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- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: PROCESS FOR MAKING VINYL PYRROLIDONE/VINYL ACETATE COPOLYMERS WITHIN A SHORT PRODUCTION CYCLE

(57) Abstract: Vinyl pyrrolidone/vinyl acetate copolymers having a very low residual vinyl pyrrolidone monomer level, i.e. < 100 ppm, preferably only 50 ppm, are made within an advantageously short production cycle, by post-treating an aqueous solution of the copolymer at an elevated temperature of about 120-150 °C, preferably about 130 °C, under pressure, in the presence of a high temperature initiator, for a period of about 1-4 hours, preferably 2 hours.



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PROCESS FOR MAKING VINYL PYRROLIDONE/VINYL ACETATE COPOLYMERS WITHIN A SHORT PRODUCTION CYCLE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for making vinyl pyrrolidone (VP)/vinyl acetate (VA) copolymers, and, more particularly, to improved manufacture of such copolymers having a very low residual VP level, within an advantageously short production cycle.

2. Description of the Prior Art

Potthoff-Karl, in U.S. Pat. 5,122,582, described a process for making VP/VA copolymers by copolymerization of the monomers in isopropanol (IPA) solvent in the presence of a radical initiator, steam distilling off the IPA, replacing it with water, (although none of the examples therein include this step) adding more initiator in IPA, post-heating the mixture at about 80°C for a period of 4½ hours, and again, removing IPA by steam distillation. However, the residual VP content of the copolymer solution obtained was high, e.g. 500 ppm (Ex. 1); 900 ppm (Ex. 2) and 1000 ppm (Ex. 3), based upon the amount of VP employed. Moreover, the duration of the post-treatment step also was excessively long.

Accordingly, it is the object of this invention to provide a new and improved process for making VP/VA copolymers having a very low residual VP level, i.e. < 100 ppm, preferably only 50 ppm, in which the post-treatment step is carried out in water only and requires a heating period of only 1-4 hours, preferably only about 2 hours.

DESCRIPTION OF THE INVENTION

What is described herein is a process of making vinyl pyrrolidone (VP)/vinyl acetate (VA) copolymers having a very low residual VP level of < 100 ppm, preferably only 50 ppm, based upon the VP monomer used, which comprises copolymerizing VP and VA in isopropanol (IPA) solvent in the presence of a radical initiator, preferably including a high temperature initiator, at about 65-90°C, stripping the IPA while simultaneously adding water, to form an aqueous solution of the copolymer, and then post-heating said aqueous solution at about 120-150°C, preferably about 130°C, under pressure, for a period of about 1-4 hours, preferably about 2 hours.

Suitably, the VP/VA copolymer includes, by wt., about 50-70% VP and about 30-50% VA.

Examples of suitable radical initiators for use herein are dimethyl 2,2'-azobisisobutyrate, dilauroyl peroxide, dibenzoyl peroxide, dicumyl peroxide, di-tert-butyl peroxide, hydrogen peroxide and, percarboxylic esters such as tert-butyl perneodecanoate, tert-amyl perpivalate, tert-butyl perpivalate, tert-butyl peroxy-2-ethylhexanoate and tert-butyl perbenzoate. Preferred initiators for use during the polymerization step are t-butyl-peroxypivalate (Lupersol® 11), and 2,2'-azodi(2-methylbutyronitrile) (Vazo® 67); while preferred high temperature initiators for use during the post-treatment step include 2,5-dimethyl-2,5-di(t-butylperoxy) hexane (Lupersol® 101); and di-t-butyl peroxide.

The invention will now be described in more detail by way of the following examples, in which:

INVENTION EXAMPLE 1

Preparation of Copolymer of VP/VA (70:30 wt.%)

1. Set up a 1-liter pressured reactor and charged
41.21 g of VP
22.01 g of vinyl acetate and
32.61 g of isopropanol.
2. Purged the reaction system 2-3 times with nitrogen to 50 psig and releasing it.
3. Heated the reactor to 80°C.
4. At 75°C, time = 0 min, started feeding a mixture of 0.95 g Vazo[®] 67, 0.93 g of Lupersol[®] 101 and 19.30 g of isopropanol. Completed the initiator feed within 340 minutes.
Also, at time = 0 min, added a mixture of 140.29 g of VP, 74.29 g of vinyl acetate and 99.94 g of isopropanol continuously during a period of 240 minutes.
5. At 255 minutes, fed 43.83 g of VP in 19.80 g of isopropanol continuously in 60 minutes.
6. After completion of initiator feeding in 340 minutes, held the reaction mixture at 80°C for 2 hours.

7. Then stripped the IPA solvent by steam distillation, while simultaneously adding water in an amount of 567 g.
8. After the solvent exchange step the solids level was about 50-60%.
9. Heated the aqueous copolymer solution under pressure to 130°C.
10. Held the reaction mixture at 130°C for about 2 hours. The residual VP level in the mixture was 50 ppm.

EXAMPLE 2

The procedure of Example 1 was followed to produce a copolymer of VP/VA having a wt. ratio of 60:40 with a similarly low VP level.

EXAMPLE 3

The procedure of Example 1 was followed to produce a VP/VA copolymer having a wt. ratio of 50:50 with a similarly low VP level.

COMPARATIVE EXAMPLE

Preparation of Copolymer of VP/VA (70:30 wt.%)

The procedure of Example 1 was followed up to step 6.

7. Heated the reaction mixture in IPA to 130°C for post-treatment.
8. Held the reaction mixture for 2 hours. The residual VP level was 1007 ppm.

WHAT IS CLAIMED IS:

1. A process of making vinyl pyrrolidone (VP)/vinyl acetate (VA) copolymers having a very low residual VP level of < 100 ppm based upon the amount of VP used in an advantageously short production cycle which comprises copolymerizing VP and VA in isopropanol (IPA) solvent in the presence of a low temperature radical initiator, continuously stripping the IPA while simultaneously adding water to form an aqueous solution of the copolymer, and post-heating said aqueous solution at about 120-150°C under pressure in the presence of a high temperature initiator, for a period of about 1-4 hours.
2. A process according to claim 1 wherein said post-heating step is carried out at about 130°C for a period of about 2 hours.
3. A process according to claim 1 wherein both said low and high temperature radical initiators are added during the polymerization step.
4. A process according to claim 1 wherein said VP/VA copolymer comprises, by wt., about 50-70% VP and about 30-50% VA.
5. A process according to claim 1 wherein said high temperature radical initiator is 2,5-dimethyl-2,5-di(t-butylperoxy) hexane.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US05/31366

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08F 2/00

US CL : 526/081

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 526/081, 71, 212, 264, 330

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,239,053 A (TSENG et al.) 24 August 1993 (24.08.1993)	1-5
A	US 5,319,041 A (ZHONG et al.) 07 JUNE 1994 (07.06.1994)	1-5
A	US 5,387,641 A (YEUNG et al.) 07 February 1995 (07.02.1995)	1-5

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Further documents are listed in the continuation of Box C.

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See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent 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 when the document is taken alone

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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

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Continuation of Item 4 of the first sheet:

Paralegal

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