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Folios: 25 1
5

Fecha (SEB) 2000-11-16 16 39 41

Trámite 002 PATENTES D 1 REGISTRO/ 444 RESPUESTA

Dependencia 2020 DIVISION DE NUEVAS CREACIONES

Señora Jefe de la

DIVISION DE NUEVAS CREACIONES

Superintendencia de Industria y Comercio

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TRAMITE 02 EVENTO 01 ACTUACION 444

Referencia

Expediente No 00 065 984

Solicitante

THE DOW CHEMICAL COMPANY

Asunto

Solicitud de patente para "POLIMERIZACIÓN DE MONÓMEROS AROMÁTICOS DE VINILO POR MEDIO DE PROCESOS DE POLIMERIZACIÓN CATIONICOS Y DE RADICAL LIBRE, PARA PRODUCIR POLÍMEROS AROMÁTICOS DE MONOVINILIDENO DE PESO MOLECULAR BIMODAL"

Fecha de la solicitud

1 de septiembre de 2000

1 Yo, Emilio FERRERO, obrando como apoderado del solicitante en el asunto antes identificado, me refiero al auto número 3144, notificado por estado del 5 de octubre de 2000

2 Mediante el auto número 3144 se puso en conocimiento del solicitante el informe que contiene las observaciones hechas por su Despacho sobre la presente solicitud de patente Atiendo a las observaciones de la manera siguiente

2 1 Título del invento Para dar mayor precisión al objeto de la invención, presento aquí nuevo título como sigue

"POLIMERIZACIÓN DE MONÓMEROS AROMÁTICOS DE VINILO POR MEDIO DE PROCESOS DE POLIMERIZACIÓN CATIONICOS Y DE RADICAL LIBRE, PARA PRODUCIR POLÍMEROS AROMÁTICOS DE MONOVINILIDENO DE PESO MOLECULAR BIMODAL"

RESPUESTA AL AUTO No 3144 DEL ESTADO

NIT 860 041 367 3

DATA 14 5 de octubre de 2000

Adicionalmente presento nuevo formato de solicitud en donde aparece el nuevo título que presento

2 2 En la descripción Para atender a la observación hecha por su Despacho con relación al término "CWC Montmorillonite clay H+", aclaro que esta es un producto de arcilla disponible comercialmente de Nanocor. La designación H+ indica que la arcilla ha sido cambiada por iones a la forma ácida, la cual es común en el estado de la técnica. En vista de que este producto es de uso común por los versados en la materia no se consideró necesario introducir explicaciones en la descripción.

2 3 Formatos adicionales Adjunto a este memorial presento nuevo extracto, nueva tarjeta temática y nueva tarjeta de archivo de propietarios (Formas P 103, P 104 y P 105), los cuales están en conformidad con las modificaciones hechas al título de la invención.

2 4 Documento de prioridad Presento con este escrito copia certificada de la solicitud de patente estadounidense número 60/152 009 del 1 de septiembre de 1999, junto con su respectiva traducción de sus reivindicaciones y certificaciones, en la cual se basa la reivindicación de la prioridad.

3 Puesto que se han atendido completamente las observaciones hechas por su Despacho sobre la presente solicitud de patente, atentamente solicito que se continúe su tramitación.

Bogotá, 16 JUL 2000
Señora Jefe,


EMILIO FERRERO
T P A. No 31 929

 COLO 00286 801 134 3
JBP/Id 1576

RETIRO FOLIOS 38, 39 y 40
DE TARJETAS Y EXTRACTO

800510

DATOS DEL SOLICITANTE

(71) Nombres y Apellidos o Razón Social

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DATOS DE LA PATENTE DE INVENCION

(73) Título de la Invención

**POLIMERIZACIÓN DE MONÓMEROS AROMÁTICOS DE VINILO POR
MEDIO DE PROCESOS DE POLIMERIZACIÓN CATIONICOS Y DE
RADICAL LIBRE, PARA PRODUCIR POLÍMEROS AROMÁTICOS DE
MONOVINILIDENO DE PESO MOLECULAR BIMODAL**

PRIORIDAD REIVINDICADA

SI ☒

NO ☐

TIPO DE PRIORIDAD

ANDINA ☐

UNIONISTA ☒

(33) País

Fecha

No Solicitud

US

01 de Septiembre de 1999

60/152.009

Convención de París

Para Publicar a los

☐ 6 meses

☐ 12 meses

☒ 18 meses a partir de la fecha de la presente solicitud

Colo 0286-801-134-3

(51) CLASIFICACIÓN INTERNACIONAL

C05F 002/000

RESUMEN CON EL OBJETO Y LA FINALIDAD DE LA INVENCION

La presente invención s refiere a un proc so para producir un polím ro aromático de monovinilideno que tiene una distribución de Mw bimodal distinta qu usa ambos procesos de polimerización catiónica y por radical libre

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ANEXOS DE LA SOLICITUD

Certificado de Existencia y Representación Legal cuando el solicitante sea Persona Jurídica	☐
Los poderes debidamente otorgados, o mención de su protocolización ante la SIC	☐
Recibo de la tasa respectiva	☐
Recibo de la tasa por concepto de excedente de palabras en la publicación	☐
Si se reivindica prioridad Andina	
Copia de la primera solicitud	☐
Traducción oficial	☐
Si se reivindica prioridad Unionista	
Copia certificada de la primera solicitud	☐
Nota Debe presentarse dentro de los tres (3) meses, contados a partir de la fecha de radicación de la solicitud posterior	
Traducción simple	☐
Capítulo descriptivo	☐
Dibujos, planos necesarios	☐
Capítulo reivindicatorio	☐
Tarjeta archivo propietarios según formato	☐
Tarjeta archivo temático según formato	☐
Extracto para publicación según formato	☐
Arte final 12 x 12 cms Y 6x6 cms	☐
Otros Documentos	☐

SOLICITO LA CONCESION DE LA PATENTE DE INVENCION Y DECLARO QUE LA INVENCION ES NUEVA Y DE MI PROPIEDAD

FIRMA

NOMBRE EMILIO FERRERO

CC 438.019 de Usaquén

TJ No. 31.929

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PA 392284



THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

August 21, 2000

**THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM
THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK
OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT
APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A
FILING DATE UNDER 35 USC 111**

APPLICATION NUMBER. 60/152,009

FILING DATE September 01, 1999



**By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS**

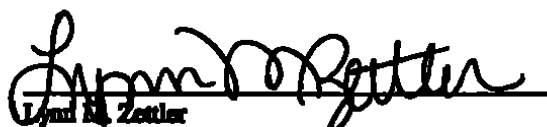
**T LAWRENCE
Certifying Officer**

PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

Docket Number		44433	Type a plus sign (+) inside this box	+
INVENTOR(s)/APPLICANT(s)				
LAST NAME	FIRST NAME	MIDDLE INITIAL	RESIDENCE (CITY AND EITHER STATE OR FOREIGN COUNTRY)	
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☐ Additional inventors are being named on separately numbered sheets attached hereto				
TITLE OF THE INVENTION (280 characters max)				
CATIONIC-FREE RADICAL POLYMERIZATION OF VINYL AROMATIC MONOMERS TO PRODUCE BIMODAL MOLECULAR WEIGHT MONOVINYLDENE AROMATIC POLYMERS				
CORRESPONDENCE ADDRESS				
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ENCLOSED APPLICATION PARTS (check all that apply)				
☒ Specification		Number of Pages 11		☐ Small Entity Statement
☐ Drawing(s)		Number of Sheets _____		☐ Other (specify)
METHOD OF PAYMENT (check one)				
☒ A check or money order is enclosed to cover the Provisional filing fees		PROVISIONAL FILING FEE AMOUNT		\$150.00
☒ The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number: 04-1512				
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government				
☒ No				
☐ Yes, the name of the U.S. Government agency and the Government contract number are:				

Respectfully submitted,


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EXPRESS MAIL MAILING NO. EL08908265208
DATE OF DEPOSIT: September 1, 1999

LMZ:cm

PROVISIONAL APPLICATION FILING ONLY

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CATIONIC-FREE RADICAL POLYMERIZATION OF VINYL AROMATIC MONOMERS
TO PRODUCE BIMODAL MOLECULAR WEIGHT MONOVINYLDENE
AROMATIC POLYMERS

BACKGROUND OF THE INVENTION

5 The process of the present invention relates to a polymerization process for producing monovinyldene aromatic polymers.

10 Generally, monovinyldene aromatic polymers have good toughness and flow properties. However, there has long been a desire to alter these properties, by increasing the flow of the polymer while maintaining or increasing toughness. Lower viscosity is normally attained by lowering the molecular weight of the polymer. However, in some applications, such as blown foams, adequate toughness cannot be attained at lower molecular weights. Plasticizers have also been used to increase the flow properties of monovinyldene aromatic polymers. However, plasticizers typically decrease the heat distortion temperature. Another method of increasing flow involves the addition of a very low molecular weight fraction to the monovinyldene aromatic polymer. However, this requires an additional compounding step and also adds cost to the polymer.

15 Therefore, there still remains a need for a process of producing a monovinyldene aromatic polymer having good toughness and improved flowability which is cost effective.

20 SUMMARY OF THE INVENTION

 The present invention relates to a process for producing a monovinyldene aromatic polymer having a distinct bimodal molecular weight distribution comprising:

- a) cationically polymerizing a vinyl aromatic monomer in the presence of a carbocation generator, to produce a first polymer composition comprising
- 25 1) a low molecular weight monovinyldene aromatic polymer fraction having a weight average molecular weight (Mw) of from 1,000 to 5,000, and
- b) polymerizing a vinyl aromatic monomer under free radical polymerization conditions in the presence of the low molecular weight monovinyldene aromatic

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polymer fraction, to a level of completion of from 70 to 95 percent, to produce a second polymer composition comprising

- ii) a high molecular weight monovinylidene aromatic polymer fraction having a Mw of from 135,000 to 400,000, and
- 5 iii) the low molecular weight monovinylidene aromatic polymer fraction having a weight average molecular weight of from 1,000 to 5,000.

This process can be utilized under batch or continuous polymerization conditions. Preferably the process is a continuous process for producing a monovinylidene aromatic polymer having a distinct bimodal molecular weight distribution comprising:

- 10 a) cationically polymerizing a vinyl aromatic monomer in the presence of a carbocation generator to a level of completion of from 1 to 10 percent, to produce a first polymer composition comprising
 - 1) a low molecular weight monovinylidene aromatic polymer fraction having a weight average molecular weight (Mw) of from 1,000 to 5,000, and
 - 15 2) unreacted vinyl aromatic monomer; and
- b) polymerizing the first polymer composition under free radical polymerization conditions to a level of completion of from 70 to 95 percent, to produce a second polymer composition comprising:
 - 20 3) a high molecular weight monovinylidene aromatic polymer fraction having a Mw of from 135,000 to 400,000, and
 - 4) the low molecular weight monovinylidene aromatic polymer fraction having a weight average molecular weight of from 1,000 to 5,000

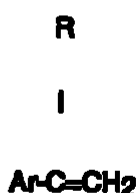
25 This process utilizes both cationic and free-radical polymerization processes to produce a monovinylidene aromatic polymer having excellent toughness and flowability properties without incorporating additional additives. In the continuous process, the low molecular weight fraction, which acts as a plasticizer, is produced in situ during the polymerization

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In one embodiment, the present invention is a process for producing a monovinylidene aromatic polymer having a distinct bimodal Mw distribution. A bimodal Mw distribution refers to a weight average molecular weight distribution of a polymer which has two distinct peaks or maxima.

Monovinylidene aromatic polymers are produced by polymerizing a vinyl aromatic monomer. Vinyl aromatic monomers include, but are not limited to those described in U S patents 4,666,987, 4,572,819 and 4,585,825, which are herein incorporated by reference. Preferably, the monomer is of the formula.

10



15 wherein R is hydrogen or methyl, Ar is an aromatic ring structure having from 1 to 3 aromatic rings with or without alkyl, halo, or haloalkyl substitution, wherein any alkyl group contains 1 to 6 carbon atoms and haloalkyl refers to a halo substituted alkyl group. Preferably, Ar is phenyl or alkylphenyl, wherein alkylphenyl refers to an alkyl substituted phenyl group, with phenyl being most preferred. Typical vinyl aromatic monomers which
20 can be used include: styrene, alpha-methylstyrene, all isomers of vinyl toluene, especially paravinyltoluene, all isomers of ethyl styrene, propyl styrene, vinyl biphenyl, vinyl naphthalene, vinyl anthracene and the like, and mixtures thereof. The vinyl aromatic monomers may also be combined with other copolymerizable monomers. Examples of such monomers include, but are not limited to acrylic monomers such as acrylonitrile,
25 methacrylonitrile, methacrylic acid, methyl methacrylate, acrylic acid, and methyl acrylate; maleimide, phenylmaleimide, and maleic anhydride. In addition, the polymerization of the vinyl aromatic monomer may be conducted in the presence of predissolved elastomer to prepare impact modified, or grafted rubber containing products, examples of which are

described in USP's 3,123,855, 3,346,520, 3,639,522, and 4,409,389, which are incorporated by reference herein

Cationic polymerization of a vinyl aromatic monomer is well known in the art and specifically disclosed in U S 4,112,209, which is incorporated herein by reference, and in
 5 JP 02180907, JP 01121305, JP 63088629, and JP 55104219 These references disclose a process wherein low molecular weight monovinylidene aromatic polymer is produced by contacting a solution of vinyl aromatic monomer with a cation generator, under substantially isothermal conditions, at a temperature between 0 °C and 180 °C.

Carbocation generators are protonic acids such as Bronsted or Lewis acids,
 10 which react with olefinic double bonds of an organic compound to generate a carbocation and can be characterized as both homogeneous and heterogeneous. The term 'homogeneous carbocation generator', as used herein, refers to any homogeneous catalyst for cationic polymerization of a vinyl aromatic monomer, including any necessary co-catalyst, as defined hereafter For example, homogeneous carbocation
 15 generators include the protonic acids such as sulfuric, hydrochloric, phosphoric, perchloric, dichloro- and trichloroacetic acids, and preferably Friedel-Crafts catalysts, such as boron trichloride, boron trifluoride, etherates thereof, stannic chloride, titanium tetrachloride, aluminum halides and alkyl aluminum halides, in conjunction with any necessary co-catalyst A small quantity of water is a common co-catalyst for most of
 20 the Friedel-Crafts catalyst and also for protonic acids, but other co-catalysts are also known and are often dependent on the solvent employed. Without such a co-catalyst, the polymerization proceeds very slowly, if at all. Preferred homogeneous carbocation generators or catalysts are BF₃ or AlCl₃ and a water co-catalyst, with BF₃ being most preferred The term 'heterogeneous carbocation generator', as used herein, refers to any
 25 heterogeneous catalyst for cationic polymerization of vinyl aromatic monomers. For example, heterogeneous carbocation generators include sulfonated ion exchange resins, heteropolyacids, perfluorinated resins such as perfluorosulfonic acid (NAFION™ resins), acidic or activated clays, and the like. These carbocation generators are essentially insoluble in vinyl aromatic monomer Preferably, the carbocation generator is
 30 heterogeneous.

If a homogeneous carbocation generator is employed, it is generally added to the vinyl aromatic monomer prior to or during polymerization and is employed in an amount that is, in total, about 1 to 10 percent of the amount of catalyst needed for 99.9 percent

polymer conversion to occur. For a BF_3 /water carbocation generator, this amount is typically from approximately 5 to 250 ppm, based on the weight of the vinyl aromatic monomer.

5 A heterogeneous carbocation generator is typically contained in a fixed or fluidized reactor through which the vinyl aromatic monomer is passed at a temperature and feed rate such that 2-15% of the monomer is converted to polymer. This reactor may be a separate vessel or part of the vessel used for free radical polymerization. The catalyst may also be used as a slurry from which the product can be decanted.

10 The carbocation generator may be added to the vinyl aromatic monomer stream prior to polymerization, in stages, or, in the case of the heterogeneous catalysts, can be contained within a fixed bed through which the monomer stream is fed.

15 Typically, the vinyl aromatic monomer is first dissolved in an inert organic solvent which is a solvent for the vinyl aromatic monomer, prior to cationic polymerization. The solvent is not reactive with the vinyl aromatic monomer or appreciably with the carbocation generator. The solvent may generally be described as an aromatic or aliphatic hydrocarbon or halohydrocarbon and include compounds such as 1,2-dichloroethane, ethylbenzene, toluene, benzene, carbon tetrachloride, ethyl chloride, ethylene dichloride, nitrobenzene, chlorobenzene, isopropyl chloride, t-butyl chloride, hexane, cyclohexane, sulfur dioxide, DMF and the like.

20 The cationic polymerization is conducted until the desired level of low molecular weight polymer is produced. Generally, molecular weights of no more than 20,000 or 30,000 are achieved by cationic polymerization. Typically the weight average molecular weight (M_w) of the low molecular weight polymer fraction is from 1,000 to 5,000; preferably from 1,000 to 4,000, more preferably from 1,000 to 3,000 and most preferably
25 from 1,000 to 2,000. M_w , as referred to throughout this application, is measured according to gel permeation chromatography (GPC).

30 The cationic polymerization can be accomplished by a batch process or as part of a continuous process. In a batch process, the low molecular weight monovinylidene aromatic polymer is produced and then combined with additional vinyl aromatic monomer, wherein the vinyl aromatic monomer is polymerized under free radical polymerization conditions.

In a continuous process, the cationic polymerization produces a first polymer composition comprising vinyl aromatic monomer, low molecular weight monovinylidene aromatic polymer, solvent (if used) and catalyst if a homogeneous catalyst has been used. Typically, a small addition of water, alcohol, e.g. methanol, or ammonia is added to the stream in order to neutralize any residual homogeneous catalyst, if used, prior to free radical polymerization. This composition is then exposed to free radical polymerization conditions. Additional vinyl aromatic monomer can also be added prior to the free radical polymerization. Free radical polymerization conditions include thermal initiation, as well as initiation using a free radical polymerization catalyst. Free radical polymerization catalysts are well known in the art, any of which can be used in the process of the present invention. Typical initiators include azo compounds and peroxides such as tert-butylperoxybenzoate, tert-butylperoxyacetate, di-tert-butylperoxide, dibenzoylperoxide, dilauroylperoxide, 1,1-bis-tert-butylperoxycyclohexane, 1,1-bis-tert-butylperoxy-3,3,5-trimethylcyclohexane and dicumylperoxide.

The amount of free radical initiator, if used, is dependent upon the Mw desired for the high molecular weight fraction. Typically, the initiator is present in an amount of from 10 to 2000 ppm based on the weight of unreacted vinyl aromatic monomer.

Suitable free radical polymerization conditions are well known in the art and described in U.S. patents such as U.S. 5,191,040, U.S. 5,087,738 and U.S. 4,275,182, all of which are incorporated by reference herein. The free radical polymerization may be a bulk, solution, emulsion or suspension process. Preferably the process of the present invention is a continuous bulk or solution polymerization.

The free radical polymerization is typically conducted at temperatures from 80 °C to 170 °C, preferably from 110 °C to 160 °C, with 115 °C to 150 °C being most preferred.

The free radical polymerization is conducted until the desired level of high molecular weight polymer is produced. Typically the Mw of the high molecular weight polymer fraction is from 135,000 to 400,000 preferably from 150,000 to 375,000, more preferably from 150,000 to 350,000 and most preferably from 150,000 to 330,000.

The amounts of low molecular weight and high molecular weight polymer fractions in the bimodal Mw polymer produced will depend upon the desired flow properties of the bimodal polymer and the molecular weight of the high molecular weight

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fraction. Higher molecular weight polymer components will require more low molecular weight fraction in order to obtain adequate flow properties. The amount of low molecular weight polymer fraction in the bimodal polymer is typically from 1 to 15 weight percent, preferably from 1 to 10 percent, more preferably from 1 to 8 percent and most preferably from 1 to 6 percent, based on the total weight of the bimodal polymer produced. The amount of high molecular weight polymer fraction in the bimodal polymer is typically from 85 to 99 weight percent, preferably from 90 to 99 percent, more preferably from 92 to 99 percent and most preferably from 94 to 99 percent, based on the total weight of the bimodal polymer produced.

10 The composition containing both high and low molecular weight vinyl aromatic polymers may be any combination of two vinyl aromatic polymers but is preferably a blend of polymers having the same composition (i.e., homopolymers of the same monomeric units or copolymers having the same comonomeric units in the similar ratios). More preferably, both polymers are polystyrene.

15 After the free radical polymerization, the polymer composition is removed from the reaction zone and devolatilized to remove unreacted monomer, solvent, and the like.

Additionally, other additives may be present in the process of the present invention including antioxidants, plasticizers, flame retarding agents, chain transfer agents and the like.

20 In one embodiment of the present invention, a monovinylidene aromatic polymer having a distinct bimodal molecular weight distribution is produced using a continuous process comprising:

a1) cationically polymerizing a vinyl aromatic monomer in the presence of a homogeneous carbocation generator to a level of completion of from 1 to 10 percent, to produce a first polymer composition comprising:

I) a low molecular weight monovinylidene aromatic polymer fraction having a weight average molecular weight (Mw) of from 1,000 to 5,000, and

II) unreacted vinyl aromatic monomer; and

III) residual homogeneous carbocation generator;

- a2) neutralizing the residual homogeneous catalyst, and
- b) further polymerizing the first polymer composition under free radical polymerization conditions to a level of completion of from 70 to 95 percent, to produce a second polymer composition comprising:

- 5 IV) a high molecular weight monovinylidene aromatic polymer fraction having a Mw of from 135,000 to 400,000, and
- V) the low molecular weight monovinylidene aromatic polymer fraction having a weight average molecular weight of from 1,000 to 5,000

10 In another embodiment of the present invention, a monovinylidene aromatic polymer having a distinct bimodal molecular weight distribution is produced using a continuous process comprising

- a1) cationically polymerizing a vinyl aromatic monomer in the presence of a heterogeneous carbocation generator to a level of completion of from 1 to 10 percent, to produce a first polymer composition comprising

- 15 1) a low molecular weight monovinylidene aromatic polymer fraction having a weight average molecular weight (Mw) of from 1,000 to 5,000, and

2) unreacted vinyl aromatic monomer; and

- 20 b) further polymerizing the first polymer composition under free radical polymerization conditions to a level of completion of from 70 to 95 percent, to produce a second polymer composition comprising:

3) a high molecular weight monovinylidene aromatic polymer fraction having a Mw of from 135,000 to 400,000, and

- 25 4) the low molecular weight monovinylidene aromatic polymer fraction having a weight average molecular weight of from 1,000 to 5,000

The following examples are provided to illustrate the present invention. The examples are not intended to limit the scope of the present invention and they should not

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GENERAL PROCEDURE FOR FIXED BED REACTOR.

- ### PREPARATION OF THE LOW MOLECULAR WEIGHT POLYMER-

15 Styrene is passed through the reactor at 50° C and 2 ml/min. to obtain a stream which contains 3 weight percent of low molecular weight polystyrene with a Mw of 1500, an Mn of 630, and a styrene-dimer content of less than 5% (based on polymer)

PREPARATION OF THE BIMODAL Mw POLYMER. A solution of styrene monomer containing 6 weight percent low molecular weight polystyrene resin having a Mw of 1600 (Mn of 700) prepared by the method described above, is thermally polymerized at 130°C to obtain a bimodal resin, wherein 90% of the resin has a Mw of 340,000 (Mn of 195,000) and 10% of the resin has a Mw of 1600 (Mn of 700).

25 A solution containing 3.5 weight percent low molecular weight polystyrene (Mw 1400, Mn 660) prepared as in Example 1, 8% ethylbenzene, 88.5% styrene monomer, and 30 ppm sulfoethylmethacrylate is passed through a stirred tube reactor with a temperature gradient from 128 to 160°C. A slurry of zinc stearate in ethylbenzene is added about halfway through the reactor such that the final concentration of zinc stearate in the product is 2400 ppm. The partial polymer is devolatilized at 230°C and 10 mm,

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WHAT IS CLAIMED IS.

1 A process for producing a monovinylidene aromatic polymer having a distinct bimodal molecular weight distribution comprising:

5 a) cationically polymerizing a vinyl aromatic monomer in the presence of a carbocation generator to produce a first polymer composition comprising:

i) a low molecular weight monovinylidene aromatic polymer having a weight average molecular weight (Mw) of from 1,000 to 5,000; and

10 b) polymerizing a vinyl aromatic monomer in the presence of the first polymer composition under free radical polymerization conditions to a level of completion of from 70 to 95 percent, to produce a second polymer composition comprising:

ii) a high molecular weight monovinylidene aromatic polymer fraction having a Mw of from 135,000 to 400,000, and

iii) the low molecular weight monovinylidene aromatic polymer fraction having a weight average molecular weight of from 1,000 to 5,000

15 2 A continuous process for producing a monovinylidene aromatic polymer having a distinct bimodal molecular weight distribution comprising:

a) cationically polymerizing a vinyl aromatic monomer in the presence of a carbocation generator to a level of completion of from 1 to 10 percent, to produce a first polymer composition comprising

20 1) a low molecular weight monovinylidene aromatic polymer fraction having a weight average molecular weight (Mw) of from 1,000 to 5,000, and

2) unreacted vinyl aromatic monomer; and

25 b) polymerizing the first polymer composition under free radical polymerization conditions to a level of completion of from 70 to 95 percent, to produce a second polymer composition comprising:

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3) a high molecular weight monovinylidene aromatic polymer fraction having a Mw of from 135,000 to 400,000 and

4) the low molecular weight monovinylidene aromatic polymer fraction having a weight average molecular weight of from 1,000 to 5,000

5 3 The process of Claim 1 or 2 wherein the vinyl aromatic monomer is styrene

 4 The process of Claim 1 or 2 wherein the low molecular weight monovinylidene aromatic polymer fraction has a Mw of from 1,000 to 2,000

 5 The process of Claim 1 or 2 wherein the high molecular weight
10 monovinylidene aromatic polymer fraction has a Mw of from 150,000 to 400,000.

 6. The process of Claim 1 or 2 wherein the monovinylidene aromatic polymer fraction of I) is from 1 to 10 weight percent of the bimodal polymer produced

 7 The process of Claim 1 or 2 wherein the carbocation generator is BF_3 .

 8. The process of Claim 1 or 2 wherein the carbocation generator is a
15 sulfonated ion exchange resin, a heteropolyacid, perfluorinated resin, or an acidic or activated clay

 9 The process of Claim 1 or 2 wherein the free radical polymerization is conducted in the presence of a free radical polymerization catalyst.

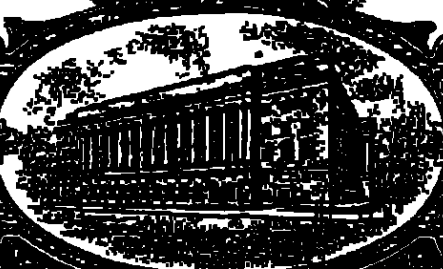
 10 The process of Claim 9 wherein the free radical polymerization catalyst is
20 1,1-bis(t-butylperoxy)cyclohexane

ABSTRACT OF THE DISCLOSURE

The present invention relates to a process for producing a monovinylidene aromatic polymer having a distinct bimodal Mw distribution using both cationic and free radical polymerization processes.

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LOS ESTADOS UNIDOS DE AMERICA

A TODO AQUEL A QUIEN CONCIERNA LO PRESENTE

DEPARTAMENTO DE COMERCIO DE LOS ESTADOS UNIDOS

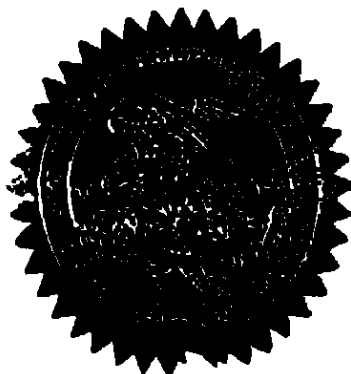
Oficina de Patentes y Marcas de los Estados Unidos

21 de Agosto de 2000

**LA PRESENTE ES PARA CERTIFICAR QUE ADJUNTA A LA MISMA HAY
UNA COPIA FIEL DE LOS REGISTROS DE LA OFICINA DE PATENTES Y
MARCAS DE LOS ESTADOS UNIDOS DE LOS DOCUMENTOS DE LA
SOLICITUD DE PATENTE IDENTIFICADA EN LO QUE SIGUE, QUE
CUMPLEN LOS REQUISITOS PARA OTORGARLE UNA FECHA DE
PRESENTACIÓN BAJO 35 USC 111**

NÚMERO DE SOLICITUD. 60/152 009

FECHA DE PRESENTACIÓN 01 de Septiembre de 1999



**Por la Autoridad del
COMISARIO DE PATENTES Y MARCAS**

T LAWRENCE

Oficial certificador

REIVINDICACIONES

1 Un proceso para producir un polimero aromático de monovinilideno que tiene una distribución de peso molecular bimodal distinta que comprende

a) polimerizar catiónicamente un monómero aromático de vinilo en la presencia de un generador de carbocatión para producir una primera composición de polimero que comprende

i) un polímero aromático de monovinilideno de bajo peso molecular que tiene un peso molecular promedio de peso molecular (Mw) desde 1,000 hasta 5,000, y

b) polimerizar un monómero de vinilo aromático en presencia de la primera composición de polimero bajo condiciones de polimerización de radical libre hasta un nivel de terminación desde 70 hasta 95 por ciento, para producir una segunda composición de polimero que comprende

ii) una fracción de polímero aromático de monovinilideno de alto peso molecular que tiene un Mw desde 135,000 hasta 400,000 y

iii) la fracción de polimero aromático de monovinilideno de bajo peso molecular que tiene un peso molecular en promedio de peso desde 1,000 hasta 5,000

2 Un proceso continuo para producir un polimero aromático de monovinilideno que tiene una distribución de peso molecular bimodal distinta que comprende

a) Polimerizar catiónicamente un monomero aromático de vinilo en la

- presencia de un generador de carbocation hasta un nivel de terminación desde 1 hasta 10 por ciento, para producir una primera composición de polímero que comprende
 - 1) una fracción de polímero aromático de monovinilideno de bajo peso molecular que tiene un peso molecular (Mw) en promedio de peso desde 1,000 hasta 5,000, y
 - 2) monómero aromático de vinilo sin reaccionar, y
- b) polimerizar la primera composición de polímero bajo condiciones de polimerización por radical libre hasta un nivel de terminación desde 70 hasta 95 por ciento, para producir una segunda composición de polímero que comprende
 - 3) una fracción de polímero aromático de monovinilideno de alto peso molecular que tiene un Mw desde 135,000 hasta 400,000, y
 - 4) la fracción de polímero aromático de monovinilideno de bajo peso molecular que tiene un peso molecular en promedio de peso desde 1,000 hasta 5 000
- 1) 3 El proceso de la reivindicación 1 o 2 en donde el monómero aromático de vinilo es estireno
- 2) 4 El proceso de la reivindicación 1 o 2 en donde la fracción de polímero aromático de monovinilideno de bajo peso molecular tiene un Mw de desde 1,000 hasta 2,000
- 5 El proceso de la reivindicación 1 o 2 en donde la fracción de polímero aromático de monovinilideno de alto peso molecular tiene un Mw desde 150,000 hasta 400,000
- 2) 6 El proceso de la reivindicación 1 o 2 en donde la fracción de

polimero aromático de monovinilideno de 1) es desde 1 hasta 10 por ciento en peso del polimero bimodal producido

7 El proceso de la reivindicación 1 o 2 en donde el generador de carbocation es BF_3

8 El proceso de la reivindicación 1 o 2 en donde el generador de carbocatión es una resina de intercambio de iones sulfonada, un heteropoliácido, resina perfluorada, o una arcilla activada o ácida

9 El proceso de la reivindicación 1 o 2 en donde la polimerización por radical libre se conduce en la presencia de un catalizador de

10 polimerización por radical libre

10 El proceso de la reivindicación 9 en donde el catalizador de polimerización por radical libre es 1,1-bis(t-butilperoxi)ciclohexano



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Industria y Comercio

SUPERINTENDENCIA

2do. EXAMEN DE FORMA PATENTE DE INVENCION

Folio 64Radicación no 00-65984Concepto Técnico no 576Clasificación Internacional de Patentes CO8 F 4/36, CO8 F 4/14
CO8 F 2 00

Practicado el examen de acuerdo a lo establecido en el Art. 38 de la Decisión 486 se determinó que esta solicitud de Patente de Invención

- SI [☒] NO [☐] Contiene un resumen de la invención (Art.26-e).
- SI [☒] NO [☐] Contiene el título o nombre de la invención (Art.27-d)
- SI [☒] NO [☐] Contiene la descripción de la invención (Art.26-b).
- SI [☐] NO [☐] NO ES APLICABLE [☒] Contiene los dibujos necesarios para comprender la invención (Art.26-d)
- SI [☒] NO [☐] Contiene una o más reivindicaciones. (Art.26-c).
- SI [☐] NO [☐] NO ES APLICABLE [☒] Han sido desarrollados los productos y/o procedimientos a partir de recursos genéticos o de sus productos derivados de los que cualquiera de los Países Miembros es país de origen. (Art. 26- h)
- SI [☐] NO [☐] NO ES APLICABLE [☒] Los productos y/o procedimientos han sido obtenidos o desarrollados a partir de los conocimientos tradicionales de las comunidades indígenas, afroamericanas, o locales de los países miembros, de acuerdo a lo establecido en la Decisión 391 y sus modificaciones y reglamentaciones vigentes.(Art.26-i)
- SI [☒] NO [☒] La invención se refiere a un producto relativo a un material biológico (Art.26-j)
- SI [☒] NO [☐] La prioridad coincide con la materia reivindicada.
- SI [☒] NO [☐] CUMPLE LOS REQUISITOS TÉCNICOS

OBSERVACIONES Y OTROS. SI [☐] NO [☒] ver hoja(s) anexa(s)

EXAMINADOR TÉCNICO

202092Bogotá D C., 27 DE JULIO 02

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Bogotá D C , Colombia

Folio 62

2020
Bogotá DC

Doctor
EMILIO FERRERO
Apoderado

REFERENCIA	Radicación No	00-65984
	Trámite	002
	Evento	001
	Actuación	416
	Oficio No	736
	Folios	001

Teniendo en cuenta que la solicitud de privilegio de patente que se tramita bajo el expediente indicado en la referencia, reúne los requisitos de forma establecidos en los artículos 26 y 27 de la Decisión 486 de la Comisión de la Comunidad Andina, y en las demás disposiciones vigentes sobre la materia, se envía el extracto de la solicitud a la Oficina de Comunicaciones para efecto de su publicación en la Gaceta de Propiedad Industrial, conforme lo establece el artículo 40 de la misma Decisión

Cúmplase
Dado en Bogotá DC, a los 17 de ABRIL del 2002

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones

Bogotá, DC, Dic-2002 El extracto de esta solicitud fue publicado en el número 516 de la Gaceta de Propiedad Industrial, de fecha 30-05-2002 El término hábil señalado por la ley expiró el 29-08-2002 y SI NOX se presentaron oposiciones por parte de terceros

202042

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