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- (21) Application No. 39966/77 (22) Filed 26 Sep. 1977
 (31) Convention Application No. 51/120591 (32) Filed 7 Oct. 1976 in
 (33) Japan (JP)
 (44) Complete Specification Published 11 Jun. 1980
 (51) INT. CL. ³ C08F 2/32 220/06
 (52) Index at Acceptance
 C3P JL

(19)



(54) PROCESS FOR PREPARATION OF SPONTANEOUSLY
 CROSSLINKED ALKALI METAL ACRYLATE POLYMERS

(71) We, KAO SOAP CO. LTD., a Japan Company, of 1, 1-chome, Nihonbashi-Kayabacho, Chuo-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a process for the preparation of spontaneously crosslinked alkali metal acrylate polymers having a high water-absorbing property and a high sanitary safety.

Paper products for absorbing human bodily excretions, such as sanitary towels and paper nappies have been used for many years, but their properties are not completely satisfactory. Most of the defects of these paper products are due to the insufficient water-absorbing properties of the paper. In paper, water is absorbed in clearance space between the fibers by capillary action. Accordingly, as the amount of water absorbed increases, the paper swells and becomes very bulky. Further, the majority of the absorbed water can be squeezed out by the application of external pressure.

In attempts to overcome this defect, there have heretofore been proposed various composite products formed by combining a water-absorbing polymer with paper, pulverized pulp, absorbent cotton or the like. For example, U.S. Patent No. 3 670 731 discloses that a low-bulk product having a high water-absorbing property even under the application of external pressure, may be prepared by distributing a partially crosslinked acrylamide-sodium acrylate copolymer in an absorbent material.

The water-absorbing polymer that can be used in this field is obtained by partially cross-linking a water-soluble polymer so that the resulting polymer can be swollen by water, but it does not dissolve in water. Because of its intended use, the water-

absorbing polymer must be sanitary and safe for contact with the human body, and it is required that the water-absorbing polymer can be manufactured at a low cost.

In general, as disclosed in U.S. Patent No 3 669 103, water-swellaable but water-insoluble polymers, such as partially crosslinked polyacrylamide and poly(alkali metal acrylate), that can be used as water-absorbing polymers, may be prepared by free radical copolymerisation of an aqueous solution of the corresponding monomer and a crosslinking monomer such as a divinyl or diallyl compound. The resulting massive hydrous gel is dried and then pulverized. Further, a water-soluble polymer prepared in advance may be crosslinked by radiation.

As an example of a water-soluble polymer having a high sanitary safety that can be used as the basic skeleton of a water-absorbing polymer, there can be mentioned poly(sodium acrylate), which is permitted for use as a food additive. In order to obtain a water-absorbing polymer, this polymer must be crosslinked. It is not preferred to copolymerize sodium acrylate using a divinyl or diallyl compound as the crosslinking monomer because the sanitary safety of a polymer prepared in the way has not been proved. Post-crosslinking by radiation is excellent from the viewpoint that an additional chemical compound is not introduced into the polymer. However, in the latter case, complicated equipment is required, so that the preparation process involves a large capital investment, and the manufacturing cost is extremely high.

It is known that in the polymerization of acrylic acid or sodium acrylate, a partially or highly crosslinked polymer can be prepared under some preparation conditions. For example, it is reported that in the aqueous solution polymerization of sodium acrylate, because the monomer concentration is high, at a pH of 4 to 6 the induction period is very

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long and after this long induction period, rapid polymerization accompanied with bumping due to accumulation of the heat of polymerization takes place and the entire mixture is converted to a granular gel which is poorly soluble in water (see "Acrylic Acid and Its Polymers", volume I, page 51, written by Eizo Ohmori and published by Shokodo in 1973). It is also reported that a polymer obtained by water-in-oil emulsion polymerization of acrylic acid is partially insoluble in water (see Japanese Patent Publication No. 10644/50). However, the primary object of these known processes is to obtain a soluble poly(sodium acrylate). In these processes the crosslinking reaction is an abnormal and unwanted reaction, and it is one of the technical problems in the conventional polymerization processes to devise procedures to eliminate the occurrence of such an abnormal crosslinking reaction.

We have noted this abnormal reaction and searched for polymerization conditions effective to cause this reaction to occur on a reliable, reproducible basis so that poly(sodium acrylate) can be uniformly and spontaneously crosslinked to produce a polymer product having a high swelling property but containing only a very small water-soluble portion.

More specifically, we prepared polymers according to the teachings of the above textbook reference and Japanese patent publication. As described in the Comparative Examples given hereinafter, the degree of swelling of a polymer obtained by aqueous solution polymerization at a high concentration of sodium acrylate is not very high and the amount of the water-soluble portion of the polymer is large. In other words, the polymer is highly sticky when it is dispersed in water. Moreover, since this reaction progresses very vigorously and rapidly, it is very difficult to conduct this polymerization process on an industrial scale while controlling the reaction appropriately. In the case of the water-in-oil emulsion polymerization of acrylic acid, the resulting polymer is obtained as a dispersion in water, and when it is neutralized with sodium hydroxide, a large quantity of a water-soluble polymer portion is formed and the resulting product is not satisfactory as a water-absorbing polymer. At any rate, in view of the intended use of the polymer, a water-absorbing polymer must be substantially neutral, and the resulting polyacrylic acid must be neutralized with an alkaline substance. Therefore, in the process in which a crosslinked polyacrylic acid is prepared and then neutralized, a gel having a high viscosity must be treated and it must be pulverized. However, the steps of removing the solvent and water from a highly viscous

gel and pulverizing and powdering the resulting solid are quite difficult and disadvantageous from the industrial viewpoint.

We have discovered that under specific conditions, namely, by adopting a water-in-oil suspension polymerization process in which the polymerization is carried out by suspending and dispersing an aqueous solution of an alkali metal acrylate having a concentration of said alkali metal acrylate of at least 40% by weight, in an aliphatic hydrocarbon solvent, in the presence of a water-soluble free radical polymerization initiator, a stable spontaneously crosslinked polymer of the alkali metal acrylate having a high swelling property (i.e. a high water-absorbing property) but having a low proportion of water-soluble polymers can be obtained in powder form.

This technique of water-in-oil polymerization as disclosed mainly for the preparation of acrylamide polymers and acrylamide copolymers in Japanese Patent Publication No. 10644/59, Japanese Patent Application Laid-Open Specification No. 1082/73, Japanese Patent Application Laid-Open Specification No. 41090/76 and Japanese Patent Application Laid-Open Specification No. 47937/76 can be employed in the process of the invention.

In the process for preparing polymers according to the present invention, because neutralization of the polymer is difficult after the polymer has been formed, the acrylic acid must be at least partially neutralized, for example, with an alkali metal hydroxide, before initiation of polymerization. The degree of neutralization of the acrylic acid, that is, the percentage of the carboxyl groups of the acrylic acid that are converted to carboxylate groups, is preferably 50 to 95% by weight, and more preferably 65 to 75% by weight.

In the present invention, it is critical that the organic medium used as the oil phase is an aliphatic hydrocarbon, preferably having a boiling point of 30 to 200°C. For example, n-hexane and ligroin are preferably employed. A particularly preferred organic solvent is n-hexane. In order to attain the intended object of the present invention, it is critical that the suspension polymerization must be conducted in the water-in-oil suspension state so that after the suspension polymerization is completed, the polymer is obtained in the form of a non-sticky powder having a particle size of 0.01 to 0.12 mm. It is important, for conducting the suspension polymerization in such a state, that a liquid aliphatic hydrocarbon medium be used as the oil phase for the suspension polymerization and that a nonionic surface active agent (e.g. a sorbitan fatty acid ester) having an HLB value of 3 to 6 be used for dispersing the aqueous solution of the alkali metal

acrylate monomer in the oil phase. It is critical that an aliphatic hydrocarbon is used as the oil phase, as pointed out hereinbefore, and the object of the present invention cannot be attained when an aromatic solvent is used. More specifically, when an aromatic solvent such as benzene, toluene, or xylene is used and a sorbitan fatty acid ester having the HLB value of 3 to 6, for example, sorbitan monostearate, is used as a surface active agent for promoting formation of water in oil-type emulsion, the resulting polymer is gelled and it cannot be powdered at all. It is believed that the reason is that the aromatic solvent is inferior to the liquid aliphatic hydrocarbon medium in an ability to stabilize the suspension phase, that the polymer product is highly soluble in the aromatic solvent so that the solvent dissolves parts of the resulting polymer particles and promotes fusion and cohesion of the polymer particles.

All of the water-soluble free radical polymerization initiators customarily used for emulsion polymerization are suitable for use in the present invention. For example, there can be mentioned water-soluble peroxides such as potassium persulfate, ammonium persulfate and hydrogenperoxide. These initiators can be combined with reducing substances such as sulfites or amines to form known redox type initiators.

The polymer prepared according to the process of the present invention is pulverized in the final step. In order to achieve efficient pulverization of the resulting polymer it is critical that the polymerization is carried out in an aqueous phase by the water-in-oil polymerization technique. Therefore, the polymerization initiator used must be water-soluble, and the use of an oil-soluble readical polymerization initiator is not permissible in the present invention. More specifically, if an attempt is made to use an oil-soluble initiator, free radicals are formed in the oil phase, and oil solution polymerization and water-in-oil type emulsion polymerization take place concurrently. Accordingly, the entire reaction mixture becomes gelled and the powdered polymer desired as a final product in the present invention cannot be obtained at all. Among the known water-soluble initiators, potassium persulfate and ammonium persulfate are preferred for their high polymerization-initiating activity.

A non-ionic surface active agent having an HLB value of 3 to 6 is used as the oil-soluble surface active agent that is used for dispersing and suspending an aqueous solution of an alkali metal acrylate in the organic solvent. Such a surface active agent that is solid at room temperature is preferred. A surface active agent that is solid at room temperature does not change the

surface condition of the resulting polymer and prevents the occurrence of undesirable phenomena such as adhesion of polymer particles or formation of agglomerates of polymer particles. In the present invention, the use of a sorbitan fatty acid ester that is solid at room temperature, especially sorbitan monostearate, is preferred. When a surface active agent having an HLB value larger than 6 is used, a water-in-oil type emulsion cannot be stably formed. When a surface active agent having an HLB value smaller than 3 is used, even though a water-in-oil type emulsion may be formed, because the surface active agent *per se* is oily, it adheres to the surfaces of the resulting polymer particles to render them sticky, and a non-sticky polymer which can be handled with ease cannot be obtained. Accordingly, the use of a surface active agent having too large or too small an HLB value is not suitable for use in the present invention.

We found that the concentration of the aqueous solution of the alkali metal acrylate to be subjected to polymerization has a very close relation to the degree of crosslinking or the degree of swelling in the resulting polymer. A higher concentration of the aqueous solution of the alkali metal acrylate results in a higher degree of crosslinking or swelling. The concentration of the alkali metal acrylate is maintained at at least 40% by weight, and preferably is maintained at the saturated concentration. The saturated concentration of sodium acrylate having a neutralization degree of 75% in water is about 45% by weight at room temperature. When polymerization is conducted at a concentration of at least 40% by weight of the alkali metal acrylate, a crosslinked polymer can be obtained without using a crosslinking agent which is ordinarily required for obtaining a crosslinked polymer.

In carrying out the process of the present invention, the ratio of the amount of the aqueous solution of the monomer to the amount of the aliphatic hydrocarbon oil phase can be varied over a broad range. In general, when the amount of the oil phase is relatively small, there is attained the advantage that the amount of the monomer that can be charged in the reaction vessel for a one-batch reaction can be increased, but it becomes difficult to remove the heat generated by the reaction. Therefore, the above-mentioned quantitative ratio of aqueous solution of alkali metal acrylate to aliphatic hydrocarbon oil phase is determined depending on the heat-removing capacity of the reaction vessel. In general, a quantitative volume ratio of aqueous phase to oil phase ranging from 1:1 to 1:4 is preferred. Removal of the heat generated by the reaction can be facilitated by adding the

aqueous solution of the monomer in batches to the oil phase.

5 The polymerization initiator is preferably in an amount of 0.01 to 1% by weight, based on the weight of the alkali metal acrylate monomer. The polymerization is preferably carried out at 30 to 80°C, more preferably 50 to 70°C.

10 A preferred amount of the surface active agent is in the range of 1 to 10% by weight, based on the weight of the alkali metal acrylate monomer. The particle size of the resulting polymer is determined by the amount incorporated of the surface active agent.

15 The polymerization according to the present invention is conducted in the following manner.

20 An initiator is dissolved in the aqueous solution of the monomer which has been neutralized in advance. The aqueous solution is mixed with a solution of a surface active agent in the oil phase. Nitrogen gas is introduced into the mixture with agitation to displace the air from the reaction system, during which time the aqueous solution phase in the reaction mixture is converted to fine liquid in the oil phase. Then, the reaction mixture is heated at a predetermined temperature to initiate polymerization. The reaction mixture is appropriately heated or cooled depending on the heat generated by the reaction. The polymerization reaction advances in the fine liquid droplets of the aqueous phase, and when agitation is stopped after completion of the reaction, the resulting water-swollen polymer particles are precipitated. The precipitated polymer particles are separated from the oil phase by a method such as decantation, filtration or centrifugal separation and they are then dried. Alternatively, the dry polymer can be directly obtained by removing the oil phase and water by distillation.

45 The particle size of the thus-obtained polymer is very small and is ordinarily in the range of 0.01 to 0.12 mm, although the particle size is dependent to some extent on the amount of surface active agent used. The resulting polymer is a powder consisting of truly globular primary particles having their surfaces coated with the surface active agent or of such primary particles and a small quantity of secondary particles by agglomeration of primary particles. Such secondary particles can easily be pulverized into finer particles by application of gentle mechanical force. This feature is very advantageous for both the preparation and the intended use of the polymer. More specifically, when a polymer gel is prepared according to customary aqueous solution polymerization and the polymer gel is dried, because the polymer is not in the powdery state, a very large mechanical force is

necessary in order to pulverize the dried polymer, and it is very difficult to obtain a fine powdery product.

70 Since the surfaces of the polymer particles obtained according to the process of the present invention are coated with the oil-soluble surface active agent, there is attained the advantage that adhesion of the particles to one another does not occur to a significant degree. Moreover, when the dry polymer is dispersed in water again and the resulting creamy product is dried, the polymer is recovered in the powdery state without agglomeration. This means that a wet method can be employed for preparing a composite product of a paper or non-woven fabric by utilizing this polymer. In contrast, when a polymer prepared according to the customary aqueous solution polymerization is dispersed in water and then dried, the polymer particles adhere to one another and form large agglomerates.

85 The polymer obtained according to the process of the present invention consists essentially of an a polymer of an alkali metal acrylate and does not contain a cross-linking monomer. Further, the oil-soluble surface active agent used as the dispersion stabilizer at the time of polymerization and which finally remains on the surfaces of the dried polymer particles is a sorbitan fatty acid ester which is safe for contact with human bodies as shown by the fact that it is allowed as a food additive. Still further, when a purified petroleum-type aliphatic hydrocarbon, for example, n-hexane of food additive grade such as is used for extraction of an edible oil, is used as the oil phase in the polymerization step, if a minute amount of it remain in the resulting polymer, it does not degrade the sanitary safety of the polymer at all. Moreover, the polymer obtained according to the present invention has the characteristic property that when it contacts water, it absorbs a large quantity of water, for example, at least 400 g of water per g of the polymer.

110 The water absorption referred to in the present specification is determined according to the following method.

115 A beaker having a capacity of 1 liter is charged with about 1 g of the polymer and 720 g of deionized water, and the contents are greatly agitated so that the polymer is sufficiently dispersed in water but the polymer chains are not broken up. The dispersion is allowed to stand at room temperature for 30 minutes to swell the polymer sufficiently, and the dispersion is filtered by an 80-mesh (Tyler Standard Series) metal screen. The weight of the polymer thus recovered is measured and the value obtained is divided by the original weight of the polymer. The value thus obtained is defined as the water absorption.

In the present invention, the particle size is determined by a micro-photograph taken at 50 magnifications by a high grade biological microscope manufactured by Olympus Co.

In the present invention, it is preferred that the starting acrylic acid is wholly neutralized so that the resulting polymer is neutral. As the alkali to be used for neutralizing the acrylic acid, there can be mentioned, for example, sodium hydroxide, potassium hydroxide and lithium hydroxide. Sodium hydroxide is most preferred as it provides a polymer having no mutual reaction with living bodies.

A preferred embodiment of the present invention will now be described.

An aqueous solution of sodium acrylate having a neutralization degree of 65 to 75%, which solution has a concentration of 40 to 45% by weight and contains potassium or ammonium persulfate in an amount of 0.01 to 1% by weight, based on the sodium acrylate, is dispersed, suspended and polymerized in n-hexane in the presence of sorbitan monostearate. Then, n-hexane and water are removed (e.g. by distillation) to obtain a powdery poly(sodium acrylate) having an excellent water-absorbing property and a high sanitary safety.

The present invention will now be described in detail by reference to the following Examples and Comparative Examples.

Comparative Example 1

An aqueous solution formed by dissolving 80.4 g of sodium hydroxide having a purity of 93% in 232 ml of water was added to 180 g of acrylic acid to effect neutralization. The solution was cooled to room temperature and 0.6 g of potassium persulfate was incorporated and dissolved in the aqueous solution. The pH value of the resulting solution was 5.7. The solution was flowed into a stainless steel tray having a height of 20 cm and a cross-sectional area of 25 cm². The top portion of the tray was covered with a thin polyethylene film and nitrogen gas was introduced in a space in the upper portion of the tray to expel oxygen. This tray was floated on a water bath maintained at 60°C. When the temperature of the reaction mixture reached 60°C, the reaction was immediately started to effect rapid polymerization which was accompanied with bumping. The reaction mixture was allowed to stand in this state for 1 hour. The resulting rubbery gel was taken out of the tray and finely cut by a knife. The cut polymer pieces were dried overnight at 70°C in a hot air oven. Then, the polymer pieces were pulverized in a mortar so as to obtain a powdery product capable of passing through a 60-mesh sieve.

The water absorption of the thus-formed

polymer determined according to the above-mentioned method was about 250 g per gram of dried polymer. Further, during the measurement, the swollen gel was highly sticky, and the filterability was poor.

Comparative Example 2

To the same starting solution as used in Comparative Example 1 there was further added a solution formed by dissolving 0.3 g of potassium metabisulfite in 8 ml of water after addition of potassium persulfate. The polymerization was carried out under the same conditions as described in Comparative Example 1 except that the temperature of the water bath was maintained at 25°C and the polymerization time was adjusted to 4 hours. The reaction was started without any substantial induction period and the maximum temperature was 30°C. The resulting polymer took a rubbery gel-like form.

The water absorption of the resulting polymer determined in the same manner as described in Comparative Example 1 was only about 180 g per gram of dried polymer. The swollen gel was highly sticky and the filterability was poor.

Comparative Example 3

A 500 ml-capacity four-neck round-bottom flask equipped with an agitator, a reflux condenser, a dropping funnel and a nitrogen inlet was charged with 175 g of xylene and 17.5 g of sorbitan monostearate, and the sorbitan monostearate was dissolved in the xylene. Then, 0.35 g of benzoyl peroxide was incorporated and dissolved in the solution. Then, a solution formed by dissolving 37.5 g of acrylic acid in 37.5 g of water was added to and emulsified in the xylene solution. Nitrogen gas was blown into the flask to expel oxygen therefrom and the reaction mixture was heated at 60 to 65°C for 8 hours. The resulting polymer was separated and dried. The polymer was insoluble in water, but when it was placed into an aqueous solution of sodium hydroxide for neutralization, the polymer was substantially dissolved and a highly viscous solution containing only a very small amount of an insoluble portion was obtained.

From the results obtained in this Comparative Example, it will readily be understood that when a 50% aqueous solution of acrylic acid is polymerized in xylene in the presence of an oil-soluble radical polymerization initiator, a water-insoluble polymer is obtained but it is dissolved in an alkaline aqueous solution, and the self-crosslinked swellable polymer desired in the present invention cannot be obtained at all.

Example 1

The same flask as used in Comparative Example 3 was charged with 228 ml of n-hexane of the food additive grade, and 1.8 g of sorbitan monostearate was added and dissolved in the n-hexane. Nitrogen gas was blown into the flask to expel dissolved oxygen. Separately, 30 g of acrylic acid was added to an alkali solution prepared from 39 g of water and 13.4 g of 93% sodium hydroxide in an Erlenmeyer flask while cooling the flask with ice from the outside, whereby 75% of the carboxyl groups of the acrylic acid were neutralized. The monomer concentration in the thus-formed aqueous solution was 45%. Then, 0.1 g of potassium persulfate was added and dissolved in the aqueous solution, and nitrogen gas was blown into the solution to expel oxygen present in the solution. The aqueous solution in the Erlenmeyer flask was dispersed in the contents of the 4-neck flask, and the mixture was agitated for 6 hours on a warm water bath while introducing nitrogen in the interior of the flask and maintaining the internal temperature at 60 to 65°C. When the agitation was stopped, there was obtained a suspension from which the resulting swollen polymer particles readily sedimented and separated. The n-hexane was removed by distillation under reduced pressure, and the residual swollen polymer was dried at 30° to 80°C under reduced pressure. The polymer was obtained in the form of a powder containing some agglomerated masses which could readily be pulverized by pressing with a finger. The particle size of the primary particles of the resulting polymer powder was in the range of 0.01 to 0.08 mm, and the average particle size was 0.05 mm. The water absorption of the resulting polymer was about 500 g per gram of dried polymer. At the time of the measurement of the water absorption, the filterability of the polymer was very good and no stickiness was observed. The pH value of a slurry containing 0.25 wt.% of this polymer was 7.4.

Example 2

A powdery polymer was prepared in the same manner as described in Example 1 except that the amount of water used for formation of the aqueous phase was changed to 49 g, namely the monomer concentration in the aqueous phase was changed to 40%.

The water absorption of the resulting polymer was about 400 g, per gram of dried polymer, and the particle size of the polymer was in the range of 0.01 to 0.08 mm and the average particle size was 0.04 mm.

Comparative Example 4

The polymerization was repeated under the same conditions as in Example 2 except that the amount of water used was increased to change the monomer concentration in the aqueous phase to 35 wt.%. When the resulting polymer was placed in water, it was in a semi-dissolved state and the water absorption could not be measured.

Example 3

A powdery polymer was prepared in the same manner as described in Example 1 except that the amounts used of 93% sodium hydroxide and water in the aqueous phase were changed to 12.5 g and 35 g, respectively, whereby the neutralization degree of the acrylic acid was changed to 70% and the monomer concentration in the aqueous phase was changed to 47%.

The water absorption of the resulting polymer was about 400 g per gram of dried polymer, and the pH value of a slurry containing 0.25 wt.% of this polymer was 7.1. The particle size of the polymer was in the range of 0.01 to 0.08 mm and the average particle size was 0.04 mm.

Comparative Example 5

A polymer was prepared in the same manner as described in Example 1 except that 0.03 g of N,N'-methylene-bis(acrylamide) was added as a crosslinking agent to the aqueous solution of sodium acrylate (0.1% by weight based on the acrylic acid). The water absorption of the resulting polymer was only 180 g per gram of dried polymer. The particle size of the polymer was in the range of from 0.01 to 0.08 mm and the average particle size was 0.04 mm.

Comparative Example 6

A polymer was prepared in the same manner as described in Example 1 except that 0.006 g of N,N'-methylene-bis(acrylamide) was added as a crosslinking agent to the aqueous solution of sodium acrylate. The water absorption of the resulting polymer was 220 g per gram of dried polymer. The particle size of the polymer was in the range of 0.01 to 0.08 mm and the average particle size was 0.04 mm.

Example 4

A powdery polymer was prepared in the same manner as in Example 1 except that commercially available ligroin of the special grade (containing more than 90% by volume of fractions boiling at 80° to 110°C) was used instead of n-hexane.

The water absorption of the resulting polymer was 450 g per gram of dried polymer. The particle size of the polymer was in the range of 0.01 to 0.8 mm and the

average particle size was 0.05 mm.

Comparative Examples 7 to 9

5 Polymerization was tried under the same conditions as described in Example 1 by using instead of n-hexane, commercially available special grade benzene, toluene and xylene separately.

10 In each case, gelation occurred midway through the reaction, and further progress of the reaction became impossible.

Comparative Example 10

15 An acrylamide-sodium acrylate copolymer was prepared in the same manner as described in Example 1 by using sodium acrylate formed by neutralizing 12 g of acrylic acid by 5.4 g of sodium hydroxide, 20 33.4 g or acrylamide, 0.02 g of potassium persulfate, 30 g of water, 220 ml of ligroin and 2.4 g of sorbitan monostearate. The water absorption of the resulting copolymer was only 240 g per gram of dried polymer. 25 The particle size of the resulting copolymer was in the range of 0.01 to 0.08 mm and the average particle size was 0.04 mm.

Comparative Example 11

30 A polymer was prepared in the same manner as described in Example 1 except that oil-soluble benzoyl peroxide was used instead of water-soluble potassium persulfate. Since benzoyl peroxide is insoluble in 35 water, it was dissolved in the n-hexane phase. The reaction progressed at a slower rate than in Example 1, and with advance of the reaction, adhesion of a gel to the wall of the reaction vessel took place. The remaining portion was a stable emulsion. Distillation of the solvent from the emulsion gave a 40 water-insoluble film. Thus, it was confirmed that when an oil-soluble polymerization initiator is used, the water-absorbing powdery polymer desired in the present invention 45 cannot be obtained.

The reason why the properties of a polymer prepared by using a water-soluble initiator are different from those of a polymer prepared by using an oil-soluble initiator as illustrated in Example 1 and Comparative 50 Example 1 is considered to be as follows.

In case of the water-soluble initiator, radical species formed from the initiator dissolved in the fine liquid droplets dispersed in the oil phase attack the monomer similarly dissolved in the fine droplets thereby to initiate the polymerization. Namely, 55 the polymerization progresses in the liquid droplets, i.e., in the aqueous phase, and the polymerization is conducted according to the so-called suspension polymerization process.

60 On the other hand, in case of the oil-soluble initiator, the neutralized monomer, 65

namely the sodium salt, is entirely present in the form of an aqueous solution in liquid droplets, and the unneutralized portion is distributed in both the liquid droplets, i.e., the aqueous phase, and the organic solvent phase. Since the initiator was dissolved only in the organic solvent, radical species formed from the initiator attack the monomer dissolved in the oil phase. In other words, polymerization of the unneutralized portion progresses in the oil phase solvent. Some of the radical species formed in the oil phase diffuse into the liquid droplets to cause polymerization of the monomer in the liquid droplets according to the so-called emulsion polymerization process. 70

In short, the former initiator causes suspension polymerization and the latter initiator causes emulsion polymerization. Therefore, the differences of properties are brought about between the polymer prepared by using the former initiator and the polymer prepared by using the latter initiator. 75 80 85 90

Example 5

A polymer was prepared in the same manner as described in Example 1 except that 1.8 g of sorbitan sesquioleate having an HLB value of 3.7 was used instead of sorbitan monostearate. 95

The water absorption of the resulting polymer was 480 g per gram of dried polymer. 100

Example 6

A polymer was prepared in the same manner as described in Example 1 except that 3.0 g of sorbitan monooleate having an HLB value of 4.3 was used instead of sorbitan monostearate. 105

The water absorption of the resulting polymer was 400 g per gram of dried polymer. 110

WHAT WE CLAIM IS:-

1. A process for the preparation of a powdery, spontaneously crosslinked, alkali metal acrylate polymer having a water absorption capacity of at least 400 grams per gram of dried polymer, said process comprising dispersing and suspending an aqueous solution of an alkali metal acrylate having a concentration of at least 40% by weight and containing a water-soluble free radical polymerization initiator in an aliphatic hydrocarbon solvent, in the presence of a non-ionic surface active agent having an HLB value of 3 to 6. 115 120

2. A process for the preparation of an alkali metal acrylate polymer according to Claim 1, wherein the alkali metal acrylate is prepared by neutralizing 50 to 95% of acrylic acid with an alkali metal hydroxide. 125

3. A process for the preparation of an 130

alkali metal acrylate polymer according to Claim 2, wherein the alkali metal hydroxide is sodium hydroxide.

5 4. A process for the preparation of an alkali metal acrylate polymer according to any preceding Claim, wherein the sorbitan fatty acid ester is sorbitan monostearate.

10 5. A process for the preparation of an alkali metal acrylate polymer according to any preceding Claim, wherein the aliphatic hydrocarbon is n-hexane.

15 6. A process for the preparation of an alkali metal acrylate polymer according to Claim 1, wherein an aqueous solution of an alkali metal acrylate having a concentration of at least 40% by weight thereof and containing potassium or ammonium persulfate in an amount of 0.01 to 1% by weight, based on the weight of the alkali metal
20 acrylate monomer, is dispersed and suspended in n-hexane in the presence of sorbitan monostearate, the alkali metal acrylate monomer is polymerized and the n-hexane and water are removed and the
25 residue dried to obtain the powdery polymer.

30 7. A powdery, crosslinked, alkali metal acrylate homopolymer prepared by the process of any preceding Claim, and having a particle size in the range of from 0.01 to 0.12 mm.

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