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Vishnupad et al.

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[54] **AQUEOUS DISPERSIONS OF POLYESTER AND POLYESTERAMIDES CROSS-LINKED WITH METALLIC IONS AND CASTS MADE THEREFROM**

4,787,984 11/1988 Hutchings 210/698
4,849,213 7/1989 Schaeffer 424/53

[75] **Inventors: Mohan Vishnupad, Monroe; Jose Ramirez, Trumbull, both of Conn.**

FOREIGN PATENT DOCUMENTS

[73] **Assignee: Imaginative Research Associates, Inc., Bridgeport, Conn.**

0022624 1/1981 European Pat. Off. .
1545403 11/1967 France .
2211474 7/1974 France .

[21] **Appl. No.: 16,806**

[22] **Filed: Feb. 11, 1993**

OTHER PUBLICATIONS

Related U.S. Patent Documents

Reissue of:

[64] **Patent No.: 4,992,508**
Issued: Feb. 21, 1991
Appl. No.: 367,183
Filed: Jun. 16, 1989

Eastman Publication No. J-257A dated May 1986 entitled "Preparation of Water-Resistant Coatings and Durable Binders Containing Eastman TM (WD3652) Water Dispersible Polymers".

"Eastman AQ TM Polymer-A Unique Dispersant For Hydrophobic Materials" by Michael J. Idacavage dated Dec. 1987.

Primary Examiner—Samuel A. Acquah
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[51] **Int. Cl.⁵ C08L 67/00**
[52] **U.S. Cl. 524/601; 528/272; 528/275; 528/281; 528/282; 524/602; 524/605; 524/608; 524/755; 524/763; 524/764; 524/767; 524/783**
[58] **Field of Search 528/272, 275, 281, 282; 524/601, 602, 605, 608, 755, 763, 764, 767, 783**

[57] **ABSTRACT**

Cross-linked aqueous dispersions and emulsions and method for producing casts of any desirable shape therefrom the dispersions comprising a water dissipatable polymer in an amount from 18 to 30 percent by weight based on the total weight of the composition; water in an amount from [67 to 130] 30-80 percent by weight based on the total weight of the composition; a source of multivalent metallic ions in an amount of 0.1 to 5 percent by weight based on the total weight of the composition; and humectant in an amount from 0.1 to 40 percent by weight based on the total weight of the composition and the emulsions comprising a water dissipatable polymer in an amount from 18 to 30 percent by weight based on the total weight of the composition; water in an amount from [67] 30 to 80 percent by weight based on the total weight of the composition; emollient oils in an amount from 0.1 to 25 percent by weight based on the total weight of the composition; a source of multivalent metallic ions in an amount from 0.1 to 5 percent by weight based on the total weight of the composition; humectants in an amount from 0.1 to 40 percent by weight based on the total weight of the composition; and emulsifier in an amount from 0.01 to 5 percent by weight based on the total weight of the composition.

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,493,550 2/1970 Schmitt et al. 525/330.2
3,562,034 2/1971 Edwards 526/240
3,734,874 5/1973 Kibler 524/603
3,879,168 4/1975 Franklin 8/115.5
3,887,756 6/1975 Gerstin et al. 428/425
3,949,742 4/1976 Nowakowski 128/155
4,022,880 5/1977 Vinson et al. 424/49
4,100,269 7/1978 Pader 424/49
4,233,196 11/1980 Sublett 524/602
4,252,885 2/1981 McGrail 430/160
4,300,580 11/1981 O'Neill 132/7
4,304,900 12/1981 O'Neil 528/290
4,304,901 2/1981 O'Neill 528/290
4,335,220 6/1982 Coney 523/414
4,393,048 7/1983 Mason 424/122
4,409,285 10/1983 Swerdlow 428/332
4,478,907 10/1984 Van Gossum 428/327
4,502,976 3/1985 Heller 252/315.4
4,704,325 11/1987 Crocker 428/323
4,724,240 2/1988 Abrutyn 514/847

3 Claims, No Drawings

**AQUEOUS DISPERSIONS OF POLYESTER AND
POLYESTERAMIDES CROSS-LINKED WITH
METALLIC IONS AND CASTS MADE
THEREFROM**

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

FIELD OF THE INVENTION

This invention relates generally to cross-linking an aqueous dispersion of polyester or polyesteramide with the water soluble multivalent metallic ions. The aqueous dispersion of polyester or polyesteramides containing ether and sulfonate groups can also contain humectants and/or emollients which when cross-linked with metallic ions and poured into any desirable shaped mold form a clear or opaque cast of therapeutic functional nature. This invention also relates to the process of cross-linking the polyester or polyesteramide aqueous dispersion with metallic ions.

BACKGROUND OF THE INVENTION

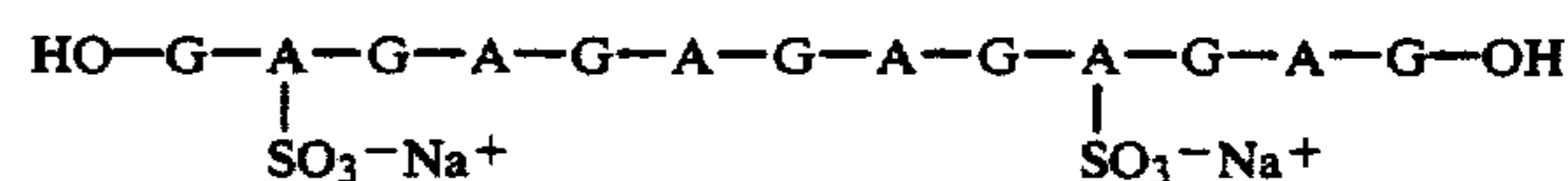
Many compositions used for skin treatment contain emollients of humectants in lotion, cream or gel form. Such products are applied by evenly spreading the product on the skin. Upon loss of water, the product dries providing humectants and emollients to the epidermis.

Water soluble gels that form protective films of various types are known. For example, U.S. Pat. No. 4,393,048 discloses a water soluble hydrogel of alkali metal alginate and glycerine that dries to a non-toxic, pliable protective film. U.S. Pat. No. 3,949,742 discloses a transparent medical dressing which performs as a synthetic film over skin wounds. Water soluble polyesters, for example U.S. Pat. No. 4,502,976, are used to form cross-linked bioerodible hydrogels. The hydrogels, suitable for carrying water soluble therapeutic macromolecules and for implantation in living mammals, are produced by a complex polymerization process without using water soluble metallic ions.

U.S. Pat. No. 3,879,168 to Franklin discloses a surgical dressing made of partially soluble alginic materials in the form of gauze or wool characterized by a pH of 4 to 7 and a calcium content of 2-6% by weight comprised of a laminate of a thin layer of non-porous segmented polyurethane sewn to foam.

U.S. Pat. Nos. 3,734,874, 4,233,196, 4,335,220, 4,304,900, 4,304,901, and 4,300,580 describe water-dissipatable, meltable polyesters that are useful as adhesives, coating materials, films, packaging materials and other products that can be dissolved, dispersed or otherwise dissipated in water or aqueous solutions. These polyesters, however, are not cross-linked using metallic ions and cast into shapes to entrap water, humectants and/or emollients within the hardened cast.

As explained in a technical publication from Eastman, the water dispersability of the AQ polymer is largely attributed to the presence of ionic substituents attached to the polymer chain. A simplified representation of the polymer is shown below:



wherein "A" is an aromatic dicarboxylic acid moiety some of which have sodiofulfo ($-\text{SO}_3-$, Na^+) substituents, "G" is an aliphatic or cycloaliphatic glycol residue and "OH" is a hydroxy end group.

It is the sodio sulfo group which impart the water dispersability to the polymer. To cross-link with multivalent metallic ions and obtain the moldable shapes of this invention, the multivalent metal salts must be added and mixed according to the teaching of this invention. Departing from this process results in non-compatible mixtures of non-commercial properties. Eastman technical publications teach the synthesis and preferred methods for crosslinking water dispersible polyesters and polyesteramides with other resins through high temperature curing process and subsequent drying of the cured resins, but specifically warn against the use of the heavy metal salts included in this invention as being not compatible with the polymers used in this invention.

OBJECTS OF THE INVENTION

It is therefore an object of the present invention to provide novel cross-linked polyester polymers with humectants and/or emollients by using water soluble metallic ions.

A further object of the present invention is to provide a convenient process of cross-linking the humectant and emollients with the polyester polymer in the presence of water soluble metallic ions.

A further object of this invention is to provide such casted patches containing water soluble medicaments and oil soluble medicaments. Such patches can be used as controlled release transdermal delivery patches.

SUMMARY OF THE INVENTION

It has been found that the objectives of this invention may be realized by forming a cast containing humectants and/or emollient oils, water, water dissipatable polyesters, and by cross-linking with water soluble multivalent metal ions. Such compositions when poured into a mold harden without pressure and have utility in wound treatment, skin treatment and controlled release drug and fragrance patches.

The casts of this invention comprise water dissipatable polyester or polyesteramide in an amount from 18 to 30 percent by weight, water in an amount from [67] 30 to 80%, humectants in an amount from 0.01 to 40% by weight, and a source of multivalent metal ions for cross-linking purposes in an amount from 0.01 to 5 percent. Casts of this invention can also be formulated using emollient oils in an amount from 0.01 to 25% by weight based on the total weight of the composition, water dissipatable polyester in an amount from 18-30% by weight, water in an amount from [67] 30-80% by weight based on the total weight of the composition, and a source of multivalent metallic ions in an amount from 0.01 to 5% based on the total weight of the composition. Optionally the composition also contains fragrance oils, medical agents or color.

DETAILED DESCRIPTION OF THE INVENTION

Cross-linked clear casts of the present invention comprise (a) a water dissipatable polyester polymer in an amount from 18-30% by weight based on the total weight of the composition; (b) water in an amount from [67]30-80% by weight based on the total weight of the composition; (c) a source of multivalent metallic ions in an amount of 0.1-5% by weight based on the total weight of the composition; (d) humectant such as propylene glycol, glycerine in an amount from 0.1-40% by weight based on the total weight of the composition.

The cross-linked cast of the present invention can also be in the form of an opaque emulsion system. Such emulsion cast of the present invention comprise (a) a water dissipatable polymer in an amount from 18 to 30% by weight based on the total weight of the composition; (b) water in an amount from [67]30 to 80% by weight based on the total weight of the composition; (c) emollient oils in an amount from 0.1 to 25% by weight based on the total weight of the composition; (d) a source of multivalent metallic ions in an amount from 0.1 to 5% by weight based on the total weight of the composition; (e) humectants in an amount from 0.01 to 40% by weight based on the total weight of the composition; (f) any suitable oil-in-water emulsifier in an amount from 0.01 to 5% by weight based on the total weight of the composition.

Polymers useful in the present invention must be capable of cross-linking with water soluble metal ions, and, when poured in liquid form into a mold hardening without pressure to form a cast of any desirable shape. Polymers suitable for use in this invention include the water-dissipatable polyester and polyesteramides described in U.S. Pat. No. 3,734,874 to Kibler, et al., U.S. Pat. No. 4,233,196 to Sublet and U.S. Pat. No. 4,304,901 to O'Neill, et al. A preferred water dissipatable polyester is commercially available on Eastman AQ 55S polymers.

Examples of organic and inorganic sources of the multivalent metal ions used to cross-link the polymers in this invention include magnesium chloride, zinc acetate, zinc gluconate, zinc oxide, titanium dioxide, and magnesium acetate. The preferred sources of multivalent metal ions are water soluble and include zinc gluconate and magnesium chloride.

In forming the clear cross-linked casts of this invention, water by itself or in combination with humectant such as propylene glycol and glycerine may be used.

In forming cross-linked emulsion casts of this invention any emollient oil may be used. Emollients useful in this invention include hydrocarbon oils and semi-solid hydrocarbons, lanolin and derivatives, silicone oils and esters commonly used in the cosmetic and dermatological fields.

The cross-linking of polymer containing emulsion systems by means of multivalent metallic ions can be achieved with or without the additional emulsifiers. The selection of an appropriate emulsifier for a given system is within the purview of one skilled in the art.

Optionally, a wide variety of agents may be incorporated into the compositions of this invention for a variety of purposes. For example, medicaments such as benzoyl peroxide, methyl nicotinate, salicylic acid, benzocaine and methanol can be cast into desirable shapes for therapeutic use.

The cross-linked hydrogels and emulsions can be cast into any desirable shape and used for various purposes. For example, casts in the form of face masks may be used for treating dry skin. Casts in the form of patches or pads may be used to cover burns and wounds for soothing and comforting the inflamed area, or for delivering active medicaments to the damaged skin as a controlled release, transdermal patch.

Both the clear and opaque emollient casts may also contain fragrance, insect repellents, sun screens and like chemicals.

The following examples illustrate how the cross-linked casts of this invention may be formed.

EXAMPLE 1

A clear cross-linked cast was produced having the following composition:

Eastman AQ 55S Polymer	24.0
Zinc Gluconate (USP)	2.0
Propylene Glycol	34.0
Water	[42.0] 40

The cross-linked cast of Example 1 was prepared by placing the appropriate amounts of water and propylene glycol into a suitable container and heating the mixture to 80° C. The appropriate amount of polymer was gradually added with a high shear mixing to dissolve the solids. When all the solids were added, high shear mixing is continued, until a clear, straw colored, thick gel was produced. The gel was then cooled to room temperature and an appropriate amount of zinc gluconate aqueous solution added by high shear mixture until cross-linking occurred. The liquid was poured into a mold of desirable shape to produce a cast of hydrogel. The metallic cross-linking can be done either at room temperature or at elevated temperatures depending on the composition.

EXAMPLE 2

An emulsion crosslinked cast was produced having the following composition:

Eastman AQ 55S Polymer	20.3
Propylene Glycol	28.0
Mineral oil	10.0
PJ	7.0
Polysorbate 20	1.0
Zinc gluconate	2.0
Water	31.7

The cross-linked emulsion casts of Example 2 were formed by placing appropriate amounts of water and propylene glycol in a suitable container and heating the mixture to 80° C. The appropriate amount of polymer was gradually added with a high shear mixing until a clear viscous liquid was produced. The polysorbate 20 was added to the clear liquid and mixing continued. The melted oil phase was then added to the aqueous phase and homogenized to form a smooth emulsion. To this emulsion the appropriate amount of aqueous solution of zinc gluconate was added with continued mixing. Pouring into a mold at appropriate viscosity formed a cast of the desired shape. The cross-linking of the emulsion can be carried out between 50° C., to 70° C., as desired, for manufacturing and suitable for pouring into the molds for casting purposes.

EXAMPLE 3

Water insoluble sources of multivalent metallic ions such as, for example, zinc oxide or titanium dioxide can be added to form more rigid cross-linked casts.

Eastman AQ55S Polymer	21.00	
Propylene Glycol	28.00	
Petroleum Jelly	15.00	
Glycerol Monostearate and Polyoxyethylene stearate	1.00	10
Zinc Oxide	2.00	
Zinc Gluconate	2.00	
Microcrystalline Wax	5.00	
Water	26.00	

EXAMPLES 4-24

The following are additional specific examples of formulations used to produce cross-linked casts of this invention:

<u>Ex. 4</u>		
Eastman AQ 55S polymer	21	
Propylene glycol	28	25
Zinc gluconate	2	
Water	49	
<u>Ex. 5</u>		
Eastman AQ 55S polymer	25.5	
Propylene glycol	34.0	
Zinc gluconate	2.0	30
Water	38.5	
<u>Ex. 6</u>		
Eastman AQ 55S polymer	20.3	
Propylene glycol	18.0	
Zinc gluconate	2.0	35
Water	59.7	
<u>Ex. 7</u>		
Eastman AQ 55S polymer	23.2	
Propylene glycol	10.0	
Zinc gluconate	2.0	40
Water	64.8	
<u>Ex. 8</u>		
Eastman AQ 55S polymer	21	
Propylene glycol	28	
Zinc gluconate	2	45
Water	49	
<u>Ex. 9</u>		
Eastman AQ 55S polymer	24	
Propylene glycol	32	
Zinc gluconate	2	50
Water	42	
<u>Ex. 10</u>		
Eastman AQ 55S polymer	27	
Propylene glycol	36	
Zinc gluconate	2	55
Water	35	
<u>Ex. 11</u>		
Eastman AQ 55S polymer	23.2	
Zinc gluconate	2.0	
Water	74.8	
<u>Ex. 12</u>		
Eastman AQ 55S polymer	23.2	
Magnesium chloride	0.5	
Water	76.3	
<u>Ex. 13</u>		
Eastman AQ 55S polymer	24	60
Glycerine	32	
Zinc gluconate	2	
Water	42	
<u>Ex. 14</u>		
Eastman AQ 55S polymer	24.0	65
Propylene glycol	32.0	
Magnesium chloride	0.3	
Water	43.7	
<u>Ex. 15</u>		

-continued

Eastman AQ 29S polymer	15.0	
Eastman AQ 55S polymer	5.4	
Propylene glycol	27.2	
Mineral oil	10.0	
Polysorbate 20	2.0	
Zinc gluconate	3.0	
Water	37.4	
<u>Ex. 16</u>		
Eastman AQ 55S polymer	20.3	
Propylene glycol	28.0	
Mineral oil	10.0	
Petroleum jelly	7.0	
Polysorbate 20	1.0	
Zinc gluconate	2.0	
Water	31.7	
<u>Ex. 17</u>		
Eastman AQ 55S polymer	20.3	
Propylene glycol	28.0	
Mineral oil	10.0	
Petroleum jelly	7.0	
Polysorbate 20	1.0	
Zinc gluconate	1.5	
Water	32.2	
<u>Ex. 18</u>		
Eastman AQ 55S polymer	18.0	
Propylene glycol	24.0	
Petroleum jelly	17.0	
Polysorbate 20	1.0	
Zinc gluconate	2.0	
Water	38.0	
<u>Ex. 19</u>		
Eastman AQ 55S polymer	21	
Propylene glycol	28	
Dimethicone	[19] 9	
Petroleum jelly	9	
Glycerolmonostearate and Polyoxyethylene Stearate	1	
Zinc gluconate	2	
Water	30	
<u>Ex. 20</u>		
Eastman AQ 55S polymer	21.0	
Propylene glycol	28.0	
Petroleum jelly	17.0	
Zinc gluconate	2.0	
Water	32.0	
<u>Ex. 21</u>		
Eastman AQ 55S polymer	21.0	
Propylene glycol	28.0	
Petroleum jelly	16.0	
Salicylic acid	2.0	
Zinc gluconate	2.0	
Water	[10.0] 31.0	
<u>Ex. 22</u>		
Eastman AQ 55S polymer	20.7	
Propylene glycol	27.6	
Petroleum jelly	15.0	
Benzoyl peroxide	2.0	
Glycerine	2.0	
Zinc gluconate	2.0	
Water	30.7	
<u>Ex. 23</u>		
Eastman AQ 55S polymer	21.0	
Propylene glycol	28.0	
Menthol	2.0	
Zinc gluconate	2.0	
Water	[26.0] 47.0	
<u>Ex. 24</u>		
Eastman AQ 55S polymer	21.0	
Propylene glycol	28.0	
Petroleum jelly	15.0	
Polysorbate 20	1.0	
Superabsorbant polymer	1.0	
Zinc gluconate	1.0	
Water	33.0	

Although particular illustrative embodiments of the present invention have been described herein, the present invention is not limited to these particular embodi-

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ments. Various changes and modifications may be made thereto by those skilled in the art without departing from the spirit or scope of the invention, which is defined in the appended claims.

What is claimed is:

1. A cross linked aqueous dispersion composition comprising:

a water dissipatable polymer in an amount from 18 to 30 percent by weight based on the total weight of the compositions;

water in an amount from [67] 30 to 80 by weight based on the total weight of the composition;

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a source of multivalent metallic ions in an amount of 0.1 to 5 percent by weight on the total weight of the composition; and

humectant in an amount from 0.1 to 40 percent by weight based on the total weight of the composition.

2. A cross-linked dispersion composition according to claim 1 wherein said source of multivalent metallic ions is selected from the group consisting of magnesium chloride, zinc acetate, zinc gluconate, zinc oxide, titanium dioxide and magnesium acetate.

3. An article manufactured using the composition of claim 1.

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