. The use of the organic dispersants mentioned above and calcium chloride, for example, can cause localized corrosion phenomena in the stripper due to the presence of free chlorides and can worsen the quality of the end-product as it can confer a certain alkalinity to the polymer obtained, thus favouring the development of undesired colourings in the final product.

The "Direct Devolatization" process, on the contrary, provides feeding the polymeric solution to a machine capable of supplying the process with the energy necessary for the evaporation of the solvent through heat exchange to the wall and dissipation of mechanical energy. These machines are capable of treating extremely viscous fluids, semi-solids, in which the mixing system, by exploiting the same viscosity of the polymeric phase, is the means through which the mechanical friction energy is dissipated as heat supplied to the polymeric phase which allows the evaporation of the solvent.

For this type of process, the contribution to the energy balance is given by the exchange of heat through the wall of the machine which, the higher the viscosity of the product (i.e. the lower the concentration of the residual solvent), the more the heat exchange will be reduced.

As the coefficients of heat exchange through the walls are low, acceptable results can be obtained by using machines having small dimensions, whereas for machines having industrial dimensions (with a reduced
5 ratio surface/volume) there is a substantial marginality of the contribution of exchange to the wall.

Said "Direct Devolatization" minimizes the energy necessary for the removal of the solvent by
10 evaporation, as only the vaporization energy of the solvent is supplied to the process, together with a small amount of sensitive heat linked to the heating of the polymeric phase. This energy, however, is supplied to the system mainly as dissipation of mechanical
15 energy, i.e. as consumption of the electric energy used for the activation of the motor of the mixing system of the machine.

The cost of electric energy is, at an equal energy used in the process, higher than that of vapour.
20 Starting from this consideration, it can be demonstrated that the minimization of the energy used in the "Direct Devolatization" process does not minimize the cost of the energy itself.

The Applicant has therefore considered the problem
25 of finding a process for the removal of the solvent from a polymeric solution, in particular from a polymeric solution comprising at least one elastomeric polymer, capable of overcoming the drawbacks mentioned above.

The Applicant has now found that the removal of the solvent from a polymeric solution can be advantageously carried out, by subjecting said polymeric solution to a stripping step by means of water vapour, in the presence of a dispersant system including at least one lamellar material and at least one cationic surfactant. Said process allows to avoid both the above-mentioned corrosion phenomena, and also the presence of colouring in the end-product. Furthermore, said process allows much lower amounts of compounds present in the dispersant system (i.e. lamellar material and cationic surfactant) to be used, than the amounts of compounds present in the dispersant system known in the art described above (i.e. organic dispersant and calcium chloride). Said process, moreover, allows lumps of polymer to be obtained, having a good compromise between apparent density and average dimension, thus avoiding problems of overheating or even self-triggering of the polymer itself during the drying of the lumps which normally takes place in one or more extruders, in addition to deterioration of the end-product.

An object of the present invention therefore relates to a process for the removal of the solvent from a polymeric solution including at least one elastomeric polymer, which comprises subjecting said polymeric solution to a stripping step by means of water vapour, in the presence of a dispersant system including:

- from 0.005% by weight to 1% by weight, preferably from 0.008% by weight to 0.8% by weight, with respect to the total weight of the dry elastomeric polymer, of at least one lamellar material;
- from 0.0005 by weight to 1% by weight, preferably from 0.0008% by weight to 0.8% by weight, with respect to the total weight of the dry elastomeric polymer, of at least one cationic surfactant.

For the purposes of the present description and of the following claims, the definitions of the numerical ranges always include the extremes, unless otherwise specified.

According to a preferred embodiment of the present invention, said elastomeric polymer can be selected from: polybutadiene (BR); polyisoprene (IR); unsaturated styrene copolymers with a random, block, tapered distribution, linear or branched such as, for example, styrene-butadiene (SB) copolymers, styrene-butadiene-styrene (SBS) copolymers, styrene-isoprene-styrene (SIS) copolymers; saturated styrene copolymers, with a random, block, tapered distribution, linear or branched such as styrene-ethylene-propylene (SEP) copolymers, styrene-ethylene/butylene-styrene (SEBS) copolymers, styrene-ethylene-propylene-styrene (SEPS) copolymers; or mixtures thereof. Styrene-butadiene (SB) copolymers and styrene-butadiene-styrene (SBS) copolymers, are preferred.

According to a preferred embodiment of the present invention, said polymeric solution comprises at least one non-polar organic solvent which can be selected, for example, from: butane, pentane, cyclopentane, 5 hexane, benzene, toluene, cyclohexane, methylcyclohexane, chlorobenzene, or mixtures thereof. Hexane, cyclohexane, or mixtures thereof, are preferred.

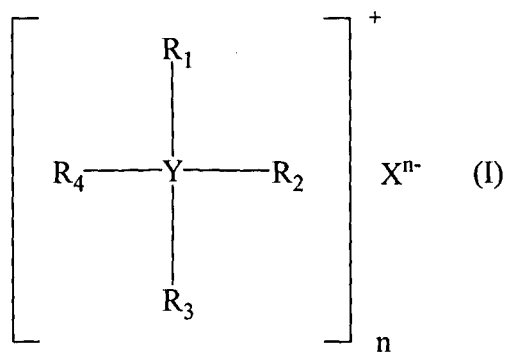
According to a preferred embodiment of the present 10 invention, said elastomeric polymer is present in said polymeric solution in a quantity ranging from 2% by weight to 30% by weight, more preferably ranging from 5% by weight to 20% by weight, with respect to the total weight of the polymeric solution.

15 According to a preferred embodiment of the present invention, said lamellar material has lamellas having a thickness ranging from 0.01 nm to 30 nm, preferably ranging from 0.2 nm to 15 nm, even more preferably ranging from 0.5 nm to 2 nm.

20 According to a preferred embodiment of the present invention, said lamellar material can be selected, for example, from phyllosilicates such as: smectites, for example montmorillonite, bentonite, nontronite, beidellite, volkonskoite, hectorite, saponite, 25 sauconite, magadite, stevensite, or mixtures thereof; vermiculite; halloysite; sericite; aluminate oxides; hydrotalcite; or mixtures thereof. Montmorillonite is preferred. Said lamellar material normally contains interchangeable cations, such as, for example, sodium

(Na⁺), calcium (Ca²⁺), potassium (K⁺), or magnesium (Mg²⁺), present on the surface of the lamellae.

According to a further preferred embodiment of the present invention, said lamellar material can be modified with alkyl ammonium or alkyl phosphonium salt, which can be selected, for example, from quaternary ammonium or phosphonium salts having general formula (I):



wherein:

- Y represents N or P;
- R₁, R₂, R₃ and R₄, equal to or different from each other, represent a linear or branched C₁-C₂₀ alkyl or hydroxyalkyl group; a linear or branched C₂-C₂₀ alkenyl or hydroxyalkenyl group; a group -R₅-SH or -R₅-NH wherein R₅ represents a linear or branched C₁-C₂₀ alkylene group; a C₆-C₁₈ aryl group; a C₇-C₂₀ arylalkyl or alkylaryl group; a C₅-C₁₈ cycloalkyl group; said cycloalkyl group optionally containing heteroatoms such as, for example, oxygen, nitrogen, sulfur;
- Xⁿ⁻ represents an anion such as, for example, a chloride ion, a sulfate ion, a phosphate ion;

- n represents 1, 2 or 3.

Said ammonium or phosphonium salt can be subjected to an ion exchange reaction with the ions which, as described above, are present on the surfaces of the lamellar materials.

If a lamellar material modified with at least one alkyl ammonium or alkyl phosphonium salt is used, its modification can be carried out by treating said lamellar material with at least one alkyl ammonium or alkyl phosphonium salt, before being used in the above-mentioned stripping step.

The treatment of the lamellar material with at least one alkyl ammonium salt or with at least one alkyl phosphonium salt, can be carried out according to methods known in the art, such as, for example, through an ion exchange reaction between the lamellar material and at least one ammonium alkyl or phosphonium alkyl salt: further details relating to this treatment can be found, for example, in American patents US 4,136,103, US 5,747,560, or US 5,952,093.

Alternatively, a lamellar material can be used, already modified with at least one ammonium alkyl or phosphonium alkyl salt which can be selected from modified lamellar materials present on the market.

Examples of lamellar materials which can be used for the purposes of the present invention and which are available on the market are the products known under the name of Dellite® LFV, Dellite® HPS, Dellite® 67G, Dellite® 72T, Dellite® 43B, of Laviosa Chimica Mineraria

S.p.A.; Cloisite® Na, Cloisite® 25A, Cloisite® 10A, Cloisite® 15A, Cloisite® 20A, of Southern Clays; Nanofil® 8, Nanofil® 9, of Süd Chemie; Bentonite® AG/3, of Dal Cin S.p.A.

5 In order to improve the activity of the lamellar material in said stripping step, said lamellar material can be subjected to a previous delamination treatment.

According to a preferred embodiment of the present invention, said lamellar material can be subjected to a
10 delamination step.

Preferably, said delamination step can be carried out by subjecting an aqueous solution of said lamellar material to stirring in a mixer or centrifuge. Said aqueous solution preferably comprises from $2.5 \times 10^{-5}\%$ by
15 weight to $5 \times 10^{-3}\%$ by weight, more preferably from $4 \times 10^{-5}\%$ by weight to $4 \times 10^{-3}\%$ by weight, of lamellar material with respect to the total weight of the aqueous solution. Preferably, said delamination step can be carried out at a rate ranging from 1,000 rpm to 20,000
20 rpm, more preferably ranging from 5,000 rpm to 10,000 rpm, at a temperature ranging from 10°C to 40°C, more preferably ranging from 15°C to 25°C, for a time ranging from 10 minutes to 3 hours, more preferably ranging from 30 minutes to 1 hour.

25 According to a preferred embodiment of the present invention, said cationic surfactant can be selected from ammonium alkyl or phosphonium alkyl salts having general formula (I) described above.

Examples of ammonium alkyl or phosphonium alkyl

salts which can be used in accordance with the present invention and which are available on the market, are the products known under the name of Arquad® HC Pastilles, Arquad® T-50, Arquad® 2HT-75, Arquad® MC-50, 5 Duoquad® T50, of Akzo Nobel, or Bardac® LF 70 of Lonza.

At the end of said stripping step, the lumps of elastomeric polymer obtained are subjected to a drying step which can be carried out, for example, by means of one or more extruders.

10 Said stripping step, in addition to said drying step, are carried out using operative conditions known in the art with respect to the above-mentioned "Traditional Technology": further details can be found, for example, in American patents US 3,337,422, US 15 3,462,347 or US 4,278,506, mentioned above.

The present invention will now be illustrated in greater detail by means of an illustrative embodiment with reference to Figure 1 indicated hereunder.

Figure 1 illustrates a first embodiment of the 20 process, object of the present invention.

As represented in Figure 1, demineralized water (2) is fed to the stripper (6), equipped with a mechanical stirrer (not represented in Figure 1), preferably until a third of its theoretical capacity is reached. The 25 stirrer of the stripper (6) is then activated and water vapour (3) is fed at such a flow-rate as to bring the temperature of the water to a value lower than or equal to 95°C, to prevent premature boiling of the water.

The lamellar material (4), for example Dellite® LVF

previously subjected to delamination, the cationic surfactant (5), for example Arquad® T-50, and the polymeric solution (1), for example a solution of styrene-butadiene-styrene (SBS) copolymer (Europrene®
5 SOL T161B of Polimeri Europa) in cyclohexane, are subsequently fed, in sequence, to the stripper (6): at this point the flow-rate of the water vapour (3) is increased, thus bringing the temperature of the water to a value lower than or equal to 98°C. Said polymeric
10 solution (1), can come directly from the production plant of the polymer (not represented in Figure 1).

The vapours produced during the mixing in the stripper (6), essentially comprising non-condensed water vapour and vapours of the solvent (7), are
15 discharged through a valve present in the head of the stripper (6) (not represented in Figure 1) and sent to the condenser (12). The aqueous phase comprising condensed water vapour and condensed solvent (13), leaving the condenser (12), is sent to the decanter
20 (14) from which a stream of water (15) together with a stream of solvent (16) are recovered which are sent for further treatments (not illustrated in Figure 1). The solvent obtained from said further treatments can optionally be anhydrified on an anhydrification column
25 and can be re-used in the polymerization process (e.g., it can be re-sent, optionally with the addition of fresh solvent, to the production plant of the polymer).

The polymeric solution (8), comprising the lumps of elastomeric polymer and water, leaves the bottom of the

stripper (6), through a valve (not represented in Figure 1), and is sent to a filter (9) from which a stream of water (10), which is sent to a specific sewer, or for further treatments (not illustrated in Figure 1), or it can be re-used in the process (i.e. it can be sent to the stripper (6)], and the lumps of the elastomeric polymer (11) that are sent to the drying step, for example, to one or more extruders (not represented in Figure 1), are recovered.

Some illustrative and non-limiting examples are provided hereunder for a better understanding of the present invention and for its embodiment.

EXAMPLES

The characterization and analysis techniques indicated hereunder were used.

Apparent density

The apparent density was obtained by filling a 2000 ml cylinder with a known volume of dried lumps of elastomeric polymer, weighing the mass, obtaining the total mass and subtracting the mass of the cylinder from the total mass. Three measurements were carried out: the above cylinder was filled with 1000 ml, with 1500 ml and with 2000 ml and the apparent density value is the average quantity weighed of the three values obtained.

Average particle-size (D50)

The average particle-size (D50) was obtained by measuring with a gauge, a representative quantity of dried polymer lumps for each test, i.e. 100 g.

EXAMPLE 1

0.1 g of Dellite® LVF (montmorillonite belonging to the family of smectites of Laviosa Chimica Mineraria S.p.A.) and 1 l of demineralized water, were introduced
5 into an Ultraturax mixer: the whole mixture was put, under stirring, at 1,000 rpm, at room temperature (25°C), for 30 minutes.

0.01 g of Arquad® T-50 (trimethylammonium chloride tallow of Akzo Nobel) were dissolved in 500 ml of
10 demineralized water.

17 l of demineralized water were fed to a 50 l stripper, equipped with a mechanical stirrer. The mechanical stirrer of the stripper was then activated at a rate of 600 rpm and water vapour was fed at such a
15 flow-rate as to bring the temperature of the water to 95°C. 2 l of the solution of Dellite® LVF obtained as described above (concentration of Dellite® LVF in the stripper equal to 0.01% by weight with respect to the total weight of the dry styrene-butadiene-styrene (SBS)
20 copolymer), 0.51 l of the solution of Arquad® T-50 obtained as described above ((concentration of Arquad® T-50 in the stripper equal to 0.001% by weight with respect to the total weight of the dry styrene-butadiene-styrene (SBS) copolymer), 7.5 kg of a
25 polymeric solution, in cyclohexane, containing 13% by weight with respect to the total weight of said polymeric solution of styrene-butadiene-styrene (SBS) copolymer (Europrene® SOL T161B of Polimeri Europa), were subsequently fed in sequence, at a flow-rate equal

to 6 kg/h: at this point, the flow-rate of the water vapour was increased thus bringing the temperature of the water to 98°C.

The vapours produced during the mixing, essentially
5 comprising non-condensed water vapour and vapours of cyclohexane, were discharged through a valve present in the head of the stripper and sent to a condenser. The aqueous phase comprising condensed water vapour and condensed cyclohexane, leaving the condenser, was sent
10 to a decanter in which a stream of water and a stream of cyclohexane are separated, which are sent for further treatments.

At the end of the feeding of the above polymeric solution, the valve was opened on the bottom of the
15 stripper and the polymeric solution comprising lumps of styrene-butadiene-styrene (SBS) copolymer and water, leaving the bottom of the stripper, was sent to a filter from which a stream of water which was sent to a specific sewer, together with lumps of styrene-
20 butadiene-styrene (SBS) copolymer which were sent to the drying step, were recovered.

The lumps of styrene-butadiene-styrene (SBS) copolymer obtained, after being sent to the drying step, were subjected to measurement of the apparent
25 density and of the average particle-size operating as described above. The results obtained are the following:

- apparent density: 93.2 g/l;
- average particle diameter: 1 cm.

EXAMPLE 2 (comparative)

17 l of demineralized water were fed to a 50 l
stripper equipped with a mechanical stirrer. The
mechanical stirrer of the stripper was then activated
5 at a rate of 600 rpm and water vapour was fed. 0.5 l of
an aqueous solution containing 1.5 g of the dispersant
Sopropon® T 36 (concentration of Sopropon® T 36 in the
stripper equal to 0.15% by weight with respect to the
total weight of the dry styrene-butadiene-styrene (SBS)
10 copolymer), 0.5 l of an aqueous solution containing
0.15 g of calcium chloride (concentration of calcium
chloride in the stripper equal to 0.015% by weight with
respect to the total weight of the dry styrene-
butadiene-styrene (SBS) copolymer), 7.5 kg of a
15 polymeric solution, in cyclohexane, containing 13% by
weight with respect to the total weight of said
polymeric solution of styrene-butadiene-styrene (SBS)
copolymer (Europrene® SOL T161B of Polimeri Europa),
were subsequently fed in sequence, at a flow-rate equal
20 to 6 kg/h: at this point, the flow-rate of the water
vapour was increased thus bringing the temperature of
the water to 98°C.

The vapours produced during the mixing, essentially
comprising non-condensed water vapour and vapours of
25 cyclohexane, were discharged through a valve present in
the head of the stripper and sent to a condenser. The
aqueous phase comprising condensed water vapour and
condensed cyclohexane, leaving the condenser, was sent
to a decanter in which a stream of water and a stream

of cyclohexane are separated, which are sent for further treatments.

At the end of the feeding of the above polymeric solution, the valve was opened on the bottom of the stripper and the polymeric solution comprising lumps of styrene-butadiene-styrene (SBS) copolymer and water, leaving the bottom of the stripper, was sent to a filter from which a stream of water which was sent to a specific sewer, together with lumps of styrene-butadiene-styrene (SBS) copolymer which were sent to the drying stepm, were recovered.

The lumps of styrene-butadiene-styrene (SBS) copolymer obtained, after being sent to the drying step, were subjected to measurement of the apparent density and of the average particle-size operating as described above. The results obtained are the following:

- apparent density: 96.2 g/l;
- average particle diameter: 1 cm

From the data reported above, it can be deduced that the apparent density and the average particle diameter of the lumps of styrene-butadiene-styrene (SBS) copolymer have values similar to those obtained in Example 1 (invention) having used, however, a quantity of compounds, i.e. Sopropo[®]n T 36 and calcium chloride, an order of magnitude higher.

CLAIMS

1. A process for the removal of the solvent from a polymeric solution including at least one elastomeric polymer, which comprises subjecting said polymeric solution to a stripping step by means of water vapour, in the presence of a dispersant system comprising:
- 5
- from 0.005% by weight to 1% by weight with respect to the total weight of the dry elastomeric polymer of at least one lamellar material;
 - 10 - from 0.0005% by weight to 1% by weight with respect to the total weight of the dry elastomeric polymer of at least one cationic surfactant.
2. The process for the removal of the solvent from a polymeric solution according to claim 1, wherein said dispersant system comprises from 0.008% by weight to 0.8% by weight with respect to the total weight of the dry elastomeric polymer of at least one lamellar material.
- 15
3. The process for the removal of the solvent from a polymeric solution according to claim 1 or 2, wherein said dispersant system comprises from 0.0008% by weight to 0.8% by weight with respect to the total weight of the dry elastomeric polymer of at least one cationic surfactant.
- 20
4. The process for the removal of the solvent from a polymeric solution according to any of the previous claims, wherein said elastomeric polymer is selected from: polybutadiene (BR); polyisoprene (IR); unsaturated styrene copolymers with a random, block,
- 25

tapered distribution, linear or branched such as styrene-butadiene (SB) copolymers, styrene-butadiene-styrene (SBS) copolymers, styrene-isoprene-styrene (SIS) copolymers; saturated styrene copolymers, with a
5 random, block, tapered distribution, linear or branched such as styrene-ethylene-propylene (SEP) copolymers, styrene-ethylene/butylene-styrene (SEBS) copolymers, styrene-ethylene-propylene-styrene (SEPS) copolymers; or mixtures thereof.

10 5. The process for the removal of the solvent from a polymeric solution according to any of the previous claims, wherein said polymeric solution comprises at least one non-polar organic solvent which is selected from: butane, pentane, cyclopentane, hexane, benzene,
15 toluene, cyclohexane, methylcyclohexane, chlorobenzene, or mixtures thereof.

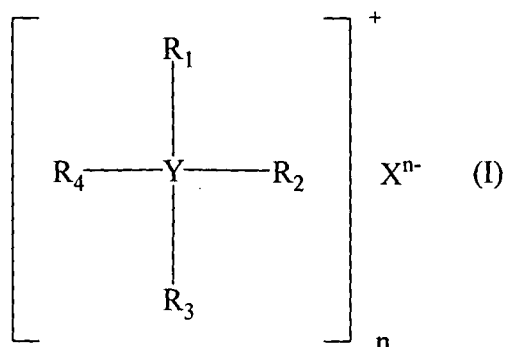
6. The process for the removal of the solvent from a polymeric solution according to any of the previous claims, wherein said elastomeric polymer is present in
20 said polymeric solution in a quantity ranging from 2% by weight to 30% by weight with respect to the total weight of the polymeric solution.

7. The process for the removal of the solvent from a polymeric solution according to any of the previous
25 claims, wherein said lamellar material has lamellae having a thickness ranging from 0.01 nm to 30 nm.

8. The process for the removal of the solvent from a polymeric solution according to any of the previous claims, wherein said lamellar material is selected from

phyllosilicates such as: smectites, such as montmorillonite, bentonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite, magadite, stevensite, or mixtures thereof; vermiculite; halloysite; sericite; aluminate oxides; hydrotalcite; or mixtures thereof.

9. The process for the removal of the solvent from a polymeric solution according to claim 8, wherein said lamellar material is modified with an alkyl ammonium or alkyl phosphonium salt which is selected from quaternary ammonium or phosphonium salts having general formula (I):



wherein:

- 15 - Y represents N or P;
- R₁, R₂, R₃ and R₄, the same or different, represent a linear or branched C₁-C₂₀ alkyl or hydroxyalkyl group; a linear or branched C₂-C₂₀ alkenyl or hydroxyalkenyl group; a group -R₅-SH or -R₅-NH
- 20 wherein R₅ represents a linear or branched C₁-C₂₀ alkylene group; a C₆-C₁₈ aryl group; a C₇-C₂₀ arylalkyl or alkylaryl group; a C₅-C₁₈ cycloalkyl group; said cycloalkyl group optionally containing

heteroatoms such as oxygen, nitrogen, sulfur;

- X^{n-} represents an anion such as a chloride ion, a sulfate ion, a phosphate ion;
- n represents 1, 2 or 3.

5 10. The process for the removal of the solvent from a polymeric solution according to any of the previous claims, wherein said lamellar material is subjected to a delamination step.

10 11. The process for the removal of the solvent from a polymeric solution according to claim 10, wherein said delamination step is carried out by subjecting an aqueous solution of said lamellar material to stirring in a mixer, or in a centrifuge, at a rate ranging from 1,000 rpm to 20,000 rpm, at a temperature ranging from
15 10°C to 40°C, for a time ranging from 10 minutes to 3 hours.

12. The process for the removal of the solvent from a polymeric solution according to claim 11, wherein said aqueous solution comprises from $2.5 \times 10^{-5}\%$ by weight to
20 $5 \times 10^{-3}\%$ by weight of lamellar material with respect to the total weight of the aqueous solution.

13. The process for the removal of the solvent from a polymeric solution according to any of the previous claims, wherein said cationic surfactant is selected
25 from alkyl ammonium or alkyl phosphonium salts having general formula (I) according to claim 9.

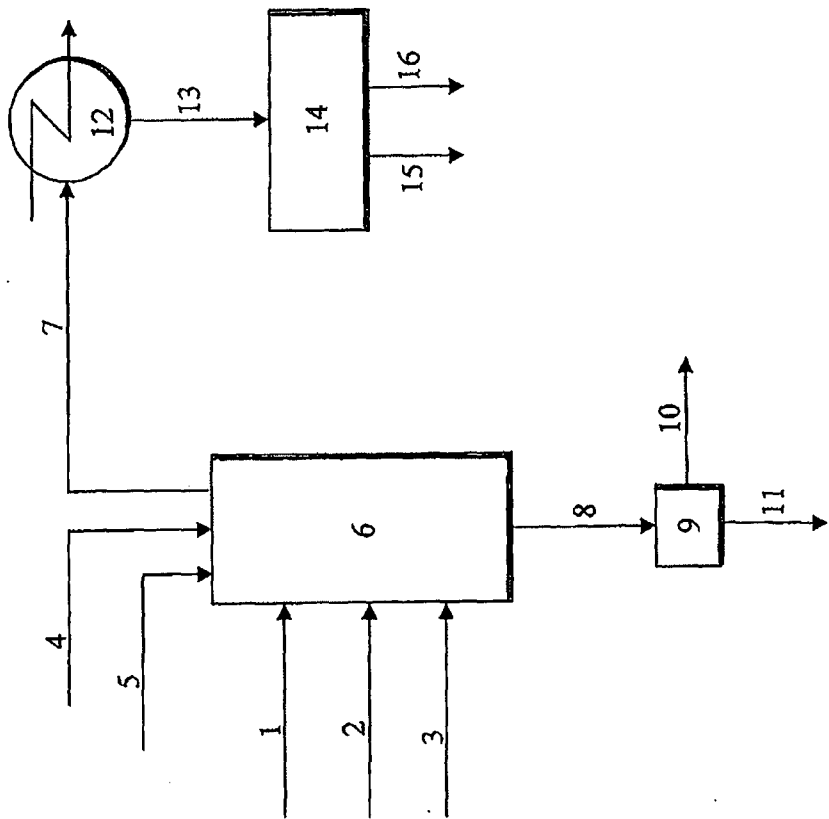


Fig.1

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2012/056680

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F6/10 C08C2/00 C08C2/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F C08C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| A | GB 1 374 709 A (MONTEDISON SPA) 20 November 1974 (1974-11-20) claims 1-3 | 1-13 |
| | ----- | |
| A | CN 100 457 814 C (CHINA GEOLOGY UNIV BEIJING [CN] UNIV CHINA GEOSCIENCES WUHAN [CN]) 4 February 2009 (2009-02-04) claims 1-3 | 1-13 |
| | ----- | |



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

20 March 2013

Date of mailing of the international search report

26/03/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Gold, Josef

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2012/056680

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|---|---|---------------------|----------------------------|---------------------|
| GB 1374709 | A | 20-11-1974 | FR 2138044 A1 | 29-12-1972 |
| | | | GB 1374709 A | 20-11-1974 |
| | | | NL 7206590 A | 21-11-1972 |
| ----- | | | | |
| CN 100457814 | C | 04-02-2009 | NONE | |
| ----- | | | | |