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DIVISION DE NUEVAS CREACIONES
Superintendencia de Industria y Comercio
E. S. D.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 07-081353- -00003-0000

Fecha: 2008-07-04 17:08:37 Dep. 2020 NUECREACIONE
Tra. 11 PATENTEIYII Eve: 378 FASENACIONALI
Act. 538 PETICION Folios: 2

Trámite : 011
Evento : 378
Actuación : 538

Referencia : Expediente No. 07.081.353
Asunto : Solicitud de Patente para **PROCESO PARA LA**
POLIMERIZACION DE MONOMEROS QUE
CONTIENEN VINILO
Solicitante : **VINNOLIT GMBH & CO. KG**
Clase : C08F 002/001, C08F 002/018, C08F 014/056, C08J 011/002
Publicada en : La Gaceta No. 588 Del 31 de enero de 2008
Fecha de Solicitud : 9 de agosto de 2007

1. Yo, Emilio FERRERO, identificado como aparece al pie de mi firma, actuando como apoderado en el asunto de la referencia, atentamente, solicito se efectúe el examen de patentabilidad de la solicitud en referencia presentada de acuerdo con el Capítulo I del PCT y según lo establecido en el artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina. Para tal efecto presento junto con este escrito el recibo por valor de \$420.000.00, que corresponde a la tasa fijada según lo dispuesto en la resolución No. 44372 de 26 de diciembre de 2007.

2. Ruego atentamente a la Señora Jefe se sirva ordenar que se anexe este recibo para que se efectúe dicho examen y se continúe con el trámite de la solicitud.

Señora Jefe,

EMILIO FERRERO
T.P.A. No. 31.929

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No. M-2008-129806\ASG

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

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OFICIAL DE CAJA : 08 - 46,120
FECHA : JUNIO 9 DE 2008

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO DE BOGOTA	062754387	2678328	09/06/2008	89,445,000.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	85 EXAMEN DE PATENTABILIDAD DE INVEN	420,000.00
TOTAL :			\$ 420,000.00

SON: CUATROCIENTOS VEINTE MIL PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

Colo 16088-841-001-8

DIVISIÓN DE NUEVAS CREACIONES

RADICACIÓN EXPEDIENTE No. 07-81353

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**
FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **588** DE
FECHA **31 DE ENERO DE 2008** EL TÉRMINO HÁBIL SEÑALADO POR LA LEY
EXPIRA EL **29 DE ABRIL DE 2008**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____ NO X

D1



US006395793B1

(12) **United States Patent**
Kadonaga et al.

(10) Patent No.: **US 6,395,793 B1**
(45) Date of Patent: **May 28, 2002**

(54) **METHOD FOR PRODUCTION OF POROUS MATERIAL**

(75) Inventors: **Kenji Kadonaga**, Takatsuki; **Akiko Mitsuhashi**, Sanda; **Hirofuma Fujimaru**, Suita; **Masazumi Sasabe**, Kakogawa; **Kazutomo Takahashi**, Moriyama; **Masuji Izubayashi**, Nishinomiya, all of (JP)

(73) Assignee: **Nippon Shokubai Co., Ltd.**, Osaka (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/712,723**

(22) Filed: **Nov. 14, 2000**

(30) **Foreign Application Priority Data**

Nov. 18, 1999 (JP) 11-328682

(51) Int. Cl.⁷ **C08J 9/28**

(52) U.S. Cl. **521/64; 521/62**

(58) Field of Search 521/64, 62

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Primary Examiner—Morton Foelak

(74) Attorney, Agent, or Firm—Fish & Richardson P.C.

(57) **ABSTRACT**

An object of this invention is to provide a method for the production of a porous material by polymerizing a water-in-oil type high internal phase emulsion in a briefer time than a conventional technique without impairing the stability of the emulsion. The object of this invention can be accomplished by a method for the production of a porous material comprising a step of polymerizing a water-in-oil type high internal phase emulsion containing a polymerization initiator, wherein the polymerization initiator is a redox type initiator combining a water-soluble oxidizing agent and a reducing agent, the reducing agent is preparatorily added to form the emulsion, and thereafter the water-soluble oxidizing agent is added to the emulsion to polymerize the added emulsion.

4 Claims, No Drawings

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A method for production of porous cross-linked polymer material which comprises separately adding an oxidizing agent and a reducing agent of a redox type initiator has been disclosed in JP-A-10-36,411. This method as disclosed therein comprises, in the polymerization of an HIPE with a redox type initiator, preparing in advance an HIPE with a water-soluble oxidizing agent added thereto, adding an aqueous solution of a reducing agent to the mixture and thereafter polymerizing the resultant HIPE mixture. This method is mainly targeted at obtaining a porous cross-linked polymer material having a decreased volume contraction ratio of the HIPE before and after the polymerization and excelling in physical properties. The present inventors have found that the method can also serve effectively as means for stably forming an HIPE and polymerizing the HIPE in a brief time as aimed at by the present invention. After further continuing the study in detail, they have found that this method has problems yet to be solved. Specifically, it has been ascertained to the inventors that while no serious problems arise when an HIPE having added sodium persulfate (as a water-soluble oxidizing agent) is emulsified at room temperature as disclosed in JP-A-10-36,411 or when the temperature exceeding the normal room temperature remains within the approximate bounds of 40° C., a possibility that the HIPE would partially be polymerized and the state of emulsification would become ununiform during the course of emulsification arises when the emulsification temperature is high. In contrast, the method for production of this invention is capable of infallibly retaining the stability of the HIPE because it comprises forming an HIPE by adding a reducing agent having no ability to initiate the polymerization and subsequently adding an oxidizing agent to the HIPE. The present inventors have further found that when the emulsification is effected after the addition of a reducing agent, the reducing agent can manifest effects of reducing and removing dissolved oxygen liable to retard the polymerization and effects of smoothly initiating the polymerization as well. They have perfected this invention based on this knowledge.

To be specific, an object of this invention can be accomplished by a method for the production of a porous material comprising a step of polymerizing a water-in-oil type high internal phase emulsion containing a polymerization initiator, wherein the polymerization initiator is a redox type initiator combining a water-soluble oxidizing agent and a reducing agent, the reducing agent is preparatorily added to form the emulsion, and thereafter the water-soluble oxidizing agent is added to the emulsion to polymerize the added emulsion.

Since this invention uses a redox type initiator combining a water-soluble oxidizing agent and a reducing agent, and comprises preparing in advance an HIPE containing the reducing agent and thereafter effecting the polymerization of the HIPE by adding the water-soluble oxidizing agent to the HIPE, it permits the polymerization to be completed in such a brief time as falling within one hour without impairing the emulsion stability during the formation of the HIPE. It may be rated as an unusually effective technique for the production of a porous material particularly by continuous polymerization.

The above and other objects, features and advantages of the present invention will become clear from the following description of the preferred embodiments.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

This invention relates to a method for the production of a porous material comprising a step of polymerizing an HIPE

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in the presence of a polymerization initiator, wherein a redox type initiator comprising a water-soluble oxidizing agent and a reducing agent in combination is used as the polymerization initiator, the reducing agent is added prior to the preparation of HIPE, and the water-soluble oxidizing agent is added to the HIPE prior to the polymerization thereof.

The component steps of the method of this invention for the production of a porous material will be described below sequentially in the order of their occurrence.

[I] Raw Material (HIPE)

(1) Composition of HIPE

The components of the HIPE which can be used in the method for the production of a porous material contemplated by this invention does not need to be particularly discriminated. It may be properly selected among compositions heretofore known in the art to suit the purpose for which the product is intended to be used. The composition of the HIPE is only required specifically to contain as essential components (a) a polymerizing monomer component containing at least one polymerizing unsaturated group in the molecular unit thereof, (b) a surfactant, (c) water, and (d) a redox type initiator using a water-soluble oxidizing agent and a reducing agent in combination. It may optionally contain (e) a salt and (f) another additive as arbitrary components as well.

(a) Polymerizing Monomer Component

The polymerizing monomer component which constitutes the HIPE mentioned above is a compound having at least one polymerizing unsaturated group in the molecular unit thereof. Though it does not need to be particularly restricted so long as it can form a water-in-oil type high internal phase emulsion and be polymerized in the emulsion, the polymerizing monomer component may preferably contain both (a-1) a polymerizing monomer having one polymerizing unsaturated group in the molecular unit thereof and (a-2) a cross-linking monomer having at least two polymerizing unsaturated groups in the molecular unit thereof.

(a-1) Polymerizing Monomer Having at Least One Polymerizing Unsaturated Group in the Molecular Unit Thereof

Though this polymerizing monomer does not need to be particularly limited, it may properly contain at least partly a (meth)acrylic ester, preferably not less than 20% by mass of a (meth)acrylic ester, and particularly preferably not less than 35% by mass of a (meth)acrylic ester. As the polymerizing monomer having one polymerizing unsaturated group in the molecular unit thereof, a polymerizing monomer containing a (meth)acrylic ester may desirably be used because the ester permits the production of a porous material excelling in flexibility and toughness.

As typical examples of the polymerizing monomer of (a-1) mentioned above, allylene monomers such as styrene; monoalkylene allylene monomers such as ethyl styrene, alpha-methyl styrene, vinyl toluene, and ethyl vinyl benzene; (meth)acrylic esters such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, isodecyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, cyclohexyl (meth)acrylate, and benzyl (meth)acrylate; chlorine-containing monomers such as vinyl chloride, vinylidene chloride, and chloromethyl styrene; acrylonitrile compounds such as acrylonitrile and methacrylonitrile; and vinyl acetate, vinyl propionate, N-octadecyl acrylamide, ethylene, propylene, and butene may be cited. These polymerizing monomers may be used either singly or in the form of a mixture of two or more members.

The content of the polymerizing monomer of (a-1) mentioned above is preferably in the range of 10 to 99.9% by

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sulfonic acid formalin condensate, sodium laureate, triethanol amine oleate, and triethanol amine apiate; polyoxyalkyl ether sulfuric esters; sulfuric esters of polyoxyethylene carboxylic ester and polyoxyethylene phenyl ether sulfuric esters; succinic acid dialkyl ester sulfonates; and polyoxy ethylene alkyl aryl sulfates may be cited. An HIPE may be prepared by using an anionic surfactant in combination with a cationic surfactant.

Incidentally, the combined use of a nonionic surfactant and a cationic surfactant may possibly result in improving the stability of the HIPE.

The content of the surfactant mentioned above may be preferably in the range of 1 to 30 parts by mass, more preferably 3 to 15 parts by mass, based on 100 parts by mass of the total mass of the monomer component of (a) mentioned above. If the content of the surfactant is less than 1 part by mass, the shortage would be at a disadvantage in possibly impairing the stability of the high dispersibility of the HIPE and preventing the surfactant from sufficiently manifesting the operation and function inherent therein. Conversely, if the content of the surfactant exceeds 30 parts by mass, the excess would be at a disadvantage in possibly rendering the produced porous material excessively brittle and disrupting the expected proportionate addition to the effects of the surfactant.

(c) Water

As the water which is an essential component for the construction of the HIPE mentioned above, in addition to purified water and deionized water, waste water to be obtained in the production of the porous material may be used either in its unmodified form or after it has been given a prescribed treatment with a view to promoting the reuse of the waste water.

The content of the water mentioned above may be properly selected to suit the purpose for which the porous material containing open cells aimed at is used (for example, a water absorbent material, an oil absorbent material, a soundproof material, and a filter). It may be decided, for example, so that the HIPE eventually produced will assume an expected water phase/oil phase (W/O) ratio which will be specifically described herein below.

(d) Polymerization Initiator

The polymerization initiator which is an essential component for the construction of the HIPE mentioned above is a redox initiator which combines a water-soluble oxidizing agent and a reducing agent. Optionally, it may be used in combination with another polymerization initiator.

The water-soluble oxidizing agent does not need to be particularly limited but water-soluble oxidizing agents which have been heretofore used for the polymerization of HIPE may be used. As typical examples of the water-soluble oxidizing agent, persulfates such as potassium persulfate, sodium persulfate, and ammonium persulfate; and peroxides such as hydrogen peroxide, potassium peracetate, sodium peracetate, potassium percarbonate, sodium percarbonate, and t-butyl hydroxyperoxide may be cited.

The amount of the water-soluble oxidizing agent mentioned above to be used may be preferably in the range of 0.05 to 15% by mass, more preferably 1.0 to 10% by mass, based on the total amount of the monomer component of (a) mentioned above. If the amount of the water-soluble oxidizing agent to be used is less than 0.05% by mass, the shortage would be at a disadvantage in suffering unaltered monomer components to increase unduly and consequently suffering the produced porous material to have an unduly large residual monomer content. Conversely, if the amount of the water-soluble oxidizing agent to be used exceeds 15%

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by mass, the excess would be at a disadvantage in rendering the polymerization difficult to control and degrading the mechanical properties of the produced porous material.

Further, the reducing agent does not need to be particularly limited and may be either an oil-soluble or water-soluble reducing agent. As typical examples of the reducing agent mentioned above, water-soluble reducing agents such as sodium hydrogen sulfite, potassium hydrogen sulfite, sodium thiosulfate, potassium thiosulfate, L-ascorbic acid, erythorbic acid, ferrous salts, formaldehyde sodium sulfoxylate, glucose, dextrose, triethanol amine, and diethanol amine; and oil-soluble reducing agents such as dimethyl aniline, diethyl aniline, dimethyl orthotoluidine, cobalt naphthenate, cobalt octanate, zirconium naphthenate, lead naphthenate, and zinc naphthenate may be cited.

The amount of the reducing agent mentioned above to be used may be preferably in the range of 0.05 to 15% by mass, more preferably 1.0 to 10% by mass, based on the total amount of the monomer component of (a) mentioned above. If the amount of the reducing agent to be used is less than 0.05% by mass, the shortage would be at a disadvantage in suffering unaltered monomer components to increase unduly and consequently suffering the produced porous material to have an unduly large residual monomer content. Conversely, if the amount of the reducing agent to be used exceeds 15% by mass, the excess would be at a disadvantage in rendering the polymerization difficult to control and degrading the mechanical properties of the produced porous material.

The ratio (mass ratio) of the amounts of the water-soluble oxidizing agent and the reducing agent to be used, i.e., the ratio of the water-soluble oxidizing agent to the reducing agent, maybe in the range of 1/0.01 to 1/10, preferably 1/0.05 to 1/2. If the ratio (mass ratio) of the amounts of the water-soluble oxidizing agent and the reducing agent to be used, i.e., the ratio of the water-soluble oxidizing agent to the reducing agent, falls outside the range of 1/0.01 to 1/10, the deviation would be at a disadvantage in degrading the efficiency of initiating the polymerization.

These redox initiators may be used either singly or in the form of a mixture of two or more members.

The redox initiator which combines a water-soluble oxidizing agent and a reducing agent as mentioned above, when necessary, may be used in combination with an oil-soluble oxidizing agent. As typical examples of the oil-soluble oxidizing agent, such peroxides as cumene hydroperoxide, t-butylhydroperoxide, di-t-butyl peroxide, diisopropyl benzene hydroperoxide, p-menthane hydroperoxide, 1,1,3,3-tetramethylbutyl hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, benzoyl peroxide, and methylethyl ketone peroxide may be cited.

(e) Salts

The salt which is one of the arbitrary components for the construction of the HIPE mentioned above may be optionally used for the purpose of improving the stability of the HIPE.

As typical examples of the salt, water-soluble salts including halogenides, sulfates, and nitrates of alkali metals and alkaline earth metals such as calcium chloride, sodium sulfate, sodium chloride, and magnesium sulfate may be cited. These salts may be used either singly or in the form of a mixture of two or more members. The salt may be preferably added to the water phase. Among other salts cited above, a polyvalent metal salt may be used advantageously from the viewpoint of the stability of the HIPE during the polymerization.

The amount of the salt to be used may be such that the concentration of the salt dissolved in water would fall in the

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Patented Sept. 13, 1949

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UNITED STATES PATENT OFFICE

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POLYMERIZATION PROCESS

William E. Elwell and Alvah L. Snow, Berkeley, Calif., assignors to California Research Corporation, San Francisco, Calif., a corporation of Delaware

Application June 19, 1945, Serial No. 600,244

13 Claims. (Cl. 260—80)

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This invention relates to polymerization processes and more particularly to the polymerization and fractionation of resulting polymers in a continuous or a repetitive type process.

In polymerization reactions, particularly those effected by the opening of a carbon unsaturated bond, the chemical law of mass action does not control the molecular weight distribution or the yield of polymer product. On the contrary, molecular weight distribution, i. e., the relative amounts of polymer molecules within given molecular weight ranges, is determined by the relationship between the rate of activation of the monomer (i. e., activation of the molecular unit being polymerized) to start chain formation, the rate of chain growth or propagation, and the rate of chain termination. Thus, the differential distribution curve for a given polymer may approximate that of an ordinary probability function, although other shapes are known in which the symmetry of the normal probability curve is decidedly modified. (See, for example, Mark and Raff, High Polymeric Reactions, volume III, pp. 54, 55.)

Linear polymer mixtures have been separated into different molecular weight fractions by means of a selective solvent. Such selective solvents are known and are characterized by the fact that they possess a relatively high solvent power for a given type polymer of lower molecular weight on the one hand, and a relatively low or even negligible solvent power for the same type polymer of a higher molecular weight, on the other hand. That is to say, such a selective solvent will selectively dissolve lower molecular weight portions of a polymer mixture or, conversely, can be made to selectively precipitate higher molecular weight portions of a dissolved polymer mixture. This selective precipitation may be effected by decreasing the solvent power of the selective solvent after the polymer has been dissolved therein. A preferred method of reducing solvent power is by adding an anti-solvent for the polymer, said anti-solvent being miscible with the selective solvent. Another method of decreasing solvent power comprises cooling the selective solvent. In some respects it is desirable to form a selective solvent of predetermined solvent power by combining a suitable solvent and anti-solvent miscible with the solvent in the range of proportions to be utilized.

An object of the present invention is to provide a process of polymerization in a selective solvent which affords good control and relatively sharp fractionation of resulting polymer products.

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Another object of the invention is to furnish an improved process for continuous or repetitive polymerization in a selective solvent.

A further object comprises the provision of an improved process for fractionating polymeric compositions.

Other objects and advantages of the invention will be apparent from the following disclosures and the attached drawing in which:

Figure I illustrates two typical basic curves showing variation in solubility and molecular weight distribution in a polymeric composition.

Figure II is a diagrammatic flow sheet of a multi-stage process utilizing a solvent and stepwise addition of an anti-solvent to vary solvent power in successive polymerization stages.

Figure III diagrammatically illustrates a process in which both solvent power and solvent ratio are varied in successive polymerization zones.

Figure IV shows a process in which solvent power temperature and pressure are varied in a polymerization process utilizing a volatile anti-solvent.

Figure V illustrates a process in which preliminary polymerization is followed by alteration of solvent power and fractionation of the polymer.

Figure VI is a flow diagram of a process utilizing the combination of a selective solvent, together with an auxiliary non-selective solvent, to effect fractionation, or polymerization and fractionation, of polymers according to molecular weight.

A study of polymerization reactions in a selective solvent reveals the phenomena illustrated in Figure I of the drawing. Referral to this figure discloses a typical solubility curve, 1, wherein average molecular weight of a linear polymer is plotted against per cent polymer miscible with a selective solvent. As will be observed, low molecular weight polymers are completely miscible with the solvent up to a given point and the solubility drops substantially to zero as molecular weight is further increased.

Curve 2 of Figure I is a typical differential distribution curve in which molecular weight of polymer is plotted against the relative amount thereof which is formed in a polymerization reaction. The molecular weight distribution here exemplified arises, as previously noted, from the three rate functions of monomer activation, chain growth, and chain termination.

When polymerization is effected in a selective solvent, a polymer chain tends to precipitate as it reaches a molecular weight above the solubility

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where the unmodified solvent phase favors the formation of a product having a molecular weight higher than is preferred in a particular case.

The precipitated polymer product, after repeated fractionation as above described, collects in the bottom of reactor 2, from which it may be removed through line 14 and suitably purified by separation from entrained solvent, anti-solvent and monomer. Components recovered from this purification may be returned to the system.

In the meantime, selective solvent, together with dissolved monomer and low and intermediate molecular weight polymers, continues to progress to the top of reactor 2. This reaction mixture and added anti-solvent then flow by way of line 3 through mixer 4 to the second polymerization and fractionation stage. The solution from mixer 4 is introduced into the bottom of second stage reactor 5 and flows upwardly there-through. Further polymerization desirably is effected in this second stage of the process to form additional low and intermediate molecular weight products.

The intermediate molecular weight polymer is precipitated and fractionated in reactor 5, as polymerization progresses, and introduction of an anti-solvent through valve controlled line 16 into the top of said reactor determines the lower molecular weight limit of polymer precipitated. The action of this anti-solvent and the repeated precipitation and solution of polymer is similar to that described in the first stage of the process. Likewise, anti-solvent may be added to mixer 4 by means of valve controlled line 17 to initially lower the solvent power of the selective solvent in the second stage of the process. The total amount of the anti-solvent introduced in the second stage of the process preferably is controlled so that the intermediate molecular weight polymer is precipitated to the point where concentration thereof in the solvent will not exceed its solubility limit upon return of the reaction mixture to reactor 2. In other words, the amount of intermediate polymer precipitated in reactor 5 preferably should equal the amount formed in both reactors 2 and 5 in order to prevent a build-up in concentration of the polymer and eventual precipitation in reactor 2 which would otherwise occur upon continuous recycle of reaction mixture from unit 5 to unit 2. This last precaution becomes unnecessary when the depolymerization feature of the process is utilized, since residual dissolved polymer is thereby removed.

Lower molecular weight polymers, in many cases, are completely miscible with the selective solvent and will reach an equilibrium point by reason of further polymerization on recycle. In any event the completely miscible polymers do not precipitate and can be removed, if desired, by depolymerization or other suitable methods.

Precipitated polymer of intermediate molecular weight collects in the bottom of second stage reactor 5 and is removed through line 18. Separation from entrained reaction mixture may be effected in any suitable manner.

Low molecular weight polymer, solvent and anti-solvent finally flow from the top of reactor 5 through line 6 to separator 7 where anti-solvent is at least partially removed and recycled through lines 11 and 15 to reactors 2 and 5. Preferably, the anti-solvent originally is selected so that it will be more volatile than the selective solvent and may be separated by a simple vaporization step. The anti-solvent may contain some monomer, depending upon the completeness of poly-

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merization and upon the relative volatility of these two components.

The remaining reaction mixture may be recycled from separator 7 to the first polymerization stage by way of outlet line 8, valve controlled return 9, and recycle line 10. This recycle reaction mixture preferably receives fresh catalyst feed prior to blending with the monomer feed as here illustrated in the drawing.

Due to the fact that the selective solvent ultimately may be contaminated with various reaction residues, the reaction mixture from separator 7 and outlet line 8 may be subjected to a purification treatment intermittently or a part of the mixture may be treated continuously, as desired. As here shown, the reaction mixture to be purified is by-passed from outlet line 8 to separator 19 and the selective solvent volatilized from higher boiling residues. Such residues may comprise, for example, low polymers, catalyst decomposition products and the like. The vaporized solvent from separator 19 is condensed and returned to the system by way of line 10a. Likewise, fresh solvent may be introduced through solvent inlet 25.

Provision is made in the process of Figure II for depolymerizing low molecular weight polymer by passing residue from separator 19 by way of line 21 to depolymerizer 22. The low polymers may be depolymerized by suitable known methods. For example, polystyrene can be depolymerized by heat and distillation. The monomer formed in depolymerizer 22 is separated and may be returned as feed through line 23. Catalyst residues, tars and the like from depolymerizer 22 may be discarded through line 24.

The process exemplified in Figure II affords close control of the type and molecular weight of polymer obtained. In reactor 2, for example, the polymer will have a relatively narrow molecular weight range as determined by difference in solubility in the solvent composition admitted to the bottom of the reactor, as an upper limiting factor, and solubility in the solvent diluted with anti-solvent in the top of the reactor, as a lower limiting factor. Likewise, the intermediate polymer separated in reactor 5 will be of a molecular weight range determined by differences in solubility in the modified solvent from the top of first stage reactor 2 on the one hand, and the total dilution of the solvent in second stage reactor 5, on the other hand. Continuous and relatively uniform operation is possible, since proper control of solvent and anti-solvent ratios in unit 5 prevents the build-up in concentration of intermediate or low polymers which might otherwise occur and cause gradual precipitation thereof on recycle to the first stage of polymerization.

Illustrated in Figure III is a second process utilizing a system in which ratio of solvent to polymer, as well as solvent power, is altered to effect and control polymerization and fractionation. In this example, an anti-solvent less volatile than the solvent is utilized and thereby permits selective removal of the solvent and alteration of solvent ratio by recycle thereof to different stages. As here shown, there is provided a multi-stage continuous process wherein polymerization and polymer fractionation are effected in a first reactor 52 and a second fractionator 55. Anti-solvent is introduced in each of these zones to effect fractionation in a desired manner, and solvent ratio is varied by introduction of additional selective solvent into the feed of second fractionator 55.

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More specifically, reference to Figure III will reveal that solvent, catalyst and monomer are fed through mixer 50 to the first polymerization and fractionating unit 52 where polymerization occurs as the solvent and its dissolved components flow upwardly through the reactor. A mixture of lower, intermediate and higher molecular weight polymers is formed, and selective precipitation of the higher polymers is effected by reducing the solvent power of the selective solvent in the upper portion of this first polymerization zone. As here indicated, solvent power is controlled by introduction of an anti-solvent through valve controlled line 56. Admission of the anti-solvent to the solution at this point effects a fractional precipitation of the polymer followed by solution and repeated precipitation of borderline polymers, as described in connection with the corresponding stage of the process of Figure II.

The precipitated polymer product is collected in the bottom of reactor 52 and removed through line 58. The polymer may be suitably purified by a separation from entrained solvent and other impurities.

As the selective solvent, together with dissolved polymers, progresses upwardly through reactor 52, it is blended with anti-solvent added through line 56, as previously indicated. This blended solution flows from the top of reactor 52 by way of line 53, mixer 54, to the second stage fractionator 55. Additional solvent is admitted to the bottom of this second fractionator through line 51 and mixer 54. Anti-solvent is introduced through valve controlled line 57 at the top of the fractionator, as in previous instances. Addition of solvent to the bottom of fractionator 55 tends to promote the formation of at least some polymer having a molecular weight overlapping the lower molecular weight range of the higher polymer precipitated in the first stage 52. However, time intervals and conditions may be controlled so that no material polymerization occurs in fractionator 55, in which event the principal function of the added selective solvent is to produce a more dilute solution and thereby effect a sharper fractionation of polymer by the addition of anti-solvent through line 57. (Dilute solutions have been found to yield sharper fractionation.)

Thus, by controlled addition of anti-solvent to reactor 52 through line 56, a relatively high molecular weight polymer fraction may be separated and removed through line 58, and by further addition of solvent to the bottom of second stage fractionator 55 and of anti-solvent near the top thereof, lower average molecular weight polymers may be fractionated and recovered through line 54. The feature of promoting additional higher molecular weight polymer in the second stage unit 55 is advantageous where a somewhat broader molecular weight range is desired in the polymer obtained from this stage of the process. Again, however, anti-solvent addition in fractionator 55 preferably should be sufficient to reduce the concentration of those polymers which are only partially miscible with the selective solvent, to a point where precipitation thereof will not occur in initial reactor 52 when and if the reaction mix is recycled.

The solvent, anti-solvent and any dissolved materials pass from fractionator 55 through line 59 to separator unit 60 where the more volatile solvent is vaporized, condensed, and recycled to initial feed and to second stage mixer 54. Anti-solvent and other less volatile residues flow from separator 60 through line 61 to a second sepa-

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rating unit 62 where anti-solvent is vaporized and recycled to the reaction and fractionation units. The remaining less volatile material is removed from separator 62 through line 63, and in suitable cases may be returned to feed or depolymerized, as described in connection with the process of Figure II. Although, as here shown, the solvent and anti-solvent are completely separated and purified before recycle, it is possible, when desired, to split the effluent from second stage fractionator 55 and purify only a portion thereof in the manner shown while returning the remainder to initial feed at mixer 50 or to second stage feed through mixer 54.

Figure IV of the drawing illustrates a multi-stage continuous process wherein a pressure differential is maintained between two stages and wherein a temperature differential likewise may be effected. In this type of process it is preferred to utilize an anti-solvent sufficiently volatile to create a superatmospheric pressure under the temperature conditions existing in at least one of the stages of the process. Controlled release of the anti-solvent pressure and the resulting vaporization thereof are then utilized to maintain a relatively lower temperature in the process stage to which the cooled reaction mixture is recycled.

As indicated in the drawing, monomer and catalyst feed are introduced into a recycled solvent and reaction mixture by way of mixer 56. Fresh solvent likewise may be introduced at this point, as desired. The recycled solvent and reaction mixture, together with fresh monomer and catalyst feed, flow from mixer 55 to the bottom of a first stage reactor and fractionator 75. Polymerization occurs as the solvent and its dissolved components flow upwardly through this reaction unit and a mixture of polymers of different molecular weights is formed. Selective precipitation of higher molecular weight polymers is effected by controlling the solvent power of the selective solvent in this first polymerization zone. As here shown, solvent power is reduced in the top of unit 75 by introduction of an anti-solvent through valve controlled line 56. Admission of anti-solvent to the solution at this point effects a fractional precipitation of the higher polymers formed in this reaction stage. The precipitated polymer then flows down the tower and is redissolved and reprecipitated to obtain fine fractionation, as previously indicated.

The fact that the reaction mixture has been cooled, in a manner to be subsequently described, maintains the average temperature of reactor 75 below that which would otherwise exist. This temperature effect may be utilized to direct the polymerization reaction. For example, in various acid catalyzed polymerizations, reduced temperature increases molecular weight, and in peroxide catalyzed reactions, reduced temperature may also increase the average molecular weight of the polymer formed, but usually substantially decreases the polymerization rate. In other words, it will generally be found that reduction in temperature in the first stage may be used with greater advantage to control primarily reaction rate in peroxide catalysis on the one hand, and molecular weight of polymer in acid type catalysis on the other hand. However, these two temperature dependent variables are not ordinarily completely separable.

The precipitated and fractionated polymer product of reactor 75 collects in the bottom thereof and may be removed as indicated at 85 in

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the drawing. In the meantime, selective solvent, together with dissolved lower molecular weight polymers, progress to the top of first stage reactor 75 and this reaction mixture, together with added anti-solvent, then flows by way of line 76, pump 77, and line 78, through mixer 79 to the second polymerization and fractionation stage which is maintained under a higher pressure than that of the first reactor 75. The solution from mixer 79 is introduced into the bottom of reactor 80 and flows upwardly therethrough. Further polymerization desirably is effected in this stage of the process to form additional lower and intermediate molecular weight polymers. Additional monomer and catalyst accordingly may be fed to reactor 80 through mixer 79 in order to obtain greater versatility in the relative yields of polymer produced in this second unit. Thus, a larger amount of the intermediate or lower polymer, or both, may be obtained in unit 80 by feeding additional monomer and catalyst thereto without unbalancing the system, since controlled addition of anti-solvent to reactor 80 will reduce the concentration of the intermediate and lower polymers to a point where precipitation or contamination of the higher polymer with the lower polymer need not occur in reactor 75.

It should be noted that a portion of effluent from pump 77 may be bypassed through valve controlled line 88 to a suitable separating system 89 where purification and removal of catalyst residues, etc., may be effected either periodically or continuously, as desired, and the solvent and anti-solvent and reaction components returned to the system through valve controlled line 90. This is desirable where the solvent becomes contaminated with non-volatile catalyst residues, tars and the like.

The reaction mixture from the top of second stage fractionator 80 passes through line 91 and pressure reducing valve 92 to vaporizer unit 93 where anti-solvent is vaporized as a result of the reduced pressure. This pressure simultaneously reduces the temperature and anti-solvent content of the recycle mixture. Relatively large amounts of anti-solvent may be vaporized to remove heat by self-refrigeration and maintain a temperature differential between the two reactors. The residual recycle mixture from vaporizer 93 is returned through line 94 and mixer 95 to reactor 75, as previously described. Anti-solvent from vaporizer 93 is re-introduced into reactors 75 and 80 through valve controlled lines 96 and 97, respectively. Suitable devices for compressing, condensing and recirculating anti-solvent and solvent will, of course, be provided.

When polymerization is slow or its initiation is delayed by a substantial induction period, a preliminary reactor may be provided with advantage. Likewise, where the anti-solvent tends to inhibit activation of the monomer and initiation of polymerization, the provision of a preliminary reactor will be found useful. This feature of the invention is illustrated in the flow sheet of Figure V.

In the process of Figure V, monomer and catalyst, together with recycle solvent, are fed through mixer 100 to a preliminary reactor 101 where initial polymerization or activation of the monomer is effected. The reaction mixture from preliminary reaction unit 101 flows through mixer 102 to a first fractionator 103. A series of polymer fractionations is effected in this first fractionator by admission of anti-solvent at a plurality of points along the path of the solvent

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as it flows upwardly therethrough. Solvent and dissolved reaction mixture, together with added anti-solvent, then pass from the first fractionator 103 through line 104 to a second fractionator 105 where further plural fractionation of dissolved lower polymer is likewise obtained. Solvent and residual materials retained in solution, together with anti-solvent, then flow from the top of this second fractionator through line 106 to a separator 107.

In this system, solvent and anti-solvent have been selected so that the monomer is the most volatile component. This permits removal of any unpolymerized monomer by vaporization in separator 107 and recycle of the vaporized monomer with or without condensation to initial feed mixer 100. Preferably, the anti-solvent is selected so that it is the next most volatile portion of the reaction mixture, and this component is accordingly separated by passing the unvaporized mixture from unit 107 through line 108 to a second separator 109 where anti-solvent is obtained as overhead, condensed and recycled through line 110 to the desired points in reactors 103, 105, etc. The residual less volatile components of the reaction mixture now flow from the anti-solvent separator 109 through line 111 and may pass either directly to feed by valve controlled line 112 or be entirely or partially by-passed through line 113 to separator 114 where solvent may be vaporized and returned either to feed or to the bottom of reactor 103 by way of line 120. This system has a number of advantages in that it is only necessary to vaporize residual monomer and anti-solvent for recycle purposes. Since the solvent is usually the larger component of the system, continuous vaporization and recycle thereof requires an increased expenditure of heat which may raise the over-all cost of operation.

Another feature of the process of Figure V involves the introduction of reaction mixture from preliminary reactor 101 and mixer 102 into the first stage fractionator 103 at a point where the anti-solvent content of the solvent from mixer 102 most nearly approaches the anti-solvent content of the solvent in reactor 103. Thus, anti-solvent content in reactor 103 increases progressively up the tower as anti-solvent is repeatedly admitted along the line of flow of the solvent, and the reaction mixture is introduced in that zone of reactor 103 where an equivalent concentration of anti-solvent is to be found. Where additional solvent is added through line 120 to the bottom of the fractionator, this point of equivalent anti-solvent concentration will be above the bottom of the fractionator, as indicated in Figure V, and somewhere in the zone of anti-solvent addition. Also, by providing preliminary reactor 101 and subsequently introducing anti-solvent through valve controlled line 115 into mixer 102, preliminary formation of a higher polymer may be promoted. At the same time, a further improvement in fractionation may be obtained by adding anti-solvent at a plurality of points in fractionators 103 and 105, to increase the number of extractions and precipitations and effect a sharper separation of polymers.

In the flow sheets and descriptions of this specification, no attempt has been made to set forth features such as valves, pumps, condensers, fractionating distillation columns, heat exchangers, and the like, which are utilized in an industrial plant. Likewise, the systems have been described on the assumption that the specific gravity of the polymer is greater than that of

Sept. 13, 1949.

W. E. ELWELL ET AL
POLYMERIZATION PROCESS

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Filed June 19, 1945

5 Sheets-Sheet 2

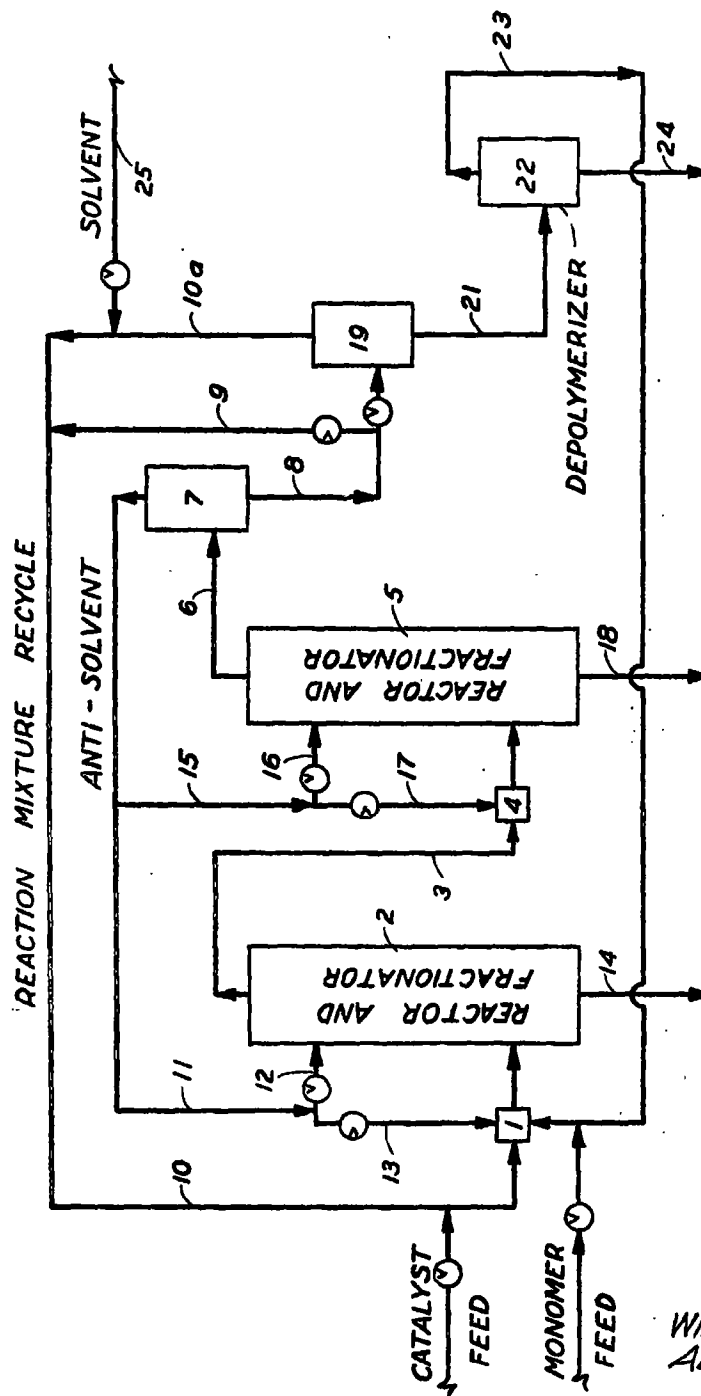


FIG. II

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BY James
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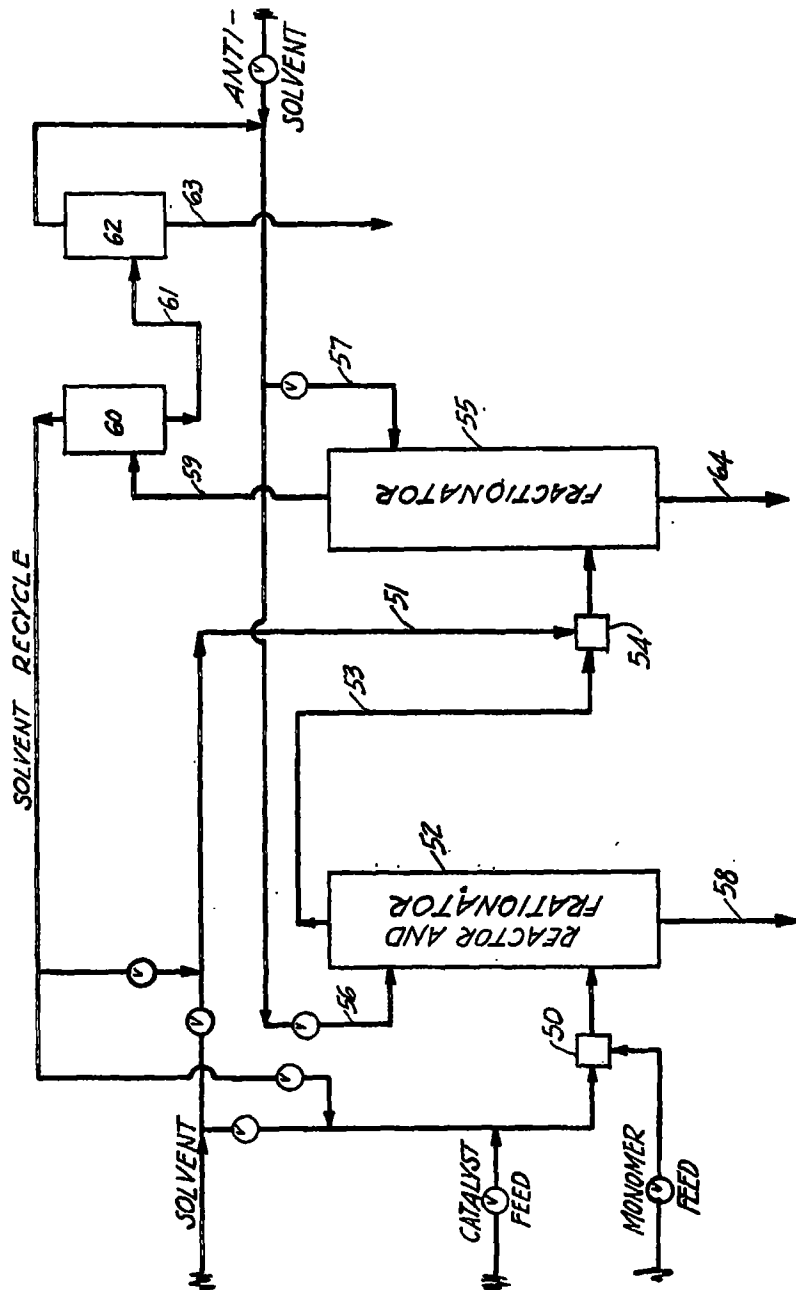
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Filed June 19, 1945

5 Sheets-Sheet 3



INVENTORS
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BY *[Signature]*
ATTORNEY

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**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIRECCIÓN DE NUEVAS CREACIONES**

2020

Bogotá, D.C., 02 de febrero de 2011

Abogado

EMILIO FERRERO

ASUNTO

Radicación 07 81353
Trámite 011
Evento 378
Actuación 519
Oficio **0 4 0 2 3**
Folios 13

Patente de Invención

☒

Vía PCT (fase nacional)

☒

Cap.I

☒

No. Solicitud Internacional

PCT/EP2006/000687

Fecha de Presentación Internacional 26/enero/2006

Como resultado del Examen de Fondo realizado, con fundamento en el Artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se comunica:

1. Documentos estudiados

Descripción: Folios 30 a 46 como se radicó inicialmente.

Reivindicaciones: Folios 48 a 50 como se radicó inicialmente

Dibujos: Folios 51 a 54 como se radicó inicialmente

Oposiciones: No se presentaron.

Respuesta del solicitante:

Prioridad: 10 2005 005 987.2 de febrero 09 de 2005

2. Análisis de la Prioridad

Se acepta la reivindicación de Prioridad porque:

Esta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486).
Y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

Título de la solicitud: "Proceso para la polimerización de monómeros que contienen vinilo"

Expediente 07 81353

El problema planteado en esta solicitud es proveer un proceso de polimerización de monómeros que contienen vinilo disminuyendo la utilización de solventes de alta pureza y utilizando de nuevo (recirculando) parte de la mezcla de reacción, también busca proveer un aparato para llevar a cabo dicho proceso de polimerización.

Para resolver este problema técnico la solicitud en estudio proporciona un proceso de polimerización de monómeros que contienen vinilo, especialmente haluros de vinilo monoméricos, que se polimerizan en una mezcla de reacción, al menos se separa un producto de polimerización de la mezcla de reacción, luego la mezcla de reacción se purifica y se utiliza de nuevo, requiriendo menos solvente fresco de alta pureza por tonelada de polímero producido y consecuentemente generando menos; además se proporciona un aparato que permite que el proceso de acuerdo con la invención sea llevado a cabo.

Clasificación Internacional de Patentes (CIP): CO8F 002/001

4. De la Solicitud de Patente

Titulo

El título no corresponde con el objeto de la solicitud porque faltaría incluir lo correspondiente al aparato para llevar a cabo el proceso, que también busca reivindicarse y aparece en el objeto de la invención, por lo cual se sugiere al Solicitante hacer la corrección necesaria.

Reivindicaciones (Art. 30 D 486, Art. 22 PCT)

Para dar mayor claridad se sugiere al Solicitante realizar lo siguiente:

- Hacer dependientes de la reivindicación 1 las reivindicaciones 4, 6, 7, 8, 9, 10, 11 y 13; y
- Hacer dependientes de la reivindicación 13 las reivindicaciones 15, 16 y 17.

Descripción (Art 28 D 486)

Se solicita hacer la conversión de Unidades (folio 34, renglón 08 y folio 35, renglón 27) al Sistema Internacional.

Se requiere al Solicitante hacer las aclaraciones necesarias.

5. Determinación del Estado de la Técnica

El Estado de la Técnica se determinó con base en la:

Fecha de Presentación de la Solicitud de Prioridad: febrero 09 de 2005

Y se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

Item	Documento	Título	Fecha de Publicación
D1	US6395793	Method for production of porous material	28/mayo/2002
D2	US2482056	Polymerization process	13/septiembre/1949

D1 divulga (página 1, resumen) un método para la producción de un material poroso por polimerización en emulsión.

D2 divulga (página 7, párrafo 2, renglones 15 - 20) un proceso de polimerización y

fraccionamiento de polímeros resultantes en un proceso tipo continuo o repetitivo.

6. Análisis de Patentabilidad (Art 14 D486)

Novedad (Art 16 D486)

La reivindicación 1 se refiere a un proceso de polimerización de monómeros que contienen vinilo en una mezcla de reacción, donde se separa al menos un producto de la mezcla y luego se purifica (filtra) dicha mezcla para utilizarla de nuevo en el proceso.

Comparación de las características técnicas **esenciales**, con las del estado de la técnica:

Características esenciales	D1	D2
Proceso de polimerización de monómeros de vinilo		
- Separar (al menos) un producto (polímero) de la mezcla de reacción	SI	SI
- Purificar (filtrar) y reutilizar la mezcla	SI	SI

Las características técnicas **esenciales** de la reivindicación 1 se ven anticipadas en los documentos del estado de la técnica, D1 y D2, en los cuáles se revela un proceso de polimerización para monómeros de vinilo donde el polímero es separado de la mezcla de reacción (D1: columna 4/línea 50–65; D2: columna 5/línea 66–columna 6/línea 25) y la mezcla de reacción es purificada y reutilizada (D1: columna 7/línea 25–33; D2: columna 8/línea 7–14), por lo tanto dicha reivindicación no se considera nueva.

Novedad (Art 16 D486)

La reivindicación 13 se refiere a un aparato para llevar a cabo el proceso de polimerización de acuerdo a la reivindicación 1, la línea de producción presenta un reactor conectado a un aparato de separación de productos de polimerización de la mezcla de reacción, el aparato de separación luego se conecta a un aparato de purificación de mezcla y dicho aparato se conecta nuevamente al reactor inicial.

Comparación de las características técnicas **esenciales**, con las del estado de la técnica:

Características esenciales	D2
Aparato para llevar a cabo proceso de polimerización	
- reactor	
- separador de productos de polimerización	SI
- purificador de mezcla	

Las características técnicas **esenciales** de la reivindicación 13 se ven anticipadas en el documento del estado de la técnica, D2, el cuál da a conocer un aparato para llevar a cabo el proceso de polimerización descrito anteriormente (D2: figuras 2 y 3), por lo tanto dicha reivindicación no se considera nueva.

7. Conclusión

Los requisitos de Patentabilidad de la presente solicitud están afectados así:

Item	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US6395793	1 - 12	Novedad
D2	US2482056	1 – 18	Novedad

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de 60 días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.



JOSÉ LUIS SALAZAR LÓPEZ
Director de Nuevas Creaciones (E)

04 MAR. 2017

El anterior requerimiento fue notificado por fijación en lista, de fecha _____

CONCEPTO TÉCNICO No. 393	EXAMINADOR TÉCNICO Código No. 2020101
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