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MAGYARORSZÁG
Szellemi Tulajdon Nemzeti Hivatala

EURÓPAI SZABADALOM
SZÖVEGÉNEK FORDÍTÁSA

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(72) Feltaláló(k):
NEUNER, Thomas-Oliver, 40721 Hilden (DE)
STANGE, Heiner, 51379 Leverkusen (DE)
JOSTEN, Rolf, 41469 Neuss (DE)
FELLER, Rolf, 40822 Mettmann (DE)
FIDAN, Mesut, 41539 Dormagen (DE)

(73) Jogosult(ak):
ARLANXEO Deutschland GmbH, 41540 Dormagen (DE)

(74) Képviselő:
Danubia Szabadalmi és Jogi Iroda Kft., Budapest

(54) **Eljárás szilárd polikloroprén kinyerésére és izolálására**

Method for obtaining and isolating polychloroprene solids

The invention relates to a process for obtaining and isolating polychloroprene solids based on rubber dispersions, and to the resultant polychloroprene solids.

The production of polychloroprene has been known for a long time. Free-radical emulsion polymerization of chloroprene (2-chloro-1,3-butadiene) produces latices made of polychloroprene. For the purposes of this application, the expression "polychloroprene latices" and "polychloroprene dispersions" are also used for said latices.

In the production process, the monomers are polymerized in an emulsion system in an aqueous medium. This is generally of anionic type, and use is also rarely made of nonionic or cationic systems. The temperature range within which the polymerization is carried out comprises values of about 0°C as far as above 80°C. The polymerization can therefore be initiated via free-radical generators that decompose thermally or via redox systems. Use is generally also made of molecular-weight regulators, such as mercaptans or xanthogen disulfides. In some cases, the molecular weight of the final product is also adjusted via copolymerization with sulfur and subsequent cleavage of the resultant sulfidic bonds. The desired conversion is established via termination of the reaction with a suitable reagent.

In the vast majority of cases, the resultant dispersion of polychloroprene in water is then demonomerized by passing water vapor through the material. Some of the resultant product here finds direct use in the form of latex in industry, but the greater part is freed from adherent water via coagulation and passed in the form of solid product to its final use.

Features of polychloroprene solids (known as "CR solids"), and also of vulcanizates produced therefrom, given appropriate mixture composition, are high resistance to weathering and to ozone, flame retardancy, very good aging properties, moderate oil resistance, and also considerable ability to resist many chemicals. They have good mechanical properties, advantageous resilience, and high wear resistance.

With respect to resilience, tensile strength, elongation at break, and modulus, vulcanizates made of polychloroprene latices (CR latices) exhibit values which are very similar to those of natural-latex vulcanizates, while vulcanizates made of polychloroprene latices at the same time exhibit good resistance to solvents, to chemicals, to oils and to fats.

As mentioned above, the separation of the CR solid from the dispersion is usually achieved via coagulation. Many different processes are known for this purpose. Mixing of the polychloroprene latices with a coagulating agent breaks the emulsion. Any conventional coagulating agent can be used for this purpose: by way of example, acidification, for example with a mineral acid or with an organic acid, can be used to coagulate the solid from CR latices produced under alkaline conditions. In many cases, simple acidification is not sufficient for complete coagulation of the polychloroprene, and it is also necessary to add strong electrolytes (salts comprising polyvalent cations, such as Mg^{2+}, Ca^{2+}, or Al^{3+}) in addition to the acid.

This method is disadvantageous because of the large amount of acid and, respectively, electrolytes needed in order to achieve complete precipitation of the solid. Relatively large amounts of precipitate remain within the product here, and this can impair important product properties. The coagulated solid is therefore washed with relatively large amounts of water in order to remove the precipitate, and this leads to economic and environmental problems. Furthermore, some of the polychloroprene is produced in the form of large clumps which in their interior still comprise unprecipitated CR latex or excess precipitate.

The prior art also discloses coagulation permitted via exposure to relatively high temperatures and/or to increased pressures, and also via additional exposure to electrolytes and to shear forces. A product of this type is exposed to considerable thermal stress, and this impairs product properties.

The usual method for separating polychloroprene from aqueous dispersions is freeze separation. Freeze separation is achieved here via cooling below the freezing point of

the aqueous phase of the CR latex. Subsequent thawing under suitable conditions gives the polychloroprene in the form of coagulate which can be separated from the aqueous phase.

In order to arrive at coagulation rates that are sufficiently high for industrial purposes, freeze separation of the CR latex in carried out in thin layers. To this end, internally coolable coagulation rolls have been developed which dip into the CR latex during rotation and thus during rotation pick up a thin latex layer and carry out freeze separation on the surface (US-B 2,187,146). The thin film made of CR coagulate and ice is scraped from the roll and passed onward.

There are other isolation processes known from the prior art. US 4,103,074 describes a process for coagulating a polymer latex using a screw extruder, where the polymer latex is coagulated during conveying within the channel of the screw.

US 3,926,877 describes a process for isolating a CR rubber where the CR latex is mixed with an aqueous carbon black dispersion before a coagulating agent is admixed with the latex. The coagulated product is separated from the aqueous phase.

DE 30 31 088 C2 discloses a process for producing a coagulated latex of a synthetic polymer where a gaseous or liquid coagulating agent is applied in the form of a mist by means of a spray nozzle to the polymer latex droplets so as to precipitate polymer beads.

US 3 437 509 A describes the coagulation of emulsions on porous substrates with steam comprising latex-destabilizing substances. There is no disclosure of coagulation for the production of polychloroprene solid.

US 4 539 396 A describes the coagulation of latex with steam and coagulant in the form of vapor or mist. Latex, coagulant and steam are sprayed simultaneously into a coagulation vessel. There is no description of the use of polychloroprene latex. The object, which is achieved via use of high temperatures, consists in the provision of round polymer particles.

EP 0 353 802 A describes the reclamation of rubber crumb produced by emulsion polymerization. Coagulation is achieved here by mechanical action rather than by contact with steam.

GB 1 397 658 A describes the coagulation of latex with steam. Before addition of the steam, a substance that destabilizes the latex can be added. The intention here is to maintain the concentration of precipitant below the threshold value at which spontaneous precipitation begins.

The best-known and most widely used process for isolating CR solids is the freeze-coagulation process. Said process has environmental and economic disadvantages, since the coagulate frozen on the roll is very difficult to separate from the roll. The iced coagulate has to be thawed again and freed from the emulsifier by using water, and this in turn is undesirable from an environmental point of view. The subsequent mechanical dewatering of the coagulate is also very energy-intensive and time-consuming. The final drying of the coagulate is usually achieved by using drying ovens in which the residual water present within the product is removed.

It is now an object of the invention to provide a process for obtaining and isolating polychloroprene solids which does not have the abovementioned disadvantages.

A process of the type mentioned in the introduction is proposed in order to achieve said object, where an aqueous polychloroprene dispersion is brought into contact with water vapor comprising coagulating agent, and the polychloroprene solid consequently coagulates.

In the process of the invention, it is preferable that the CR solid coagulates in the form of a strand or in the form of crumb.

Surprisingly, it has been found that the process of the invention can be used with all polychloroprene dispersions, irrespective of the conventional polymerization process used to produce same.

The process of the invention is more energy-efficient, uses less resources, and is therefore more environmentally compatible.

The precipitated polychloroprene solid is then separated from the coagulation suspension and is then preferably dewatered in a dewatering apparatus. An example of equipment that can be used here is a screw-based strainer or dewatering rolls. Other known dewatering apparatuses can likewise be used.

The dewatered polychloroprene solid is then dried by means of a drying apparatus. The drying apparatus involves by way of example a twin-screw extruder, a screw-based dryer, or a kneader dryer. In the drying apparatus, additives and/or inert materials can preferably be added. By this means the other properties of the polychloroprene solid of the invention can be influenced in ideal manner for any requirement, and this can also be achieved after work-up. Preferred examples of additives for influencing product properties are stabilizers, accelerators, emulsifiers, liquors, antioxidants, and viscosity-influencing processing aids. Any conventional additives can be used. Examples of inert materials are nitrogen, argon, and carbon dioxide, where these can be added in order to influence polymer melting points.

The polychloroprene solid of the invention is preferably pelletized and cooled by means of the underwater pelletization process.

The polychloroprene dispersion preferably involves a latex which has been produced by means of emulsion polymerization. The polymerization takes place at a polymerization temperature of from 5°C to 50°C. Conversion in the polymerization is usually in the range from 50% to 80%. After polymerization, excess monomer is removed by means of vacuum devolatilization to give a value in the range from 1000 ppm to 1 ppm. Emulsion polymerization processes are known from the prior art, and these can be used here.

It is optionally also possible to add one or more different comonomers, such as 2,3-dichlorobutadiene, alongside chloroprene (2-chloro-1,3-butadiene) for control of crystallization in the polymerization process.

The solids content of the polychloroprene dispersion from which the CR solid of the invention is obtained is preferably from 20 to 45% by weight, and the gel content of said dispersion is preferably in the range from 0 to 10% by weight. However, the gel content can also be increased in a controlled manner.

The water vapor comprising coagulating agent is preferably formed from water vapor and from an aqueous coagulating-agent solution. Coagulating-agent solution preferably used comprises an aqueous solution of a coagulating agent made of inorganic salts, preferably of metals of the second and third main group of the Periodic Table of the Elements.

Coagulating agent preferably used comprises calcium chloride, magnesium chloride, magnesium sulfate, aluminum chloride, and/or aluminum sulfate.

The coagulating-agent solution preferably has a coagulating-agent concentration of from 1% by weight to 60% by weight, preferably from 2% by weight to 55% by weight, particularly preferably from 10% by weight to 35% by weight, based on the coagulating-agent solution.

It is preferable that prior to contact with the water vapor comprising coagulating agent, the polychloroprene dispersion is diluted.

It is preferable here that the polychloroprene dispersion is diluted to a solids content of from 38% by weight to 45% by weight, preferably from 28% by weight to 35% by weight, and particularly preferably from 20% by weight to 28% by weight, based on the polychloroprene dispersion.

The dilution process preferably uses water, particularly demineralized water.

The dilution is important not only because the intention is to prevent or reduce caking and blocking of the flow/coagulation apparatus but also because it is possible to ensure ideal coagulation brought about via the contact between the CR dispersion and the water vapor comprising coagulating agent.

From 80 to 1000 kg of water vapor per metric ton of solid of the polychloroprene dispersion are particularly preferably used, preferably from 80 to 300 kg of water vapor per metric ton of solid of the polychloroprene dispersion.

From 10 to 40 kg of coagulating agent per metric ton of solid of the polychloroprene dispersion are moreover used, preferably from 10 to 25 kg of coagulating agent per metric ton of solid of the polychloroprene dispersion.

For the coagulation process, the aqueous polychloroprene dispersion passes through a flow/coagulation apparatus, where the flow/coagulation apparatus has apertures through which the water vapor comprising coagulating agent can pass and encounters the polychloroprene dispersion in the flow/coagulation apparatus. The polychloroprene solid of the invention coagulates here.

It is preferable that the polychloroprene solid is dewatered in the dewatering apparatus as far as a residual moisture level of from 10% by weight to 15% by weight, preferably from 1.0 % by weight to 9% by weight, based on the polychloroprene solid.

It is preferable that the dewatered polychloroprene solid is dried in the drying apparatus as far as a residual moisture level of from 1% by weight to 1.5% by weight, particularly preferably from 0.5% by weight to 1% by weight, and very particularly preferably from 0.1% by weight to 0.5% by weight, based on the dewatered polychloroprene solid.

At the end of the drying phase in the drying apparatus, the polychloroprene solid takes the form of rubber melt. The melt is discharged through a die, and is processed through a cutting apparatus, and cooled and transported by water in the underwater pelletization process.

It is preferable that a release agent is added to the water in the underwater pelletization process. Examples of release agents that can be used here are talc powder and metal stearates. Other conventional release agents can likewise be used.

The resultant polychloroprene solid can be used for producing vulcanizates, rubber mixtures, and adhesives, or adhesive raw materials.

The invention is explained in more detail below with reference to a drawing:

Process for isolating and obtaining a polychloroprene solid of the invention

Fig. 1 shows a diagram of the structure of a process of the invention.

A polychloroprene dispersion is first produced by a conventional process.

Production of a polychloroprene dispersion

A polychloroprene dispersion is produced with use of the main formulation mentioned below (data being in parts by weight per 100 parts by weight of chloroprene used):

125 pts. by wt.	of water
100 pts. by wt.	of chloroprene
3 pts. by wt.	of sodium salt of disproportionated abietic acid
0.5 pt. by wt.	of potassium hydroxide
0.2 pt. by wt.	of n-dodecyl mercaptan
0.5 pt. by wt.	of sodium salt of formaldehyde-condensed naphthalenesulfonic acid

The polychloroprene dispersion is produced via free-radical emulsion polymerization at from 40°C to 45°C from the abovementioned components by conventional methods (e.g. Ullmanns Encyclopedia of Industrial Chemistry, vol. 23A, pp. 252-262.). The

polymerization is terminated at a conversion of from 50% to 70%, and the dispersion is freed from residual monomers via vacuum devolatilization.

Said dispersion is worked up with the aid of the process of the invention, which can be described as follows:

The abovementioned polychloroprene dispersion is conveyed from a storage container 1 into a flow/coagulation apparatus 3. The polychloroprene dispersion can be diluted with water prior to input into the flow/coagulation apparatus 3.

The aqueous coagulating agent, which has been mixed in advance with water vapor, is introduced from another storage container 2 into the flow/coagulation apparatus 3, and by way of apertures therein is brought into contact with the polychloroprene dispersion. The polychloroprene dispersion here is quantitatively precipitated in the flow/coagulation apparatus 3 and in the precipitation tube 4 that follows.

The precipitation tube 4 leads to the intake region of the dewatering apparatus 5, where the precipitated polychloroprene solid of the invention is dewatered.

The dewatered polychloroprene solid either in the form of a strand or in the form of crumb is introduced into the drying apparatus 7 and is dried. Additives or inert materials can be metered into the material within the feed screw 6 or the subsequent region of the drying apparatus 7, in order to influence the properties of the polychloroprene solid of the invention.

The vapors are drawn off by way of evacuated upward protuberances 8, within which there are stuffing screws to ensure that rubber particles are retained. Beyond the upward protuberances 8 there are separators 9 in which entrained rubber particles are separated and then introduced into an extracted air scrubber 10.

The hot rubber melt from the drying apparatus 7 is chipped in the underwater pelletization process by way of a die and chopping blades. The cooling and the

transport of the chips is achieved by way of a stream 11 of water which optionally can have admixed additives (e.g. release agent).

The chips are first separated from the water by way of a sieve chute. The residual energy in the chips vaporizes the water adhering on the surface. This can be supplemented by a stream of warm air to promote removal of the adherent water.

The chips are then further cooled, and talc powder is optionally applied thereto. They are then weighed into sacks and packaged on pallets or in crates.

Szabadalmi igénypontok

1. Eljárás szilárd polikloroprén izolálására és kinyerésére, **azzal jellemezve**, hogy vizes polikloroprén--diszperziót érintkezésbe hozunk koagulánst tartalmazó vízgőzzel, ezáltal a szilárd polikloroprén koagulál.

2. Az 1. igénypont szerinti eljárás, **azzal jellemezve**, hogy a szilárd polikloroprént a koagulációs szuszpenziótól elválasztjuk.

3. A 2. igénypont szerinti eljárás, **azzal jellemezve**, hogy a szilárd polikloroprént egy víztelenítő berendezés alkalmazásával víztelenítjük.

4. A 3. igénypont szerinti eljárás, **azzal jellemezve**, hogy a víztelenített szilárd polikloroprént egy szárító berendezés alkalmazásával megszárítjuk.

5. A 4. igénypont szerinti eljárás, **azzal jellemezve**, hogy a víztelenített szilárd polikloroprénhez a szárítóberendezésben adalékot és/vagy közömbös anyagot adunk.

6. Az 5. igénypont szerinti eljárás, **azzal jellemezve**, hogy a megszárított víztelenített szilárd polikloroprént víz alatti granulálással granuláljuk és lehűtjük.

7. A 6. igénypont szerinti eljárás, **azzal jellemezve**, hogy a polikloroprén-diszperzió egy látex.

8. A 7. igénypont szerinti eljárás, **azzal jellemezve**, hogy a polikloroprén-diszperziót emulziós polimerizációval állítjuk elő.

9. A 8. igénypont szerinti eljárás, **azzal jellemezve**, hogy a koagulánst tartalmazó vízgőzt vízgőz és vizes koaguláns-oldat alkalmazásával állítjuk elő.

10. A 9. igénypont szerinti eljárás, **azzal jellemezve**, hogy koaguláns-oldatként szervetlen sókból (koagulánsból), előnyösen az elemek periódusos rendszerének második és harmadik főcsoportjába tartozó fémek sóiból előállított vizes oldatot alkalmazunk.

11. A 10. igénypont szerinti eljárás, **azzal jellemezve**, hogy koagulánsként kalcium-kloridot, magnézium-kloridot, magnézium-szulfátot, alumínium-kloridot és/vagy alumínium-szulfátot alkalmazunk.

12. A 11. igénypont szerinti eljárás, **azzal jellemezve**, hogy a koaguláns-oldat koaguláns koncentrációja 1 tömeg% és 60 tömeg% között van, előnyösen 2 tömeg% és 45 tömeg% között van, különösen előnyösen 10 tömeg% és 35 tömeg% között van a koaguláns-oldatra vonatkoztatva.

13. A 12. igénypont szerinti eljárás, **azzal jellemezve**, hogy a polikloroprén-diszperziót a koagulánst tartalmazó vizgőzzel való érintkeztetés előtt hígítjuk.

14. A 13. igénypont szerinti eljárás, **azzal jellemezve**, hogy a polikloroprén-diszperziót 38 tömeg% - 45 tömeg%, előnyösen 28 tömeg% - 35 tömeg% és különösen előnyösen 20 tömeg% - 28 tömeg% szilárdanyag--tartalomra hígítjuk a polikloroprén-diszperzióra vonatkoztatva.

15. A 9. igénypont szerinti eljárás, **azzal jellemezve**, hogy a polikloroprén-diszperzió szilárdanyag--tartalmának 1 tonnájára vonatkoztatva 80 kg – 1000 kg vizgőzt, előnyösen 80 kg – 250 kg vízgőzt alkalmazunk.

16. A 11. igénypont szerinti eljárás, **azzal jellemezve**, hogy a polikloroprén-diszperzió szilárdanyag--tartalmának 1 tonnájára vonatkoztatva 10-40 kg koagulánst, előnyösen 10 kg - 25 kg koagulánst alkalmazunk.

17. A 16. igénypont szerinti eljárás, **azzal jellemezve**, hogy a vizes polikloroprén-diszperzió átáramlik egy áramlásos/koagulációs berendezésen, amely áramlásos/koagulációs berendezésnek nyílásai vannak, amelyen a koagulánst tartalmazó vizgőz átjutva találkozik a polikloroprén-diszperzióval az áramlásos/koagulációs berendezésben.

18. A 3. igénypont szerinti eljárás, **azzal jellemezve**, hogy a víztelenítő berendezésben a szilárd polikloroprént 10 tömeg% - 15 tömeg%, előnyösen 1,0 tömeg% - 9 tömeg% maradék nedvességtartalomra víztelenítjük a szilárd polikloroprénre vonatkoztatva.

19. A 4. igénypont szerinti eljárás, **azzal jellemezve**, hogy a szárító berendezésben a víztelenített szilárd polikloroprént 1 tömeg% - 1,5 tömeg%, előnyösen 0,5 tömeg% - 1 tömeg%, különösen előnyösen 0,1 tömeg% - 0,5 tömeg% maradék nedvességtartalomra szárítjuk a víztelenített szilárd polikloroprénra vonatkoztatva.

20. A 19. igénypont szerinti eljárás, **azzal jellemezve**, hogy a megszárított szilárd polikloroprén a szárítóberendezésben a szárítási szakasz végén gumiömledék formájú.

21. A 20. igénypont szerinti eljárás, **azzal jellemezve**, hogy a víz alatti granulálás során a vízhez elválasztó anyagokat adunk.

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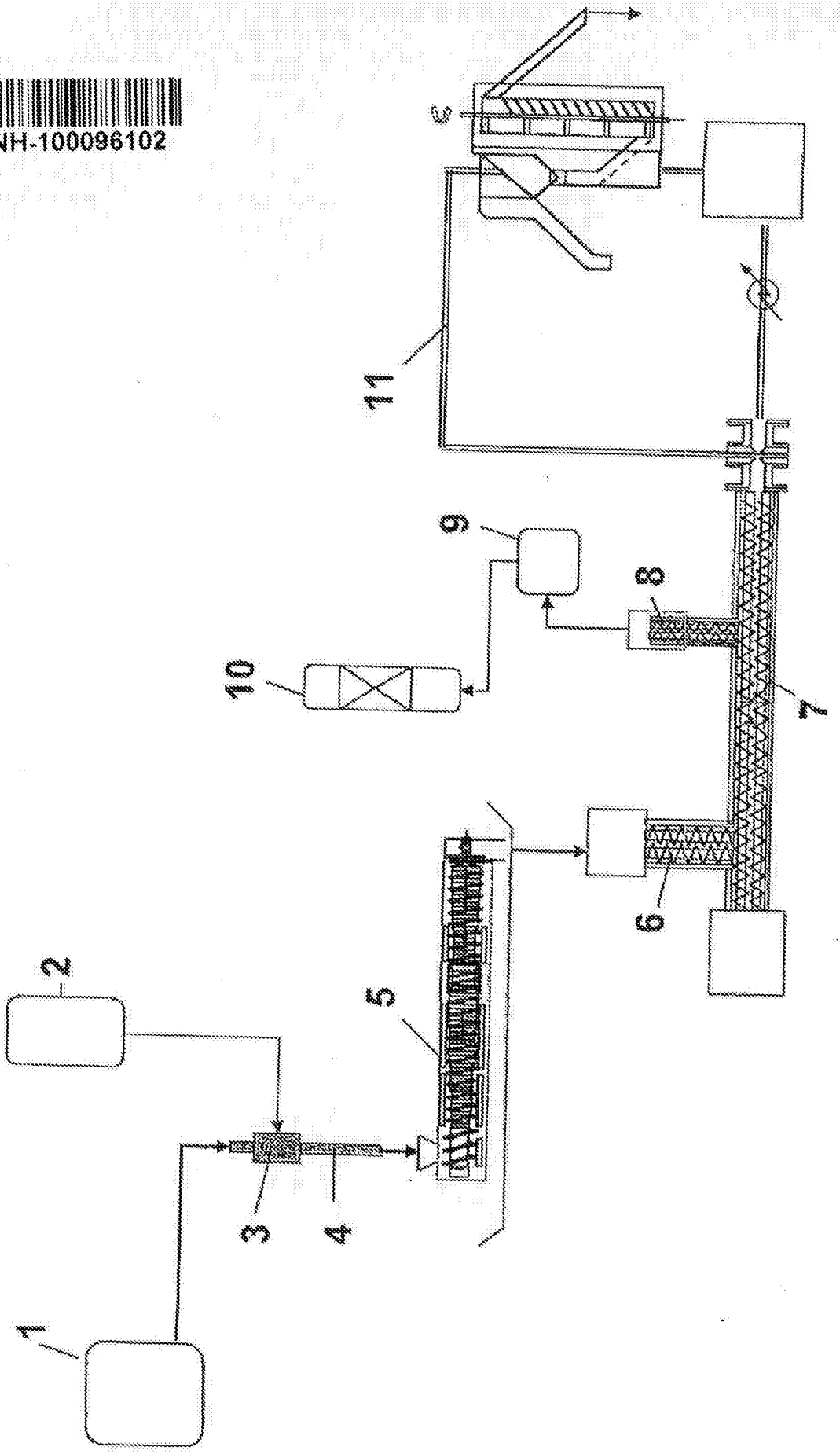

Fig. 1