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(54) Title: PROCESS FOR PRODUCING PVP-H ₂ O ₂ PRODUCTS (57) Abstract A process for the production of PVP-H₂O₂ products in the form of free-flowing powders, or a free-standing, porous solid or foam, is described. To prepare free-flowing powders, a fluidized bed is maintained at a reaction temperature of about room temperature to 60 °C and is contacted with finely divided droplets of a 30 to 85 % by weight aqueous H₂O₂ solution. Preferably the fluidized bed temperature is about 35°-45 °C, a 5-70 % H₂O₂ solution is used, and the feed rate of introduction of the H₂O₂ solution is about 5-50 g/minute/kg PVP present. The PVP-H₂O₂ product preferably contains about 15-24 %, preferably 18-22 %, H₂O₂ (1:1 molar ratio) and less than about 5 % water.		

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PROCESS FOR PRODUCING PVP-H₂O₂ PRODUCTS

This invention relates to a process for making a polyvinylpyrrolidone-hydrogen peroxide (PVP-H₂O₂) product, and more particularly, to a fluidized bed process for the production of such material in the form of free-flowing powders or a free-standing, porous solid of foam.

Stabilized H₂O₂ compositions have found wide utility in commercial and industrial applications, e.g. as antiseptics, disinfectants, sterilization agents, bleaching materials, washing concentrates, etchants, in cosmetic preparations, and as a catalyst in polymerizations requiring a free radical source. In biological applications which require an antiseptic, disinfectant or sterilization agent, such H₂O₂ compositions require release of an effective amount of oxygen at a desired rate.

Shiraeff, in U.S. Patents 3,376,110 and 3,480,557, disclosed that a solid, stabilized hydrogen peroxide composition of hydrogen peroxide and a polymeric N-vinyl heterocyclic compound could be prepared from an aqueous solution of the components. The process involved mixing PVP and a substantial excess of aqueous H₂O₂ and evaporating the solution to dryness. The H₂O₂ content of the composition was given as being at least 2%, and preferably 4.5 to 70% by weight. Prolonged drying of the composition, in an attempt to reduce the water content, however, resulted in a substantial loss of H₂O₂ from the complex. The product was a brittle, transparent, gummy, amorphous material, and had a variable H₂O₂ content ranging from about 3.20 to 18.07% by weight, depending upon the drying times.

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The Shiraeff process did not attain commercial success because (1) the product was not a free-flowing powder and thus could not be handled easily; (2) its water and hydrogen peroxide content varied over a wide range; (3) the complex was not stable; and (4) the aqueous process could not be carried out on a commercial scale.

Rossberger et al., in German Patent OLS 3,444,552, published June 12, 1986, described a process for making urea peroxyhydrate using a fluidized bed of urea having a particle size of less than 1000 μm onto which was sprayed an aqueous solution of concentrated H_2O_2 . This technique was practical only because urea is a stable, crystalline compound which readily formed a free-flowing powdery complex upon addition of aqueous hydrogen peroxide solutions.

Production of free-flowing or foam complexes of PVP- H_2O_2 from amorphous, polymeric, polyvinylpyrrolidone and aqueous H_2O_2 , however, has not been easy to achieve commercially because, during production, the PVP polymer can alter its physical state, and/or retain excess water and/or free H_2O_2 , even at elevated drying temperatures, resulting in a gummy rather than a free-flowing of foam product.

The invention provides a process for the production of PVP- H_2O_2 products in the form of free-flowing powders in which a fluidized bed of PVP powders maintained at a reaction temperature of from about ambient temperature to 60°C . is contacted with finely divided droplets of a 30 to 85% by weight aqueous H_2O_2 solution.

With gelling agent present, e.g. hydroxyethyl cellulose in an amount of about 20-60%, the bulk density and porosity is substantially lower.

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Thus, if an individual uses a sunscreen for protection from ultraviolet radiation, he or she is forced to forego a tanned appearance. Therefore, it would be highly desirable to provide protection from the harmful effects of ultraviolet radiation, and yet at the same time deliver a tanned appearance to the skin.

Furthermore, even if an individual is willing to accept the risks associated with exposure to ultraviolet radiation in order to obtain a tan, there are situations in which it may not be practical or even possible to do so because of time constraints, weather conditions, time of day, season of the year, geographic limitations, unavailability of an artificial ultraviolet radiation source, and the like. Therefore, it would be highly desirable to provide products that can deliver a tanned appearance whenever desired without the need for ultraviolet radiation.

Therefore, it would be highly desirable to provide a dihydroxyacetone containing emulsion for delivering both an artificial tan and also for providing protection from ultraviolet radiation. The combination of 3% dihydroxyacetone with 0.25% lawsone as a sunscreen active combination is described in the Federal Register, Vol. 43, No. 166, pp. 38206-38269, August 25, 1978, this reference being incorporated herein by reference in its entirety. However, this combination is unsuitable for high SPF products. Furthermore, lawsone is a high melting bright yellow solid which is difficult to formulate and which is not readily available from suppliers in the United States. U.S. Patent No. 3,177,120, to Black et al., issued April 6, 1965 and U.S. Patent No. 4,434,154, to McShane, issued February 28, 1984 disclose dihydroxyacetone containing formulations which also incorporate a sunscreen. The '120 patent teaches compositions limited to the use of a single sunscreen not containing active amino groups (e.g., either homomenthyl salicylate or 2-ethoxy ethyl p-methoxy cinnamic acid); the '154 patent is limited to the use of octyl dimethyl PABA. However, homomenthyl salicylate is a very weak sunscreen unsuitable for use in products designed to delivered a high sun protection factor (i.e. SPF). Similarly, it is difficult to deliver high SPFs using either 2-ethoxy ethyl p-methoxy cinnamic acid or octyl dimethyl PABA, alone. Furthermore, due to growing consumer concerns over the use of PABA and PABA esters in

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In accordance with the present invention, a fluidized bed containing a charge of PVP powders is reacted with an aqueous solution of concentrated hydrogen peroxide. The PVP polymer can be obtained from GAF Chemicals Corporation in the form of a water-soluble or water-insoluble polymer, which has a molecular weight ranging from the K-15 to K-90 designations. These PVP polymers, which generally have a water content of about 5% by weight, or less, and a particle size of about 10 to 100 microns, may be used directly in the process of the invention, or pre-dried, if desired, to reduce its moisture content.

The hydrogen peroxide solution used herein usually contains about 30 to 85% hydrogen peroxide. A 50 to 70% H_2O_2 solution, however, is preferred because of the inherent danger present in use of the higher H_2O_2 concentrations.

The fluidized bed of PVP powders can be maintained in the fluidized condition by directing a current of dry air through the powders, by mechanical agitation of the powders, or by a combination of both techniques.

The fluidized bed is maintained at a suitable bed (reaction) temperature at which formation of the desired PVP- H_2O_2 complex product can occur readily without affecting the powdery state of the PVP polymer, and at which excess water from the H_2O_2 solution can be quickly removed both from the product and the PVP bed itself. The selected bed temperature also will enhance the formation of a free-flowing powder rather than a gum. Such suitable reaction temperatures range from about ambient temperature to 60°C., preferably about 35° to 45°C.

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The aqueous concentrated H_2O_2 solution preferably is contacted with the PVP powders as finely divided droplets of liquid. Such desired droplets may be formed by pumping the H_2O_2 solution through a spray nozzle and onto the PVP bed at a selected rate and for a predetermined period of time. Any spray nozzle capable of producing a fine dispersion of droplets may be used for this purpose. If necessary, however, a stream of air may be introduced into such nozzle with the solution to assist in atomizing the solution into finely divided droplets.

The spray solution of aqueous H_2O_2 thus formed preferably is introduced into the fluidized bed of PVP powders at a selected rate such that excess water can be removed therein during formation of the complex without retaining free H_2O_2 therein. A suitable feed rate for introduction of the H_2O_2 solution is about 5-50 g/minute/kg PVP. Under these flow rate conditions, a free-flowing powder of the desired PVP- H_2O_2 complex is obtained containing about 15-24% H_2O_2 , preferably 18-22%, and about 5% or less water therein.

In the preferred form of the process of the invention, the spray solution of H_2O_2 is directed onto the PVP bed for a period sufficient to form a free-flowing powder having an H_2O_2 content of about 15 to 24% by weight, preferably 18-22%, which is indicative of a complex having a 1:1 molar ratio of PVP to H_2O_2 . At this point in the process, the feed is discontinued to preclude excess water and/or free H_2O_2 from forming on the free-flowing powder which can cause it to become gummy. The appearance of a gummy product is indicative of the presence of excess water and/or free H_2O_2 in the product.

The spray solution of H_2O_2 may be directed onto the fluidized bed as a vertical, horizontal or by downward flow of droplets.

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If a fluidizing air stream is used to create the fluid bed, it is usually directed upwardly against the PVP powders. Such air currents also can assist in carrying water away from the bed. The fluidized state of the bed also may be maintained using mechanical agitation, or a combination of both air and mechanical means.

The process of the invention can be carried out in one or two steps, i.e. removal of water from the product and bed can take place either (a) simultaneous with or after mixing of the reaction components in the same apparatus, or (b) in a downstream drying step, or (c) by a combination of both steps. The particular method of drying will depend upon the type of equipment used. For example, if a fluidized bed mixer is used, such as a plowshare, belt screw or paddle mixer, then the moist PVP-H₂O₂ product can be dried further in a separate dryer. This sequence is characterized as a two-step process. Any suitable dryer can be used for this purpose, such as a vacuum, radiant heat or contact dryer.

Furthermore, if desired, application of the spray H₂O₂ solution onto the PVP bed, followed by downstream drying, may be carried out in several stages in order to increase the H₂O₂ content of the product towards the desired 1:1 molar ratio, and to reduce its water content.

Moreover, a fluid bed dryer may be used in the process which has the dual capabilities of providing both the fluidized bed and drying functions. Accordingly, drying of the product will begin and be completed during reaction between the PVP charge and the aqueous H₂O₂ solution. Such a process may be considered as taking place in a one-step.

Preferably, reaction and dehydration are continued until the product reaches a desired H₂O₂ content, suitably about 15-24% H₂O₂, and usually about 18-22%, with less than about 5% water, generally about 1-3%.

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However, it is essential that the product remain in the free-flowing state after completion of addition of the H_2O_2 solution.

The size of the fluidized bed reactor, the rate of addition of the hydrogen peroxide solution, and the reaction times will vary with the particular equipment used, as well as the concentration of the hydrogen peroxide solution and the reaction temperature, keeping in mind the purposes intended to be achieved with respect to each of these process parameters.

The free-standing, porous solid or foam PVP- H_2O_2 product also is made by freeze-drying an aqueous solution of PVP powders complexed with an aqueous solution of hydrogen peroxide. The starting PVP polymer material preferably is a water-soluble polymer.

The resulting aqueous solution of PVP and H_2O_2 for freeze-drying suitably contains about 4-10% by weight of H_2O_2 , about 15-25% by weight of PVP, and about 65-85% by weight of water. Most preferably, the aqueous solution of PVP and H_2O_2 for freeze-drying contains about 6% H_2O_2 , 20% PVP and 74% water.

The aqueous solution thus obtained then is frozen at a temperature of less than -20°C . which forms a soft ice of these materials. The soft ice material then is vacuum dried at these low temperatures under high vacuum, preferably, at about 0.1 mm or less. The water which is removed is condensed in a suitable condenser maintained at about -90°C .

After the freeze-drying step is carried out for some period of time, it is observed that the soft ice is transformed into a free-standing, porous, hard solid which comprises an integral network of PVP molecules hydrogen-bonded to H_2O_2 molecules. The open system in this product result from the loss of water from the

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interior of the ice body thus providing a porous structure. During transition of the soft ice starting material into the porous, hard network solid, a tacky and porous intermediate product is obtained in which some water is present on the outside of the structure. However, by keeping this material well dispersed and cold, the exterior water content can be readily vacuum-sublimed to provide the advantageous porous and hard solid or foam while avoiding the undesired glassy state.

The final product is a PVP-H₂O₂ complex, which is free-standing and foam-like, and is composed of an integral network of about 70-90% by weight PVP which is hydrogen-bonded to about 10-24% by weight H₂O₂, and where the amount of water present therein is less than 10%. Preferably, the PVP content of this product is about 75-85%, the amount of H₂O₂ is about 15-20%, and its water content is less than about 7-1/2%. Suitably, the total amount of H₂O₂ and water therein is about 25% or less by weight of the product. In the preferred embodiment of the invention, PVP is 77-82%, H₂O₂ is 17-19% and water is about 2-7-1/2%.

In another embodiment of the invention, a water-soluble gelling agent is incorporated within the porous foam during formation to increase its porosity. Suitable gelling agents include hydroxyalkyl cellulose e.g. hydroxyethyl cellulose, propylene and ethylene glycols, polyalkylene glycols, and the like. The resultant porous foam product then comprises about 25-70% PVP, 5-20% H₂O₂, about 20-60% gelling agent; and 0-8% water, by weight of the product.

As a foam, the product has a bulk density of about 0.3 to about 0.5 g/cc and a porosity of about 60-70%.

Of course, if desired, free-flowing powders of such PVP-H₂O₂ products may be obtained by grinding the porous solid.

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The invention herein also contemplates the formation of compositions, or mixtures, of the porous solid PVP-H₂O₂ product herein admixed with diluents, carriers, or other active materials. For example, an improved filter material may be provided by forming admixtures of the PVP-H₂O₂ product of the invention with such diluents as inorganic substances such as silica gel, alumina, diatomaceous earth and the like, or organic substances such as polyolefins, polystyrene, polyvinyl chloride and the like, while retaining the desirable pore volume of the porous solid complex. The resultant pore volume of such mixtures for filter application should be between about 0.1 and 2.5 cc per granular of total granular material.

The invention will be illustrated now by reference to the following examples.

EXAMPLE 1

PRODUCTION OF PVP-H₂O₂ AS FREE-FLOWING POWDERS USING A FLUIDIZED BED REACTOR AND VACUUM DRYING

0.35 kg of polyvinylpyrrolidone (PVP K-30, CI grade) having particle sizes of predominately 40-50 microns, and a moisture content of 2-3%, was introduced into a 0.4 l fluid bed reactor. The PVP powders were fluidized by passing a stream of dry air upwardly through the charge. The bed temperature was set at 35°-45°C. Then an aqueous solution of 70% H₂O₂ was metered through a spray nozzle with the assistance of an air stream and directed vertically onto the bed. The rate of addition of the solution was 15-25 g of solution/minute/kg PVP for 20 minutes. Adsorption of the solution onto the bed produced a wet product containing 18% H₂O₂ and 6% water.

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Subsequent downstream vacuum drying of the wet material at 25°-35°C. for 10 hours produced a free-flowing powder which had a 20-22% H_2O_2 content and only 3% water therein.

EXAMPLE 2

FREE-FLOWING PVP- H_2O_2 POWDERS USING FLUIDIZED BED DRYER

3.6 kg of polyvinylpyrrolidone (PVP K-30, CI grade), having a particle size of 40-50 microns, was packed into a 22 liter fluidized bed dryer and fluidized at 35°-45°C. using a dry air stream. Then a 70% H_2O_2 solution was introduced during 20 minutes at a feed rate of 10-15 g/minute/kg PVP. During the addition, water was being removed continuously from the product and the bed. Following completion of the H_2O_2 addition, the resultant product was dried further for 10 minutes. The resultant product was a free-flowing powdery complex of PVP- H_2O_2 having a peroxide content of 20% and a moisture content of only 2%.

EXAMPLE 3

PVP- H_2O_2 POWDERS USING 30% H_2O_2

The procedure of Example 1 was followed using a 30% H_2O_2 solution at a feed rate of 20 g/minute/kg PVP for 20 minutes. Successive additions of H_2O_2 were followed by vacuum drying. After three stages of application and drying, the free-flowing product contained 19% H_2O_2 and 3% water.

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Technology, disclose numerous suitable agents. Specific suitable sunscreens include, but are not limited to, for example: Ethylhexyl-p-methoxycinnamate (available as Parsol MCX from Givaudan Corporation), p-Aminobenzoic acid, its salts and its derivatives (ethyl, isobutyl, glyceryl esters; p-dimethylaminobenzoic acid; 2-ethylhexyl N,N-dimethylaminobenzoate); p-Methoxycinnamic Acid Diethanolamine Salt (available as Bernel Hydro from Bernel Chemical Co.); Anthranilates (i.e., o-aminobenzoates; methyl, octyl, amyl, menthyl, phenyl, benzyl, phenylethyl, linalyl, terpinyl, and cyclohexenyl esters); Salicylates (octyl, amyl, phenyl, benzyl, menthyl, glyceryl, and dipropyleneglycol esters); Cinnamic acid derivatives (menthyl and benzyl esters, -phenyl cinnamitrile; butyl cinnamoyl pyruvate); Dihydroxycinnamic acid derivatives (umbelliferone, methylumbelliferone, methylaceto-umbelliferone); Trihydroxycinnamic acid derivatives (esculetin, methylesculetin, daphnetin, and the glucosides, esculin and daphnin); Hydrocarbons (diphenylbutadiene, stilbene); Dibenzalacetone and benzalacetophenone; 2-Phenyl-benzimidazole-5-sulfonic acid and its salts; Naphtholsulfonates (sodium salts of 2-naphthol 3,6-disulfonic and of 2-naphthol-6,8-disulfonic acids); Dihydroxy-naphthoic acid and its salts; o- and p-Hydroxybiphenyldisulfonates; Coumarin derivatives (7-hydroxy, 7-methyl, 3-phenyl); Diazoles (2-acetyl-3-bromoindazole, phenyl benzoxazole, methyl naphthoxazole, various aryl benzothiazoles); Quinine salts (bisulfate, sulfate, chloride, oleate, and tannate); Quinoline derivatives (8-hydroxyquinoline salts, 2-phenylquinoline); Hydroxy- or methoxy-substituted benzophenones; Uric and vilouric acids; Tannic acid and its derivatives (e.g., hexaethyl-ether); (Butyl carbityl) (6-propyl piperonyl) ether; Hydroquinone; Benzophenones (Oxybenzene, Sulisobenzene, Dioxybenzone, Benzoescorcinol, 2,2',4,4'-Tetrahydroxybenzophenone, 2,2'-Dihydroxy-4,4'-dimethoxybenzophenone, Octabenzene; 4-Isopropyl-dibenzoylmethane; Butylmethoxydibenzoylmethane; Octocrylene; 4-isopropyl-di-benzoylmethane; and camphor derivatives such as methyl benzylidene or benzylidene camphor; and mixtures thereof. Other sunscreens include the solid physical sunblocks such as titanium dioxide (micronized titanium dioxide, 0.03 microns), zinc oxide, silica, iron oxide and the like. Without being limited by theory,

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EXAMPLE 7PVP-H₂O₂ POWDERS FROM PVP
CROSPOVIDONE USING FLUID BED DRYER

The procedure of Example 6 was followed using a fluid bed dryer, at a H₂O₂ solution feed rate of 13 g/minute/kg PVP. The product contained 18% H₂O₂ and 2% water.

EXAMPLE 8PVP-H₂O₂ POWDERS FROM PVP K-15

The procedure of Example 1 was followed using PVP K-15 having a particle size of 50-80 microns. Two stages of addition and vacuum drying were required to produce a free-flowing product with a 15% H₂O₂ and 2% water content.

EXAMPLE 9PVP-H₂O₂ AS FREE-STANDING, POROUS SOLID

An aqueous solution of PVP/hydrogen peroxide was prepared by mixing 20 parts by weight of polyvinyl pyrrolidone (PVP K-30) with 80 parts by weight of a 7.6 weight % hydrogen peroxide solution. This solution was then cooled to a temperature below -20°C. whereupon a solid was formed. This solid material was then cryogenically ground while its temperature remained below -20°C. by prechilling a grinder and grinding the frozen solution with dry ice. The granulated material then was charged into a prechilled vacuum jar. A high vacuum of <0.1 mm Hg was

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applied to the contents while maintaining the jar in a chilled bath at $<-20^{\circ}\text{C}$. A condenser element was maintained at -95°C . to freeze out any moisture before entering the vacuum pump. After 28 hours, nearly all of the water in the solid was removed leaving porous solid at room temperature containing 15-18% hydrogen peroxide, 3-4-1/2% water and the remainder PVP.

EXAMPLE 10

PVP-H₂O₂ AS POROUS FOAM

The procedure of Example 9 was followed except that the aqueous solution was frozen into pieces 2-3 inches thick; then vacuum dried while in the chilled state. The resulting material was foam-like with a bulk density of about 0.43 g/cc and a porosity of 66%. This material had a hydrogen peroxide content of 17-1/2% and a moisture content of 7-1/2% after 48 hours of vacuum drying under the above conditions.

EXAMPLE 11

90 parts of an aqueous solution of 20% polyvinylpyrrolidone (PVP C-30/CI grade) and 6% aqueous hydrogen peroxide were mixed with 10 parts of hydroxyethyl cellulose (HEC) and allowed to gel for 20 to 30 minutes. The gelled material had an overall composition of: 18.0% PVP, 10.0% HEC, 5.4% H₂O₂, and 66.6% water. The material then was placed in a freeze-dryer at ambient temperature and evacuated to about 0.1 mm Hg for about 18 hours. The resulting solid retained a volume similar to the initial gel, however, the water loss had reduced the sample to 32% of its original weight. Analysis of the product showed a composition as follows: 55.2% PVP, 30.7% HEC, 12.8% H₂O₂ and 1.3% water.

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WHAT IS CLAIMED IS:

1. A process for the production of free-flowing powders of PVP-H₂O₂, optionally including a gelling agent, comprising reacting a fluidized bed of PVP polymer, optionally with a gelling agent, maintained at a reaction temperature of from ambient temperature to about 60°C. with finely divided droplets of a 5 to 85% by weight aqueous solution of H₂O₂, and drying the product.

2. A process according to claim 1 wherein introduction of said H₂O₂ solution is continued until the resultant product contains about 15 to 24% by weight H₂O₂.

3. A process according to claim 2 wherein said H₂O₂ solution is introduced at a feed rate of about 5-50 g/minute/kg PVP.

4. A process according to claim 1 wherein drying is carried out in the fluidized bed during formation of the product, or in a downstream dryer, said reaction and drying steps are carried out in a fluidized bed dryer, or the reaction is carried out in a fluidized bed reactor, and further drying of the wet product is performed in a downstream dryer, optionally wherein air is used to fluidize the PVP powders and to assist in removing water from the fluidized bed during the process.

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5. A process according to claim 1 wherein the PVP powders are selected from water-soluble and water-insoluble PVP powders in a range of molecular weights corresponding to the designations K-15 to K-90.

6. A process according to claim 1 wherein the product contains about 5% or less water therein, and said PVP has a particle size of about 10-100 microns.

7. A product comprising a PVP-H₂O₂ complex in the form of a free-standing, porous, hard solid or foam having an integral network of PVP molecules hydrogen bonded to H₂O₂ molecules, the H₂O₂ content being about 10-24% by weight, the water content being less than 10% by weight, and the PVP content being about 70-90% by weight, of the product.

8. A product according to claim 7 where the H₂O₂ content is about 15-20%, the water content is less than 7-1/2%, the PVP content is about 75-85%, and the total amount of H₂O₂ and water is 25% or less.

9. A product according to claim 7 which is a foam having a bulk density of about 0.3 to about 0.5 g/cc and a porosity of about 60-70%.

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10. A process for making the product of claim 7 which comprises:

(a) providing an aqueous solution of H_2O_2 and PVP in the proportions of:

about 4-10% by weight H_2O_2 ,

about 15-25% by weight PVP, and

about 65-85% by weight water;

(b) freezing the solution at below $-20^{\circ}C$. to form a soft ice,

(c) vacuum drying at a reduced pressure of less than about 0.1 mm to remove water therefrom.

11. A process according to claim 10 which includes up to 60% by weight of a gelling agent such as a hydroxyethyl cellulose.

12. A free-standing, porous foam product consisting essentially of an integral network of PVP molecules hydrogen bonded to H_2O_2 molecules, the PVP content being about 25-70% by weight, the H_2O_2 content being about 5-20% by weight, and including about 20-60% by weight of a water-soluble gelling agent to increase the porosity of the foam.

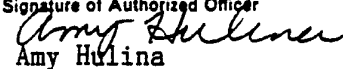
13. A porous foam product according to claim 12 where the PVP content is about 55.2%, the H_2O_2 content is about 12.8%, and the gelling agent is about 30.7%.

14. A porous foam product according to claim 13 which contains less than about 8% water therein.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US92/02287

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): A61R 7/40, 31/79 U.S. CL. 424/405, 78.24; 427/213		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	424/405, 78.24; 427/213	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X,P	US, A, 5,008,106 (MERIANOS) 16 APRIL 1991 See the entire document.	7-9, 12-14
Y	US, A, 3,908,045 (ALTERMAN) 23 SEPTEMBER 1975 See particularly Example 1 column 14 and Example 4 column 17.	1-6, 10, 11
$\frac{X}{Y}$	US, A, 3,480,557 (SHIRAEFF) 25 NOVEMBER 1969 See the entire document.	$\frac{7-9}{12-14}$
* Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
08 June 1992	09 JUL 1992	
International Searching Authority	Signature of Authorized Officer	
ISA/US	 Amy Hulina	