

明細書

吸水性樹脂の製造方法

技術分野

本発明は、吸水性樹脂の製造方法、特に、水溶性エチレン性不飽和単量体を重合反応させることにより吸水性樹脂を製造する方法に関する。

背景技術

吸水性樹脂は、生理用品や紙おむつなどの衛生材用途、保水剤や土壤改良剤などの農園芸用途、或いは止水剤や結露防止剤などの工業資材用途などの広範な分野で利用されている。このうち、特に衛生材関連において吸水性樹脂がさかんに利用されている。これらの各種用途で用いられる吸水性樹脂は、通常、軽度に架橋された高分子樹脂であり、例えば、澱粉－アクリロニトリルグラフト共重合体の加水分解物（特公昭49－43395号）や澱粉－アクリル酸グラフト共重合体の中和物（特開昭51－125468号）などの澱粉系吸水性樹脂、酢酸ビニル－アクリル酸エステル共重合体のケン化物（特開昭52－14689号）およびポリアクリル酸部分中和物（特開昭62－172006号、特開昭57－158209号、特開昭57－21405号）などが知られている。

ところで、吸水性樹脂、特に衛生材用途に用いられる吸水性樹脂に求められる特性として、吸水量が大きく吸水速度が速いこと、吸水後のゲル強度が高いこと、並びに微粉が少なく粒度分布が狭いことなどが挙げられる。このうち、吸水速度は、衛生材などの用途において、パルプ材と複合化して吸水体を形成する場合、そのような吸水体に求められる特性、即ち、吸収した液体（被吸収液）の吸水体外部への逆戻り量が少ないこと、および吸収した液体の吸水体内部への拡散性を高めるのに影響を及ぼす重要な要因である。

例えば、上述の吸水体において、吸水速度が比較的遅い吸水性樹脂を用いた場合は、被吸収液の吸水体への拡散性は良好である。しかし、この場合は、吸水に長時間を要するため、吸水体に圧力が加わった際（例えば、当該吸水体が採用されたおむつをした乳児が排尿直後に座ったとき）に被吸収液の逆戻り量が多くなる。また、吸水体に対する被吸収液の供給速度が吸水性樹脂の吸水速度を上回る場合は、余剰の被吸収液が吸水体から漏れ出ることもある。

逆に、上述の吸水体において、吸水速度が比較的速い吸水性樹脂を用いた場合は、吸水体に対する被吸収液の供給位置付近で吸水性樹脂が被吸収液を局部的に吸収し、膨潤した吸水性樹脂がゲル化してブロッキングを起こすことが多い。この場合は、吸水体に対する被吸収液の拡散性がゲル化した吸水性樹脂により阻害され、被吸収液が吸水体全体に行き渡りにくくなるので、結果として被吸収液の逆戻り量が多くなる。

したがって、このような吸水体において、被吸収液の逆戻り量を低減させながら拡散性を高めるためには、初期の吸水速度が速く、その後は緩やかな吸水速度に変化し得る吸水性樹脂を用いる必要がある。このような特性を発揮し得る吸水性樹脂としては、吸水速度が速い吸水性樹脂と吸水速度が遅い吸水性樹脂とを混合したものが考えられる。しかし、このような吸水性樹脂は、粒径や嵩比重が異なる複数種の吸水性樹脂を混合することにより調製されるため、均一性に欠け、依然として上述の問題点を解決できるには至っていない。

本発明の目的は、吸水性樹脂について、被吸収液の逆戻り量を低減させながら、同時に被吸収液の拡散性を高めることにある。

また、本発明の目的は、特に衛生材用途に用いられる吸水性樹脂について、被吸収液の逆戻り量を低減させながら、同時に被吸収液の拡散性を高めることにある。

発明の開示

本発明に係る吸水性樹脂の製造方法は、水溶性エチレン性不飽和単

量体の重合反応により吸水性樹脂を製造するためのものである。この方法は、前記水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂の存在下で、前記水溶性エチレン性不飽和単量体を重合反応させる工程を含んでいる。

このような本発明の好ましい態様では、前記重合反応が逆相懸濁重合法により行なわれる。

本発明の他の観点による吸水性樹脂の製造方法は、水溶性エチレン性不飽和単量体の重合反応により吸水性樹脂を製造するための方法である。この方法は、前記水溶性エチレン性不飽和単量体が溶解されかつ前記水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂を含有する水溶液を調製する工程と、前記水溶液を炭化水素溶媒中に添加して分散させる工程と、前記水溶液が分散された前記炭化水素溶媒を加熱して、前記水溶液中に含まれる前記水溶性エチレン性不飽和単量体を重合する工程と、を含んでいる。

本発明のさらに他の観点による吸水性樹脂の製造方法は、水溶性エチレン性不飽和単量体の重合反応により吸水性樹脂を製造するための方法である。この方法は、前記水溶性エチレン性不飽和単量体を含む水溶液を炭化水素溶媒中に添加して分散させる工程と、前記水溶液が分散された前記炭化水素溶媒中に、前記水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂を添加する工程と、前記水溶液および前記他の吸水性樹脂を含む前記炭化水素溶媒を加熱して、前記水溶液中に含まれる前記水溶性エチレン性不飽和単量体を重合する工程と、を含んでいる。

本発明のさらに他の観点による吸水性樹脂の製造方法は、水溶性エチレン性不飽和単量体の重合反応により吸水性樹脂を製造するための方法である。この方法は、前記水溶性エチレン性不飽和単量体を重合反応させてスラリーを得るための工程と、前記スラリーに前記水溶性

エチレン性不飽和単量体を追加して、追加された前記水溶性エチレン性不飽和単量体の重合反応をさらに行なうための工程とを含んでいる。上述の両工程においては、そのうちの少なくとも1つの工程において、前記水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂の存在下で前記重合反応を行なう。

本発明のさらに他の観点による吸水性樹脂の製造方法は、水溶性エチレン性不飽和単量体の重合反応により吸水性樹脂を製造するための方法である。この方法は、前記水溶性エチレン性不飽和単量体を重合反応させてスラリーを得るための工程と、前記スラリーに、前記水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂を添加しかつ前記水溶性エチレン性不飽和単量体を追加して、追加された前記水溶性エチレン性不飽和単量体の重合反応をさらに行なうための工程と、を含んでいる。

このような本発明に係る吸水性樹脂の製造方法では、水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂の存在下で水溶性エチレン性不飽和単量体を重合反応させているので、互いに吸水速度が異なる吸水性樹脂が複合した吸水性樹脂、すなわち、重合反応系に存在させる吸水性樹脂と水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂とが複合した吸水性樹脂を製造することができる。このような吸水性樹脂は、被吸収液の逆戻り量を低減させながら同時に被吸収液の拡散性を高めることができる。

また、本発明に係る吸水性樹脂は、水溶性エチレン性不飽和単量体を重合反応させることにより得られた第1の吸水性樹脂成分と、前記第1の吸水性樹脂成分に複合された、前記第1の吸水性樹脂成分とは吸水速度が異なる第2の吸水性樹脂成分と、を含んでいる。

このような吸水性樹脂は、吸水速度が互いに異なる第1の吸水性樹脂成分と第2の吸水性樹脂成分とを含んでいるので、被吸収液の逆戻り

り量を低減させながら同時に被吸収液の拡散性を高めることができる。

本発明の他の目的および効果は、以下の詳細な説明から明かになるであろう。

発明の詳細な説明

本発明の製造方法で採用される重合方法は、特に限定されるものではなく、逆相懸濁重合法や水溶液重合法などの一般的に知られた種々の重合法である。但し、本発明では、より望ましい効果が得られることから逆相懸濁重合法を採用するのが好ましい。以下、重合反応として逆相懸濁重合法を採用することを前提として、本発明の製造方法を説明する。

本発明で用いられる水溶性エチレン性不飽和単量体は、特に限定されるものではなく、重合用として通常用いられるものである。具体的には、アクリル酸、メタアクリル酸、2-アクリルアミド-2-メチルプロパンスルホン酸、2-メタアクリルアミド-2-メチルプロパンスルホン酸およびそれらのアルカリ塩（アンモニウム塩やアルカリ金属塩など）、アクリルアミド、メタアクリルアミド、N, N-ジメチルアクリルアミド、2-ヒドロキシエチルアクリレート、2-ヒドロキシエチルメタアクリレート、N-メチロールアクリルアミド、N-メチロールメタアクリルアミドなどの非イオン性単量体、ジエチルアミノエチルアクリレート、ジエチルアミノエチルメタアクリレート、ジエチルアミノプロピルアクリレート、ジエチルアミノプロピルメタアクリレート、ジエチルアミノプロピルアクリルアミド、ジエチルアミノプロピルメタアクリルアミドなどのアミノ基含有不飽和単量体やそれらの4級化物などを挙げることができる。このような水溶性エチレン性不飽和単量体は、2種以上混合して用いられてもよい。

なお、上述の水溶性エチレン性不飽和単量体のうち好ましいものは、工業的に入手が容易な点でアクリル酸、メタアクリル酸およびこれらのアルカリ塩、アクリルアミド、メタアクリルアミド、N, N-ジメ

チルアクリルアミドである。

本発明において、上述の水溶性エチレン性不飽和単量体は、通常水溶液の状態で用いられる。このような水溶性エチレン性不飽和単量体水溶液では、水溶性エチレン性不飽和単量体の濃度を25重量%～飽和濃度に設定するのが好ましい。

このような水溶性エチレン性不飽和単量体を逆相懸濁重合させる際には、当該水溶性エチレン性不飽和単量体の水溶液を炭化水素溶媒中に添加して分散させる。ここで用いられる炭化水素溶媒は、脂肪族炭化水素溶媒、脂環族炭化水素溶媒または芳香族炭化水素溶媒である。脂肪族炭化水素溶媒としては、例えば、*n*-ヘキサン、*n*-ヘプタンおよびリグロインなどが挙げられる。脂環族炭化水素溶媒としては、例えば、シクロペンタン、メチルシクロペンタン、シクロヘキサンおよびメチルシクロヘキサンなどが挙げられる。芳香族炭化水素溶媒としては、ベンゼン、トルエンおよびキシレンなどが挙げられる。これらの炭化水素溶媒のうち好ましいものは、工業的に品質が一定しておりかつ入手が容易で安価な*n*-ヘキサン、*n*-ヘプタン、シクロヘキサン、トルエンおよびキシレンである。

なお、上述の炭化水素溶媒は、2種以上が混合して用いられてもよい。

炭化水素溶媒中には、界面活性剤または高分子保護コロイドを予め添加しておくのが好ましい。界面活性剤と高分子保護コロイドとは併用されてもよい。

ここで用いられる界面活性剤は、水溶性エチレン性不飽和単量体水溶液を逆相懸濁重合できるものであれば特に限定されない。利用可能な界面活性剤の具体例としては、ソルビタン脂肪酸エステル、ポリグリセリン脂肪酸エステル、ショ糖脂肪酸エステル、ソルビトール脂肪酸エステルおよびポリオキシエチレンアルキルフェニルエーテルなどの非イオン性界面活性剤が挙げられる。このような非イオン性界面活性剤は、2種以上が混合して用いられてもよい。

一方、高分子保護コロイドとしては、例えば、エチルセルロース、

エチルヒドロキシエチルセルロース、酸化変性ポリエチレン、無水マレイン酸変性ポリエチレン、無水マレイン酸変性ポリブタジエン、無水マレイン酸変性EPDM（エチレン・プロピレン・ジエン・ターポリマー）などが用いられる。

上述の非イオン性界面活性剤および高分子保護コロイドは、脂肪酸塩、アルキルベンゼンスルホン酸塩、アルキルメチルタウリン酸塩、ポリオキシエチレンアルキルフェニルエーテル硫酸エステル塩、ポリオキシエチレンアルキルエーテルスルホン酸塩などのアニオン性界面活性剤と併用することもできる。

なお、界面活性剤または高分子保護コロイド、若しくは界面活性剤と高分子保護コロイドとの混合物の使用量は、通常、水溶性エチレン性不飽和単量体水溶液の0.1～5重量%、好ましくは0.2～3重量%である。使用量が0.1重量%未満の場合は、乳化が不十分となる。逆に、5重量%を超えても、それに比例した効果が得られず却って不経済である。

本発明の重合反応では、所望により、架橋剤が用いられてもよい。当該架橋剤は、通常、上述の水溶性エチレン性不飽和単量体水溶液中に予め添加しておくのが好ましい。ここで用いることができる架橋剤は、重合性不飽和基または反応性官能基を2個以上有するものである。重合性不飽和基を2個以上有する架橋剤としては、エチレングリコール、プロピレングリコール、トリメチロールプロパン、グリセリンポリオキシエチレングリコール、ポリオキシプロピレングリコール、ポリグリセリンなどのポリオール類のジまたはトリアクリル酸エステル類若しくはジまたはトリメタアクリル酸エステル類、上述のポリオール類とマレイン酸、フマル酸などの不飽和酸類とを反応させて得られる不飽和ポリエステル類、N, N'-メチレンビスアクリルアミドなどのビスアクリルアミド類、ポリエポキシドとアクリル酸若しくはメタアクリル酸とを反応させて得られるジまたはトリアクリル酸エステル類若しくはジまたはトリメタアクリル酸エステル類、トリレンジイソシアネート、ヘキサメチレンジイソシアネートなどのポリイソシ

アネートとアクリル酸ヒドロキシエチルまたはメタアクリル酸ヒドロキシエチルとを反応させて得られるジアクリル酸カルバミルエステル類またはジメタアクリル酸カルバミルエステル類、アリル化デンプン、アリル化セルロース、ジアリルフタレート、N, N', N''-トリアリルイソシアヌレート、ジビニルベンゼンなどが例示できる。

上述の重合性不飽和基を2個以上有する架橋剤のうち好ましいものは、エチレングリコールジアクリレート、エチレングリコールジメタクリレート、ジエチレングリコールジアクリレート、ジエチレングリコールジメタクリレート、プロピレングリコールジアクリレート、プロピレングリコールジメタクリレート、ポリエチレングリコールジアクリレート、ポリエチレングリコールジメタクリレート、ジアリルフタレート、N, N'-メチレンビスアクリルアミドである。

一方、反応性官能基を2個以上有する架橋剤としては、例えば、ジグリシジルエーテル化合物、ハロエポキシ化合物、イソシアネート化合物などを用いることができ、このうち、ジグリシジルエーテル化合物が好ましい。

ジグリシジルエーテル化合物の具体例としては、例えば、エチレングリコールジグリシジルエーテル、ポリエチレングリコールジグリシジルエーテル、プロピレングリコールジグリシジルエーテル、ポリプロピレングリコールジグリシジルエーテル、グリセリンジグリシジルエーテル、ポリグリセリンジグリシジルエーテルなどが挙げられる。このうち特に好ましいものは、エチレングリコールジグリシジルエーテルである。

また、ハロエポキシ化合物としては、エピクロルヒドリン、エピブロムヒドリン、 α -メチルエピクロルヒドリンなどが例示できる。さらに、イソシアネート化合物としては、2, 4-トリレンジイソシアネート、ヘキサメチレンジイソシアネートなどが例示できる。

なお、上述の架橋剤は、重合性不飽和基と反応性官能基とをそれぞれ2個以上同時に有していてもよい。

上述の架橋剤を使用する場合、その使用量は、通常、水溶性エチレ

ン性不飽和単量体の0.001～5重量%に設定される。使用量が0.001重量%未満の場合は、得られる樹脂の水溶性が高まり、当該樹脂が吸水性樹脂として機能しにくくなる場合がある。逆に、5重量%を超えると、満足な吸水性が得られない。

本発明での重合反応を行う際には、ラジカル重合開始剤を用いる。ラジカル重合開始剤としては、過硫酸カリウム、過硫酸アンモニウム、過硫酸ナトリウムなどの、一般的に使用される水溶性ラジカル重合開始剤を用いるのが好ましい。このようなラジカル重合開始剤は、亜硫酸塩などと併用してレドックス系開始剤として用いることもできる。

また、ラジカル重合開始剤としては、油溶性ラジカル重合開始剤を用いることもできる。ただし、油溶性ラジカル重合開始剤を用いる場合は、生成する重合体が一般に水溶性となるため、本発明の吸水性樹脂を得るためには上述の架橋剤を用いる必要がある。なお、油溶性ラジカル重合開始剤としては、過酸化ベンゾイル、アゾビスイソブチロニトリルなどを用いるのが好ましい。

ラジカル重合開始剤の使用量は、通常、水溶性エチレン性不飽和単量体の0.005～1.0モル%である。使用量が0.005モル%よりも少ない場合は重合反応に長時間を要することになり、1.0モル%を超える場合は急激な重合反応が起こるため危険である。

重合反応を行う際の重合温度は、使用する重合開始剤により異なるが、通常、20～110℃、好ましくは40～80℃である。重合温度が20℃よりも低い場合は、重合速度が低下して重合時間が長くなるので経済的ではない。逆に、110℃より高い場合は、重合熱を除去するのが困難になり、円滑な重合反応を行うのが困難になる。かくして得られた水溶性エチレン性不飽和単量体の重合物は、通常、スラリーとして得られる。

上述の重合反応を実施する際に反応系に存在させる吸水性樹脂は、上述の水溶性エチレン性不飽和単量体の重合により製造される吸水性樹脂の吸水速度とは異なる吸水速度を有するものである。すなわち、製造される吸水性樹脂の吸水速度よりも速い吸水速度を有する吸水性

樹脂、または製造される吸水性樹脂の吸水速度よりも遅い吸水速度を有する吸水性樹脂である。

このような吸水性樹脂は、特に限定されず、市販されている一般的な吸水性樹脂であれば種々のものを用いることができる。具体的には、澱粉-アクリロニトリルグラフト共重合体の加水分解物や澱粉-アクリル酸グラフト共重合体の中和物などの澱粉系吸水性樹脂、酢酸ビニル-アクリル酸エステル共重合体のケン化物、ポリアクリル酸部分中和物、無水マレイン酸-イソブチレン共重合体および上述の水溶性エチレン性不飽和単量体の重合体などが挙げられる。なお、これらの吸水性樹脂は、2種以上が併用されてもよい。

但し、上述の水溶性エチレン性不飽和単量体の重合により製造されるものと同種類の吸水性樹脂を用いるのが好ましい。より具体的には、アクリル酸、メタアクリル酸、2-アクリルアミド-2-メチルプロパンスルホン酸、2-メタアクリルアミド-2-メチルプロパンスルホン酸およびそれらのアルカリ塩（アンモニウム塩やアルカリ金属塩など）、アクリルアミド、メタアクリルアミド、N、N-ジメチルアクリルアミド、2-ヒドロキシエチルアクリレート、2-ヒドロキシエチルメタアクリレート、N-メチロールアクリルアミド、N-メチロールメタアクリルアミドなどの非イオン性単量体、ジエチルアミノエチルアクリレート、ジエチルアミノエチルメタアクリレート、ジエチルアミノプロピルアクリレート、ジエチルアミノプロピルメタアクリレート、ジエチルアミノプロピルアクリルアミド、ジエチルアミノプロピルメタアクリルアミドなどのアミノ基含有不飽和単量体やそれらの4級化物などの水溶性エチレン性不飽和単量体を逆相懸濁重合法により単独重合または共重合することにより得られる吸水性樹脂を用いるのが好ましい。特に、アクリル酸、メタアクリル酸およびこれらのアルカリ塩、アクリルアミド、メタアクリルアミド、並びにN、N-ジメチルアクリルアミドの単独重合体または共重合体からなる吸水性樹脂を用いるのが好ましい。

重合反応系に存在させる上述の吸水性樹脂の量は、通常、重合反応

させる水溶性エチレン性不飽和単量体に対して1～100重量%に設定するのが好ましく、5～50重量%に設定するのがより好ましい。1重量%未満の場合は、本発明が目的とする吸水性樹脂が得られにくい。逆に、100重量%を超えると、経済的でないばかりではなく、逆相懸濁重合反応において重合反応系が不安定になり、塊状化が起こりやすくなる。

重合反応系に上述の吸水性樹脂を存在させる方法としては、水溶性エチレン性不飽和単量体の重合反応時に当該吸水性樹脂を存在させることができる方法であれば種々の方法が採用され得る。具体的には、水溶性エチレン性不飽和単量体水溶液中に最初から存在させておく方法、水溶性エチレン性不飽和単量体水溶液を炭化水素溶媒中に添加して分散させた後、当該炭化水素溶媒中に吸水性樹脂を添加する方法などが採用される。

なお、本発明では、目的とする吸水性樹脂を多段重合法により製造することもできる。このような多段重合法を採用する場合、先ず、1段目の重合反応で上述の水溶性エチレン性不飽和単量体を重合させる。そして、1段目の重合反応により得られたスラリーに水溶性エチレン性不飽和単量体をさらに添加して2段目の重合反応を実施する。この場合、重合反応系に存在させる吸水性樹脂は、1段目の重合反応系に存在させてもよいし、2段目の重合反応系に存在させてもよい。また、1段目および2段目の両重合反応系に存在させることもできる。

本発明の製造方法により製造された吸水性樹脂は、吸水速度が速い吸水性樹脂成分と、吸水速度が遅い吸水性樹脂成分とが複合されたものである。吸水速度が異なる両吸水性樹脂成分が複合して得られる吸水性樹脂の形態は、特に限定されるものではないが、例えば、粉末状、顆粒状、球状、りん片状等種々の形態をとりうる。

このような本発明の製造方法により得られる吸水性樹脂において、吸水速度が速い部分を構成する吸水性樹脂成分の吸水速度は、10秒未満が好ましく、5秒未満がより好ましい。この吸水速度が10秒以上の場合は、吸水初期に満足な吸水性が発揮されにくくなる。一方、

吸水速度が遅い部分を構成する吸水性樹脂成分の吸水速度は、20秒を超えるのが好ましく、30秒を超えるのがより好ましい。この吸水速度が20秒以下の場合、吸水速度が速すぎるために吸水性樹脂がゲル化してブロッキングを起こしやすくなる。従って、吸水性樹脂を構成する、2つの吸水性樹脂成分の吸水速度がこのような条件を満たさない場合、当該吸水性樹脂は、被吸収液の逆戻り量を低減させながら同時に被吸収液の拡散性を高めるのが困難になる。

なお、本発明において、吸水速度とは、1gの吸水性樹脂が、攪拌下において25mlの0.9%食塩水を完全に吸水するまでに要する時間を云う。この吸水速度は、長さが20mm、直径が7mmφの回転子を入れた50mlのビーカーに0.9%食塩水25mlを入れ、マグネチックスターラーを使用して500rpmで攪拌しながら吸水性樹脂を1.0g加え、目視により完全に遊離水がない状態が確認できるまでに要した時間を測定することにより求めることができる。

本発明により得られる吸水性樹脂は、上述のように吸水速度が異なる複数種の吸水性樹脂成分が複合化されたものであるため、吸水速度が異なる複数種の吸水性樹脂を単に混合した場合とは異なり、それを用いた吸水体、例えば生理用品や紙おむつなどの衛生材全体に均質な吸水性能を付与することができる。したがって、本発明による吸水性樹脂は、従来の吸水性樹脂では実現が困難であった吸水特性、即ち、被吸収液の逆戻り量を低減させながら同時に被吸収液の拡散性を高めることが可能になる。具体的には、本発明による吸水性樹脂をパルプ材などに散布することにより形成された吸水体は、被吸収液をすばやく吸収し、同時に被吸収液を吸水体に広く拡散させることができるので、被吸収液の供給速度が速い場合でも、供給された被吸収液の漏れを起こしにくい。

本発明により得られる吸水性樹脂は、生理用品や紙おむつなどの衛生材用途、保水剤や土壌改良剤などの農園芸用途、或いは止水剤や結露防止剤などの工業資材用途などの広範な分野で利用可能であるが、特に、衛生材用途に適している。

以下、実施例により本発明を詳細に説明する。ここでは、各実施例をそれに対応する比較例と対応させて示しているが、実施例の説明および理解の便のために対応する比較例を先に記載している。

比較例 1

攪拌機、還流冷却器、滴下ロートおよび窒素ガス導入管を備えた 1 ℓ の四つ口円筒型丸底フラスコに n-ヘプタンを 550 ml 加えた。これに、HLB が 8.6 のソルビタンモノラウレート（界面活性剤：日本油脂株式会社製のノニオン LP-20R）を 0.97 g 添加して分散させ、50℃まで昇温して界面活性剤を溶解した後 30℃まで冷却した。

一方、500 ml の三角フラスコを別に用意し、これに 80 重量% のアクリル酸水溶液 92 g を加えた。これに、外部から氷冷しつつ 20.1 重量% の水酸化ナトリウム水溶液 152.6 g を滴下して 75 モル% の中和を行い、アクリル酸部分中和水溶液を調製した。その後、過硫酸カリウム 0.11 g をさらに加えて溶解した。

次に、上述の 500 ml の三角フラスコの内容物の全量を上述の四つ口円筒型丸底フラスコに加えて分散させ、系内を窒素で置換した後に昇温し、浴温を 70℃に保持して 3 時間重合反応を行った。水および n-ヘプタンを蒸留により除去して乾燥し、吸水性樹脂 97.2 g を得た。得られた吸水性樹脂の吸水速度は 3 秒であった。

実施例 1-a

攪拌機、還流冷却器、滴下ロートおよび窒素ガス導入管を備えた 1 ℓ の四つ口円筒型丸底フラスコに n-ヘプタンを 550 ml 加えた。これに、HLB が 8.6 のソルビタンモノラウレート（界面活性剤：日本油脂株式会社製のノニオン LP-20R）を 0.97 g 添加して分散させ、50℃まで昇温して界面活性剤を溶解した後 30℃まで冷却した。

一方、500mℓの三角フラスコを別に用意し、これに80重量%のアクリル酸水溶液92gを加えた。これに、外部から氷冷しつつ20.1重量%の水酸化ナトリウム水溶液152.6gを滴下して75モル%の中和を行い、その後、過硫酸カリウム0.11gをさらに加えて溶解した。このようにして得られたアクリル酸部分中和水溶液に吸水速度が45秒の吸水性樹脂（住友精化株式会社製のポリアクリル酸部分中和物の重合体：商品名”アクアキープ”）18.4gをさらに添加した。

次に、上述の500mℓの三角フラスコの内容物の全量を上述の四つ口円筒型丸底フラスコに加えて分散させ、系内を窒素で置換した後に昇温し、浴温を70℃に保持して3時間重合反応を行った。水およびn-ヘプタンを蒸留により除去して乾燥し、複合化吸水性樹脂115.7gを得た。

実施例 1-b

比較例1の場合と同様に、界面活性剤を溶解した四つ口円筒型丸底フラスコ中の溶媒に三角フラスコ内のアクリル酸部分中和水溶液を加えて分散させた後、これに吸水速度が45秒の吸水性樹脂（住友精化株式会社製のポリアクリル酸部分中和物の重合体：商品名”アクアキープ”）46.0gをさらに添加した。以後、実施例1-aの場合と同様にして重合操作を実施し、複合化吸水性樹脂144.5gを得た。

比較例 2

攪拌機、還流冷却器、滴下ロートおよび窒素ガス導入管を備えた1ℓの四つ口円筒型丸底フラスコにn-ヘプタンを550mℓ加えた。これに、HLBが13.1のヘキサグリセリルモノベヘニレート（界面活性剤：日本油脂株式会社製のノニオンGV-106）を1.38g添加して分散させ、50℃まで昇温して界面活性剤を溶解した後30℃まで冷却した。

一方、500 ml の三角フラスコを別に用意し、これに80重量%のアクリル酸水溶液92 gを加えた。これに、外部から氷冷しつつ20.1重量%の水酸化ナトリウム水溶液152.6 gを滴下して75モル%の中和を行い、その後、過硫酸カリウム0.11 gと架橋剤としてのエチレングリコールジグリシジルエーテル0.019 gとをさらに加えて溶解した。これにより、アクリル酸部分中和水溶液が得られた。

次に、上述の500 ml の三角フラスコの内容物の全量を上述の四つ口円筒型丸底フラスコに加えて分散させた。そして、系内を窒素で置換した後に昇温し、浴温を70℃に保持して3時間重合反応を行った。水およびn-ヘプタンを蒸留により除去して乾燥し、吸水性樹脂98.3 gを得た。得られた吸水性樹脂の吸水速度は48秒であった。

実施例 2

比較例2の場合と同様に、界面活性剤を溶解した四つ口円筒丸底フラスコ中の溶媒に三角フラスコ内のアクリル酸部分中和水溶液を加えて分散させた後、これに吸水速度が2秒の吸水性樹脂（住友精化株式会社製のポリアクリル酸部分中和物の重合体：商品名“アクアキープ”）9.2 gをさらに添加した。以後、比較例2の場合と同様に重合操作を実施し、複合化吸水性樹脂106.0 gを得た。

比較例 3

攪拌機、還流冷却器、滴下ロートおよび窒素ガス導入管を備えた1ℓの四つ口円筒型丸底フラスコにn-ヘプタンを550 ml加えた。これに、HLBが13.1のヘキサグリセリルモノベヘニレート（界面活性剤：日本油脂株式会社製のノニオンGV-106）を1.38 g添加して分散させ、50℃まで昇温して界面活性剤を溶解した後30℃まで冷却した。

一方、500 ml の三角フラスコを別に用意し、これに80重量%

のアクリル酸水溶液 92 g を加えた。これに、外部から氷冷しつつ 20.1 重量%の水酸化ナトリウム水溶液 152.6 g を滴下して 75 モル%の中和を行い、その後、過硫酸カリウム 0.11 g と架橋剤としてのエチレングリコールジグリシジルエーテル 0.019 g とをさらに加えて溶解した。これにより、アクリル酸部分中和水溶液が得られた。

次に、上述の 500 ml の三角フラスコの内容物の全量を上述の四つ口円筒型丸底フラスコに加えて分散させ、系内を窒素で置換した後昇温し、浴温を 70℃に保持して 3 時間 1 段目の重合反応を行った。

1 段目の重合反応により得られた重合スラリー液を 20℃に冷却し、これに上述のものと同様に調製した同量のアクリル酸部分中和水溶液をさらに滴下した。そして、30 分間系内を窒素により十分に置換して昇温し、浴温を 70℃に保持して 3 時間 2 段目の重合反応を行った。水および n-ヘプタンを蒸留により除去して乾燥し、吸水性樹脂 196.5 g を得た。得られた吸水性樹脂の吸水速度は 57 秒であった。

実施例 3

2 段目の重合反応系に用いるアクリル酸部分中和水溶液に吸水速度が 2 秒の吸水性樹脂（住友精化株式会社製のポリアクリル酸部分中和物の重合体：商品名“アクアキープ”）18.4 g を予め添加しておいた点を除いて比較例 3 の場合と同様に重合操作を実施し、複合化吸水性樹脂 212.2 g を得た。

評価

実施例 1～3 および比較例 1～3 で得られた吸水性樹脂について、吸水量、初期吸水速度、吸水速度、逆戻り量および拡散長を調べた。評価方法は下記の通りである。結果を表 1 に示す。

(1) 吸水量 (g/g)

回転子入りの 300 ml ビーカーに 0.9%食塩水を 200 ml 入れ、マグネチックスターラーで攪拌しながら吸水性樹脂 1.0 g を加

えた。1時間攪拌後、200メッシュの金網で濾過して金網に残留した膨潤樹脂量を測定し、吸水性樹脂1g当たりの吸水量(g)を測定した。

(2) 初期吸水速度

長さが20mm、直径が7mmφの回転子を入れた50mlのビーカーに0.9%食塩水10mlを入れ、マグネチックスターラーを使用して500rpmで攪拌しながら吸水性樹脂を1.0g加え、目視により完全に遊離水がない状態が確認できるまでに要した時間を測定することにより求めた。

(3) 吸水速度

既述の方法により測定した。

(4) 逆戻り量および拡散長

80g/m²の坪量を有する、40cm×14cmの大きさに裁断したパルプシートの上に5gの吸水性樹脂を均一に散布し、その上に同様のパルプシートを重ね合わせた。次に、パルプシート面全体に2kg/cm²の加重を加えてプレスし、吸水体を作成した。作成した吸水体の中心付近に1.6%食塩水150mlを1分間かけて注ぎ、5分間放置した。その後、10cm×10cmに裁断したろ紙(東洋ろ紙No. 2)20枚を重ねて吸収体の中心付近に置き、その上から3.5kgのおもり(底面積=10cm×10cm)を載せて3分間加重した。ろ紙に吸収された食塩水量を測定し、これを逆戻り量とした。また、吸水体に吸収された食塩水について、吸水体の長手方向の拡がりを測定し、これを拡散長とした。

表 1

		吸水量 (g / g)	初期吸水速度 (秒)	吸水速度 (秒)	逆戻り量 (g)	拡散長 (cm)
実 施 例	1-a	6.7	2	1.8	1.5	2.2
	1-b	6.5	5	2.5	1.3	2.4
	2	6.3	7	3.5	0.5	2.8
	3	6.2	8	4.2	0.2	2.9
比 較 例	1	7.2	1	3	15.2	1.5
	2	6.1	1.8	4.8	5.5	3.0
	3	6.3	2.9	5.7	6.2	3.2

本発明は、その精神または主要な特徴から逸脱することなく、他のいろいろな形で実施することができる。そのため、上述の実施例はあらゆる点で単なる例示に過ぎず、限定的に解釈してはならない。本発明の範囲は、請求の範囲によって示すものであって、明細書本文にはなんら拘束されない。さらに、請求の範囲の均等範囲に属する変形や変更は、すべて本発明の範囲内のものである。

請求の範囲

1. 水溶性エチレン性不飽和単量体の重合反応により吸水性樹脂を製造するための方法であって、

前記水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂の存在下で、前記水溶性エチレン性不飽和単量体を重合反応させる工程を含む、吸水性樹脂の製造方法。

2. 前記水溶性エチレン性不飽和単量体が、アクリル酸、メタアクリル酸、アクリル酸のアルカリ塩、メタアクリル酸のアルカリ塩、アクリルアミド、メタクリルアミドおよびN, N-ジメチルアクリルアミドからなる群から選ばれた少なくとも1種である、請求の範囲1に記載の吸水性樹脂の製造方法。

3. 前記重合反応を逆相懸濁重合法により行なう、請求の範囲1に記載の吸水性樹脂の製造方法。

4. 前記重合反応時に存在させる前記吸水性樹脂の量が、前記水溶性エチレン性不飽和単量体の1～100重量%である、請求の範囲1に記載の吸水性樹脂の製造方法。

5. 前記重合反応時に存在させる前記吸水性樹脂が、澱粉-アクリロニトリルグラフト共重合体の加水分解物、澱粉-アクリル酸グラフト共重合体の中和物、酢酸ビニル-アクリル酸エステル共重合体のケン化物、ポリアクリル酸部分中和物、無水マレイン酸-イソブチレン共重合体および水溶性エチレン性不飽和単量体の重合物からなる群から選ばれた少なくとも1種である、請求の範囲4に記載の吸水性樹脂の製造方法。

6. 前記水溶性エチレン性不飽和単量体の重合物が、アクリル酸、メタアクリル酸、アクリル酸のアルカリ塩、メタアクリル酸のアルカリ塩、アクリルアミド、メタクリルアミドおよびN, N-ジメチルアクリルアミドからなる群から選ばれた単量体の単独重合体および共重合体から選ばれた少なくとも1種である、請求の範囲5に記載の吸水性



樹脂の製造方法。

7. 前記重合反応時に存在させる前記吸水性樹脂が、前記水溶性エチレン性不飽和単量体の重合により得られる吸水性樹脂と同種類のものである、請求の範囲4に記載の吸水性樹脂の製造方法。

8. 水溶性エチレン性不飽和単量体の重合反応により吸水性樹脂を製造するための方法であって、

前記水溶性エチレン性不飽和単量体が溶解されかつ前記水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂を含有する水溶液を調製する工程と、

前記水溶液を炭化水素溶媒中に添加して分散させる工程と、

前記水溶液が分散された前記炭化水素溶媒を加熱して、前記水溶液中に含まれる前記水溶性エチレン性不飽和単量体を重合する工程と、を含む吸水性樹脂の製造方法。

9. 前記炭化水素溶媒には、界面活性剤および高分子保護コロイドのうちの少なくとも1種が予め添加されている、請求の範囲8に記載の吸水性樹脂の製造方法。

10. 前記水溶液に含有される前記吸水性樹脂の使用量が、前記水溶性エチレン性不飽和単量体の1～100重量%に設定されている、請求の範囲8に記載の吸水性樹脂の製造方法。

11. 前記水溶液に含有される前記吸水性樹脂が、澱粉-アクリロニトリルグラフト共重合体の加水分解物、澱粉-アクリル酸グラフト共重合体の中和物、酢酸ビニル-アクリル酸エステル共重合体のケン化物、ポリアクリル酸部分中和物、無水マレイン酸-イソブチレン共重合体および水溶性エチレン性不飽和単量体の重合物からなる群から選ばれた少なくとも1種である、請求の範囲10に記載の吸水性樹脂の製造方法。

12. 前記水溶性エチレン性不飽和単量体の重合物が、アクリル酸、メタアクリル酸、アクリル酸のアルカリ塩、メタアクリル酸のアルカリ塩、アクリルアミド、メタクリルアミドおよびN, N-ジメチルア



クリルアミドからなる群から選ばれた単量体の単独重合体および共重合体から選ばれた少なくとも1種である、請求の範囲11に記載の吸水性樹脂の製造方法。

13. 前記水溶液に含有される前記吸水性樹脂が、前記水溶性エチレン性不飽和単量体の重合により得られる吸水性樹脂と同種類のものである、請求の範囲10に記載の吸水性樹脂の製造方法。

14. 前記水溶液が架橋剤をさらに含んでいる、請求の範囲8に記載の吸水性樹脂の製造方法。

15. 前記架橋剤の使用量が、前記水溶性エチレン性不飽和単量体の0.001～5重量%に設定されている、請求の範囲14に記載の吸水性樹脂の製造方法。

16. 水溶性エチレン性不飽和単量体の重合反応により吸水性樹脂を製造するための方法であって、

前記水溶性エチレン性不飽和単量体を含む水溶液を炭化水素溶媒中に添加して分散させる工程と、

前記水溶液が分散された前記炭化水素溶媒中に、前記水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂を添加する工程と、

前記水溶液および添加された前記吸水性樹脂を含む前記炭化水素溶媒を加熱して、前記水溶液中に含まれる前記水溶性エチレン性不飽和単量体を重合する工程と、
を含む吸水性樹脂の製造方法。

17. 前記炭化水素溶媒には、界面活性剤および高分子保護コロイドのうちの少なくとも1種が予め添加されている、請求の範囲16に記載の吸水性樹脂の製造方法。

18. 前記炭化水素溶媒中に添加された前記吸水性樹脂の添加量が、前記水溶性エチレン性不飽和単量体の1～100重量%に設定されている、請求の範囲16に記載の吸水性樹脂の製造方法。

19. 前記炭化水素溶媒中に添加された前記吸水性樹脂が、澱粉－アクリロニトリルグラフト共重合体の加水分解物、澱粉－アクリル酸グ



ラフト共重合体の中和物、酢酸ビニル-アクリル酸エステル共重合体のケン化物、ポリアクリル酸部分中和物、無水マレイン酸-イソブチレン共重合体および水溶性エチレン性不飽和単量体の重合物からなる群から選ばれた少なくとも1種である、請求の範囲18に記載の吸水性樹脂の製造方法。

20. 前記水溶性エチレン性不飽和単量体の重合物が、アクリル酸、メタアクリル酸、アクリル酸のアルカリ塩、メタアクリル酸のアルカリ塩、アクリルアミド、メタクリルアミドおよびN, N-ジメチルアクリルアミドからなる群から選ばれた単量体の単独重合体および共重合体から選ばれた少なくとも1種である、請求の範囲19に記載の吸水性樹脂の製造方法。

21. 前記炭化水素溶媒中に添加された前記吸水性樹脂が、前記水溶性エチレン性不飽和単量体の重合により得られる吸水性樹脂と同種類のものである、請求の範囲18に記載の吸水性樹脂の製造方法。

22. 前記水溶性エチレン性不飽和単量体を含む前記水溶液が架橋剤をさらに含んでいる、請求の範囲16に記載の吸水性樹脂の製造方法。

23. 前記架橋剤の使用量が、前記水溶性エチレン性不飽和単量体の0.001～5重量%に設定されている、請求の範囲22に記載の吸水性樹脂の製造方法。

24. 水溶性エチレン性不飽和単量体の重合反応により吸水性樹脂を製造するための方法であって、

前記水溶性エチレン性不飽和単量体を重合反応させてスラリーを得るための工程と、

前記スラリーに前記水溶性エチレン性不飽和単量体を追加して、追加された前記水溶性エチレン性不飽和単量体の重合反応をさらにこなうための工程とを含み、

前記両工程のうちの少なくとも1つの工程において、前記水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂の存在下で前記重合反応を行なう、



吸水性樹脂の製造方法。

25. 水溶性エチレン性不飽和単量体の重合反応により吸水性樹脂を製造するための方法であって、

前記水溶性エチレン性不飽和単量体を重合反応させてスラリーを得るための工程と、

前記水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂が予め添加された前記水溶性エチレン性不飽和単量体を前記スラリーに追加して、追加された前記水溶性エチレン性不飽和単量体の重合反応をさらに行なうための工程と、

を含む吸水性樹脂の製造方法。

26. 請求の範囲1の製造方法により得られる吸水性樹脂。

27. 請求の範囲8の製造方法により得られる吸水性樹脂。

28. 請求の範囲16の製造方法により得られる吸水性樹脂。

29. 請求の範囲24の製造方法により得られる吸水性樹脂。

30. 請求の範囲25の製造方法により得られる吸水性樹脂。

31. 水溶性エチレン性不飽和単量体を重合反応させることにより得られる第1の吸水性樹脂成分と、

前記第1の吸水性樹脂成分に複合された、前記第1の吸水性樹脂成分とは吸水速度が異なる第2の吸水性樹脂成分と、
を含む吸水性樹脂。



SPECIFICATION

PROCESS FOR PREPARING WATER-ABSORBENT RESIN

FIELD OF THE INVENTION

The present invention relates to processes for preparing a water-absorbent resin and, more particularly, to processes for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer.

BACKGROUND OF THE INVENTION

Water-absorbent resins have found wide application in the fields of sanitary materials such as menstrual articles and disposable diapers, agricultural materials such as water retention agents and soil conditioning agents, and industrial materials such as cutoff materials and anti-dewing agents. Particularly, the water-absorbent resins are advantageously used in the field of the sanitary materials. Generally known as the water-absorbent resins for use in the aforesaid fields are lightly crosslinked polymeric resins. Examples thereof include starch type water-absorbent resins such as a hydrolyzate of a graft copolymer of starch and

acrylonitrile (Japanese Examined Patent Publication No. 49-43395 (1974)) and a neutralized graft copolymer of starch and acrylic acid (Japanese Unexamined Patent Publication No. 51-125468 (1976)), a saponified copolymer of vinyl acetate and acrylic acid ester (Japanese Unexamined Patent Publication No. 52-14689 (1977)), and a partially neutralized polyacrylic acid (Japanese Unexamined Patent Publications No. 62-172006 (1987), No. 57-158209 (1982) and No. 57-21405 (1982)).

Properties required for a water-absorbent resin, particularly, in the field of the sanitary materials include a high water-absorbency, a high water-absorbing rate, a high gel strength after water absorption, a low content of fine particles, and a sharp distribution of particle size. Where the water-absorbent resin is compounded with a pulp material to form a water-absorbent material for the sanitary materials, the water-absorbing rate is an important factor which influences the properties of the water-absorbent material, i.e., the reduction in the release amount of once absorbed liquid from the water-absorbent material and the increase in the diffusibility of the absorbed liquid into interior of the water-absorbent material.

Where a water-absorbent resin having a relatively low water-absorbing rate is employed, for example, the

resulting water-absorbing material exhibits an excellent liquid diffusibility. However, when the water-absorbent material is pressed (e.g., when a baby wearing a disposable diaper comprised of such a water-absorbent material sits immediately after urination), the release amount of liquid is increased because the water-absorbent resin requires much time for the liquid absorption. In addition, if the liquid supply rate to the water-absorbent material is higher than the water-absorbing rate of the water-absorbent resin, excess liquid may leak from the water-absorbent material.

Where a water-absorbent resin having a relatively high water-absorbing rate is employed for the water-absorbing material, on the other hand, liquid absorption by the water-absorbent resin locally occurs in a portion of the water-absorbent material to which liquid is supplied, and the water-absorbent resin in that portion swells and gelatinizes to cause blocking. In such a case, the liquid diffusion into the water-absorbent material is blocked by the gelatinous water-absorbent resin, so that the liquid is prevented from spreading throughout the water-absorbent material. As a result, the release amount of the absorbed liquid is increased.

Therefore, a water-absorbent resin exhibiting

initially a high water-absorbing rate and thereafter a moderate water-absorbing rate is desirable for a water-absorbent material in order to reduce the liquid release amount and increase the liquid diffusibility. A mixture of a water-absorbent resin component having a high water-absorbing rate and a water-absorbent resin component having a low water-absorbing rate may afford a water-absorbent resin having such properties. The water-absorbent resin mixture, however, is less homogeneous because it is prepared by mixing a plurality of kinds of water-absorbent resins having different particle diameters and different bulk densities. Hence, no practical solution to the aforesaid problem has been found yet.

It is, therefore, an object of the present invention to prepare a water-absorbent resin ensuring the reduction in the liquid release amount and the increase in the liquid diffusibility.

It is another object of the present invention to prepare a water-absorbent resin ensuring the reduction in the liquid release amount and the increase in the liquid diffusibility, particularly, for use in sanitary materials.

SUMMARY OF THE INVENTION

In accordance with one aspect of the present invention, there is provided a process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, which comprises the step of polymerizing the water-soluble ethylenic unsaturated monomer in the presence of a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer.

In a preferred mode of the present invention, the polymerization is performed by a reversed-phase suspension polymerization method.

In accordance with another aspect of the present invention, there is provided a process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, which comprises the steps of: preparing an aqueous solution containing the water-soluble ethylenic unsaturated monomer dissolved therein and a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer; adding the aqueous solution to a hydrocarbon solvent and dispersing the aqueous solution therein; and heating the



hydrocarbon solvent containing the aqueous solution dispersed therein to polymerize the water-soluble ethylenic unsaturated monomer contained in the aqueous solution.

In accordance with further another aspect of the present invention, there is provided a process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, which comprises the steps of: adding an aqueous solution containing the water-soluble ethylenic unsaturated monomer to a hydrocarbon solvent and dispersing the aqueous solution therein; adding a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer to the hydrocarbon solvent which contains the aqueous solution dispersed therein; and heating the hydrocarbon solvent containing the aqueous solution and the added water-absorbent resin to polymerize the water-soluble ethylenic unsaturated monomer contained in the aqueous solution.

In accordance with still another aspect of the present invention, there is provided a process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, which



comprises the steps of: polymerizing the water-soluble ethylenic unsaturated monomer to afford a slurry; and further adding the water-soluble ethylenic unsaturated monomer to the slurry, and polymerizing the added water-soluble ethylenic unsaturated monomer. In at least one of the aforesaid steps, the polymerization is allowed to take place in the presence of a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer.

In accordance with yet another aspect of the present invention, there is provided a process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, which comprises the steps of: polymerizing the water-soluble ethylenic unsaturated monomer to afford a slurry; and adding to the slurry a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer, and adding the water-soluble ethylenic unsaturated monomer to the slurry, and polymerizing the added water-soluble ethylenic unsaturated monomer.

In the aforesaid processes according to the

present invention, a water-soluble ethylenic unsaturated monomer is polymerized in the presence of a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer. Thus, a water-absorbent resin can be prepared in which there is a compound of the two components of water-absorbent resin having different water-absorbing rates, i.e., a compound of the water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer and the water-absorbent resin present in the polymerization reaction system. The water-absorbent resin thus prepared ensures the reduction in the release amount of liquid as well as the increase in the liquid diffusibility.

A water-absorbent resin according to the present invention comprises a first water-absorbent resin component resulting from polymerization of a water-soluble ethylenic unsaturated monomer and a second water-absorbent resin component having a water-absorbing rate different from that of the first water-absorbent resin component and compounded with the first water-absorbent resin component.

Since the water-absorbent resin contains the

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

first and second water-absorbent resin components having different water-absorbing rates, the reduction in the release amount of liquid as well as the increase in the liquid diffusibility can be ensured.

The foregoing and other objects and effects will become apparent from the following detailed description.

DETAILED DESCRIPTION OF THE INVENTION

The polymerization method to be employed in the preparation processes of the present invention is not particularly limited, but any of various known polymerization methods such as reversed-phase suspension polymerization and aqueous solution polymerization can be employed. To produce a better effect, however, the reversed-phase suspension polymerization method is preferably employed. The preparation processes will hereinafter be described on the premise that the reversed-phase suspension polymerization method is employed.

The water-soluble ethylenic unsaturated monomer to be used in the present invention is not particularly limited, but any of those generally used for polymerization may be employed. Examples of specific water-soluble ethylenic unsaturated monomers include:



acrylic acid, methacrylic acid, 2-acrylamide-2-methylpropanesulfonic acid, 2-methacrylamide-2-methylpropanesulfonic acid, and alkali salts (e.g., ammonium salts, alkali metal salts and the like) thereof; nonionic monomers such as acrylamide, methacrylamide, N,N-dimethylacrylamide, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, N-methylol acrylamide and N-methylol methacrylamide; and unsaturated monomers containing amino-group such as diethylaminoethyl acrylate, diethylaminoethyl methacrylate, diethylaminopropyl acrylate, diethylaminopropyl methacrylate, diethylaminopropyl acrylamide and diethylaminopropyl methacrylamide, and quaternary compounds thereof. These water-soluble ethylenic unsaturated monomers may be used either alone or in combination.

Among the aforesaid water-soluble ethylenic unsaturated monomers, acrylic acid and methacrylic acid and alkali salts thereof, acrylamide, methacrylamide and N,N-dimethylacrylamide are preferred in terms of industrial availability.

In the present invention, the water-soluble ethylenic unsaturated monomer is typically used in a state of an aqueous solution. The concentration of the water-soluble ethylenic unsaturated monomer in the

aqueous solution is preferably between 25wt% and a saturated concentration.

The aqueous solution of the water-soluble ethylenic unsaturated monomer is added to a hydrocarbon solvent and dispersed therein for the reversed-phase suspension polymerization of the water-soluble ethylenic unsaturated monomer. Usable as the hydrocarbon solvent are aliphatic hydrocarbon solvents, alicyclic hydrocarbon solvents and aromatic hydrocarbon solvents. Examples of specific aliphatic hydrocarbon solvents include n-hexane, n-heptane and ligroin. Examples of specific alicyclic hydrocarbon solvents include cyclopentane, methylcyclopentane, cyclohexane and methylcyclohexane. Examples of specific aromatic hydrocarbon solvents include benzene, toluene and xylene. Among these hydrocarbon solvents, n-hexane, n-heptane, cyclohexane, toluene and xylene are preferred because they are stable in quality and available at a low cost.

The aforesaid hydrocarbon solvents may be used either alone or in combination.

Preferably, a surface active agent or a polymer protective colloid is preliminarily added to the hydrocarbon solvent. The surface active agent and the polymer protective colloid may be used in combination.

The surface active agent to be used is not particularly limited, as long as the reversed-phase suspension polymerization of the water-soluble ethylenic unsaturated monomer can be effected in the aqueous solution. Examples of usable surface active agents include nonionic surface active agents such as sorbitan fatty acid esters, polyglycerin fatty acid esters, sucrose fatty acid esters, sorbitol fatty acid esters and polyoxyethylenealkyl phenyl ether. These nonionic surface active agents may be used either alone or in combination.

Examples of specific polymer protective colloids include ethyl cellulose, ethylhydroxyethyl cellulose, oxidized polyethylene, polyethylene modified with maleic anhydride, polybutadiene modified with maleic anhydride, and EPDM (ethylene-propylene-diene terpolymer) modified with maleic anhydride .

The aforesaid nonionic surface active agent and the polymer protective colloid may be used in combination with an anionic surface active agent such as a fatty acid salt, alkylbenzenesulfonate, alkylmethyltaurine salt, polyoxyethylenealkyl phenyl ether sulfate or polyoxyethylenealkyl ether sulfonate.

The surface active agent, the polymer protective colloid or a mixture of the surface active agent and the

polymer protective colloid is typically used in an amount of 0.1wt% to 5wt%, preferably 0.2wt% to 3wt%, with respect to the aqueous solution of the water-soluble ethylenic unsaturated monomer. If the amount is less than 0.1wt%, insufficient emulsification may result. The use in an amount of greater than 5wt% is uneconomical, because an effect to be produced is not corresponding to the usage.

A crosslinking agent may be optionally used, for the polymerization. Preferably, the crosslinking agent is preliminarily added to the aqueous solution of the water-soluble ethylenic unsaturated monomer. The crosslinking agent to be used herein has two or more polymerizable unsaturated groups or reactive functional groups. Examples of specific crosslinking agents having two or more polymerizable unsaturated groups include di- or triacrylic esters and di- or trimethacrylic esters of polyols such as ethylene glycol, propylene glycol, trimethylolpropane, glycerol, polyoxyethylene glycol, polyoxypropylene glycol and polyglycerol; unsaturated polyesters obtained by reacting the aforesaid polyols with an unsaturated acid such as maleic acid and fumaric acid; bisacrylamides such as N,N'-methylenebisacrylamide; di- or triacrylic esters and di- or trimethacrylic esters obtained by

reacting polyepoxides with acrylic acid and with methacrylic acid, respectively; carbamyl diacrylate and carbamyl dimethacrylate obtained by reacting polyisocyanates such as tolylene diisocyanate and hexamethylene diisocyanate with hydroxyethyl acrylate and with hydroxyethyl methacrylate, respectively; allylated starch, allylated cellulose, diallyl phthalate, N,N',N''-triallyl isocyanurate, and divinylbenzene.

Among the aforesaid crosslinking agents having two or more polymerizable unsaturated groups, ethylene glycol diacrylate, ethylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, propylene glycol diacrylate, propylene glycol dimethacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, diallyl phthalate and N,N'-methylenebisacrylamide are preferred.

Examples of the crosslinking agents having two or more reactive functional groups include diglycidyl ether compounds, haloepoxy compounds and isocyanate compounds. Among those, the diglycidyl ether compounds are preferred.

Examples of specific diglycidyl ether compounds include ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, propylene glycol diglycidyl

ether, polypropylene glycol diglycidyl ether, glycerol diglycidyl ether, and polyglycerol diglycidyl ether. Among those, ethylene glycol diglycidyl ether is particularly preferred.

Examples of specific haloeпоxy compounds include epichlorohydrin, epibromohydrin and α -methylepichlorohydrin. Examples of specific isocyanate compounds include 2,4-tolylene diisocyanate and hexamethylene diisocyanate.

The aforesaid crosslinking agent may have two or more polymerizable unsaturated groups and two or more reactive functional groups.

The crosslinking agent is typically used in an amount of 0.001wt% to 5wt% with respect to the water-soluble ethylenic unsaturated monomer. If the amount is less than 0.001wt%, the resulting resin has a high water-solubility and is hence less functional as a water-absorbent resin. If the amount exceeds 5wt%, the resulting resin does not exhibit satisfactory water-absorbing properties.

A radical polymerization initiator is used in the polymerization according to the present invention. The radical polymerization initiator to be used is preferably selected from conventional water-soluble radical polymerization initiators such as potassium

persulfate, ammonium persulfate and sodium persulfate. The radical polymerization initiator can be used in combination with a sulfite as a redox-type initiator.

An oil-soluble radical polymerization initiator may also be used as the radical polymerization initiator. Where such an oil-soluble radical polymerization initiator is used, the resulting polymer is generally water-soluble, hence the crosslinking agent should be used to prepare the water-absorbent resin of the present invention. Preferably used as the oil-soluble radical polymerization initiator are benzoyl peroxide, and azobisisobutyronitrile.

The radical polymerization initiator is typically used in an amount of 0.005mol% to 1.0mol% with respect to the water-soluble ethylenic unsaturated monomer. If the amount is less than 0.005mol%, much time is required for the polymerization. If the amount exceeds 1.0mol%, a rapid polymerization reaction entailing a danger may result.

The polymerization temperature varies depending upon the polymerization initiator to be used, but typically 20°C to 110°C, preferably 40°C to 80°C. If the polymerization temperature is lower than 20°C, the polymerization rate is reduced, so that the polymerization process requires much time and is hence

uneconomical. If the polymerization temperature is higher than 110°C, it is difficult to remove polymerization heat to facilitate the polymerization. The polymer of the water-soluble ethylenic unsaturated monomer is generally obtained in a state of a slurry.

The water-absorbent resin to be present in the polymerization reaction system has a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer, i.e., a water-absorbing rate higher or lower than that of the water-absorbent resin to be prepared.

The water-absorbent resin to be present in the polymerization reaction system is not particularly limited, but any of various commercially available water-absorbent resins may be used. Examples of specific water-absorbent resins include starch type water-absorbent resins such as a hydrolyzate of a graft copolymer of starch and acrylonitrile and a neutralized graft copolymer of starch and acrylic acid, a saponified copolymer of vinyl acetate and acrylic acid ester, partially neutralized polyacrylic acid, a copolymer of maleic anhydride and isobutylene, and a polymer of the aforesaid water-soluble ethylenic unsaturated monomer. These water-absorbent resins may be used either alone

or in combination.

Preferably used as the water-absorbent resin to be present in the polymerization reaction system is of the same type as the water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer. Examples of specific water-absorbent resins to be preferably used are water-absorbent resins resulting from reversed-phase suspension homopolymerization or copolymerization of water-soluble ethylenic unsaturated monomers including acrylic acid, methacrylic acid, 2-acrylamide-2-methylpropanesulfonic acid, 2-methacrylamide-2-methylpropanesulfonic acid, and alkali salts (e.g., ammonium salts, alkali metal salts and the like) thereof; nonionic monomers such as acrylamide, methacrylamide, N,N-dimethylacrylamide, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, N-methylol acrylamide and N-methylol methacrylamide; amino-containing unsaturated monomers such as diethylaminoethyl acrylate, diethylaminoethyl methacrylate, diethylaminopropyl acrylate, diethylaminopropyl methacrylate, diethylaminopropyl acrylamide and diethylaminopropyl methacrylamide, and quaternary compounds thereof. Among those, a water-absorbent resin comprised of a homopolymer or copolymer

of acrylic acid or methacrylic acid or an alkali salt thereof, acrylamide, methacrylamide or N,N-dimethylacrylamide is preferred.

The amount of the water-absorbent resin to be present in the polymerization reaction system is preferably 1wt% to 100wt%, more preferably 5wt% to 50wt% with respect to the water-soluble ethylenic unsaturated monomer to be polymerized. If the amount is less than 1wt%, it is difficult to afford the water-absorbent resin of interest in the present invention. If the amount exceeds 100wt%, an uneconomical process may result and, in addition, the polymerization reaction system for the reversed-phase suspension polymerization becomes unstable, so that the resulting resin tends to bulk.

The method of allowing the water-absorbent resin to be present in the polymerization reaction system is not particularly limited. The water-absorbent resin is allowed to be present in any of various methods in the course of polymerization of the water-soluble ethylenic unsaturated monomer. More specifically, the water-absorbent resin is allowed to be present in the aqueous solution of the water-soluble ethylenic unsaturated monomer from the beginning. Alternatively, the aqueous solution of the water-soluble ethylenic unsaturated

monomer is first added to the hydrocarbon solvent and dispersed therein, and then the water-absorbent resin is added to the hydrocarbon solvent.

In accordance with the present invention, the water-absorbent resin of interest may be prepared by a multi-stage polymerization process. At the first polymerization stage, the water-soluble ethylenic unsaturated monomer is polymerized. At the second polymerization stage, the water-soluble ethylenic unsaturated monomer is added to a slurry obtained by the polymerization at the first stage, and polymerized. In this case, the water-absorbent resin may be allowed to be present either in the first-stage polymerization reaction system or in the second-stage polymerization reaction system or, alternatively, in both of the first- and second-stage polymerization reaction systems.

The water-absorbent resin prepared by the preparation process of the present invention is a compound of a water-absorbent resin component having a higher water-absorbing rate and a water-absorbent resin component having a lower water-absorbing rate. The water-absorbent resin containing the water-absorbent resin components having different water-absorbing rates does not take a particular form, but can be in any of various forms such as powdery, granular, spherical and

scale forms.

In the water-absorbent resin prepared by the preparation process of the present invention, the resin component having the higher water-absorption rate preferably offers a water-absorbing time of less than 10 seconds, more preferably less than 5 seconds. If the water-absorbing time is not less than 10 seconds, the resulting water-absorbent resin does not exhibit a satisfactory initial water-absorbency. On the other hand, the resin component having the lower water-absorbing rate preferably offers a water-absorbing time of longer than 20 seconds, more preferably longer than 30 seconds. If the water-absorbing time is not longer than 20 seconds, the water-absorbing rate is so high that the resulting water-absorbent resin is gelatinized and tends to cause blocking. Therefore, if the two water-absorbent resin components of the present water-absorbent resin do not satisfy the aforesaid requirements for the water-absorbing time, it is difficult for the water-absorbent resin to ensure the reduction in the amount of liquid released as well as the increase in the liquid diffusibility.

It is noted that the term "water-absorbing rate" is herein meant by the time required for 1g of a water-absorbent resin to completely absorb 25ml of a

0.9% saline solution with stirring. The water-absorbing rate can be determined in the following manner. First, 25ml of the 0.9% saline solution is poured into a 50-ml beaker containing a rotator having a length of 20mm and a diameter of 7mm ϕ , and then 1.0g of the water-absorbent resin is added to the saline solution with stirring at a rotation speed of 500rpm by means of a magnetic stirrer. The water-absorbing rate is determined by measuring the elapsed time before it is visually confirmed that there is no free water in the beaker.

As described above, the water-absorbent resin prepared by the preparation process of the present invention is a compound of a plurality of water-absorbent resin components having different water-absorbing rates. Therefore, a water-absorbent material, for example, a sanitary material such as a menstrual article or a disposable diaper which employs the present water-absorbent resin can be imparted with a homogeneous water-absorbing property, unlike a case where a water-absorbent resin mixture prepared by simply mixing a plurality of water-absorbent resin having different water-absorbing rates is employed. Thus, the present invention can impart the water-absorbent resin with superior water-absorbing properties which is

difficult to be achieved by the conventional water-absorbent resins. That is, the water-absorbent resin according to the present invention ensures the reduction in the release amount of the liquid as well as the increase in the liquid diffusibility. More specifically, a water-absorbent material produced by spreading the water-absorbent resin of the present invention in a pulp material can rapidly absorb liquid and extensively diffuse the absorbed liquid therein. Therefore, even if the supply rate of the liquid is high, the supplied liquid hardly leaks.

The water-absorbent resin according to the present invention can be used in a wide range of application fields including sanitary materials such as menstrual articles and disposable diapers, agricultural materials such as water retention agents and soil conditioning agents, and industrial materials such as cutoff materials and anti-dewing agents, but is particularly suitable for the sanitary materials.

The present invention will hereinafter be described in greater detail by way of examples thereof. In the following description, Examples are set forth in conjunction with corresponding Comparative Examples, which each precede Examples for easy understanding.

Comparative Example 1

First, 550ml of n-heptane was put in a 1-liter four-necked round flask provided with a stirrer, a reflux condenser, a dropping funnel and a nitrogen gas introduction tube. Then, 0.97g of sorbitan monolaurate (surface active agent NONION LP-20R available from Nippon Yushi Co.) having an HLB of 8.6 was added to the solvent and dispersed therein. The solution was once heated up to 50°C to dissolve the surface active agent therein, and then cooled to 30°C.

In turn, 92g of an 80wt% acrylic acid aqueous solution was prepared in a 500-ml Erlenmeyer's flask, and 152.6g of a 20.1wt% sodium hydroxide aqueous solution was added thereto drop by drop for 75mol% neutralization in an ice bath to afford an aqueous solution of partially neutralized acrylic acid. Then, 0.11g of potassium persulfate was added to the partially neutralized acrylic acid aqueous solution and dissolved therein.

The aqueous solution contained in the 500-ml Erlenmeyer's flask was all added to the solution in the four-necked round flask, and dispersed therein. After the atmosphere of the reaction system was replaced with nitrogen gas, the reaction system was heated up to 70°C, at which polymerization was allowed to proceed for 3 hours. Then, water and n-heptane were distilled off, and the resulting product was dried. Thus, 97.2g of a

water-absorbent resin was obtained. The water-absorbing time of the water-absorbent resin thus obtained was 3 seconds.

Example 1-a

First, 550ml of n-heptane was put in a 1-liter four-necked round flask provided with a stirrer, a reflux condenser, a dropping funnel and a nitrogen gas introduction tube. Then, 0.97g of sorbitan monolaurate (surface active agent NONION LP-20R available from Nippon Yushi Co.) having an HLB of 8.6 was added to the solvent and dispersed therein. The solution was once heated up to 50°C to dissolve the surface active agent therein, and then cooled to 30°C.

In turn, 92g of an 80wt% acrylic acid aqueous solution was prepared in a 500-ml Erlenmeyer's flask, and 152.6g of a 20.1wt% sodium hydroxide aqueous solution was added thereto drop by drop for 75mol% neutralization in an ice bath. Then, 0.11g of potassium persulfate was added to the resulting solution and dissolved therein. To a partially neutralized acrylic acid aqueous solution thus obtained was added 18.4g of a water-absorbent resin (polymer of partially neutralized polyacrylic acid available under the trade name of "AQUAKEEP" from Sumitomo Seika Chemicals Co.) having a water-absorbing time of 45 seconds.

The solution contained in the 500-ml Erlenmeyer's flask was all added to the solution in the four-necked round flask, and dispersed therein. After the atmosphere of the reaction system was replaced with nitrogen gas, the reaction system was heated up to 70° C, at which polymerization was allowed to proceed for 3 hours. Then, water and n-heptane were distilled off, and the resulting product was dried. Thus, 115.7g of a compounded water-absorbent resin was obtained.

Example 1-b

In the same manner as in Comparative Example 1, the partially neutralized acrylic acid aqueous solution in the Erlenmeyer's flask was added to the solution containing the surface active agent dissolved therein in the four-necked round flask, and dispersed therein. To the resulting solution mixture was added 46.0g of a water-absorbent resin (polymer of partially neutralized polyacrylic acid available under the trade name of "AQUAKEEP" from Sumitomo Seika Chemicals Co.) having a water-absorbing time of 45 seconds. Thereafter, the polymerization and subsequent steps were carried out in the same manner as in Example 1-a. Thus, 144.5g of a compounded water-absorbent resin was obtained.

Comparative Example 2

First, 550ml of n-heptane was put in a 1-liter

four-necked round flask provided with a stirrer, a reflux condenser, a dropping funnel and a nitrogen gas introduction tube. Then, 1.38g of hexaglyceryl monobehenylate (surface active agent NONION GV-106 available from Nippon Yushi Co.) having an HLB of 13.1 was added to the solvent, and dispersed therein. The solution was once heated up to 50°C to dissolve the surface active agent therein, and then cooled to 30°C.

In turn, 92g of an 80wt% acrylic acid aqueous solution was prepared in a 500-ml Erlenmeyer's flask, and 152.6g of a 20.1wt% sodium hydroxide aqueous solution was added thereto drop by drop for 75mol% neutralization in an ice bath. Then, 0.11g of potassium persulfate and 0.019g of ethylene glycol diglycidyl ether as a crosslinking agent were added to the resulting solution, and dissolved therein. Thus, a partially neutralized acrylic acid aqueous solution was prepared.

The aqueous solution contained in the 500-ml Erlenmeyer's flask was all added to the solution in the four-necked round flask, and dispersed therein. After the atmosphere of the reaction system was replaced with nitrogen gas, the reaction system was heated up to 70°C, at which polymerization was allowed to proceed for 3 hours. Then, water and n-heptane were distilled off,

and the resulting product was dried. Thus, 98.3g of a water-absorbent resin was obtained. The water-absorbing time of the water-absorbent resin thus obtained was 48 seconds.

Example 2

In the same manner as in Comparative Example 2, the partially neutralized acrylic acid aqueous solution in the Erlenmeyer's flask was added to the solution containing the surface active agent dissolved therein in the four-necked round flask, and dispersed therein. To the resulting solution mixture was added 9.2g of a water-absorbent resin (polymer of partially neutralized polyacrylic acid available under the trade name of "AQUAKEEP" from Sumitomo Seika Chemicals Co.) having a water-absorbing time of 2 seconds. Thereafter, the polymerization and subsequent steps were carried out in the same manner as in Comparative Example 2. Thus, 106.0g of a compounded water-absorbent resin was obtained.

Comparative Example 3

First, 550ml of n-heptane was put in a 1-liter four-necked round flask provided with a stirrer, a reflux condenser, a dropping funnel and a nitrogen gas introduction tube. Then, 1.38g of hexaglyceryl monobehenylate (surface active agent NONION GV-106

available from Nippon Yushi Co.) having an HLB of 13.1 was added to the solvent, and dispersed therein. The solution was once heated up to 50°C to dissolve the surface active agent therein, and then cooled to 30°C.

In turn, 92g of an 80wt% acrylic acid aqueous solution was prepared in a 500-ml Erlenmeyer's flask, and 152.6g of a 20.1wt% sodium hydroxide aqueous solution was added thereto drop by drop for 75mol% neutralization in an ice bath. Then, 0.11g of potassium persulfate and 0.019g of ethylene glycol diglycidyl ether as a crosslinking agent were added to the resulting solution, and dissolved therein. Thus, a partially neutralized acrylic acid aqueous solution was prepared.

The aqueous solution contained in the 500-ml Erlenmeyer's flask was all added to the solution in the four-necked round flask, and dispersed therein. After the atmosphere of the reaction system was replaced with nitrogen gas, the reaction system was heated up to 70°C, at which first-stage polymerization was allowed to proceed for 3 hours.

A polymer slurry resulting from the first-stage polymerization was cooled to 20°C, and then a partially neutralized acrylic acid aqueous solution prepared in the aforesaid manner was added thereto drop by drop in

the same amount as used in the first-stage polymerization. After the atmosphere of the reaction system was fully replaced with nitrogen gas for 30 minutes, the reaction system was heated up to 70°C, at which second-stage polymerization was allowed to proceed for 3 hours. Then, water and n-heptane were distilled off, and the resulting product was dried. Thus, 196.5g of a water-absorbent resin was obtained. The water-absorbing time of the resin thus obtained was 57 seconds.

Example 3

The polymerization process was performed in substantially the same manner as in Comparative Example 3, except that 18.4g of a water-absorbent resin (polymer of partially neutralized polyacrylic acid available under the trade name of "AQUAKEEP" from Sumitomo Seika Chemicals Co.) having a water-absorbing time of 2 seconds was preliminarily added to the partially neutralized acrylic resin aqueous solution to be used in the second-stage polymerization. Thus, 212.2g of a compounded water-absorbent resin was obtained.

Evaluation

The amount of water absorbed, initial water-absorbing time, water-absorbing time, release amount of water and longitudinal diffusion expanse of water-absorbent resins prepared in Examples 1 to 3 and

Comparative Examples 1 to 3 were measured in the following manner for evaluation of the resins. The results are shown in Table 1.

(1) Water absorption amount (g/g)

A rotator and 200ml of a 0.9% saline solution were put in a 300-ml beaker, and 1.0g of a water-absorbent resin was added thereto with stirring by means of a magnetic stirrer. After the solution was stirred for 1 hour, the swollen water-absorbent resin was filtered by means of a 200-mesh wire gauze and weighed for determination of the amount of water absorbed (g) per gram of the water-absorbent resin.

(2) Initial water-absorbing time

A rotator having a length of 20mm and a diameter of 7mm ϕ and 10ml of a 0.9% saline solution were put in a 50-ml beaker. Then, 1.0g of a water-absorbent resin was added thereto with stirring at a rotation speed of 500rpm by means of a magnetic stirrer, and the elapsed time before it was visually confirmed that there was no free water was measured.

(3) Water-absorbing time

The water-absorbing time was measured in the manner previously mentioned.

(4) Release amount and longitudinal diffusion expanse

First, 5g of a water-absorbent resin was uniformly spread on a cut pulp sheet having dimensions of 40cm×14cm and a unit weight of 80g/m², and then another cut pulp sheet having the same dimensions and weight was overlaid thereon. Next, the combined pulp sheets thus formed were pressed with a load of 2kg/cm², thereby a water-absorbent material was prepared. Subsequently, 150ml of a 1.6% saline solution was poured around the center of the water-absorbent material within 1 minutes, and the water-absorbent material was allowed to stand for 5 minutes. Then, a pile of 20 cut filter paper sheets (Toyo filter paper No.2) having dimensions of 10cm×10cm were placed on the center of the water-absorbent material, and a 3.5kg weight (having a bottom area of 10cm×10cm) was placed on the filter paper sheets to impose a load thereon for 3 minutes. The amount of the saline solution absorbed by the filter paper sheets was measured for determination of the release amount. The longitudinal expanse of the saline solution absorbed and diffused in the water-absorbent material was measured for determination of the longitudinal diffusion expanse.

Table 1

	Amount of water absorbed (g/g)	Initial water- absorbing time(sec)	Water- absorbing time (sec)	Release amount (g)	Longitudinal diffusion expanse (cm)
Ex.1-a	67	2	18	1.5	22
Ex.1-b	65	5	25	1.3	24
Ex.2	63	7	35	0.5	28
Ex.3	62	8	42	0.2	29
Com.Ex.1	72	1	3	15.2	15
Com.Ex.2	61	18	48	5.5	30
Com.Ex.3	63	29	57	6.2	32

The present invention can be embodied in various forms without departing from the spirit and principal features of the present invention. Therefore, the aforementioned embodiments are merely illustrative of the invention in every aspect, and not limitative of the same. The scope of the present invention is defined by the appended claims, and is not restricted by the description herein set forth. Further, various changes and modifications to be made within the scope of the appended claims and equivalents thereof are to fall within the scope of the present invention.



REPLACED SHEETS

SG

- ☐ Description : paged to paged
☒ Claim(s) : paged 34 to paged 41.....
☐ Drawing(s) : paged to paged
☐ Abstract : paged to paged

CLAIMS

1. A process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, comprising the step of:

polymerizing the water-soluble ethylenic unsaturated monomer in the presence of a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer.

2. A process as set forth in claim 1, wherein the water-soluble ethylenic unsaturated monomer is at least one selected from the group consisting of acrylic acid, methacrylic acid, an alkali salt of acrylic acid, an alkali salt of methacrylic acid, acrylamide, methacrylamide and N,N-dimethylacrylamide.

3. A process as set forth in claim 1, wherein the polymerization is performed by a reversed-phase suspension polymerization method.

4. A process as set forth in claim 1, wherein the amount of the water-absorbent resin to be present during the polymerization is 1wt% to 100wt% with respect to the water-soluble ethylenic unsaturated monomer.

5. A process as set forth in claim 4, wherein the





water-absorbent resin to be present during the polymerization is at least one selected from the group consisting of a hydrolyzate of a graft copolymer of starch and acrylonitrile, a neutralized graft copolymer of starch and acrylic acid, a saponified copolymer of vinyl acetate and acrylic acid ester, partially neutralized polyacrylic acid, a copolymer of maleic anhydride and isobutylene, and a polymer of a water-soluble ethylenic unsaturated monomer.

6. A process as set forth in claim 5, wherein the polymer of the water-soluble ethylenic unsaturated monomer is at least one selected from homopolymers and copolymers of monomers selected from the group consisting of acrylic acid, methacrylic acid, an alkali salt of acrylic acid, an alkali salt of methacrylic acid, acrylamide, methacrylamide and N,N-dimethylacrylamide.

7. A process as set forth in claim 4, wherein the water-absorbent resin to be present during the polymerization is of the same type as the water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer.

8. A process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, comprising the steps of:





preparing an aqueous solution containing the water-soluble ethylenic unsaturated monomer dissolved therein and a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer;

adding the aqueous solution to a hydrocarbon solvent and dispersing the aqueous solution therein; and

heating the hydrocarbon solvent containing the aqueous solution dispersed therein to polymerize the water-soluble ethylenic unsaturated monomer contained in the aqueous solution.

9. A process as set forth in claim 8, wherein at least one of a surface active agent and a polymer protective colloid is preliminarily added to the hydrocarbon solvent.

10. A process as set forth in claim 8, wherein the amount of the water-absorbent resin contained in the aqueous solution is 1wt% to 100wt% with respect to the water-soluble ethylenic unsaturated monomer.

11. A process as set forth in claim 10, wherein the water-absorbent resin contained in the aqueous solution is at least one selected from the group consisting of a hydrolyzate of a graft copolymer of starch and acrylonitrile, a neutralized graft copolymer of starch





and acrylic acid, a saponified copolymer of vinyl acetate and acrylic acid ester, partially neutralized polyacrylic acid, a copolymer of maleic anhydride and isobutylene, and a polymer of a water-soluble ethylenic unsaturated monomer.

12. A process as set forth in claim 11, wherein the polymer of the water-soluble ethylenic unsaturated monomer is at least one selected from homopolymers and copolymers of monomers selected from the group consisting of acrylic acid, methacrylic acid, an alkali salt of acrylic acid, an alkali salt of methacrylic acid, acrylamide, methacrylamide and N,N-dimethylacrylamide.

13. A process as set forth in claim 10, wherein the water-absorbent resin contained in the aqueous solution is of the same type as the water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer.

14. A process as set forth in claim 8, wherein the aqueous solution further contains a crosslinking agent.

15. A process as set forth in claim 14, wherein the amount of the crosslinking agent to be used is 0.001wt% to 5wt% with respect to the water-soluble ethylenic unsaturated monomer.

16. A process for preparing a water-absorbent resin





by polymerization of a water-soluble ethylenic unsaturated monomer, comprising the steps of:

adding an aqueous solution containing the water-soluble ethylenic unsaturated monomer to a hydrocarbon solvent and dispersing the aqueous solution therein;

adding a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer to the hydrocarbon solvent which contains the aqueous solution dispersed therein; and

heating the hydrocarbon solvent containing the aqueous solution and the added water-absorbent resin to polymerize the water-soluble ethylenic unsaturated monomer contained in the aqueous solution.

17. A process as set forth in claim 16, wherein at least one of a surface active agent and a polymer protective colloid is preliminarily added to the hydrocarbon solvent.

18. A process as set forth in claim 16, wherein the amount of the water-absorbent resin added to the hydrocarbon solvent is 1wt% to 100wt% with respect to the water-soluble ethylenic unsaturated monomer.

19. A process as set forth in claim 18, wherein the





water-absorbent resin added to the hydrocarbon solvent is at least one selected from the group consisting of a hydrolyzate of a graft copolymer of starch and acrylonitrile, a neutralized graft copolymer of starch and acrylic acid, a saponified copolymer of vinyl acetate and acrylic acid ester, partially neutralized polyacrylic acid, a copolymer of maleic anhydride and isobutylene, and a polymer of a water-soluble ethylenic unsaturated monomer.

20. A process as set forth in claim 19, wherein the polymer of the water-soluble ethylenic unsaturated monomer is at least one selected from homopolymers and copolymers of monomers selected from the group consisting of acrylic acid, methacrylic acid, an alkali salt of acrylic acid, an alkali salt of methacrylic acid, acrylamide, methacrylamide and N,N-dimethylacrylamide.

21. A process as set forth in claim 18, wherein the water-absorbent resin added to the hydrocarbon solvent is of the same type as the water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer.

22. A process as set forth in claim 16, wherein the aqueous solution containing the water-soluble ethylenic unsaturated monomer further contains a





crosslinking agent.

23. A process as set forth in claim 22, wherein the amount of the crosslinking agent to be used is 0.001wt% to 5wt% with respect to the water-soluble ethylenic unsaturated monomer.

24. A process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, comprising the steps of:

polymerizing the water-soluble ethylenic unsaturated monomer to afford a slurry; and

further adding the water-soluble ethylenic unsaturated monomer to the slurry, and polymerizing the added water-soluble ethylenic unsaturated monomer,

wherein, in at least one of the aforesaid steps, the polymerization is allowed to take place in the presence of a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer.

25. A process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, comprising the steps of:

polymerizing the water-soluble ethylenic unsaturated monomer to afford a slurry; and

adding to the slurry the water-soluble ethylenic





unsaturated monomer preliminarily mixed with a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer, and polymerizing the added water-soluble ethylenic unsaturated monomer.

26. A water-absorbent resin prepared by a process as recited in claim 1.

27. A water-absorbent resin prepared by a process as recited in claim 8.

28. A water-absorbent resin prepared by a process as recited in claim 16.

29. A water-absorbent resin prepared by a process as recited in claim 24.

30. A water-absorbent resin prepared by a process as recited in claim 25.

31. A water-absorbent resin comprising:

a first water-absorbent resin component resulting from polymerization of a water-soluble ethylenic unsaturated monomer; and

a second water-absorbent resin component compounded with the first water-absorbent resin component and having a water-absorbing rate different from that of the first water-absorbent resin component.



ABSTRACT

A process for preparing a water-absorbent resin is provided which enables the water-absorbent resin to ensure the reduction in the release amount of liquid and the increase in the liquid diffusibility. In the preparation process, the water-absorbent resin is prepared by polymerization of a water-soluble ethylenic unsaturated monomer. The polymerization of the water-soluble ethylenic unsaturated monomer is allowed to take place in the presence of a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer. In a preferred mode, the polymerization is performed by a reversed-phase suspension polymerization method.

THIS SHEET HAS BEEN
REPLACED

This Sheet Has Been Replaced



REPLACEMENT SHEETS SG

- ☐ Description : paged to paged
☒ Claim(s) : paged 34 to paged 42
☐ Drawing(s) : paged to paged
☐ Abstract : paged to paged

DATE OF RECEIPT 2/11/00

-34-

Substitute sheet - 1 November 2000



Claims

1. A process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, comprising the step of:

polymerizing the water-soluble ethylenic unsaturated monomer in the presence of a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer, wherein, a water-absorbing time of the water-absorbent resin to be present during the polymerization is less than 10 seconds or longer than 20 seconds.

2. A process as set forth in claim 1, wherein the water-soluble ethylenic unsaturated monomer is at least one selected from the group consisting of acrylic acid, methacrylic acid, an alkali salt of acrylic acid, an alkali salt of methacrylic acid, acrylamide, methacrylamide and N,N-dimethylacrylamide.

3. A process as set forth in claim 1, wherein the polymerization is performed by a reversed-phase suspension polymerization method.

4. A process as set forth in claim 1, wherein the amount of the water-absorbent resin to be present during the

This is the replacement sheet

Date:

02 NOV 2000

9702999-5
2/11/00



polymerization is 1wt% to 100wt% with respect to the water-soluble ethylenic unsaturated monomer.

5. A process as set forth in claim 4, wherein the water-absorbent resin to be present during the polymerization is at least one selected from the group consisting of a hydrolyzate of a graft copolymer of starch and acrylonitrile, a neutralized graft copolymer of starch and acrylic acid, a saponified copolymer of vinyl acetate and acrylic acid ester, partially neutralized polyacrylic acid, a copolymer of maleic anhydride and isobutylene, and a polymer of a water-soluble ethylenic unsaturated monomer.

6. A process as set forth in claim 5, wherein the polymer of the water-soluble ethylenic unsaturated monomer is at least one selected from homopolymers and copolymers of monomers selected from the group consisting of acrylic acid, methacrylic acid, an alkali salt of acrylic acid, an alkali salt of methacrylic acid, acrylamide, methacrylamide and N,N-dimethylacrylamide.

7. A process as set forth in claim 4, wherein the water-absorbent resin to be present during the polymerization is of the same type as the water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer.

8. A process for preparing a water-absorbent resin

This is the replacement sheet

Date: 02 NOV 2000



by polymerization of a water-soluble ethylenic unsaturated monomer, comprising the steps of:

preparing an aqueous solution containing the water-soluble ethylenic unsaturated monomer dissolved therein and a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer;

adding the aqueous solution to a hydrocarbon solvent and dispersing the aqueous solution therein; and

heating the hydrocarbon solvent containing the aqueous solution dispersed therein to polymerize the water-soluble ethylenic unsaturated monomer contained in the aqueous solution,

wherein, a water-absorbing time of the water-absorbent resin contained in the aqueous solution is less than 10 seconds or longer than 20 seconds.

9. A process as set forth in claim 8, wherein at least one of a surface active agent and a polymer protective colloid is preliminarily added to the hydrocarbon solvent.

10. A process as set forth in claim 8, wherein the amount of the water-absorbent resin contained in the aqueous solution is 1wt% to 100wt% with respect to the water-soluble ethylenic unsaturated monomer.

11. A process as set forth in claim 10, wherein the

This is the replacement sheet

Date: 02 NOV 2000



water-absorbent resin contained in the aqueous solution is at least one selected from the group consisting of a hydrolyzate of a graft copolymer of starch and acrylonitrile, a neutralized graft copolymer of starch and acrylic acid, a saponified copolymer of vinyl acetate and acrylic acid ester, partially neutralized polyacrylic acid, a copolymer of maleic anhydride and isobutylene, and a polymer of a water-soluble ethylenic unsaturated monomer.

12. A process as set forth in claim 11, wherein the polymer of the water-soluble ethylenic unsaturated monomer is at least one selected from homopolymers and copolymers of monomers selected from the group consisting of acrylic acid, methacrylic acid, an alkali salt of acrylic acid, an alkali salt of methacrylic acid, acrylamide, methacrylamide and N,N-dimethylacrylamide.

13. A process as set forth in claim 10, wherein the water-absorbent resin contained in the aqueous solution is of the same type as the water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer.

14. A process as set forth in claim 8, wherein the aqueous solution further contains a crosslinking agent.

15. A process as set forth in claim 14, wherein the amount of the crosslinking agent to be used is 0.001wt%

This is the replacement sheet

Date: 02 NOV 2000



to 5wt% with respect to the water-soluble ethylenic unsaturated monomer.

16. A process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, comprising the steps of:

adding an aqueous solution containing the water-soluble ethylenic unsaturated monomer to a hydrocarbon solvent and dispersing the aqueous solution therein;

adding a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer to the hydrocarbon solvent which contains the aqueous solution dispersed therein; and

heating the hydrocarbon solvent containing the aqueous solution and the added water-absorbent resin to polymerize the water-soluble ethylenic unsaturated monomer contained in the aqueous solution,

wherein, a water-absorbing time of the water-absorbent resin added to the hydrocarbon solvent is less than 10 seconds or longer than 20 seconds.

17. A process as set forth in claim 16, wherein at least one of a surface active agent and a polymer protective colloid is preliminarily added to the hydrocarbon solvent.

This is the replacement sheet

Date: 02 NOV 2000



18. A process as set forth in claim 16, wherein the amount of the water-absorbent resin added to the hydrocarbon solvent is 1wt% to 100wt% with respect to the water-soluble ethylenic unsaturated monomer.

19. A process as set forth in claim 18, wherein the water-absorbent resin added to the hydrocarbon solvent is at least one selected from the group consisting of a hydrolyzate of a graft copolymer of starch and acrylonitrile, a neutralized graft copolymer of starch and acrylic acid, a saponified copolymer of vinyl acetate and acrylic acid ester, partially neutralized polyacrylic acid, a copolymer of maleic anhydride and isobutylene, and a polymer of a water-soluble ethylenic unsaturated monomer.

20. A process as set forth in claim 19, wherein the polymer of the water-soluble ethylenic unsaturated monomer is at least one selected from homopolymers and copolymers of monomers selected from the group consisting of acrylic acid, methacrylic acid, an alkali salt of acrylic acid, an alkali salt of methacrylic acid, acrylamide, methacrylamide and N,N-dimethylacrylamide.

21. A process as set forth in claim 18, wherein the water-absorbent resin added to the hydrocarbon solvent is of the same type as the water-absorbent resin resulting from the polymerization of the water-soluble ethylenic



unsaturated monomer.

22. A process as set forth in claim 16, wherein the aqueous solution containing the water-soluble ethylenic unsaturated monomer further contains a crosslinking agent.

23. A process as set forth in claim 22, wherein the amount of the crosslinking agent to be used is 0.001wt% to 5wt% with respect to the water-soluble ethylenic unsaturated monomer.

24. A process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, comprising the steps of:

polymerizing the water-soluble ethylenic unsaturated monomer to afford a slurry; and

further adding the water-soluble ethylenic unsaturated monomer to the slurry, and polymerizing the added water-soluble ethylenic unsaturated monomer,

wherein, in at least one of the aforesaid steps, the polymerization is allowed to take place in the presence of a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer.

25. A process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic



unsaturated monomer, comprising the steps of:

polymerizing the water-soluble ethylenic
unsaturated monomer to afford a slurry; and

adding to the slurry the water-soluble ethylenic
unsaturated monomer preliminarily mixed with a
water-absorbent resin having a water-absorbing rate
different from that of a water-absorbent resin resulting
from the polymerization of the water-soluble ethylenic
unsaturated monomer, and polymerizing the added
water-soluble ethylenic unsaturated monomer.

26. A water-absorbent resin prepared by a process as
recited in claim 1.

27. A water-absorbent resin prepared by a process as
recited in claim 8.

28. A water-absorbent resin prepared by a process as
recited in claim 16.

29. A water-absorbent resin prepared by a process as
recited in claim 24.

30. A water-absorbent resin prepared by a process as
recited in claim 25.

31. A water-absorbent resin comprising:

a first water-absorbent resin component having a
water-absorbing time of less than ten seconds; and
a second water-absorbent resin component
compounded with the first water-absorbent resin component



and having a water-absorbing time of longer than 20
seconds.

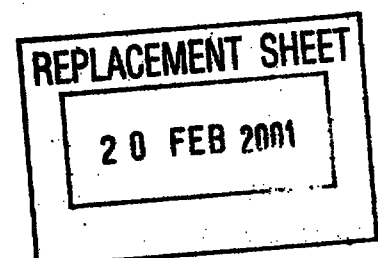
This is the replacement sheet

Date: 02 NOV 2000

In accordance with one aspect of the present invention, there is provided a process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, which comprises the step of polymerizing the water-soluble ethylenic unsaturated monomer in the presence of a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer. A water-absorbing time of the water-absorbent resin to be present during the polymerization is less than 10 seconds or longer than 20 seconds.

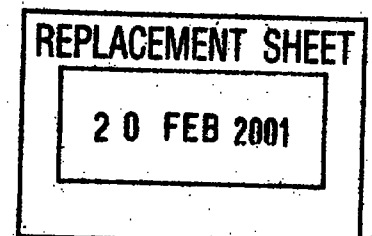
In a preferred mode of the present invention, the polymerization is performed by a reversed-phase suspension polymerization method.

In accordance with another aspect of the present invention, there is provided a process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, which comprises the steps of: preparing an aqueous solution containing the water-soluble ethylenic unsaturated monomer dissolved therein and a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the



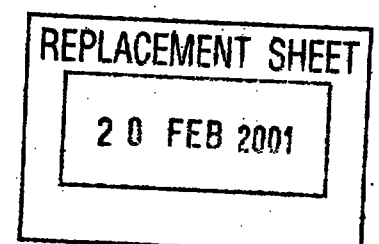
water-soluble ethylenic unsaturated monomer; adding the aqueous solution to a hydrocarbon solvent and dispersing the aqueous solution therein; and heating the hydrocarbon solvent containing the aqueous solution dispersed therein to polymerize the water-soluble ethylenic unsaturated monomer contained in the aqueous solution. A water-absorbing time of the water-absorbent resin contained in the aqueous solution is less than 10 seconds or longer than 20 seconds.

In accordance with further another aspect of the present invention, there is provided a process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, which comprises the steps of: adding an aqueous solution containing the water-soluble ethylenic unsaturated monomer to a hydrocarbon solvent and dispersing the aqueous solution therein; adding a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer to the hydrocarbon solvent which contains the aqueous solution dispersed therein; and heating the hydrocarbon solvent containing the aqueous solution and the added water-absorbent resin to polymerize the water-soluble ethylenic unsaturated



monomer contained in the aqueous solution. A water-absorbing time of the water-absorbent resin added to the hydrocarbon solvent is less than 10 seconds or longer than 20 seconds.

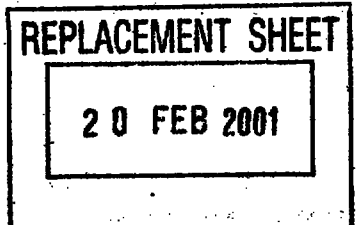
In accordance with still another aspect of the present invention, there is provided a process for preparing a water-absorbent resin by polymerization of a water-soluble ethylenic unsaturated monomer, which



present invention, a water-soluble ethylenic unsaturated monomer is polymerized in the presence of a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer. Thus, a water-absorbent resin can be prepared in which there is a compound of the two components of water-absorbent resin having different water-absorbing rates, i.e., a compound of the water-absorbent resin resulting from the polymerization of the water-soluble ethylenic unsaturated monomer and the water-absorbent resin present in the polymerization reaction system. The water-absorbent resin thus prepared ensures the reduction in the release amount of liquid as well as the increase in the liquid diffusibility.

A water-absorbent resin according to the present invention comprises a first water-absorbent resin component having a water-absorbing time of less than ten seconds and a second water-absorbent resin component compounded with the first water-absorbent resin component and having a water-absorbing time of longer than 20 seconds.

Since the water-absorbent resin contains the



first and second water-absorbent resin components having different water-absorbing times, the reduction in the release amount of liquid as well as the increase in the liquid diffusibility can be ensured.

The foregoing and other objects and effects will become apparent from the following detailed description.

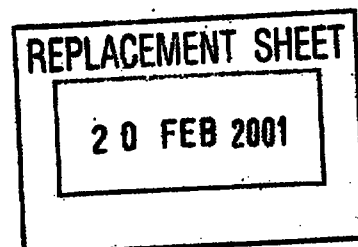
DETAILED DESCRIPTION OF THE INVENTION

The polymerization method to be employed in the preparation processes of the present invention is not particularly limited, but any of various known polymerization methods such as reversed-phase suspension polymerization and aqueous solution polymerization can be employed. To produce a better effect, however, the reversed-phase suspension polymerization method is preferably employed. The preparation processes will hereinafter be described on the premise that the reversed-phase suspension polymerization method is employed.

The water-soluble ethylenic unsaturated monomer to be used in the present invention is not particularly limited, but any of those generally used for polymerization may be employed. Examples of specific water-soluble ethylenic unsaturated monomers include:

ABSTRACT

A process for preparing a water-absorbent resin is provided which enables the water-absorbent resin to ensure the reduction in the release amount of liquid and the increase in the liquid diffusibility. In the preparation process, the water-absorbent resin is prepared by polymerization of a water-soluble ethylenic unsaturated monomer. The polymerization of the water-soluble ethylenic unsaturated monomer is allowed to take place in the presence of a water-absorbent resin having a water-absorbing rate different from that of a water-absorbent resin resulting from polymerization of the water-soluble ethylenic unsaturated monomer. A water-absorbing time of the water-absorbent resin to be present during the polymerization is less than 10 seconds or longer than 20 seconds. In a preferred mode, the polymerization is performed by a reversed-phase suspension polymerization method.



PCT

世界知的所有権機関
国際事務局

特許協力条約に基づいて公開された国際出願

CA02999-5
IP05

(51) 国際特許分類6 C08F 291/00, 2/32, 2/44, 265/02, 220/06	A1	(11) 国際公開番号 WO97/19968 (43) 国際公開日 1997年6月5日(05.06.97)
(21) 国際出願番号 PCT/JP96/03454 (22) 国際出願日 1996年11月25日(25.11.96) (30) 優先権データ 特願平7/337752 / 1995年11月30日(30.11.95) JP (71) 出願人 (米国を除くすべての指定国について) 住友精化株式会社 (SUMITOMO SEIKA CHEMICALS CO., LTD.)[JP/JP] 〒675-01 兵庫県加古郡播磨町宮西346番地の1 Hyogo, (JP) (72) 発明者: および (75) 発明者/出願人 (米国についてのみ) 藤掛正人(FUJIKAKE, Masato)[JP/JP] 縄田康博(NAWATA, Yasuhiro)[JP/JP] 白川孫大(SHIRAKAWA, Magoto)[JP/JP] 山盛勝一(YAMAMORI, Masakazu)[JP/JP] 古仲塩子(YOSHINAKA, Shioko)[JP/JP] 中村守男(NAKAMURA, Morio)[JP/JP] 〒672 兵庫県姫路市飾磨区入船町1番地 住友精化株式会社 第2研究所内 Hyogo, (JP)		(74) 代理人 弁理士 市川恒彦(ICHIKAWA, Tsunehiko) 〒530 大阪府大阪市北区南森町1丁目1番25号 八千代ビル南館7階 Osaka, (JP) (81) 指定国 CN, KR, <u>SG</u> , US, 欧州特許 (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, I.U, MC, NL, PT, SE). 添付公開書類 国際調査報告書
(54)Title: PROCESS FOR PREPARING WATER-ABSORBENT RESIN (54)発明の名称 吸水性樹脂の製造方法 (57) Abstract A process for preparing a water-absorbent resin, which can reduce the amount of back flow of a liquid to be absorbed and, at the same time, can enhance the diffusibility of the liquid to be absorbed. The process comprises conducting the polymerization of a water-soluble ethylenically unsaturated monomer in the presence of a water-absorbent resin having a water absorption rate different from that of the water-absorbent resin prepared by the polymerization of the above monomer. According to a preferred embodiment, the polymerization is carried out by reversed phase suspension polymerization.		

(57) 要約

被吸収液の逆戻り量を低減させながら同時に被吸収液の拡散性を高めることができる吸水性樹脂の製造方法である。この製造方法では、水溶性エチレン性不飽和単量体の重合反応により吸水性樹脂を製造する。この際、水溶性エチレン性不飽和単量体の重合反応により得られる吸水性樹脂の吸水速度とは異なる吸水速度を有する吸水性樹脂の存在下で、水溶性エチレン性不飽和単量体を重合反応させる。好ましい態様では、重合反応を逆相懸濁重合法により行う。

簡報としての用途のみ

PCTに基づいて公開される国際出願をパンフレット第一頁にPCT加盟国を特定するために使用されるコード

AL	アルバニア	EE	エストニア	LR	リベリア	RU	ロシア連邦
AM	アルメニア	FI	フィンランド	LT	リトアニア	DE	ドイツ
AT	オーストリア	FR	フランス	LU	ルクセンブルグ	SG	シンガポール
AU	オーストラリア	GB	イギリス	LV	ラトヴィア	SK	スロバキア
AZ	アゼルバイジャン	GE	グルジア	MC	モナコ	SI	スロベニア
BB	バルバドス	GH	ガーナ	MD	モルドバ	SS	スウェーデン
BG	ブルガリア	GN	ギニア	MG	マダガスカル	SN	セネガル
BJ	ベナン	GR	ギリシャ	MK	マケドニア	NZ	ニュージーランド
BR	ブラジル	HU	ハンガリー	UA	ウクライナ	TD	チャド
BY	ベラルーシ	IE	アイルランド	ML	マリ	TG	トーゴ
CC	カカ	IT	イタリア	MN	モンゴル	TM	トルクメニスタン
CF	中央アフリカ共和国	JP	日本	MR	モーリタニア	TR	トルコ
CG	コンゴ	KE	ケニア	MW	モザンビーク	TT	トリニダード・トバゴ
CH	スイス	KR	韓国	MX	メキシコ	TV	ツバル
CI	コート・ジボワール	KG	キルギス	NE	ニジェール	UG	ウガンダ
CM	カメルーン	KP	朝鮮民主主義人民共和国	NL	オランダ	US	米国
CN	中国	KZ	カザフスタン	NO	ノルウェー	UZ	ウズベキスタン
CO	コロンビア	LI	リヒテンシュタイン	NZ	ニュージーランド	VN	ベトナム
DE	ドイツ	RS	セルビア	PL	ポーランド	YU	ユーゴスラビア
DK	デンマーク	SK	スウェーデン	RO	ルーマニア		