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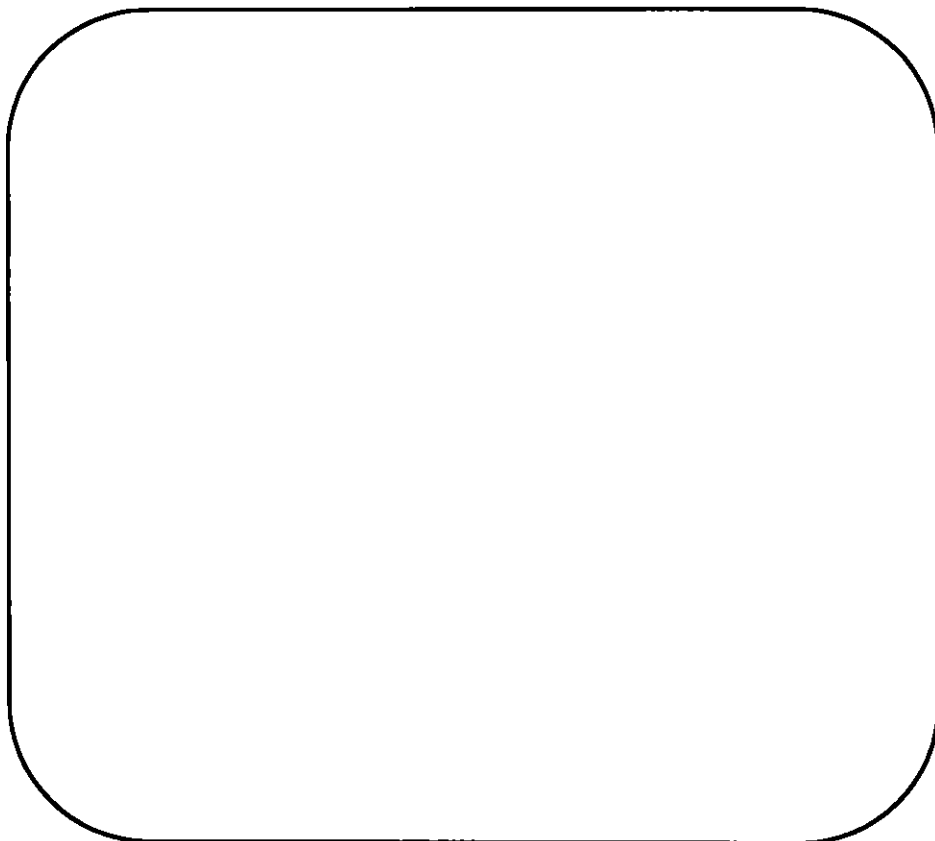
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Anexos:

- ☒ Comprobante de pago de la tasa de presentación de la solicitud por \$ 378.000.00.
- ☐ Comprobante de pago por reivindicación de prioridad.
- ☒ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☒ Poderes, si fuere el caso.
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☐ Declaraciones.
- ☒ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Copia del examen preliminar efectuado por la IPEA.
- ☐ Traducción del examen preliminar efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de acceso.
- ☐ De ser el caso, documento que acredite la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☐ Arte final 12x12
- ☐ De ser el caso, Información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☐ Otros

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FIGURA CARACTERISTICA:

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(54) Title: MONOVINYLIDENE AROMATIC POLYMERS WITH IMPROVED TOUGHNESS AND RIGIDITY AND A PROCESS FOR THEIR PREPARATION

(57) Abstract: Disclosed are rubber-modified monovinylidene aromatic polymers with improved toughness and rigidity as well as a process for the process thereof. The polymer comprises: a) a monovinylidene aromatic polymer matrix, b) rubber particles dispersed therein, characterized in that the rubber particles are produced from a diene rubber having I) from 20 to 80 percent, based on the total weight of said rubber particles, of a high solution viscosity component having a viscosity value ranging from 110 to 500 centipoise and II) from 80 to 20 percent, based on the total weight of said rubber particles, of a low solution viscosity component having a viscosity value ranging from 1 to 100 centipoise, further characterized in that the ratio of solution viscosity of high solution viscosity component to the solution viscosity of low solution viscosity ranges from 1.1 to 500, wherein both component I and II have a 1.4 cis content of greater than 30 percent, and III) the rubber is grafted with monovinylidene aromatic polymer to the extent that there is at least 30 percent monovinylidene aromatic polymer present as grafts on the rubber.

MONOVINYLIDENE AROMATIC POLYMERS WITH IMPROVED TOUGHNESS AND RIGIDITY AND A PROCESS FOR THEIR PREPARATION

The present invention relates to rubber-reinforced monovinylidene aromatic polymer compositions of the type commonly referred to as "high impact polystyrene" or "HIPS". More particularly, the invention relates to such compositions, in which the rubber-reinforcing particles are produced from a specific polybutadiene rubber, have a specific particle size distribution and a process for the production of such compositions.

Rubber-reinforced polymer compositions of the HIPS type are widely used in many applications because of their ease of molding, good gloss, and generally good mechanical properties. It has been known for some time that improved combinations of gloss and mechanical properties can be achieved in such rubber-reinforced polymers by providing a so-called "bimodal" distribution in the sizes of the rubber reinforcing particles, that is the particles show two distinct peaks in their size distribution. This can be achieved by combining two or more such resins or components, each having a group of rubber particles having a different average particle size. Various monovinylidene aromatic polymer compositions are known having at least two groups of rubber particles wherein the groups have different average particle sizes. See for example US-A-4,146,589, US-A-4,214,056 and US-A-4,334,039 and EP-A-0 096 447, EP-A-0 158 258 and EP-A-0 152 752 which disclose such compositions.

US-A-4,493,922 also discloses rubber-reinforced polystyrene compositions having bimodal rubber particle size distributions. The average rubber particle sizes disclosed for the groups of particles are 2 to 8 micrometers (especially from 5 to 6 micrometers) for the group of larger particles and 0.2 to 2.0 micrometers for the group of smaller particles.

As mentioned, a number of methods are proposed for achieving such a bimodal particle distribution. For example, US-A-4,153,645 discloses a method for the preparation of a HIPS-type polymer in which two polymer compositions are prepared using standard production processes, the compositions having different average particle

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sizes. These two polymer compositions are then mixed by a subsequent mechanical blending process.

An alternative approach to producing HIPS polymers with a bimodal rubber distribution has been to introduce feed streams of monomer and rubber at two different points in the polymerization system. This results in a polymer product which generally has a fairly broad spread of rubber particle sizes. Examples of this are described in EP 0 015 752, U.S. 4,334,039 and EP 0 096 447. A disadvantage of such methods is that the mechanical properties of the resulting product can be somewhat poor and difficult to control.

Yet a further approach is disclosed in U.S. 4,146,589 and EP 0 048 389. In this method, two prepolymer compositions are prepared containing rubber particles with different particle sizes. The prepolymer compositions are then mixed and further polymerized to provide a polymer having a bimodal particle size distribution.

Other references in this area include EP-418,042 wherein the rubber comprises a partially coupled radial or star rubber, having a cis content of less than or equal to 70 percent, JP 02762722 wherein the rubber is a mixture of a high cis polybutadiene of high molecular weight and a low cis polybutadiene of low molecular weight, and JP 95005789 wherein the rubber is a mixture of a high molecular weight polybutadiene and a low molecular weight polybutadiene, both having a cis structure of greater than 80 percent. However, a desirable balance of impact strength and tensile strength is still not attained for some specific applications.

Therefore, it is still desirable to obtain a rubber modified monovinylidene aromatic polymer having an improved balance of impact and tensile properties for select applications.

The present invention is a rubber modified monovinylidene aromatic polymer comprising:

- a) a monovinylidene aromatic polymer matrix,
- b) rubber particles dispersed therein, characterized in that the rubber particles are produced from a diene rubber having 1) from 20 to 80 percent, based on the total weight of said rubber particles, of a high solution viscosity component having a viscosity value ranging from 110

to 500 centipoise and II) from 80 to 20 percent, based on the total weight of said rubber particles, of a low solution viscosity component having a viscosity value ranging from 1 to 100 centipoise, further characterized in that the ratio of solution viscosity of high solution viscosity component to the solution viscosity of low solution viscosity ranges from 1.1 to 500, wherein both components I and II have a 1,4 cis content of greater than 30 percent, and III) the rubber is grafted with monovinylidene aromatic polymer to the extent that there is at least 30 percent monovinylidene aromatic polymer present as grafts on the rubber.

In a preferred embodiment the present invention is a rubber modified monovinylidene aromatic polymer comprising:

- a) a monovinylidene aromatic polymer matrix,
- b) rubber particles dispersed therein in the form of small and large particles, wherein the volume average particle diameter of the small particles is from 0.1 to 2 micrometers and the volume average particle diameter of the large particles is from 2 to 6 micrometers, characterized in that the rubber particles are produced from a diene rubber having I) from 20 to 80 percent, based on the total weight of said rubber particles, of a high solution viscosity component having a viscosity value ranging from 110 to 500 centipoise and II) from 80 to 20 percent, based on the total weight of said rubber particles, of a low solution viscosity component having a viscosity value ranging from 1 to 100 centipoise, further characterized in that the ratio of solution viscosity of high solution viscosity component to the solution viscosity of low solution viscosity ranges from 1.1 to 500, wherein both components I and II have a 1,4 cis content of greater than 30 percent, and III) the rubber is grafted with monovinylidene aromatic polymer to the extent that there is at least 30 percent monovinylidene aromatic polymer present as grafts on the rubber, wherein the amount of rubber in the polymer represents 2 to 20 percent based on the total weight of the polymer.

Another aspect of the present invention is a process for preparing a rubber-modified monovinylidene aromatic polymer comprising the steps of: (a) continuously supplying a reaction mixture comprising monovinylidene aromatic monomer and a dissolved diene rubber to a reactor means, (b) continuously polymerizing the

5 monovinylidene aromatic monomer in the presence of the dissolved diene rubber in the reactor means under conditions whereby phase inversion subsequently occurs, (c) continuously removing from the reactor means a diene rubber-reinforced monovinylidene aromatic polymer, which process is characterized in that: (d) the diene rubber which is dissolved in the reaction mixture has I) from 20 to 80 percent, based on

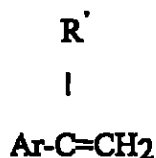
10 the total weight of said diene rubber, of a high solution viscosity component having a viscosity value ranging from 120 to 500 centipoise and II) from 80 to 20 percent, based on the total weight of said diene rubber, of a low solution viscosity component having a viscosity value ranging from 1 to 100 centipoise, further characterized in that the ratio of solution viscosity of high solution viscosity component to the solution viscosity of

15 low solution viscosity ranges from 1.2 to 500, wherein both components I and II have a 1,4 cis content of greater than 30.

In a preferred embodiment, the process further comprises (e) wherein the process conditions prior to phase inversion are adjusted to produce different groups of diene rubber particles from the high and low molecular weight components of the diene

20 rubber, each group having a different average rubber particle size.

Monovinylidene aromatic polymers suitable for the present invention are those produced by polymerizing a vinyl aromatic monomer. Vinyl aromatic monomers include, but are not limited to those described in US-A-4,666,987, US-A-4,572,819 and US-A-4,585,825. Preferably, the monomer is of the formula:



wherein R' is hydrogen or methyl, Ar is an aromatic ring structure having from 1 to 3

30 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 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, and vinyl anthracene, 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, methacrylonitrile, methacrylic acid, methyl methacrylate, acrylic acid, and methyl acrylate; maleimide, phenylmaleimide, and maleic anhydride. It is preferred, however, for the practice of the present invention to use either less than 10 percent by weight or substantially no other copolymerizable monomer. The specified particle size distribution is no longer optimal for larger amounts of one or more of these monomers. In general, the preferred monovinylidene aromatic monomers are styrene, alpha methyl styrene, one or more of the vinyl toluene isomers, and/or mixtures of two or more of these, with styrene being the most preferred monovinylidene aromatic compound.

The monovinylidene aromatic polymer typically has a weight average molecular weight (Mw) of from approximately 120,000 to 500,000.

The rubbers preferably employed in the practice of the present invention are those polymers and copolymers which exhibit a second order transition temperature which is not higher than 0°C, preferably not higher than -200°C and more preferably not higher than -400°C as determined or approximated using conventional techniques, for example, ASTM Test Method D-746-52 T.

Highly preferred rubbers are alkadiene polymers. Suitable alkadienes are 1,3-conjugated dienes such as butadiene, isoprene, chloroprene or piperylene. Most preferred are homopolymers (excepting any coupling monomers) prepared from 1,3-conjugated dienes, with such homopolymers of 1,3-butadiene being especially preferred. Alkadiene copolymer rubbers containing small amounts, for example less than 15, preferably less than 10 weight percent, of other monomers such as monovinylidene aromatics can also be employed if the rubbers meet the other qualifications described herein. The most preferred rubbers are the linear, radial, star,

or randomly branched homopolymers of 1,3-butadiene which have a cis content of at least 30 percent

The rubbers suitable for the present invention can be made by anionic polymerization or Ziegler-Netta polymerization well known to those skilled in the art.

5 Regarding the rubber materials suitable for use according to the present invention, the essential requirement for the rubber material is that it has a relatively high solution viscosity component and a relatively low solution viscosity component, wherein both components have a 1,4 cis content of at least 30 percent. Suitable rubbers for use herein are the linear, partially coupled rubbers, also called radial or star rubbers, 10 completely coupled rubbers as well as randomly-branched rubbers, other branched polymers and blends of rubbers, such as a blend of linear and branched polymers, meeting the requirements for rubber materials to be employed in this invention. The molecules of these rubber materials have three or more polymer segments coupled by a single polyfunctional element or compound. Radial or star polymers having this 15 designed branching are conventionally prepared using a polyfunctional coupling agent. Methods for preparing star or radial polymers having designed branching are well-known in the art. Methods for preparing a polymer of butadiene of this type using a coupling agent are illustrated in US-A-4,183,877, US-A-4,340,690, US-A-4,340,691 and US-A-3,668,162 and Japanese Patent 59-24 711.

20 As used herein, the molecular weights referred to are the weight average molecular weights or Mw's for the rubber components as determined by the gel permeation chromatographic techniques described by ASTM Test Method designated D-3536 (polystyrene standard) and expressed without correction for the differences between rubber and polystyrene standards.

25 The diene rubbers most suitable for this invention contain two distinct components, which are comprised of a relatively high solution viscosity diene rubber and a relatively low solution viscosity diene rubber. More particularly, the low solution viscosity component of diene rubber useful for the present invention has solution viscosity values from 1, generally from 5, preferably from 10 and more preferably from 30 20, to 100, generally to 95, preferably to 85 and more preferably to 75. The high solution viscosity component of diene rubber useful for the present invention has

solution viscosity values from 110, generally from 115, preferably from 120 and more preferably from 150 to 500, generally to 450, preferably to 430 and more preferably to 400. The low and high solution viscosity components of diene rubbers useful for the present invention are further characterized in that the ratio of solution viscosity of high
5 solution viscosity component to the solution viscosity of low solution viscosity ranges from 1.1, generally from 1.26, preferably from 1.53 and more preferably from 1.76, to 500, generally to 90, preferably to 40 and more preferably to 21.5.

In addition, in order to obtain the proper proportions of the small and large rubber particles, it is preferred if the low solution viscosity component of the rubber
10 material constitutes from 20 to 80 weight percent of the total rubber content of the resin, preferably from 30 to 70 weight percent. Most preferably neither component is more than 80 percent of the total rubber in the composition.

Advantageously, to prepare a rubber-reinforced resin using mass or mass/suspension polymerization techniques, the solution viscosity of the rubber of the
15 alkadiene polymer, as measured as a 5 weight percent solution in styrene, will be greater than 40 and less than 400 centipoise (cps) at 25°C when the viscosity is measured using a Canon-Fenske capillary viscometer (Capillary No. 400, 1.92 mm inside diameter).

The Mooney viscosity values of the radial-type rubbers should be less than
20 90, preferably less than 70 as measured by DIN 53523. In general, to have a rubber, which is sufficiently solid to be handled and processed in a normal fashion, the Mooney viscosity value should be at least 20 and values of at least 30 are preferred. The preferred range for the Mooney value is between 20 and 90, more preferably between 30 and 85, most preferably between 35 and 80.

25 Although the rubber may contain a small amount of a crosslinking agent, excessive crosslinking can result in loss of the rubbery characteristics and/or render the rubber insoluble in the monomer.

The rubber is advantageously employed in amounts such that the rubber-reinforced polymer product contains from 2 to 20 percent, preferably from 3 to 17
30 percent, more preferably 3 to 15 weight percent rubber or rubber equivalent, based on the total weight of the rubber modified monovinylidene aromatic polymer.

The term "rubber" or "rubber equivalent" as used herein to indicate weight amounts of rubber material is intended to mean, for a rubber homopolymer (such as polybutadiene), simply the amount of rubber, and for a block copolymer, the amount of the copolymer made up from monomer(s) which, when homopolymerized form a rubbery polymer. For example, for calculating the amount of rubber in a composition where a butadiene-styrene block copolymer rubber has been employed, the "rubber" or "rubber equivalent" of the composition is calculated based on only the butadiene component in the block copolymer. Obviously where physical properties or other aspects of the rubber material are measured, the complete rubber material including any comonomers is referred to.

The product of the present invention can be viewed as having a generally broadened rubber particle size distribution. In one embodiment the present invention has a bimodal rubber particle size distribution with a critical amount of large and small rubber particles. The present invention having such distributions results in a resin product which, in the form of molded articles, possesses improved combinations of impact resistance, and tensile strength.

In one embodiment, according to this invention, it has surprisingly been discovered that products having a rubber particle size distribution of this type have better combinations of properties when, based on 100 parts by weight rubber or rubber equivalent, (a) particles constituting from 20 to 60 parts by weight of the rubber have diameters of from 0.1 to 2 micrometers, (b) particles constituting from 60 to 20 parts by weight of the rubber have diameters of from 2 to 8 micrometers.

In terms of a bimodal distribution, it is found that as groups of particles, the group of smaller particles should have a volume average particle diameter of from 0.2 to 2 micrometers, preferably to 1.8 micrometers and most preferably to 1.5 micrometers and the group of larger particles should have a volume average particle diameter of from 2.0, preferably from 2.5 to 5 micrometers. In terms of broad distribution, it is found that 80 percent of particles are in the range of from 0.2 to 8 micrometers.

As used herein, the said particle size is the diameter of the rubber particles as measured in the resultant product, including all occlusions of matrix polymer within rubber particles, which occlusions are generally present in the disperse rubber particles

of a rubber-reinforced polymer prepared using mass polymerization techniques. Rubber particle morphologies, sizes and distributions may be determined using conventional techniques such as (for larger particles) using a Coulter Counter (Coulter Counter is a Trade Mark) or, particularly for smaller particles, transmission electron microscopy.

5 Regarding morphology of the rubber particles in the different groups, as is well known, the smaller particles typically have a core-shell (single, major occlusion) or cellular (multiple, minor occlusions) morphology. The larger particles would generally have a cellular or similar multiple-occlusion morphology.

10 The process of the present invention is characterized by the utilization of a rubber having specific high and low molecular weight components under process conditions whereby the above-specified rubber particle size distribution can be obtained with standard polymerization processes and equipment.

15 In the preparation of the rubber-reinforced polymers, a reaction mixture is prepared by dissolving the rubber in the monomer(s) and the resulting monomer/rubber solution, referred to herein as the reaction mixture, is supplied to a reactor means and subsequently polymerized. The amount of rubber initially dissolved in the reaction mixture is dependent on the desired concentration of rubber in the final rubber-reinforced polymer product, the degree of conversion during polymerization and the viscosity of the reaction mixture solution. Specifically, the viscosity of the reaction mixture solution is advantageously less than 3000 centipoise. At higher viscosities, the reaction mixture solution is difficult to process. Provided the viscosity of the reaction mixture is not undesirably high, the reaction mixture solution will generally comprise from 5 to 15, weight percent of the rubber, said weight percent being based on the total amounts of rubber and monomers employed.

25 Optionally, the reaction mixture will contain an organic liquid diluent. Organic liquid diluents suitably employed are normally liquid organic materials which do not boil at the polymerization conditions employed and which form a solution with the polymerizable monomer(3) and the polymer prepared therefrom. Representative organic liquid diluents include aromatic (and inertly substituted aromatic) hydrocarbons such as toluene, benzene, ethylbenzene and xylene; saturated or inertly substituted, 30 saturated aliphatics having either straight or branched chains of five or more carbon

atoms such as heptane, hexane and octane; alicyclic or inertly substituted alicyclic hydrocarbons having five or six carbon atoms such as cyclohexane. Preferred of such organic liquid diluents are the inertly substituted aromatics, with ethylbenzene and xylene being most preferred. In general, the organic liquid is employed in amounts
5 sufficient to improve the processability and heat transfer during polymerization, for example, flow characteristics of the polymerization mixture. Such amounts will vary depending on the rubber, monomer and diluent employed, the process equipment and the desired degree of polymerization. In general, if employed, the reaction mixture will normally contain from 2 to 30 weight percent of the diluent based on the total weight of
10 the rubber, monomer and diluent.

During the polymerization of the resulting reaction mixture, the polymerization conditions are maintained such that phase inversion subsequently occurs. Under such conditions the monomer is polymerized both with the rubber (grafted) and separately (free polymer), which dissolved rubber thereby becomes
15 grafted with a portion of polymerized monomer. The balance of free polymer, basically incompatible with the rubber, forms a discontinuous smaller volume polymer/monomer phase dispersed throughout the larger volume continuous phase of the monomer/rubber (including grafted rubber) solution.

Eventually, at a point after sufficient amounts of free polymer are formed,
20 the free polymer converts from a discontinuous phase dispersed in the continuous phase of the unpolymerized monomer(s), through a point where there is no distinct continuous or discontinuous phases in the polymerization mixture, to a continuous polymer phase having the rubber dispersed as discrete particles there through. As the polymer/monomer phase becomes the larger volume phase and hence the continuous
25 phase, the grafted rubber forms a discontinuous phase. This is the point in the polymerization when phase inversion occurs and the rubber becomes dispersed in the form of particles through the continuous polymer phase resulting in a product having rubber particles dispersed in a matrix of monovinylidene aromatic polymer.

Preferably, at phase inversion, the rubber is sufficiently grafted such that
30 the disperse rubber particles, following initial sizing, are capable of retaining essentially the same average particle size and morphological properties throughout the remainder

of the polymerization process. In a preferred embodiment, the amount of grafted rubber is at least 30 percent of the total rubber at phase inversion. The degree of grafting of the diene rubber at the point of phase inversion has a significant impact on the properties of the resultant rubber modified polymer produced. Generally, the number of grafts per chain contributes to the particle size, the structure and the amount of occluded matrix polymer within the rubber particles. Higher grafting level results in higher gel content, a larger amount of grafted rubber and higher graft and occluded matrix polymer content within the rubber particles. The increased gel content is highly desirable in that it enables an increased rubber phase volume to be achieved. Increased rubber phase volume can also be achieved by using a high molecular weight polybutadiene rubber, however increasing the molecular weight typically increases the solution viscosity as well, making handling and processing more difficult. In general, the higher solution viscosity rubber will result in larger rubber particles, and low solution viscosity rubber will result in smaller rubber particles.

Careful control of back mixing during the polymerization process is critical in achieving the desired rubber particle size. Accordingly, one essential feature of the present invention is that prior to phase inversion the polymerization must proceed in a plug-flow form with a limited or minimum amount of back mixing;. The desired rubber particle size will not be realized if the polymerization reaction mixture is allowed to be back mixed extensively or, worse yet, totally. Therefore, it is preferable that the degree of back mixing be controlled or limited to such an extent that the desired rubber particle size can be obtained. The degree and type of control for the amount of back mixing will depend on, in part, the geometric features of the equipment being employed in the polymerization process, the achievement of which control is well within the capability of those who are skilled in the art using conventional process control techniques without undue experimentation.

When preparing bimodal compositions in the practice of the present invention the polymerization process should be conducted at conditions such that at the point of phase inversion, the high and low solution viscosity components of the rubber form separate groups of rubber particles having different average particle sizes.

The polymerization process features that are utilized to achieve the requisite rubber particle distribution include the use of a graft promoting chemical initiator, such as the peroxide initiators including the peresters, for example, tertiary butyl peroxybenzoate, tertiary butyl peroxyacetate, dibenzoyl peroxide, and dilauroyl peroxide, the perketals, for example, 1,1-bis tertiary butyl peroxy cyclohexane, 1,1-bis tertiary butyl peroxy-3,3,5-trimethyl cyclohexane, and di-cumyl peroxide, and the percarbonates; and photo chemical initiation techniques. Preferred initiators include tertiary butyl peroxy benzoate, 1,1-bis tertiary butyl peroxy cyclohexane 1,1-bis tertiary butyl peroxy-3,3,5 trimethyl cyclohexane and tertiary butyl peroxy acetate.

Initiators may be employed in a range of concentrations dependent on a variety of factors including the specific initiator employed, the desired levels of polymer grafting and the conditions at which the mass polymerization is conducted. Specifically, in the preferred mass polymerization process for preparing rubber-reinforced polymers, from 50 to 2000, preferably from 100 to 1500, weight parts of the initiator are employed per million weight parts of monomer resulting in a product having rubber particles dispersed in a matrix of monovinylidene aromatic polymer.

With such an initiator the grafting onto the high molecular weight component of the rubber is promoted and multiple grafts are formed. This stabilizes these rubber molecules in the reaction mixture and facilitates the separation of the high molecular weight rubber molecules from the lower molecular weight rubber. This contributes to the formation of the larger rubber particles.

The lower molecular weight component of the rubber, on the other hand, being less grafted, tends to form the smaller particles somewhat later than the larger particles are formed. It is also desirable to facilitate the formation of separate, smaller particles to provide an increased amount of agitation to the reaction mixture during and well after the point of phase inversion. Phase inversion has usually taken place at a point in the polymerization process where the reaction mixture contains a solids level which, in weight percent based on reaction mixture, is 2.5 or 3 times the weight content of the added rubber material. Therefore, a relatively high agitation level is preferably maintained until a point in the polymerization process where the reaction mixture

contains a solids level which, in weight percent based on reaction mixture, is at least 3, preferably 4 times the weight content of the added rubber material.

For example, when there is 5 to 10 weight percent rubber added to the reaction mixture, relatively high agitation is maintained until the reaction mixture contains 30 percent by weight solids. As used herein, the term solids refers to the polymeric components of the reaction mixture such as the rubber which was added initially and the monovinylidene aromatic polymer which has been formed.

Depending upon particular production equipment there may also be other process features that can be utilized to further facilitate the formation of the specified rubber particle size distribution.

In general, continuous methods are employed for mass polymerizing the monovinylidene aromatic compound in the reaction mixture. In the practice of the present invention it is generally preferred to utilize a stratified, linear flow, stirred tower type reactor, also referred to as a plug flow type reactor. Such reactors are well known. See, for example US-A-2,727,884.

An important aspect of such polymerization processes is that a significant portion of the polymerization of the monovinylidene aromatic monomer in the reaction mixture can take place in the presence of the dissolved rubber. Phase inversion and precipitation and dispersion of the rubber particles does not occur until after sufficient grafting of monovinylidene aromatic polymer onto the rubber, which primarily takes place when the rubber is in solution.

This is a major advantage over polymerization in completely mixed, stirred tank type reactors (non-stratified, non-plug flow) which are operated at a predetermined level of conversion. Typically, due to the presence of significant levels of the already polymerized monovinylidene aromatic polymer, the rubber which may be dissolved in the feed stream to such a reactor, is immediately dispersed as particles before graft polymerization can occur and, more importantly, before the high and low solution viscosity components of an appropriate rubber material can separate and form separate groups of rubber particles.

Moreover, the process according to the present invention can be practiced advantageously on standard mass polymerization process equipment not otherwise

capable of the preparation of monovinylidene aromatic polymers with bimodal rubber particle distributions without significant equipment modifications. Such standard equipment typically utilizes a single supply of the unpolymerized reaction mixture comprising a solution of rubber, monomer, optional diluent and other additives. The reaction mixture is then polymerized as it proceeds through one or a series of such reactor vessels. At the end of the reactor vessel (series) the product is removed and diluent and any residual monomer removed.

The polymerization mixture may also contain other additive materials and/or polymerization aids such as plasticizers or lubricants such as mineral oil, butyl stearate or diethyl phthalate; stabilizers including antioxidants (for example, alkylated phenols such as di-tert-butyl-p-cresol or phosphates such as trisnonyl phenyl phosphate); chain transfer agent, such as an alkyl mercaptan such as n-dodecyl mercaptan; or mold release agents, for example, zinc stearate; all of which additives and/or polymerization aids are added to the reaction mixture where appropriate including before, during or after polymerization.

The use of a chain transfer agent is optional and is usually employed only in the production of a composition or prepolymer containing larger size rubber particles (for example having an average particle size of at least one micrometer). If employed, the chain transfer agent is generally employed in an amount of from 0.001 to 0.5 weight percent based on the total weight of the polymerization mixture to which it is added.

The temperatures at which polymerization is most advantageously conducted are dependent on the specific components, particularly initiator, employed but will generally vary from 60 to 190°C.

Crosslinking of the rubber in the resulting product and removal of the unreacted monomers, as well as any reaction diluent, if employed, and other volatile materials is advantageously conducted employing conventional techniques.

The rubber modified monovinylidene aromatic polymer of the present invention has an excellent balance of impact and tensile modulus properties, allowing for its use in various applications including injection molding applications, extrusion applications, foam applications including large appliances, consumer electronics, air conditioners, refrigerators, freezers, small appliances, cassettes, radio, TV, stereo

cabinets, furniture and furnishings, toys, housewares, building and construction applications, footwear, medical applications, packaging, disposables such as tumblers, glasses, dishes, cups, bowls, flatware, cutlery, blowmolded items, foam board, sheet, and films.

5 **EXAMPLES**

The following examples are given to illustrate the present invention relating to rubber-modified monovinylidene aromatic polymers, and should not be interpreted as limiting the invention in any way.

10 Samples of rubber-modified monovinylidene aromatic polymer compositions were prepared in a miniplant having a linear three stirred tube reactor system. Each reactor had 2.5L internal volume with an L/D ratio of 22, and an agitator with pins attached to the shaft. Each reactor contained three temperature zones that were electrically heated. The reactor system was computer controlled within a predefined narrow range to ensure uniformity. After the third reactor, the partial polymers were devolatilized with a devolatilizing extruder, 15 stranded, then cut to form pellets. All the testing was done using these pellets. Extruder temperature controlled the degree of cross-linking of the rubber. Generally higher temperatures resulted in higher degree of cross-linking.

A certain amount of the main feed was added into the middle zone of the second reactor as a second addition to further improve the toughness and rigidity balance of the 20 products. At around 20 percent, second addition level, the properties were usually optimum. If these experiments were to be repeated without second addition, the values would be proportionately lower but would have same relative ranking in terms of toughness rigidity balance.

NDm (n-dodecyl mercaptan) was added to the second reactor as a chain transfer 25 agent to maintain the melt flow rate of the final products.

In total three sets of rubbers were used. As a control, (that is, a comparative example) a standard low-cis diene rubber from Bayer AG BUNA 640 was used (example 1). A high-cis rubber which has a bimodal molecular weight distribution available from UBE Industries of Japan under the tradename UBE 23H was used for examples 2 and 3. In the 30 fourth example of the present invention, a bimodal mixture was prepared by *in situ* solution blending of two rubbers commercially available from The Dow Chemical Company. under the tradename of 1202B (lower molecular weight) and 1202J (higher molecular weight). The amounts are given in the examples.

The measurements of certain physical properties and corresponding test methods were follows:

Property	Method	Units	Remarks
Izod Impact	ASTM D256-93A	J/m	Injection moulded bars
Charpy Impact	ISO 179-2C-82	kJ/m ²	Injection moulded bars
Tensile Yield	ASTM D638M-93	Mpa	Injection moulded bars (5 mm/min)
Tensile rupture	ASTM D638M-93	Mpa	Injection moulded bars (5 mm/min)
Elongation	ASTM D638M-93	percent	Injection moulded bars (5 mm/min)
Tensile modulus (E-modulus)	ASTM D638	N/mm ²	Injection moulded bars (1 mm/min)
MFR	ASTM D1238-94	°C	
Vicat	ASTM D1525-91	g	Injection moulded bars
Mw and Mn	GPC	g/mol	
Rubber Particle Size (RPS)	Coulter 50 micron tube	µm	
Rubber content	Mass Balance	percent	
M.O. content	Liquid Chromatography	percent	
Solids	Gravimetric	percent	

In general, the results of the experiments clearly demonstrate that the examples of the present invention provide a better balance of toughness and rigidity despite having somewhat higher melt flow rate than the comparative example.

At similar particle size and rubber composition, the examples of the present invention provide higher Izod and Charpy impact values as well as higher tensile yield strength and tensile modulus.

Variable	Date	07/24/1999	07/22/1999	07/28/1999	05/26/2000
		Comp. Ex. 1	Example 1	Example 2	Example 3
Linear Feed rate	g/h	1000	1000	1000	1080
Second Add	g/h	200	200	200	120
Percent Second Add	percent	20	20	20	10
Total Feed Rate	g/h	1200	1200	1200	1200
Linear reactor	Z1-L	111	111	111	110
	Z2-L	115	115	115	113
	Z3-L	119	119	119	121
	Z4-L	126	126	126	127
	Z5-L	135	135	135	133
	Z6-L	145	145	145	142
	Z7-L	155	155	155	148
	Z8-L	162	162	162	155
	Z9-L	170	170	170	160
Agitation / rom	STR1	150	225	225	175
	STR2	60	60	60	60
	STR3	40	40	40	40

Devolatilization conditions					
Mid Barrel/screw T	C	240	240	240	240
Second vacuum chamber T	C	230	230	230	230
End barrel/screw T	C	220	220	220	220

Adds					
Initiator DP275 / ppm	SM12	380	380	380	465
nDM to second reactor / ppm	SM13	1200	1100	1200	1150
EB / percent	Feed	7	7	7	7
M.O. / percent	Feed	0.8	0.8	0.8	0.4
Irganox 1076 / Ppm	Feed	1000	1000	1000	1000
Rubber HX-528 / AX-640 A	percent	5.75			
Ubepol Br 23 HB	percent		5.75	5.75	
1202B	percent				2.8
1202J	percent				2.8

Process control parameters					
Solids / percent	STR1	34.7	36.8	35.8	35.7
	STR2	60.9	61.8	59.5	59.8
	Conversio	83.1	82.4	82.9	81.6

End product properties					
R.P.S. mean / μm (Coulter) (50 μm tube) (1)		2.80	3.00	2.70	2.30
Mw / g/mol		178700	187000	187200	185500
Mn / g/mol		65900	68100	69600	69600
Polydispersity		2.71	2.75	2.69	2.67
M.F.R. / g/10 min		4.90	5.80	5.20	5.20
Charpy Impact / kJ/m ²		6.9	7.6	7.6	10.7
Izod / J/m		86	107	102	109
Vicat / C		102.1	101.8	101.7	103.7
Tensile Yield / Mpa		24.3	23.7	23.9	25.1
Tensile Rupture / Mpa		23.8	23.1	23.2	21.8
Elongation / percent		47.2	58.1	57.4	26.9
Tensile Modulus / N/mm ²		1938	2146	2183	2201
Mineral oil content / percent		0.9	1.0	1.0	0.5
Rubber content / percent (mass balance)		6.9	7.0	6.9	6.9

The following table has the rubber specific data. They are based on polystyrene standards and no universal calibration correction is made.

- 5 The solution viscosities are measured in styrene monomer at 5 percent by weight of rubber solution at 23°C. The component data from UBE23H is calculated from overall GPC plots and are estimates. Also, the solution viscosities for the UBE23H components are estimates based on known relationships of MW versus solution viscosity. The results are quoted in centiPoise (cP).

Sample ID	Dow Measurements (PS Standards)					Sol. Viscosity
	Mw	Mn	Mp	Mz	PDI	
1202B #182 BCP 817 lot 81116A	426400	134700	224800	1114200	3.2	40.6
1202J #139 BCP 820 lot 90921A	661800	267400	539600	1393600	2.5	275.1
Diene 55 BUNA 640	485000	222000	369		2.2	170
UBE23H Overall	576300	151351	824500	1430300	3.8	155
UBE23H LOW MW Component	165000	70000	145000		2.3	8
UBE23H High MW component	1020000					1100

WHAT IS CLAIMED IS:

1. A rubber modified monovinylidene aromatic polymer comprising:
 - a) a monovinylidene aromatic polymer matrix,
 - b) rubber particles dispersed therein, characterized in that the rubber
- 5 particles are produced from a diene rubber having I) from 20 to 80 percent, based on the total weight of said rubber particles, of a high solution viscosity component having a viscosity value ranging from 110 to 500 centipoise and II) from 80 to 20 percent, based on the total weight of said rubber particles, of a low solution viscosity component having a
- 10 viscosity value ranging from 1 to 100 centipoise, further characterized in that the ratio of solution viscosity of high solution viscosity component to the solution viscosity of low solution viscosity ranges from 1.1 to 500, wherein both components I and II have a 1,4 cis content of greater than 30 percent, and III) the rubber is grafted with monovinylidene aromatic
- 15 polymer to the extent that there is at least 30 percent monovinylidene aromatic polymer present as grafts on the rubber.
2. The rubber modified monovinylidene aromatic polymer of Claim 1, wherein the high solution viscosity component has a viscosity value ranging from 120 to 450 centipoise, the low solution viscosity component has viscosity value ranging
- 20 from 5 to 95 centipoise, and the ratio of solution viscosity is from 1.26 to 90.
3. The rubber modified monovinylidene aromatic polymer of Claim 1, wherein the high solution viscosity component has a viscosity value ranging from 150 to 430 centipoise, the low solution viscosity component has viscosity value ranging
- 25 from 20 to 85 centipoise, and the ratio of solution viscosity is from 1.76 to 21.5.
4. The rubber modified monovinylidene aromatic polymer of Claim 1, wherein the amount of rubber in said polymer is 2 to 20 percent based on the total weight of said polymer.
5. The rubber modified monovinylidene aromatic polymer of Claim 1, wherein the rubber particles are dispersed in the form of small and large particles, wherein
- 30 the volume average particle diameter of the small particles is from 0.1 to 2

micrometers and the volume average particle diameter of the large particles is from 2 to 6 micrometers.

6. The rubber modified monovinylidene aromatic polymer of Claim 1 wherein the monovinylidene aromatic polymer is polystyrene.
- 5 7. The rubber modified monovinylidene aromatic polymer of Claim 1 wherein the rubber is polybutadiene.
8. The rubber modified monovinylidene aromatic polymer of Claim 1, wherein the diene rubber is branched.
9. The rubber modified monovinylidene aromatic polymer of Claim 1 wherein the
10 diene rubber has a 1,4 cis content of greater than 30 percent.
10. A process for preparing a rubber-modified monovinylidene aromatic polymer comprising the steps of: (a) continuously supplying a reaction mixture comprising monovinylidene aromatic monomer and a dissolved diene rubber to a reactor means, (b) continuously polymerizing the monovinylidene aromatic
15 monomer in the presence of the dissolved diene rubber in the reactor means under conditions whereby phase inversion subsequently occurs, (c) continuously removing from the reactor means a diene rubber-reinforced monovinylidene aromatic polymer, which process is characterized in that: (d) the diene rubber which is dissolved in the reaction mixture has I) from 20 to 80 percent, based on
20 the total weight of said diene rubber, of a high solution viscosity component having a viscosity value ranging from 120 to 500 centipoise and II) from 80 to 20 percent, based on the total weight of said diene rubber, of a low solution viscosity component having a viscosity value ranging from 1 to 100 centipoise, further characterized in that the ratio of solution viscosity of high solution
25 viscosity component to the solution viscosity of low solution viscosity ranges from 1.2 to 500, wherein both components I and II have a 1,4 cis content of greater than 30 and, optionally, (e) the process conditions prior to phase inversion are adjusted to produce different groups of diene rubber particles from the high and low solution viscosity components of the diene rubber, each group
30 having a different average rubber particle size.

11. The process of Claim 10 wherein the monovinylidene aromatic polymer is polystyrene.
12. The process of Claim 10 wherein the rubber is polybutadiene.
13. The process of Claim 10, wherein the diene rubber is branched.
- 5 14. The process of Claim 10 wherein the diene rubber has a 1,4 cis content of greater than 30 percent.
15. An article produced from the rubber modified polymer of Claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/15001

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F279/02

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)
IPC 7 C08F

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 practical, 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.
X	EP 0 832 904 A (ENICHEM SPA) 1 Apr11 1998 (1998-04-01) claims 1,4,5	1-15
X	EP 0 825 208 A (BAYER AG) 25 February 1998 (1998-02-25) claim 1	1-15

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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 document but published on or after the international filing date
- *L* document which may throw doubt 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
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *Z* document member of the same patent family

Date of the actual completion of the international search

12 November 2001

Date of mailing of the international search report

21/11/2001

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
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Fax: (+31-70) 340-3010

Authorized officer

Meulemans, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/15001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0832904 A	01-04-1998	IT MI961978 A1	27-03-1998
		AT 186921 T	15-12-1999
		BR 9704917 A	22-12-1998
		DE 69700829 D1	30-12-1999
		DE 69700829 T2	18-05-2000
		DK 832904 T3	17-04-2000
		EP 0832904 A1	01-04-1998
		ES 2138851 T3	16-01-2000
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		JP 2922484 B2	26-07-1999
		JP 10130343 A	19-05-1998
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		SI 832904 T1	29-02-2000
		US 5942575 A	24-08-1999
EP 0825208 A	25-02-1998	DE 19632926 A1	19-02-1998
		CA 2212844 A1	16-02-1998
		EP 0825208 A2	25-02-1998
		JP 10087951 A	07-04-1998

IPEA/EP

CHAPTER II

PCT DEMAND

under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the International application specified below be the subject of
international preliminary examination according to the Patent Cooperation Treaty and
hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only

Identification of IPEA		Date of receipt of DEMAND	
Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION		Applicant's or agent's file reference 60858A	
International application No. PCT/US01/15001	International filing date 09 May 2001 09.05.01	(Earliest) Priority date 02 June 2000 02.06.00	
Title of invention MONOVINYLIDENE AROMATIC POLYMERS WITH IMPROVED TOUGHNESS AND RIGIDITY AND A PROCESS FOR THEIR PREPARATION			
Box No. II APPLICANT(S)			
Name and address: DOW GLOBAL TECHNOLOGIES INC. Washington Street 1790 Building Midland, Michigan 48674 United States of America		Telephone No. (989) 636-5214 Facsimile No. (989) 636-3237 Teleprinter No. Applicant's Registration No. with the Office	
State (that is, country) of nationality: US		State (that is, country) of residence: US	
Name and address:			
State (that is, country) of nationality:		State (that is, country) of residence:	
Name and address:			
State (that is, country) of nationality:		State (that is, country) of residence:	
Name and address:			
State (that is, country) of nationality:		State (that is, country) of residence:	
☐ Further applicants are indicated on a continuation sheet.			

International application No.

PCT/US01/15001

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is ☒ agent ☐ common representative
 and ☒ has been appointed earlier and represents the applicant(s) also for international preliminary examination.
☐ is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.
☐ is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address:

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Agent's Registration No. with the
 Office
 35,797

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. IV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION

Statement concerning amendments:

1. The applicant wishes the international preliminary examination to start on the basis of:

☒ the international application as originally filedthe description ☒ as originally filed☐ as amended under Article 34the claims ☒ as originally filed☐ as amended under Article 19 (together with any accompanying statement)☐ as amended under Article 34the drawings ☐ as originally filed☐ as amended under Article 342. ☐ The applicant wishes any amendment to the claims under Article 19 to be considered as reversed.

3. ☐ The applicant wishes the start of the international preliminary examination to be postponed until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). (This check-box may be marked only where the time limit under Article 19 has not yet expired.)

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: English.....

☒ which is the language in which the international application was filed.☒ which is the language of a translation furnished for the purposes of international search.☒ which is the language of publication of the international application.☐ which is the language of the translation (to be) furnished for the purposes of international preliminary examination.**Box No. V ELECTION OF STATES**

The applicant hereby elects all eligible States (that is, all States which have been designated and which are bound by Chapter II of the PCT)

excluding the following States which the applicant wishes not to elect:

Corresponds to: Form PCT/IPEA/401 (second sheet) (January 2002)

CONFIRMATION
 OF FAX

International application No.

PCT/US01/15001

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of International preliminary examination:

- | | | |
|--|---|--------|
| 1. translation of international application | : | sheets |
| 2. amendments under Article 34 | : | sheets |
| 3. copy (or, where required, translation) of amendments under Article 19 | : | sheets |
| 4. copy (or, where required, translation) of statement under Article 19 | : | sheets |
| 5. letter | : | sheets |
| 6. other (specify) | : | sheets |

For International Preliminary
Examining Authority use only
received not received

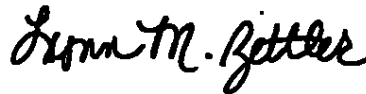
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|--------------------------|--------------------------|
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |
| ☐ | ☐ |

The demand is also accompanied by the item(s) marked below:

- | | |
|--|--|
| 1. ☒ fee calculation sheet | 5. ☐ statement explaining lack of signature |
| 2. ☐ original separate power of attorney | 6. ☐ sequence listing in computer readable form |
| 3. ☐ original general power of attorney | 7. ☐ other (specify): |
| 4. ☐ copy of general power of attorney; reference number, if any: | |

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

DOW GLOBAL TECHNOLOGIES INC.



By: _____
Lynn M. Zettler

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:

2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 80.1(b):

3. ☐ The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and Item 4 or 5, below, does not apply. ☐ The applicant has been informed accordingly.

4. ☐ The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.

5. ☐ Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 80.5. For International Bureau use only

Demand received from IPEA on:

Corresponds to: Form PCT/IPEA/401 (last sheet) (January 2002)

**CONFIRMATION
OF FAX**
See Notes to the demand form

PCT
FEE CALCULATION SHEET
Annex to the Demand

CHAPTER II

International application No. PCT/US01/15001		For International Preliminary Examining Authority use only	
Applicant's or agent's file reference 60858A		Date stamp of the IPEA	
Applicant DOW GLOBAL TECHNOLOGIES INC.			
CALCULATION OF PRESCRIBED FEES			
1. Preliminary examination fee	<u>Euro 1,533</u> P		
2. Handling fee	<u>Euro 147</u> H		
3. Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	<u>Euro 1,680</u> <u>TOTAL</u>		
MODE OF PAYMENT			
☒ authorization to charge deposit account with the IPEA (see below)		☐ cash	
☐ cheque		☐ revenue stamps	
☐ postal money order		☐ coupons	
☐ bank draft		☐ other (specify):	
AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT (This mode of payment may not be available at all IPEAs)		IPEA/ : EP	
☒ Authorization to charge the total fees indicated above.		Deposit Account No.: : 28300015	
☒ (This check-box may be marked only if the conditions for deposit accounts of the IPEA so permit) Authorization to charge any deficiency or credit any overpayment in the total fees indicated above.		Date: : December 20, 2001	
		Name: : Lynn M. Zettler	
		Signature: : <u>Lynn M. Zettler</u>	

**CONFIRMATION
OF FAX**

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITYFD 202
PCT

To:

ZETTLER, Lynn M.
The Dow Chemical Company
Intellectual Property
P.O.Box 1967
Midland, Michigan 48641-1967
ETATS-UNIS D'AMERIQUE

NIF

NOTIFICATION OF TRANSMITTAL OF
INTERNATIONAL PRELIMINARY
EXAMINATION REPORT

(PCT Rule 71.1)

Date of mailing
(day/month/year)

23/04/2002

Applicant's or agent's file reference

60858A

IMPORTANT NOTIFICATION

International application No.

PCT/US 01/ 15001

International filing date (day/month/year)

09/05/2001

Priority date (day/month/year)

02/06/2000

Applicant

THE DOW CHEMICAL COMPANY et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

RECEIVED

Name and mailing address of the IPEA/

European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0, Tx: 523656 epmu d
Fax: (+49-89) 2399-4465

Authorized officer

PATENT MAIL ROOM
KENNEDY M B
Tel. (+49-89) 2399 2828

Form PCT/IPEA/416 (July 1992) P20473

5-3-02
5/3/02 L.M.H.

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 60858A	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US 01/ 15001	International filing date (day/month/year) 09/05/2001	Priority date (day/month/year) 02/06/2000
International Patent Classification (IPC) or national classification and IPC C08F279/02		
Applicant THE DOW CHEMICAL COMPANY et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of <u>2</u> sheets, including this cover sheet. ☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT). These annexes consists of a total of _____ sheets.
3. This report contains indications relating to the following items: I ☒ Basis of the report II ☐ Priority III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV ☐ Lack of unity of invention V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI ☐ Certain documents cited VII ☐ Certain defects in the international application VIII ☐ Certain observations on the international application

Date of submission of the demand 24/12/2001	Date of completion of this report 18/04/2002
Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer VAN THIELEN J B Tel. (+49-89) 2399 2828

Form PCT/IPEA/409 (cover sheet) (July 1998)



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**International application No PCT/US 01/ 15001

I. Basis of the report

The basis of this international preliminary examination is the application as originally filed.

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability

In light of the documents cited in the international search report, it is considered that the invention as defined in at least some of the claims does not appear to meet the criteria mentioned in Article 33(1) PCT, i.e. does not appear to be novel and/or to involve an inventive step (see international search report, in particular the documents cited X and/or Y and corresponding claim references).

Certificate of Express Mailing (37 CFR 1.10)

EL 636 832 554
"Express Mail" Mailing Number

09 May 2001
Date of Deposit

I hereby certify that this application is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Carla S. Samuel
(Typed or printed name of person mailing application)

Carla S. Samuel
(Signature of person mailing application)

PCT INTERNATIONAL APPLICATION COVER LETTER

Regarding the International Application of:

Docket or Reference Number: Dow Case No. 60858A

Applicant(s): The Dow Chemical Company

Entitled: MONOVINYLDENE AROMATIC POLYMERS WITH IMPROVED TOUGHNESS AND RIGIDITY
AND A PROCESS FOR THEIR PREPARATION

Corresponding to the following application(s):

<u>Serial No.</u>	<u>Filing Date</u>	<u>Country</u>
60/209,035	June 2, 2000	United States of America

To the United States Receiving Office (RO/US):

Accompanying this cover letter is the above-identified International Application, including a completed Request Form PCT/RO/101 and Fee Sheet. Please process the application according to the provisions of the Patent Cooperation Treaty.

Respectfully submitted,

Tai-Sam Choo
Tai-Sam Choo
Agent for the Applicant(s)
Reg. No. 28,370

Date: 09 May 2001

PCT

REQUEST

The undersigned requests that the present
international application be processed
according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of Receiving Office and "PCT International Application"

Applicant's or Agent's file reference
60858A

Box No. I TITLE OF INVENTION MONOVINYLIDENE AROMATIC POLYMERS WITH IMPROVED TOUGHNESS AND RIGIDITY AND A PROCESS FOR THEIR PREPARATION	
Box No. II APPLICANT ☐ This person is also inventor.	
Name and address: THE DOW CHEMICAL COMPANY 2030 Dow Center Midland, Michigan 48674 United States of America	Telephone No. (989) 636-8133 Facsimile No. (989) 636-3237 Teleprinter No. Applicant's registration No. with the Office
State (that is, country) of nationality: US	State (that is, country) of residence: US
This person is applicant for the purposes of: ☒ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address: DEMIRORS, Mehmet 2866 N. Tupelo Drive Midland, Michigan 48642 United States of America	This person is: ☐ applicant only ☐ applicant and inventor ☒ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative	
Name and address: CHOO, Tai-Sam The Dow Chemical Company Intellectual Property P.O. Box 1967 Midland, Michigan 48641-1967 United States of America	Telephone No. (989) 636-8133 Facsimile No. (989) 636-3237 Teleprinter No. Applicant's registration No. with the Office 28,370
☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.	

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
<i>If none of the following sub-boxes is used, this sheet is not to be included in the request.</i>	
Name and address: MAUGHON, Dianne J. M. 601 West Main Street Midland, Michigan 48640 United States of America	This person is: ☐ applicant only ☐ applicant and inventor ☒ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: REGO, Jose M. Vlasstraat, 31 Helkant, Hulst Netherlands	This person is: ☐ applicant only ☐ applicant and inventor ☒ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: SCHRADER, David 4158 East Baker Road Midland, Michigan 48642 United States of America	This person is: ☐ applicant only ☐ applicant and inventor ☒ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
Name and address: 	This person is: ☐ applicant only ☐ applicant and inventor ☐ inventor only (If this check-box is marked, do not fill in below.) Applicant's registration No. with the Office
State (that is, country) of nationality:	State (that is, country) of residence:
This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box	
☐ Further applicants and/or (further) inventors are indicated on another continuation sheet	

Box No. V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

Regional Patent

- ☒ **AP** ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, MZ Mozambique, SD Sudan, SL Sierra Leone, SZ Swaziland, TZ United Republic of Tanzania, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☒ **EA** Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP** European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, TR Turkey, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☒ **OA** OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on line)

National Patent (if other kind of protection or treatment desired, specify on line):

- | | | |
|--|---|---|
| ☒ AE United Arab Emirates | ☒ GE Georgia | ☒ MW Malawi |
| ☒ AG Antigua & Barbuda | ☒ GH Ghana | ☒ MX Mexico |
| ☒ AL Albania | ☒ GM Gambia | ☒ MZ Mozambique |
| ☒ AM Armenia | ☒ HR Croatia | ☒ NO Norway |
| ☒ AT Austria | ☒ HU Hungary | ☒ NZ New Zealand |
| ☒ AU Australia | ☒ ID Indonesia | ☒ PL Poland |
| ☒ AZ Azerbaijan | ☒ IL Israel | ☒ PT Portugal |
| ☒ BA Bosnia and Herzegovina | ☒ IN India | ☒ RO Romania |
| | ☒ IS Iceland | ☒ RU Russian Federation |
| ☒ BB Barbados | ☒ JP Japan | |
| ☒ BG Bulgaria | ☒ KE Kenya | ☒ SD Sudan |
| ☒ BR Brazil | ☒ KG Kyrgyzstan | ☒ SE Sweden |
| ☒ BY Belarus | ☐ KP Democratic People's Republic of Korea | ☒ SG Singapore |
| ☒ BZ Belize | ☒ KR Republic of Korea | ☒ SI Slovenia |
| ☒ CA Canada | ☒ KZ Kazakhstan | ☒ SK Slovakia |
| ☒ CH & LI Switzerland and Liechtenstein | ☒ LC Saint Lucia | ☒ SL Sierra Leone |
| ☒ CN China | ☒ LK Sri Lanka | ☒ TJ Tajikistan |
| ☒ CO Colombia | ☒ LR Liberia | ☒ TM Turkmenistan |
| ☒ CR Costa Rica | ☒ LS Lesotho | ☒ TR Turkey |
| ☐ CU Cuba | ☒ LT Lithuania | ☒ TT Trinidad and Tobago |
| ☒ CZ Czech Republic | ☒ LU Luxembourg | |
| ☒ DE Germany | ☒ LV Latvia | ☒ TZ United Republic of Tanzania |
| ☒ DK Denmark | ☒ MA Morocco | ☒ UA Ukraine |
| ☒ DM Dominica | ☒ MD Republic of Moldova | ☒ UG Uganda |
| ☒ DZ Algeria | | ☐ US United States of America |
| ☒ EE Estonia | ☒ MG Madagascar | |
| ☒ ES Spain | ☒ MK The former Yugoslav Republic of Macedonia | ☒ UZ Uzbekistan |
| ☒ FI Finland | ☒ MN Mongolia | ☐ VN Viet Nam |
| ☒ GB United Kingdom | | ☒ YU Yugoslavia |
| ☒ GD Grenada | | ☒ ZA South Africa |
| | | ☒ ZW Zimbabwe |

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet

☐	☐	☐
☐	☐	☐

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)

Box No. VI PRIORITY CLAIM				
The priority of the following earlier application(s) is hereby claimed:				
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) 02 June 2000 (02.06.00)	60/209,035	US		
item (2)				
item (3)				
item (4)				
item (5)				

☐ Further priority claims are indicated in the Supplemental Box.

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as:

☒ all items ☐ item (1) ☐ item (2) ☐ item (3) ☐ item (4) ☐ item (5) ☐ other, see Supplemental Box

* Where the earlier application is an ARIPO application, indicate at least one country party to the Paris Convention for the Protection of Industrial Property or one Member of the World Trade Organization for which that earlier application was filed (Rule 4.10(b)(i)).

Box No. VII INTERNATIONAL SEARCHING AUTHORITY		
Choice of International Searching Authority (ISA) (if two or more international Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):		
ISA / EP		
Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the international Searching Authority):		
Date (day/month/year)	Number	Country (or regional Office)

Box No. VIII DECLARATIONS		
The following declarations are contained in Boxes Nos. VIII (i) to (v) (mark the applicable check-boxes below and indicate in the right column the number of each type of declaration):		Number of Declarations
☐ Box No. VIII(i)	Declaration as to the identity of the inventor	:
☐ Box No. VIII(ii)	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	:
☐ Box No. VIII(iii)	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	:
☐ Box No. VIII(iv)	Declaration of inventorship (only for the purposes of the designation of the United States of America)	:
☐ Box No. VIII(v)	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	:

Box No. IX CHECK LIST; LANGUAGE OF FILING

This international application contains:		This international application is accompanied by the following item(s) (mark the applicable check-boxes below and indicate in right column the number of each item):		Number of items
(a) the following number of sheets in paper form:				
request (including declaration sheets)	: 5	1. ☒ fee calculation sheet	:	1
description (excluding sequence listing part)	: 18	2. ☐ original separate power of attorney	:	
claims	: 3	3. ☐ original general power of attorney	:	
abstract	: 1	4. ☒ copy of general power of attorney; reference number, if any: _____	:	1
drawings	: 0	5. ☐ statement explaining lack of signature	:	
Sub-total number of sheets	: 27	6. ☐ priority document(s) identified in Box No. VI as item(s): _____	:	
sequence listing part of description (actual number of sheets if filed in paper form, whether or not also filed in computer readable form: see (b) below)	: _____	7. ☐ translation of international application into (language): _____	:	
Total number of sheets	: 27	8. ☐ separate indications concerning deposited microorganism or other biological material	:	
(b) sequence listing part of description filed in computer readable form		9. ☐ sequence listing in computer readable form (indicate also type and number of carriers (diskette, CD-ROM, CD-R or other))	:	
(i) ☐ only (under Section 801(a)(i))		(i) ☐ copy submitted for the purposes of international search under Rule 13ter only (and not as part of the international application)	:	
(ii) ☐ in addition to being filed in paper form (under Section 801(a)(ii))		(ii) ☐ (only where check-box (b)(i) or (b)(ii) is marked in left column) additional copies including, where applicable, the copy for the purposes of international search under Rule 13ter	:	
Type and number of carriers (diskette, CD-ROM, CD-R or other) on which the sequence listing part is contained (additional copies to be indicated under item 9(ii), in right column): _____		(iii) ☐ together with relevant statement as to the identity of the copy or copies with the sequence listing part mentioned in left column	:	
Figure of the drawings which should accompany the abstract: 0		10. ☒ other (specify): cover letter to USRO; Return Postcard	:	2
Language of Filing of the International application: English				

Box No. X SIGNATURE OF APPLICANT, AGENT, OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

The Dow Chemical Company

By: Tai-Sam Choo
Tai-Sam Choo

1. Date of actual receipt of the purported international application:		2. Drawings: ☐ received: ☐ not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA/	6. ☐ Transmittal of search copy delayed until search fee is paid.	

Date of receipt of the record copy by the International Bureau:

PCT

FEE CALCULATION SHEET

Annex to the Request

For Receiving office use only

International application No.

Applicant's or agent's
file reference 60858A

Date stamp of the receiving Office

Applicant
The Dow Chemical Company

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE \$ 240.00 T

2. SEARCH FEE \$ 846.00 S

International search to be carried out by ISA/EP

3. INTERNATIONAL FEE

Basic Fee

Where item (b) of Box No. IX applies, enter Sub-total number of sheets

Where item (b) of Box No. IX does not apply, enter Total number of sheets

b1 first 30 sheets \$ 382.00 b1

b2 0 x \$ 9.00 = \$ 0.00 b2
number of sheets fee per sheet
in excess of 30b3 Additional component (only if sequence listing part of description is
filed in computer readable form under Section 801(a)(i), or both in
that form and on paper, under Section 801(a)(ii):400 X \$ \$ b3
fee per sheet

Add amounts entered at b1, b2 and b3 and enter total at B \$ 382.00 B

Designation Fees

The international application contains 87 designations.

6 x \$ 82.00 = \$ 492.00 D

number of designations amount of designation fee
payable (maximum 6)

Add amounts entered at B and D and enter total at I \$ 874.00 I

4. FEE FOR PRIORITY DOCUMENT (if applicable) \$ 15.00 P

5. TOTAL FEES PAYABLE \$ 1,975.00

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

TOTAL

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

- ☒
- authorization to charge
-
- deposit account (see below)
- ☐
- postal money order
- ☐
- cash
- ☐
- coupons
-
- ☐
- cheque
- ☐
- bank draft
- ☐
- revenue stamps
- ☐
- other (specify):

AUTHORIZATION TO CHARGE (OR CREDIT) DEPOSIT ACCOUNT

This mode of payment may not be available at all receiving Offices)

Receiving Office: RO/US

Deposit Account No.: 04-1512

Date: 09 May 2001

Name: Tai-Sam Choo

☒ Authorization to charge the total fees indicated above.☒ (This check-box may be marked only if the conditions for deposit accounts
of the receiving Office so permit) Authorization to charge any deficiency
or credit any overpayment in the total fees indicated above.☒ Authorization to charge the fee for priority document

Signature: Tai Sam Choo

42

PCT

GENERAL POWER OF ATTORNEY - PATENT COOPERATION TREATY
General Appointment of Agent

The undersigned applicant, THE DOW CHEMICAL COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, and whose official address is 2030 Dow Center, Midland, Michigan 48674, United States of America, hereby appoints as individual agents:

Attorney/Agent Name	USPTO Reg. No.	Attorney/Agent Name	USPTO Reg. No.	Attorney/Agent Name	USPTO Reg. No.
BLACK, Edward W.	36,454	JOZWIAK, Elisabeth T.	41,101	SCHULTZ, Dale H.	36,287
CAVENDER, Carol J.	27,619	KANUCH, Bruce M.	24,623	SHEPHERD, Philip D.	28,905
CHOO, Tai-Sam	28,370	KARADZIC, Dragan J.	28,024	SIMS, Norman L.	30,685
CHRISTY, M. Robert	42,414	KIMBLE, Karen L.	26,895	SPENCER, Lee	43,353
DAMOCLES, Nemia C.	28,368	KORFHAGE, Glenn H.	27,204	STORER, Shelley D.	45,135
DELINE, Douglas N.	29,146	KRUPP, Stephen P.	34,366	TREANGEN, John B.	38,343
DICKERSON, James H., Jr.	29,297	LELKES, Robert S.	33,730	ULMER, Duane C.	34,941
DRAKE, James J.	34,584	MAURER, Charles J., III	33,065	WAKEFIELD, Charles P.	37,749
FARRELL, Daniel R.	28,599	MCKINNEY, Osborne K.	40,084	WARRICK, Noreen D.	34,573
FIFIELD, David H.	26,729	MILLER, William B.	32,922	WILLIS, Reid S.	39,429
GLENN, Michael L.	28,849	MORSE, Jonathan W.	30,200	ZERULL, Susan M.	38,387
HALLDORSON, Burke M.	24,642	NILSEN, Kevin	41,510	ZETTLER, Lynn M.	35,797
HANSBRO, Kevin R.	38,485	PELTON, James M.	24,551		
HAYHURST, Paul D.	30,180	PRIETO, Joe R.	30,887		
HOPPE, James T.	35,899	RUHR, Paula Sanders	32,585		
HOWARD, Dan R.	30,070	SCOTT, Mark S.	43,101		

all of THE DOW CHEMICAL COMPANY or its affiliated companies for which The Dow Chemical Company has control, to act on behalf of THE DOW CHEMICAL COMPANY before the competent International Authorities in connection with any and all international applications filed by THE DOW CHEMICAL COMPANY and of which THE DOW CHEMICAL COMPANY is an applicant.

The applicant also hereby appoints as agents: Beatrice E. Goldaner, Dorothee Von Cunow and Niek H.M. de Jong, all of affiliated companies for which The Dow Chemical Company has control and all registered to practice before the European Patent Office to act on behalf of THE DOW CHEMICAL COMPANY before the European Patent Office as International Searching Authority and International Preliminary Examining Authority in connection with any and all international applications filed by THE DOW CHEMICAL COMPANY and of which THE DOW CHEMICAL COMPANY is an applicant.

Signed at: Midland, Michigan 48674, United States of America this 26 day of March, 2001.

CORP.
SEAL

THE DOW CHEMICAL COMPANY

By: Graham E. Taylor
GRAHAM E. TAYLOR
Associate General Counsel, Intellectual Property

NOTARIAL CERTIFICATE (Corporation)

UNITED STATES OF AMERICA)
STATE OF Michigan) SS
County/Parish of Midland)

On this 26 day of March, 2001, personally appeared before me, GRAHAM E. TAYLOR, Associate General Counsel, Intellectual Property, THE DOW CHEMICAL COMPANY, known or identified to me to be the individual described in and who executed the foregoing document and acknowledged the same as a free act and deed for uses and purposes therein expressed by authority of the said Corporation incorporated under the laws of the State of Delaware, United States of America.

I further certify that said authority, dated September 7, 1999, is based on a Resolution of the Board of Directors of the said Corporation which I have seen, appointing the said individual Attorney-In-fact with full power to sign the foregoing document on behalf of the said corporation and that the purposes for which said document is granted are within the scope of the objects or activities of said corporation.

SEAL

Ann Heritier
Notary Public

ANN HERITIER
NOTARY PUBLIC, BAY COUNTY, MICHIGAN
~~ACTING IN MIDLAND COUNTY, MICHIGAN~~
MY COMMISSION EXPIRES DECEMBER 3, 2002



CERTIFIED RESOLUTION

The Dow Chemical Company
Midland, Michigan 48674

Graham E. Taylor Granted Authority to Sign Patent Documents

RESOLVED, that Graham E. Taylor, the Company's Assistant General Counsel - Intellectual Property, be and is hereby authorized, empowered and made Attorney-in-Fact, to sign on behalf of The Dow Chemical Company such formal papers as must bear a Company signature for use in the Patent Office of any nation (a) to accompany or to complete applications for patent, design, or utility model, or reissues, extensions or renewals thereof; (b) to make statutory disclaimers of the remaining term of patents; (c) to initiate at any administrative level on behalf of this Company oppositions, nullity actions or cancellation proceedings with respect to the patents, or applications for patents of others; (d) to endorse patents as available for license; and (e) to constitute the acceptance by this Company of an assignment from inventors, or the certification that such assignment exists; and

FURTHER RESOLVED, that the signature of Graham E. Taylor on behalf of The Dow Chemical Company on such patent papers shall have the same force and effect as that of any duly qualified officer of The Dow Chemical Company, and the signature of Graham E. Taylor on any of the above-specified papers that may require the corporate seal of The Dow Chemical Company may be attested and the seal affixed by the Secretary or an Assistant Secretary of this Company; and

FURTHER RESOLVED, that this resolution and the power herein granted shall remain in force until revoked by action of this Board of Directors; and

FURTHER RESOLVED, that this resolution and the power herein granted is effective September 15, 1999, upon which date the resolution adopted by this Board of Directors on July 14, 1994, which granted a power similar to that herein granted and the power therein granted shall be revoked and superseded by this resolution and the power herein granted; and

FURTHER RESOLVED, that the Secretary or an Assistant Secretary of this Company may certify copies of this resolution and power, as may be required from time to time, for use in various nations in respect to matters occurring while the power is in force.

Certification

I, Tina S. Van Dam, Assistant Secretary of The Dow Chemical Company (the "Company"), do hereby certify that the foregoing is a full, true and correct copy of a resolution adopted at a meeting of the Executive Committee of the Board of Directors of the Company, held at the offices of the Company in Midland, Michigan, on the 7th day of September, 1999, at which meeting a quorum of the Board of Directors was present, and that, as of the date below, such resolution has not been revoked, annulled or modified in any manner whatsoever, and is in full force and effect.

IN WITNESS WHEREOF, I have hereunto set my hand and affixed the corporate seal of the Company this 7th day of September, 1999.


Tina S. Van Dam, Assistant Secretary

PATENT COOPERATION TREATY

A 211-02
PCT 24

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:
ZETTLER, Lynn M.
The Dow Chemical Company
Intellectual Property
P.O. Box 1967
Midland, Michigan 48641-1967
ETATS-UNIS D'AMERIQUE

NIF

INVITATION TO CORRECT
DEFECTS IN THE DEMAND
By letter in annex
(PCT Rule 60.1)

Applicant's or agent's file reference 60858A	Date of mailing (day/month/year) 11.01.02
International application No. PCT/US 01/ 15001	REPLIQUE within ONE MONTH from the above date of mailing. See also below. International filing date (day/month/year) 09/05/2001
Applicant DOW GLOBAL TECHNOLOGIES INC. et al.	
JAN 17 2002	

PATENT MAIL ROOM

The applicant is hereby invited within the time limit indicated above to correct the following defects which this International Preliminary Examining Authority has found in the demand for international preliminary examination:

- ☐ It does not contain the election of at least one Contracting State bound by Chapter II (Rules 53.2(a)(iv) and 53.7).
- ☐ It does not permit identification of the international application to which it relates (Rule 60.1(b)).
- ☐ It does not contain the required petition (Rules 53.2(a)(i) and 53.3).
- ☐ It does not contain the required indications concerning the agent as specified in the Annex (Rules 53.2(a)(ii) and 53.5).
- ☐ It does not contain the required indications concerning the international application as specified in the Annex (Rules 53.2(a)(iii) and 53.6).
- ☐ It is not submitted in the required language which is: _____ (Rule 55.1).
- ☐ It is not made on the printed form (rule 53.1(a)).
- ☐ It is presented as a computer print-out the particulars of which do not comply with the Administrative Instructions (Rule 53.1(a)).
- ☒ It does not contain the required indications concerning the applicant as specified in the Annex (Rules 53.2(a)(ii) and 53.4).
- ☐ It does not contain the required signature as specified in the Annex (Rules 53.2(b) and 53.8).

Effects of the date of receipt of the corrections on the date of receipt of the demand:

(i) If the defects noted under items 1 and 2 are corrected within the time limit indicated above, the demand shall be considered as if it had been received on the date when the corrections are received (Rule 60.1(b)). If that date is later than the expiration of 19 months from the priority date, entry into the national phase before the elected Offices will NOT be postponed until the expiration of 30 months from the priority date.

(ii) If the defects noted under items 3 to 10 are corrected within the time limit indicated above, the demand shall be considered as if it had been received on its actual filing date (Rule 60.1(b)).

Effects of failure to correct the defects within the time limit indicated above:

(i) In the case of defects noted under items 1 to 8, this Authority will declare that the demand is considered as if it had not been submitted.

(ii) In the case of defects noted under items 9 and 10, this Authority will declare that the election(s) of the State(s) concerned is (are) considered as if it (they) had not been made.

A copy of this invitation has been sent to the International Bureau.

Name and mailing address of the IPEA/  European Patent Office D-80298 Munich Tel. (+49-89) 2399-0, Tx: 523656 epmu d Fax: (+49-89) 2399-4465	Authorized officer KENNEDY M B Tel. (+49-89) 2399-2976
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1-24-02

ANNEX TO
FORM PCT/IPEA/404

International application No.
PCT/US 01/ 15001

U5

Continuation of item 4: As to indications concerning the agent (Rule 4.4), the demand:

- a. ☐ does not properly indicate the agent's name (*specify*):
- b. ☐ does not indicate the agent's address.
- c. ☐ does not properly indicate the agent's address (*specify*):

Continuation of item 5: As to indications concerning the international application, the demand does not indicate:

- a. ☐ the international filing date.
- b. ☐ the international application number.
- c. ☐ the name of the receiving Office, where the international application number was not known to the applicant at the time the demand was filed.
- d. ☐ the title of the invention.

Continuation of item 9: As to indications concerning the applicant (Rules 4.4 and 4.5), the demand:

- a. ☐ does not indicate all the applicants for the elected States.
- b. ☒ does not properly indicate the applicant's name (*specify*):
- c. ☐ does not indicate the applicant's address.
- d. ☐ does not properly indicate the applicant's address (*specify*):

See GULU Technology, ex. Dr. Chemical Company?
Please clarify

- e. ☐ does not indicate the applicant's nationality.
- f. ☐ does not indicate the applicant's residence.

Continuation of item 10: As to indications concerning signature (Rules 4.15 and 90.4), the demand:

- a. ☐ is not signed.
- b. ☐ is not signed by all the applicants for the elected States.
- c. ☐ is not accompanied by the statement referred to in the check list in Box No. VI of the demand explaining the lack of the signature of an applicant for the election of the United States of America.
- d. ☐ is signed by what appears to be an agent/common representative but
- ☐ the demand is not accompanied by a power of attorney appointing him.
- ☐ the power of attorney accompanying the demand is not signed by all the applicants for the elected States.

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

To:

ZETTLER, Lynn M.
The Dow Chemical Company
Intellectual Property
P.O.Box 1967
Midland, Michigan 48641-1967
ETATS-UNIS D'AMERIQUE

NOTIFICATION OF RECEIPT
OF DEMAND BY COMPETENT INTERNATIONAL
PRELIMINARY EXAMINING AUTHORITY(PCT Rules 59.3(e) and 61.1(b), first sentence
and Administrative Instructions, Section 601(a))Date of mailing
(day/month/year)

11 01 02

Applicant's or agent's file reference

60858A

IMPORTANT NOTIFICATION

International application No.

PCT/US 01/ 15001

International filing date (day/month/year)

09/05/2001

Priority date (day/month/year)

02/06/2000

Applicant

DOW GLOBAL TECHNOLOGIES INC. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority considers the following date as the date of receipt of the demand for international preliminary examination of the international application:

24/12/2001

2. This date of receipt is:

- ☒ the actual date of receipt of the demand by this Authority (Rule 61.1(b)).
☐ the actual date of receipt of the demand on behalf of this Authority (Rule 59.3(e)).
☐ the date on which this Authority has, in response to the invitation to correct defects in the demand (Form PCT/IPEA/404), received the required corrections.

3. ☐ ATTENTION: That date of receipt is AFTER the expiration of 19 months from the priority date. Consequently, the election(s) made in the demand does (do) not have the effect of postponing the entry into the national phase until 30 months from the priority date (or later in some Offices) (Article 39(1)). Therefore, the acts for entry into the national phase must be performed within 20 months from the priority date (or later in some Offices) (Article 22). For details, see the PCT Applicant's Guide, Volume II.

- ☐ (If applicable) This notification confirms the information given by telephone, facsimile transmission or in person on:

4. Only where paragraph 3 applies, a copy of this notification has been sent to the International Bureau.

Name and mailing address of the IPEA/

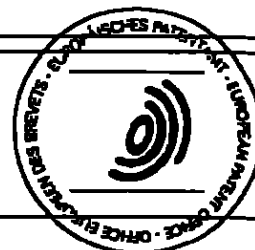


European Patent Office
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Authorized officer

KENNEDY M B

Tel. (+49-89) 2399-2976



PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

43-7-02
PCT 48

To:

ZETTLER, Lynn M.
The Dow Chemical Company
Intellectual Property
P.O. Box 1967
Midland, Michigan 48641-1967
ETATS-UNIS D'AMERIQUE

NI

WRITTEN OPINION

(PCT Rule 66)

Date of mailing
(day/month/year)

07/02/2002

Applicant's or agent's file reference

60858A

REPLY DEADLINE

within 1 / 00 months/days
from the above date of mailing

International application No.

PCT/US 01/15001

International filing date (day/month/year)

09/05/2001

Priority date (day/month/year)

02/06/2000

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

C08F279/02

Applicant

THE DOW CHEMICAL COMPANY et al.

1. This written opinion is the first drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also For an additional opportunity to submit amendments, see Rule 66.4. For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4b. For an informal communication with the examiner, see Rule 66.6.

RECEIVED

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

FEB 15 2002

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is:

02/10/2002

PATENT MAIL ROOM

Name and mailing address of the IPEA/



European Patent Office
D-80298 Munich
Tel. (+49-89) 2399-0, Tx: 523656 epmu d
Fax: (+49-89) 2399-4465

Authorized officer

Examiner

Formalities officer

(incl. extension of time limits)
Tel. (+49-89) 2399 2828



Form PCT/IPEA/408 (cover sheet) (July 1998)

2-20-02

I. Basis of the opinion

1. The basis of this written opinion is the application as originally filed.

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

2. The question of whether the claimed invention appears to be novel, to involve an inventive step, or to be industrially applicable has not been and will not be the subject of the international preliminary examination (Article 34 (4) (a) (i) (ii) PCT; see also international search report) in respect of:

- 2.1 Applications having an unnecessary plurality of independent claims (generally not more than 1 independent claim in the same category is necessary; Article 6 PCT);

- 2.2 unsearched subject-matter (Article 17 (2) (a), Rule 66.1 (e) PCT), e.g.

- 2.2.1 claimed subject-matter under Rule 39.1 PCT,

- 2.2.2 applications where the description, the claims, or the drawings fail to comply with the prescribed requirements to such an extent that no meaningful search could have been carried out;

- 2.3 claimed subject-matter under Rule 67.1 PCT.

V. Reasoned statement under Rule 66.2(a)(II) with regard to novelty, inventive step or industrial applicability

3. To the extent that the international preliminary examination has been carried out (see item III above), the following is pointed out:

In light of the documents cited in the international search report, it is considered that the invention as claimed in at least one of the independent claims does not appear to meet the criteria mentioned in Article 33 (1) PCT, i.e. does not appear to be novel and/or to involve an inventive step.

4. If amendments are filed, the Applicant must comply with the requirements of Rule 66.8 PCT and indicate the basis in the originally filed application of the amendments made (Article 34 (2) (b) PCT) otherwise these amendments will not be taken into consideration for the establishment of international preliminary examination.
The attention of the applicant is drawn to the fact that if the application contains an unjustified plurality of independent claims no examination of any of the claims will be carried out.

POLIMEROS AROMATICOS DE MONOVINILIDENO CON DUREZA Y RIGIDEZ MEJORADAS Y UN PROCESO PARA SU PREPARACIÓN

La presente invención se refiere a composiciones de polímeros aromáticos de monovinilideno reforzadas con hule del tipo aludido comúnmente como "poliestireno de alto impacto" o "HIPS". Más particularmente, la invención se refiere a tales composiciones en las cuales las partículas reforzadoras de hule se producen a partir de un hule de polibutadieno específico, tienen una distribución específica de tamaño de partículas y un proceso para la producción de tales composiciones.

Las composiciones poliméricas reforzadas con hule del tipo HIPS se usan ampliamente en muchas aplicaciones debido a su facilidad de moldeo, buen brillo y generalmente buenas propiedades mecánicas. Se sabe desde algún tiempo que las combinaciones mejoradas de brillo y propiedades mecánicas pueden ser logradas en tales polímeros reforzados con hule mediante la provisión de una distribución así llamada "bimodal" en los tamaños de las partículas reforzadoras de hule, es decir las partículas muestran dos picos distintos en su distribución de tamaño. Esto se puede lograr combinando dos o más de tales resinas o componentes, teniendo cada uno un grupo de partículas de hule que tienen un tamaño diferente de partícula promedio. Se conocen varias composiciones de polímeros aromáticos de monovinilideno que tienen por lo menos dos grupos de partículas de hule en donde los grupos tienen tamaños

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diferentes de partícula promedio. Ver por ejemplo las US-A-4,146,589, US-A-4,214,056 y US-A-4,334,039 y EP-A-0 096 447, EP-A- 0 158 258 y EP-A- 0 152 752 que describen tales composiciones.

La US-A-4,493,922, describe también composiciones de poliestireno reforzadas con hule que tienen distribuciones de tamaño de partícula de hule bimodales. Los tamaños promedio de partículas de hule descritos para los grupos de partículas son de 2 a 8 micrómetros (especialmente de 5 a 6 micrómetros) para el grupo de partículas más grandes y 0.2 a 2.0 micrómetros para el grupo de partículas más pequeñas.

Como se dijo, se proponen un número de métodos para lograr tal distribución bimodal de partículas. Por ejemplo, la US-A-4,153,645 describe un método para la preparación de un polímero tipo HIPS en el cual se preparan dos composiciones poliméricas usando procesos normales de producción, las composiciones que tienen diferentes tamaños promedio de partículas. Estas dos composiciones poliméricas se mezclan entonces mediante un proceso de mezclado mecánico subsecuente.

Un enfoque alternativo para producir polímeros de HIPS con una distribución bimodal de hule ha sido introducir corrientes de alimentación de monómero y hule en dos puntos diferentes en el sistema de polimerización. Esto resulta en un producto polimérico que tiene generalmente un buen despliegue amplio de tamaños de partícula de hule. Ejemplos de esto se describen en EP 0 015 752, US 4,334,039 y EP 0 096 447. Una desventaja de tales métodos es que las propiedades mecánicas del producto resultante

pueden ser algo pobres y difíciles de controlar.

Un enfoque adicional todavía se describe en US 4,146,589 y EP 0 048 389. En este método, se preparan dos composiciones de pre-polímero que contienen partículas de hule con diferentes tamaños de partículas. Las composiciones de pre-polímero se mezclan entonces y polimerizan después para proporcionar un polímero que tiene una distribución bimodal de tamaño de partícula.

Otras referencias en esta área incluye la EP-418,042 en donde el hule comprende un hule radial o de estrella parcialmente acoplado, que tiene un contenido de cis de menos de o igual a 70 por ciento, JP 02762722 en donde el hule es una mezcla de un polibutadieno elevado en cis de alto peso molecular y un polibutadieno de bajo cis de bajo peso molecular, y JP 95005789 en donde el hule es una mezcla de un polibutadieno de alto peso molecular y un polibutadieno de bajo peso molecular, ambos teniendo una estructura de cis de más de 80 por ciento. Sin embargo, aún no se obtiene un balance deseable de resistencia al impacto y resistencia a la tensión para algunas aplicaciones específicas.

Por lo tanto, es deseable aún obtener un polímero aromático de monovinilideno modificado con hule que tenga un balance mejorado de propiedades de impacto y tensión para aplicaciones selectas.

La presente invención es un polímero aromático de monovinilideno modificado con hule que comprende:

a) una matriz de polímero aromático de monovinilideno,

b) partículas de hule dispersas en esa, caracterizada porque las partículas de hule se producen a partir de un hule dino que tiene I) de 20 a 80 por ciento, con base en el peso total de dichas partículas de hule, de un componente de alta viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 110 hasta 500 centipoise y II) de 80 a 20 por ciento, con base en el peso total de dichas partículas de hule, de un componente de baja viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 1 a 100 centipoise, caracterizada además porque la relación de viscosidad en solución del componente de alta viscosidad en solución a la viscosidad en solución del componente de baja viscosidad en solución fluctúa desde 1.1 hasta 500, en donde ambos componentes I y II tienen un contenido de 1,4 cis de más de 30 por ciento, y III) el hule está injertado con polímero aromático de monovinilideno hasta el punto en que hay por lo menos 30 por ciento de polímero aromático de monovinilideno presente como injerto en el hule.

c)

En una modalidad preferida la presente invención es un polímero aromático de monovinilideno modificado con hule que comprende:

a) una matriz de polímero aromático de monovinilideno,

b) partículas de hule dispersas en esa en la forma de partículas pequeñas y grandes, en donde el

diámetro de volumen de partícula promedio de las partículas pequeñas es de 0.1 a 2 micrómetros y el diámetro de volumen de partícula promedio de las partículas grandes es de 2 a 6 micrómetros, caracterizada porque las partículas de hule se producen a partir de un hule de dieno que tiene I) de 20 a 80 por ciento, con base en el peso total de dichas partículas de hule, de un componente de alta viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 110 hasta 500 centipoise y II) de 80 a 20 por ciento, con base en el peso total de dichas partículas de hule, de un componente de baja viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 1 a 100 centipoise, caracterizada además porque la relación de viscosidad en solución del componente de alta viscosidad en solución a la viscosidad en solución del componente de baja viscosidad en solución fluctúa desde 1.1 hasta 500, en donde ambos componentes I y II tienen un contenido de 1,4 cis de más de 30 por ciento, y III) el hule está injertado con polímero aromático de monovinilideno hasta el punto en que hay por lo menos 30 por ciento de polímero aromático de monovinilideno presente como injerto en el hule, en donde la cantidad de hule en el polímero representa de 2 a 20 por ciento con base en el peso total del polímero.

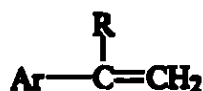
Otro aspecto de la presente invención es un proceso para preparar un polímero aromático de monovinilideno modificado con hule que comprende los

pasos de: (a) suministrar continuamente una mezcla de reacción que comprende un monómero aromático de monovinilideno y un hule dieno disuelto a un medio de reactor, (b) polimerizar continuamente el monómero aromático de monovinilideno en la presencia del hule dieno disuelto en el medio de reactor bajo condiciones por las que ocurre subsecuentemente la inversión de fase, (c) remover continuamente del medio de reactor un polímero aromático de monovinilideno reforzado con hule dieno, dicho proceso está caracterizado porque: (d) el hule dieno que está disuelto en la mezcla de reacción tiene I) de 20 a 80 por ciento, con base en el peso total de dicho hule dieno, de un componente de alta viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 120 hasta 500 centipoise y II) de 80 a 20 por ciento, con base en el peso total de dicho hule dieno, de un componente de baja viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 1 a 100 centipoise, caracterizado además porque la relación de viscosidad en solución del componente de alta viscosidad en solución a la viscosidad en solución del componente de baja viscosidad en solución fluctúa desde 1.2 hasta 500, en donde ambos componentes I y II tienen un contenido de 1,4 cis de más de 30.

En una modalidad preferida, el proceso comprende además (e) en donde las condiciones del proceso antes de la inversión de fase se ajustan para producir diferentes grupos de partículas de hule dieno a partir de los componentes de alto y bajo pesos moleculares del hule dieno, cada grupo teniendo un

tamaño promedio diferente de partícula de hule.

Los polímeros aromáticos de monovinilideno adecuados para la presente invención son aquellos producidos mediante polimerización de un monómero aromático de vinilo. Los monómeros aromáticos de vinilo incluyen, pero no están limitados a aquellos descritos en US-A-4,666,987, US-A-4,572,819 y US-A-4,585,825. De preferencia, el monómero es de la fórmula:



en donde R' es hidrógeno o metilo, Ar es una estructura de anillos aromáticos que tiene de 1 a 3 anillos aromáticos con o sin substitución con alquilo, halo o haloalquilo, en donde cualquier grupo alquilo contiene de 1 a 6 átomos de carbono y haloalquilo se refiere a un grupo alquilo substituido con halo. De preferencia, Ar es fenilo o alquilfenilo, en donde alquilfenilo se refiere a un grupo fenilo substituido con alquilo, siendo el fenilo el más preferido. Los monómeros aromáticos de vinilo típicos que se pueden usar incluyen: estireno, alfa-metilestireno, todos los isómeros de vinil tolueno, especialmente paraviniltolueno, todos los isómeros de etil estireno, propil estireno, vinil bifenilo, vinil naftaleno, y vinil antraceno y sus mezclas. Los monómeros aromáticos de vinilo se pueden combinar también con otros monómeros copolimerizables. Ejemplos de tales monómeros incluyen, pero no están limitados a monómeros acrílicos tales como acrilonitrilo, metacrilonitrilo, ácido metacrílico, metacrilato de metilo, ácido

acrílico, y acrilato de metilo; maleimida, fenilmaleimida y anhídrido maleico. Se prefiere, sin embargo, para la práctica de la presente invención usar ya sea menos de 10 por ciento en peso o substancialmente ningún otro monómero copolimerizable. La distribución específica de tamaño de partícula ya no es óptima para grandes cantidades de uno o más de estos monómeros. En general, los monómeros aromáticos de monovinilideno preferidos son estireno, alfa metil estireno, uno o más de los isómeros de vinil tolueno, y/o mezclas de dos o más de estos, siendo el estireno el compuesto aromático de monovinilideno más preferido.

El polímero aromático de monovinilideno tiene típicamente un peso molecular (Mw) en promedio de peso desde aproximadamente 120,000 hasta 500,000.

Los hules empleados de preferencia en la práctica de la presente invención son aquellos polímeros y copolímeros que exhiben una temperatura de transición de segundo orden la cual no es mayor de 0° C, de preferencia no mayor de -200° C y más preferiblemente no mayor de -400° C según determinación o aproximación usando técnicas convencionales, por ejemplo, Método de Prueba ASTM D-746-52 T.

Los hules altamente preferidos son polímeros de alcadieno. Los alcadienos adecuados son dienos conjugados en 1,3 tales como butadieno, isopreno, cloropreno o piperileno. Los más preferidos son homopolímeros (exceptuando cualesquier monómeros de acoplamiento) preparados a partir de dienos conjugados en 1,3, con tales homopolímeros de 1,3-butadieno siendo especialmente preferidos. Los hules

de copolímero de alcadieno que contienen cantidades pequeñas, por ejemplo menos de 15, de preferencia menos de 10% en peso, de otros monómeros tales como aromáticos de monovinilideno pueden emplearse también si los hules cumplen las otras calificaciones descritas en la presente. Los hules más preferidos son homopolímeros lineales, radiales, de estrella o ramificados aleatoriamente del 1,3-butadieno que tienen un contenido de cis de por lo menos 30%.

Los hules adecuados para la presente invención pueden hacerse mediante polimerización aniónica o polimerización de Ziegler-Natta bien conocidas por aquellos expertos en la técnica.

Con respecto a los materiales de hule adecuados para uso de acuerdo con la presente invención, el requerimiento esencial para el material de hule es que tenga un componente de relativamente alta viscosidad en solución y un componente de relativamente baja viscosidad en solución, en donde ambos componentes tengan un contenido de cis 1,4 de por lo menos 30 por ciento. Los hules adecuados para uso en la presente son hules lineales, parcialmente acoplados, llamados también hules radiales o de estrella, hules acoplados completamente así como hules ramificados aleatoriamente, otros polímeros ramificados y mezclas de hules, tal como una mezcla de polímeros lineales y ramificados, que reúnen los requisitos para los materiales de hule a ser empleados en esta invención. Las moléculas de estos materiales de hule tienen tres o más segmentos de polímero acoplados mediante un elemento o compuesto polifuncional sencillo. Los polímeros radiales o de

estrella que tienen este ramificado designado se preparan convencionalmente usando un agente polifuncional de acoplamiento. Los métodos para preparar polímeros radiales o de estrella que tienen ramificado diseñado son bien conocidos en la técnica. Métodos para preparar un polímero de butadieno de este tipo usando un agente de acoplamiento se ilustran en US-A-4,183,877, US-A-4,340,690, US-A-4,340,691 y US-A-3,668,162 y la Patente Japonesa 59-24 711.

Como se usa en la presente, los pesos moleculares aludidos son los pesos moleculares en promedio de peso o Mw's para los componentes de hule según determinación mediante las técnicas cromatográficas de permeación en gel descritas por el Método de Prueba ASTM designado D-3536 (poliestireno estándar) y expresado sin corrección para las diferencias entre hule y poliestireno estándares.

Los hules dieno más adecuados para esta invención contienen dos componentes distintos, los cuales están constituidos por un hule dieno de relativamente alta viscosidad en solución y un hule dieno de relativamente baja viscosidad en solución. Más particularmente, el componente de baja viscosidad en solución de hule dieno útil para la presente invención tiene valores de viscosidad en solución desde 1, generalmente desde 5, de preferencia desde 10 y más preferiblemente desde 20, hasta 100, generalmente hasta 95, de preferencia hasta 85 y lo más preferible hasta 75. El componente de alta viscosidad en solución de hule dieno útil para la presente invención tiene valores de viscosidad en

solución desde 110, generalmente desde 115, de preferencia desde 120 y más preferiblemente desde 150, hasta 500, generalmente hasta 450, de preferencia hasta 430 y lo más preferible hasta 400. Los componentes de baja y alta viscosidad en solución de hules dieno útiles para la presente invención están caracterizados además porque la relación de viscosidad en solución del componente de alta viscosidad en solución a la viscosidad en solución de baja viscosidad en solución fluctúa desde 1.1, generalmente desde 1.26, de preferencia desde 1.53 y más preferiblemente desde 1.76, hasta 500, generalmente hasta 90, de preferencia hasta 40 y más preferiblemente hasta 21.5.

Además, con el fin de obtener las proporciones apropiadas de las partículas de hule pequeñas y grandes, se prefiere si el componente de baja viscosidad en solución del material de hule constituye de 20 a 80 por ciento en peso del contenido total de hule de la resina, de preferencia de 30 a 70 por ciento en peso. Lo más preferible ningún componente es más de 80 por ciento del hule total en la composición.

Ventajosamente, para preparar una resina reforzada con hule usando técnicas de polimerización en masa o masa/suspensión, la viscosidad en solución del hule del polímero de alcadieno, según medición como una solución al 5 por ciento en peso en estireno, será mayor de 40 y menor de 400 centipoise (cps) a 25° C cuando la viscosidad se mide usando un viscosímetro capilar Canon-Fenske (capilar No. 400, 1.92 mm de diámetro interno).

Los valores de la viscosidad Mooney de los hules tipo radial deben ser menores de 90, de preferencia menores de 70 según medición mediante DIN 53523. En general, para tener un hule, que sea suficientemente sólido para ser manejado y procesado de una manera normal, el valor de viscosidad Mooney debe ser por lo menos 20 y se prefieren los valores de por lo menos 30. El rango preferido para el valor Mooney está entre 20 y 90, más preferiblemente entre 30 y 85, lo más preferible entre 35 y 80.

Aunque el hule puede contener una pequeña cantidad de un agente de entrelazamiento, el entrelazamiento excesivo puede resultar en pérdida de las características ahuladas y/o volver al hule insoluble en el monómero.

El hule se emplea ventajosamente en cantidades tales que el producto de polímero reforzado con hule contiene de 2 a 20 por ciento, de preferencia de 3 a 17 por ciento, más preferible de 3 a 15 por ciento en peso de hule o equivalente de hule, con base en el peso total del polímero aromático de monovinilideno modificado con hule.

El término "hule" o "equivalente de hule" como se usa en la presente para indicar cantidades en peso de material de hule pretende significar, para un homopolímero de hule (tal como polibutadieno), simplemente la cantidad de hule, y para un copolímero de bloque, la cantidad del copolímero hecho a partir de monómero(s) los cuales, cuando se homopolimerizan forman un polímero ahulado. Por ejemplo, para

calcular la cantidad de hule en una composición donde se ha empleado un hule de copolímero de bloque butadieno-estireno, el "hule" o "equivalente de hule" de la composición se calcula con base en solamente el componente de butadieno en el copolímero de bloque. Obviamente cuando se miden propiedades físicas u otros aspectos del material de hule, se refiere al material de hule completo incluyendo cualesquier comonómeros.

El producto de la presente invención puede verse como teniendo una distribución de tamaño de partícula de hule generalmente ampliada. En una modalidad la presente invención tiene una distribución bimodal de tamaño de partícula de hule con una cantidad crítica de partículas de hule grandes y pequeñas. La presente invención que tiene tales distribuciones resulta en un producto de resina el cual, en la forma de artículos moldeados, tiene combinaciones mejoradas de resistencia al impacto y resistencia a la tensión.

En una modalidad, de acuerdo con esta invención, se ha descubierto de manera sorprendente que los productos que tienen una distribución de tamaño de partículas de hule de este tipo tienen mejores combinaciones de propiedades cuando, con base en 100 partes en peso de hule o equivalente de hule, (a) partículas que constituyen de 20 a 60 partes en peso del hule tienen diámetros de 0.1 a 2 micrómetros, (b) partículas que constituyen de 60 a 20 partes en peso del hule tienen diámetros desde 2 hasta 8 micrómetros.

En términos de una distribución bimodal, se encuentra que como grupos de partículas, el grupo de

partículas más pequeñas debe tener un diámetro de partícula promedio volumen desde 0.2 hasta 2 micrómetros, de preferencia hasta 1.8 micrómetros y lo más preferido hasta 1.5 micrómetros y el grupo de partículas más grandes debe tener un diámetro de partícula en promedio de volumen desde 2.0, de preferencia desde 2.5 hasta 5 micrómetros. En términos de distribución amplia, se encuentra que 80 por ciento de partículas están en el rango desde 0.2 hasta 8 micrómetros.

Como se usa en la presente, dicho tamaño de partícula es el diámetro de la partícula de hule según medición en el producto resultante, incluyendo todas las oclusiones del polímero de matriz con partículas de hule, dichas oclusiones están presentes generalmente en las partículas de hule dispersas de un polímero reforzado con hule preparado usando técnicas de polimerización en masa. Las morfologías tamaños y distribuciones de partículas de hule, se pueden determinar usando técnicas convencionales tales como (para partículas más grandes) usando un Coulter Counter (Coulter Counter es una marca registrada) o, particularmente para partículas más pequeñas microscopia de transmisión de electrón.

Con relación a la morfología de las partículas de hule en los diferentes grupos, como es bien conocido, las partículas más pequeñas tienen típicamente una morfología de cubierta de núcleo (sencilla, oclusión mayor) o celular (múltiple, oclusiones menores). Las partículas más grandes tendrían generalmente una morfología celular o de oclusión múltiple similar.

El proceso de la presente invención está caracterizado por la utilización de un hule que tiene componentes específicos de alto y bajo pesos moleculares bajo condiciones de proceso por las que la distribución de tamaño de partícula de hule antes especificada se puede obtener con procesos y equipo de polimerización estándares.

En la preparación de los polímeros reforzados con hule, se prepara una mezcla de reacción disolviendo el hule en el (los) monómero(s) y la solución de monómero/hule resultante, aludida en la presente como la mezcla de reacción, se suministra a un medio de reactor y se polimeriza subsecuentemente. La cantidad de hule disuelta inicialmente en la mezcla de reacción depende de la concentración deseada de hule en el producto final de polímero reforzado con hule, el grado de conversión durante la polimerización y la viscosidad de la solución de mezcla de reacción. Específicamente, la viscosidad de la solución de la mezcla de reacción es ventajosamente menor de 3,000 centipoise. A viscosidades más altas, la solución de mezcla de reacción es difícil de procesar. Siempre que la viscosidad de la mezcla de reacción no sea indeseablemente alta, la solución de mezcla de reacción comprenderá generalmente de 5 a 15, por ciento en peso del hule, dicho por ciento en peso siendo con base en las cantidades totales de hule y monómeros empleados.

Opcionalmente, la mezcla de reacción contendrá un diluyente líquido orgánico. Los diluyentes líquidos orgánicos adecuadamente empleados son materiales

orgánicos normalmente líquidos que no hierven en las condiciones de polimerización empleadas y que forman una solución con el monómero (3) polimerizable y el polímero preparado a partir de los mismos. Los diluyentes líquidos orgánicos representativos incluyen hidrocarburos aromáticos (y aromáticos sustituidos de manera inerte) tales como tolueno, benceno, etil benceno y xileno; alifáticos saturados, saturados o sustituidos de manera inerte, que tienen cadenas ya sea rectas o ramificadas de 5 o más átomos de carbono tales como heptano, hexano y octano; hidrocarburos alicíclicos o alicíclicos sustituidos de manera inerte que tienen 5 o 6 átomos de carbono tal como ciclohexano. Preferidos de tales diluyentes líquidos orgánicos son los aromáticos sustituidos de manera inerte, siendo los más preferidos etil benceno y xileno. En general, el líquido orgánico se emplea en cantidades suficientes para mejorar la procesabilidad y transferencia de calor durante la polimerización, por ejemplo, características de flujo de la mezcla de polimerización. Tales cantidades variarán dependiendo del hule, monómero y diluyente empleados, el equipo de proceso y el grado de polimerización deseado. En general, si se emplea, la mezcla de reacción contendrá normalmente de dos a 30 por ciento en peso del diluyente con base en el peso total del hule, monómero y diluyente.

Durante la polimerización de la mezcla de reacción resultante, las condiciones de polimerización se mantienen de tal manera que ocurre subsecuentemente la inversión de fase. Bajo tales condiciones el monómero se polimeriza tanto con el hule (injetado) y separadamente (polímero libre),

dicho hule disuelto se convierte con esto injertado con una porción de monómero polimerizado. El resto del polímero libre, básicamente incompatible con el hule, forma una fase de polímero/monómero de volumen más pequeño discontinua dispersa en toda la fase continua del volumen más grande de la solución de monómero/hule (incluyendo el hule injertado).

Eventualmente, en un punto después que se han formado cantidades suficientes de polímero libre, el polímero libre se convierte de una fase discontinua dispersa en la fase continua del (de los) monómero(s) sin polimerizar, a través de un punto en donde no hay fases continua o discontinua distintas en la mezcla de polimerización, hasta una fase continua de polímero que tiene el hule disperso como partículas discretas a través de la misma. Conforme la fase de polímero/monómero se convierte en la fase de volumen más grande y por ende en la fase continua, el hule injertado forma una fase discontinua. Este es el punto en la polimerización cuando ocurre la inversión de fase y el hule se vuelve disperso en la forma de partículas a través de la fase continua de polímero que resulta en un producto que tiene partículas de hule dispersas en una matriz de polímero aromático de monovinilideno.

De preferencia, en la inversión de fase, el hule está suficientemente injertado de manera que las partículas de hule dispersas, siguiendo el dimensionado inicial, son capaces de retener esencialmente los mismos tamaños de partícula promedio y propiedades morfológicas en todo el resto del proceso de polimerización. En una modalidad

preferida, la cantidad de hule injertado es por lo menos 30 por ciento del hule total en la inversión de fase. El grado de injertado del hule de dieno en el punto de inversión de fase tiene un impacto significativo en las propiedades del polímero modificado con hule resultante producido. Generalmente, el número de injertos por cadena contribuye al tamaño de partícula, la estructura y la cantidad de polímero de matriz ocluida dentro de las partículas de hule. Niveles mayores de injertado resultan en mayor contenido de gel, una cantidad más grande de hule injertado y contenido de polímero injertado mayor y de matriz ocluida dentro de las partículas de hule. El contenido de gel incrementado es altamente deseable porque permite que se alcance un volumen incrementado de fase de hule. El volumen incrementado de fase de hule se puede alcanzar también usando un hule de polibutadieno de alto peso molecular, sin embargo, incrementando el peso molecular incrementa típicamente la viscosidad de la solución también, haciendo el manejo y procesamiento más difíciles. En general, el hule de mayor viscosidad en solución resultará en partículas de hule más grandes y el hule de baja viscosidad en solución resultarán en partículas de hule más pequeñas.

El control cuidadoso de retro-mezclado durante el proceso de polimerización es crítico para alcanzar el tamaño deseado de partícula de hule. En consecuencia, un aspecto esencial de la presente invención es que antes de la inversión de fase la polimerización debe proceder en una forma de tapón-flujo con una cantidad limitada o mínima de retro-

mezclado. El tamaño deseado de partícula de hule no será obtenido si la mezcla de reacción de polimerización se permite que se retro-mezcle extensivamente o, pero aún, totalmente. Por lo tanto, es preferible que se controle o limite el grado de retro-mezclado hasta un grado en que se pueda obtener el tamaño deseado de partícula de hule. El grado y tipo de control para la cantidad de retro-mezclado dependerá, en parte, de los aspectos geométricos del equipo que se emplee en el proceso de polimerización, el logro de tal control está completamente dentro de la capacidad de aquellos que son expertos en la técnica usando técnicas convencionales de control de proceso sin experimentación indebida.

Al preparar composiciones bimodales en la práctica de la presente invención el proceso de polimerización se debe conducir en condiciones tales que en el punto de inversión de fase, los componentes de alta y baja viscosidad en solución del hule forman grupos separados de partículas de hule que tienen diferentes tamaños promedio de partículas.

Los aspectos del proceso de polimerización que se utilizan para alcanzar la distribución de partícula de hule requerida incluye el uso de un iniciador químico promotor de injerto, tales como los iniciadores de peróxido incluyendo los perésteres, por ejemplo, peróxibenzoato de butilo terciario, peróxiacetato de butilo terciario, peróxido de dibenzoilo, y peróxido de dilauroilo, los peracetales, por ejemplo, 1,1-bis peroxiciclohexano de butilo terciario, 1,1-bis peroxi-3,3,5-trimetilciclohexano de butilo terciario, y peroxido

de di-cumilo, y los percarbonatos; y técnicas de iniciación fotoquímica. Los iniciadores preferidos incluyen peroxibenzoato de butilo terciario, 1,1-bis peroxiciclohexano de butilo terciario 1,1-bis peroxi-3,3,5-trimetil ciclohexano de butilo terciario y peroxiacetato de butilo terciario.

Los iniciadores pueden ser empleados en un rango de concentraciones dependiendo de una variedad de factores que incluyen el iniciador específico empleado, los niveles deseados de injerto de polímero y las condiciones en las cuales se conduce la polimerización en masa. Específicamente, en el proceso de polimerización en masa preferido para preparar polímeros reforzados con hule, se emplea de 50 a 2000, de preferencia de 100 a 1500 partes en peso del iniciador por millón de partes en peso de monómero lo que resulta en un producto que tiene partículas de hule dispersas en una matriz de polímero aromático de monovinilideno.

Con tal iniciador el injertado en el componente de alto peso molecular del hule es promovido y se forman injertos múltiples. Esto estabiliza estas moléculas de hule en las mezclas de reacción y facilita la separación de las moléculas de hule de alto peso molecular del hule de menor peso molecular. Esto contribuye a la formación de las partículas de hule más grandes.

El componente de menor peso molecular del hule, por otra parte, que es el menos injertado, tiende a formar las partículas más pequeñas algo más tarde de lo que se forman las partículas más grandes. También

es deseable facilitar la formación de partículas más pequeñas, separadas para proporcionar una cantidad incrementada de agitación a la mezcla de reacción durante y bastante después del punto de la inversión de fase. La inversión de fase tiene lugar usualmente en un punto en el proceso de polimerización donde la mezcla de reacción contiene un nivel de sólidos el cual, con base en por ciento en peso en la mezcla de reacción, es de 2.5 a 3 veces el contenido en peso del material de hule agregado. Por lo tanto, de preferencia se mantiene un nivel de agitación relativamente alto hasta un punto en el proceso de polimerización donde la mezcla de reacción contiene un nivel de sólidos el cual, con base en por ciento en peso en la mezcla de reacción, es por lo menos 3, de preferencia 4 veces el contenido en peso del material de hule agregado.

Por ejemplo, cuando se agrega de 5 a 10 por ciento en peso de hule a la mezcla de reacción, se mantiene agitación relativamente alta hasta que la mezcla de reacción contiene 30 por ciento en peso de sólidos. Como se usa en la presente, el término sólidos se refiere a los componentes poliméricos de la mezcla de reacción tal como el hule que se agregó inicialmente y el polímero aromático de monovinilideno que se ha formado.

Dependiendo del equipo de producción en particular puede haber también otros aspectos del proceso que se pueden utilizar para facilitar más la formación de la distribución específica de tamaño de partícula de hule.

En general, se emplean métodos continuos para polimerizar en masa el compuesto aromático de monovinilideno en la mezcla de reacción. En la práctica de la presente invención se prefiere generalmente utilizar un reactor de tipo torre con agitación, de flujo lineal, estratificado, aludido también como reactor de tipo tapón flujo. Tales reactores son bien conocidos. Ver, por ejemplo la Patente de E. U., No. 2,727,884.

Un aspecto importante de tales procesos de polimerización es que una porción significativa de la polimerización del monómero aromático de monovinilideno en la mezcla de reacción puede tener lugar en la presencia del hule disuelto. La inversión de fase y precipitación y dispersión de las partículas de hule no ocurren hasta después de suficiente injertado de polímero aromático de monovinilideno en el hule, lo cual tiene lugar principalmente cuando el hule está en solución.

Esta es una ventaja principal en la polimerización en reactores de tipo de tanque con agitación, completamente mezclados (no estratificados, no de tapón flujo) que son operados en un nivel predeterminado de conversión. Típicamente, debido a la presencia de niveles significativos del polímero aromático de monovinilideno ya polimerizado, el hule que puede ser disuelto en la corriente de alimentación a tal reactor, es inmediatamente dispersado como partículas antes de que pueda ocurrir la polimerización de injerto y, de manera más importante, antes de que se

puedan separar los componentes de alta y de baja viscosidad en solución de un material de hule apropiado y formar grupos separados de partículas de hule.

Además, el proceso de acuerdo con la presente invención se puede practicar ventajosamente en equipo estándar de proceso de polimerización en masa no capaces de otra manera de la preparación de polímeros aromáticos de monovinilideno con distribuciones bimodales de partículas de hule sin modificaciones significativas del equipo. Tal equipo estándar utiliza típicamente un suministro sencillo de la mezcla de reacción sin polimerizar que comprende una solución de hule, monómero, diluyente opcional y otros aditivos. La mezcla de reacción se polimeriza después conforme es procedente a través de uno o una serie de tales recipientes de reactor. Al final del recipiente de reactor (serie) el producto se remueve y se remueve el diluyente y cualquier monómero residual.

La mezcla de polimerización puede contener también otros materiales aditivos y/o auxiliares de polimerización tales como plastificantes o lubricantes tales como aceite mineral, estearato de butilo o ftalato de dietilo; estabilizadores incluyendo antioxidantes (por ejemplo, fenoles alquilados tales como di-ter-butil-p-cresol o fosfatos tal como fosfato de trisnonil fenilo); agente de transferencia de cadena, tal como un mercaptano de alquilo tal como n-dodecil mercaptano; o agentes de liberación de molde, por ejemplo, estearato de zinc; todos los dichos aditivos y/o

auxiliares de polimerización se agregan a la mezcla de reacción cuando es apropiado incluyendo antes, durante o después la polimerización.

El uso de un agente de transferencia de cadena es opcional y se emplea usualmente solamente en la producción de una composición o prepolímero que contiene partículas de hule de tamaño más grande (por ejemplo que tienen un tamaño de partícula promedio de por lo menos un micrómetro). Si se emplea, el agente de transferencia de cadena se emplea generalmente en una cantidad desde 0.001 hasta 0.5 por ciento en peso con base en el peso total de la mezcla de polimerización a la cual se agrega.

Las temperaturas a las cuales se conduce de manera más ventajosa la polimerización dependen de los componentes específicos, particularmente el iniciador, empleados, pero variarán generalmente de 60 a 190° C.

El entrelazamiento del hule en el producto resultante y la remoción de los monómeros sin reaccionar, así como cualquier diluyente de reacción, si se emplea, y otros materiales volátiles se conduce ventajosamente empleando técnicas convencionales.

El polímero aromático de monovinilideno modificado con hule de la presente invención tiene un equilibrio excelente de propiedades de impacto y módulo de tensión, que permite su uso en varias aplicaciones incluyendo aplicaciones de moldeo por inyección, aplicaciones de extrusión, aplicaciones de espuma incluyendo artículos grandes, electrónicos de

consumo, acondicionadores de aire, refrigeradores, congeladores, electrodomésticos pequeños, casetes, gabinetes de radio, televisión, estéreo, muebles y amueblamientos, juguetes, artículos domésticos, aplicaciones en edificios y construcción, calzado, aplicaciones médicas, embalaje, desechables tales como tambores giratorios, vasos, platos, tasas, tazones, cubertería, cuchillería, artículos moldeados por sople, paneles, láminas y películas de espuma.

EJEMPLOS

Los siguientes ejemplos se dan para ilustrar la presente invención con relación a los polímeros aromáticos de monovinilideno modificados con hule, y no deben interpretarse como limitativos de la invención en cualquier manera.

Se prepararon muestras de composiciones de polímero aromático de monovinilideno modificado con hule en una mini planta que tiene un sistema de tres reactores de tubo con agitación lineal. Cada reactor tenía un volumen interno de 2.5 L con una relación de L/D de 22, y un agitador con chavetas unido a la flecha. Cada reactor contenía tres zonas de temperatura que estaban calentadas eléctricamente. El sistema de reactor estaba controlado por computadora dentro de un rango angosto predefinido para asegurar la uniformidad. Después del tercer reactor, los polímeros parciales se desvolatilizaron con una extrusora para desvolatilizar, formados en hilos, cortados después para formar gránulos. Toda la prueba se hizo usando estos gránulos. La temperatura de la extrusora controló el grado de

entrelazamiento del hule. Generalmente temperaturas mayores resultaron en mayor grado de entrelazamiento.

Se agregó una cierta cantidad de la alimentación principal a la zona media del segundo reactor como una segunda adición para mejorar más el balance de dureza y rigidez de los productos. En alrededor del 20 por ciento, segundo nivel de adición, las propiedades fueron usualmente óptimas. Si estos experimentos fueran a ser repetidos sin segunda adición, los valores serían proporcionalmente menores, pero tendrían la misma clasificación relativa en términos de balance de dureza y rigidez.

Se agregó NDm (n-dodecil mercaptano) al segundo reactor como un agente de transferencia de cadena para mantener el régimen de flujo de fundido de los productos finales.

En total se usaron tres conjuntos de hules. Como un control, (es decir, un ejemplo comparativo) se usó un hule dieno estándar de bajo cis de Bayer AG BUNA 640 (ejemplo 1). Un hule de alto cis que tiene una distribución bimodal de peso molecular disponible de UBE Industries de Japón bajo la marca registrada UBE 23H se usó para los ejemplos 2 y 3. En el cuarto ejemplo de la presente invención, se preparó una mezcla bimodal mediante mezclado de solución *in situ* de dos hules disponibles comercialmente de The Dow Chemical Company, bajo la marca registrada de 1202B (peso molecular menor) y 1202J (peso molecular más alto). Las cantidades se dan en los ejemplos.

Las mediciones de ciertas propiedades físicas y métodos de prueba correspondientes fueron los siguientes:

Propiedad	Método	Unidades	Observaciones
Impacto Izod	ASTM D256-93A	J/m	Barras moldeadas por inyección
Impacto Charpy	ISO 179-2C-82	kJ/m ²	Barras moldeadas por inyección
Deformación por tensión	ASTM D638M-93	Mpa	Barras moldeadas por inyección (5 mm/min)
Ruptura por Tensión	ASTM D638M-93	Mpa	Barras moldeadas por inyección (5 mm/min)
Elongación	ASTM D638M-93	Por ciento	Barras moldeadas por inyección (5 mm/min)
Módulo de Tensión (módulo-E)	ASTM D638	N/mm ²	Barras moldeadas por inyección (1 mm/min)
MFR	ASTM D1238-94	° C	
Vicat	ASTM D1525-91	g	Barras moldeadas por inyección
Mw y Mn	GPC	g/mol	
Tamaño de partícula de hule (RPS)	Tubo Coulter de 50 micrones	µm	
Contenido de Hule	Balance de Masa	Por ciento	
Contenido de M.O.	Cromatografía líquida	Por ciento	
Sólidos	Gravimétrico	Por ciento	

En general, los resultados de los experimentos demuestran claramente que los ejemplos de la presente invención proporcionan un mejor balance de dureza y rigidez a pesar de tener un régimen de flujo de fundido algo mayor que el ejemplo comparativo.

A un tamaño de partícula y composición de hule similares, los ejemplos de la presente invención proporcionan valores de impacto Charpy e Izod más altos así como resistencia a la deformación por tensión y módulo de tensión mayores.

Variable Fecha		07/24/1999	07/22/1999	07/28/1999	05/26/2000
		Ej. comp. 1	Ejemplo 1	Ejemplo 2	Ejemplo 3
Régimen Alimentación Lineal g/h		1000	1000	1000	1080
Segunda Adición g/h		200	200	200	120
Por ciento segunda adición %		20	20	20	10
Régimen Alimentación Total g/h		1200	1200	1200	1200
Reactor Lineal	Z1-L	111	111	111	110
	Z2-L	115	115	115	113
	Z3-L	119	119	119	121
	Z4-L	126	126	126	127
	Z5-L	135	135	135	133
	Z6-L	145	145	145	142
	Z7-L	155	155	155	148
	Z8-L	162	162	162	155
	Z9-L	170	170	170	160
Agitación/rpm	STR1	150	225	225	175
	STR2	60	60	60	60
	STR3	40	40	40	40

Condiciones Desvolatilización					
Barril Medio/Tornillo T	C	240	240	240	240
Segunda Cámara Vacío T	C	230	230	230	230
Barril Final/Tornillo T	C	220	220	220	220
Adiciones					
Iniciador DP275/ppm	SM12	380	380	380	465
NDM a segundo reactor/ppm	SM13	1200	1200	1200	1150
EB/por ciento	Alim.	7	7	7	7
M.O./por ciento	Alim.	0.8	0.8	0.8	0.4
Irganox 1076/Pppm	Alim.	1000	1000	1000	1000
Hule HX-528/AX-640 A	‡	5.75			
Ubepol Br 23 HB	‡		5.75	5.75	
1202B	‡				2.8
1202J	‡				2.8
Parámetros de Control de Proceso					
Sólidos/por ciento	STR1	34.7	36.8	35.8	35.7
	STR2	60.9	61.8	59.5	59.8
	Conv.	83.1	82.4	82.9	81.6
Propiedades de Producto Final					
R.P.S. media/µm (Coulter) (tubo 50 µm) (1)		2.80	3.00	2.70	2.30
Mw/g/mol		178700	187000	187200	185500
Mn/g/mol		65900	68100	69600	69600
Polidispersidad		2.71	2.75	2.69	2.67
M.F.R./g/10 min		4.90	5.80	5.20	5.20
Impacto Charpy/kJ/m²		6.9	7.6	7.6	10.7
Izod/J/m		86	107	102	109
Vicat/C		102.1	101.8	101.7	103.7
Deformación Tensión/Mpa		24.3	23.7	23.9	25.1
Ruptura Tensión/Mpa		23.8	23.1	23.2	21.8
Elongación/por ciento		47.2	58.1	57.4	26.9
Módulo Tensión/N/mm²		1938	2146	2183	2201
Contenido Aceite Mineral/por ciento		0.9	1.0	1.0	0.5
Contenido Hule/por ciento (balance masa)		6.9	7.0	6.9	6.9

La siguiente Tabla tiene la información específica de hule. Está basada en estándares de poliestireno y no se hace corrección de calibración universal.

Las viscosidades en solución se miden en monómero de estireno al 5 por ciento en peso de solución de hule a 23° C. La información del componente de UBE23H se calcula a partir de gráficas globales de GPC y es estimada. También, las viscosidades en solución para los componentes de UBE23H son estimadas con base en relaciones conocidas de MW vs viscosidad de la solución. Los resultados están expresados en centiPoise (cP).

ID muestra			Mediciones Dow (estándares PS)					Viscosidad de sol.
			Mw	Mn	Mp	Mz	PDI	cPoise
1202B#182 BCP 817 lote 81116A			426400	134700	224800	1114200	3.2	40.6
1202J#139 BCP 820 lote 90921A			661800	267400	539600	1393600	2.5	275.1
Dieno 55 BUNA 640			485000	222000	369		2.2	170
UBE23H global			576300	151351	824500	1430300	3.8	155
Componente bajo MW UBE23H			165000	70000	145000		2.3	8
Componente alto MW UBE23H			1020000					1100

REIVINDICACIONES

1. Un polímero aromático de monovinilideno modificado con hule que comprende:

- a) una matriz de polímero aromático de monovinilideno,
- b) partículas de hule dispersas en esa, caracterizada porque las partículas de hule se producen a partir de un hule dieno que tiene I) de 20 a 80 por ciento, con base en el peso total de dichas partículas de hule, de un componente de alta viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 110 hasta 500 centipoise y II) de 80 a 20 por ciento, con base en el peso total de dichas partículas de hule, de un componente de baja viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 1 a 100 centipoise, caracterizada además porque la relación de viscosidad de solución del componente de alta viscosidad en solución a la viscosidad de solución de baja viscosidad en solución fluctúa desde 1.1 hasta 500, en donde ambos componentes I y II tienen un contenido de 1,4 cis de más de 30 por ciento, y III) el hule está injertado con polímero aromático de monovinilideno hasta el punto en que hay por lo menos 30 por ciento de polímero aromático de monovinilideno presente como injerto en el hule.

2. El polímero aromático de monovinilideno

modificado con hule de la reivindicación 1, en donde el componente de alta viscosidad en solución tiene un valor de viscosidad que fluctúa desde 120 hasta 450 centipoise, el componente de baja viscosidad en solución tiene un valor de viscosidad que fluctúa desde 5 a 95 centipoise, y la relación de viscosidad en solución es desde 1.26 hasta 90.

3. El polímero aromático de monovinilideno modificado con hule de la reivindicación 1, en donde el componente de alta viscosidad en solución tiene un valor de viscosidad que fluctúa desde 150 hasta 430 centipoise, el componente de baja viscosidad en solución tiene un valor de viscosidad que fluctúa desde 20 a 85 centipoise, y la relación de viscosidad en solución es desde 1.76 hasta 21.5.

4. El polímero aromático de monovinilideno modificado con hule de la reivindicación 1, en donde la cantidad de hule en dicho polímero es de 2 a 20 por ciento con base en el peso total de dicho polímero.

5. El polímero aromático de monovinilideno modificado con hule de la reivindicación 1, en donde las partículas están dispersas en la forma de partículas pequeñas y grandes, en donde el diámetro promedio de volumen de partícula de las partículas pequeñas es desde 0.1 a 2 micrómetros y el diámetro promedio de volumen de partícula de las partículas grandes es desde 2 a 6 micrómetros.

6. El polímero aromático de monovinilideno modificado con hule de la reivindicación 1, en donde el polímero aromático de monovinilideno es poliestireno.

7. El polímero aromático de monovinilideno modificado con hule de la reivindicación 1, en donde el hule es polibutadieno.

8. El polímero aromático de monovinilideno modificado con hule de la reivindicación 1, en donde el hule dieno es ramificado.

9. El polímero aromático de monovinilideno modificado con hule de la reivindicación 1, en donde el hule dieno tiene un contenido de 1,4 cis de más de 30 por ciento.

10. Un proceso para preparar un polímero aromático de monovinilideno modificado con hule que comprende los pasos de: (a) suministrar continuamente una mezcla de reacción que comprende un monómero aromático de monovinilideno y un hule dieno disuelto a un medio de reactor, (b) polimerizar continuamente el monómero aromático de monovinilideno en la presencia del hule dieno disuelto en el medio de reactor bajo condiciones por las que ocurre subsecuentemente la inversión de fase, (c) remover continuamente del medio de reactor un polímero aromático de monovinilideno reforzado con hule dieno, dicho proceso está caracterizado porque: (d) el hule dieno que está disuelto en la mezcla de reacción

tiene I) de 20 a 80 por ciento, con base en el peso total de dicho hule dieno, de un componente de alta viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 120 hasta 500 centipoise y II) de 80 a 20 por ciento, con base en el peso total de dicho hule dieno, de un componente de baja viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 1 a 100 centipoise, caracterizado además porque la relación de viscosidad de solución del componente de alta viscosidad en solución a la viscosidad de solución de baja viscosidad en solución fluctúa desde 1.2 hasta 500, en donde ambos componentes I y II tienen un contenido de 1,4 cis de más de más 30 y, opcionalmente, (e) las condiciones de proceso antes de la inversión de fase se ajustan para producir diferentes grupos de partículas de hule dieno a partir de los componentes de alta y baja viscosidades en solución del hule dieno, cada grupo teniendo un tamaño promedio diferente de partícula de hule.

11. El proceso de la reivindicación 1, en donde el polímero aromático de monovinilideno es poliestireno.

12. El proceso de la reivindicación 10, en donde el hule es polibutadieno.

13. El proceso de la reivindicación 10, en donde el hule dieno es ramificado.

14. El proceso de la reivindicación 10, en donde

el hule dieno tiene un contenido de 1,4 cis de más de 30 por ciento.

15. Un artículo producido a partir del polímero .
modificado con hule de la reivindicación 1.

RESUMEN

Se describen polímeros aromáticos de monovinilideno modificados con hule con dureza y rigidez modificadas así como también un proceso para la preparación de los mismos. El polímero que comprende:

- a) una matriz de polímero aromático de monovinilideno,
- b) partículas de hule dispersas en esa, caracterizada porque las partículas de hule se producen a partir de un hule dieno que tiene I) de 20 a 80 por ciento, con base en el peso total de dichas partículas de hule, de un componente de alta viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 110 hasta 500 centipoise y II) de 80 a 20 por ciento, con base en el peso total de dichas partículas de hule, de un componente de baja viscosidad en solución que tiene un valor de viscosidad que fluctúa desde 1 a 100 centipoise, caracterizada además porque la relación de viscosidad de solución del componente de alta viscosidad en solución a la viscosidad de solución de baja viscosidad en solución fluctúa desde 1.1 hasta 500, en donde ambos componentes I y II tienen un contenido de 1,4 cis de más de 30 por ciento, y III) el hule está injertado con polímero aromático de monovinilideno hasta el punto en que hay por lo menos 30 por ciento de polímero aromático de monovinilideno presente como injertos en el hule.

Representación y Poder con autenticación notarial y Apostille para patentes, modelos de utilidad, diseños industriales, marcas de fábrica, nombres comerciales, enseñas, nombres de dominio, lemas comerciales, licencias.

Representation and Power-of-Attorney with notarial authentication and Apostille for patents, utility models, industrial designs, trademarks, commercial names, trade emblems, domain names, slogans, licenses.

REPRESENTACION Y PODER

REPRESENTATION AND POWER-OF-ATTORNEY

Yo (nosotros), abajo firmado (s)/I (we), the undersigned

DOW GLOBAL TECHNOLOGIES INC.

domiciliado (s) en/of 1790 Building, Washington Street

Midland, Michigan 48676, U.S.A.

por el presente nombramos a EMILIO FERRERO, tpa. 31929; GONZALO PERDOMO, tpa. 831; LUZ CLEMENCIA DE PAEZ, tpa. 23555; y GERMAN CAVELIER, tpa. 832, domiciliados en la Carrera 4a N° 72-35, Bogotá, Colombia, en obediencia a lo dispuesto en el párrafo 1o del Artículo 543 del Código de Comercio, el primero como principal y los demás como suplentes, en su orden, como mis (nuestros) representantes en todos los asuntos de propiedad industrial con facultad para recibir notificaciones y nombrar apoderados judiciales o extrajudiciales. El primer representante suplente reemplazará al principal en caso de ausencia o impedimento temporal o definitivo de aquél. La misma regla se aplicará cuando el segundo representante suplente haya de reemplazar al primero, o el tercero al segundo. En tales casos, el representante principal, o el primero, o segundo suplente, en su caso, o ambos, declararán su intención de no ejercer la representación mediante declaración autenticada por Notario Público en Colombia, o por Notario u otro Funcionario Público, o Cónsul de Colombia, en el extranjero; y si se tratare de impedimento, con el certificado respectivo. Si alguno de los nombrados faltare definitivamente, el siguiente tomará su lugar. Cuando cesare la ausencia o impedimento del representante principal, o de su primero o segundo suplentes, en su caso, podrán ejercer la representación, en su orden, uno u otros según el caso, asumiéndola por el solo hecho de ejercerla, cesando en ese momento el ejercicio de la representación por el primero, segundo o tercer suplente en su caso.

Además, confiero (conferimos) poder a los abogados arriba nombrados, para obtener la protección de mi (nuestra) propiedad industrial y contra la competencia desleal, a cuyo efecto autorizo (amos) a los dichos apoderados para que me (nos) representen ante cualesquiera entidades o personas, ejerzan o no jurisdicción, especialmente ante las del orden administrativo, contencioso-administrativo y judicial, así como los tribunales de arbitramento, en todo lo concerniente a los siguientes asuntos: a) Obtención de patentes de invención, modelos de utilidad y diseños industriales; el registro de marcas de fábrica, colectivas, defensivas, de servicio, lemas comerciales, nombres comerciales, enseñas, nombres de dominio, variedades vegetales y denominaciones de origen; su renovación, traspaso, cambio de nombre o domicilio, cancelación voluntaria; y el registro de licencias de uso de esos derechos; b) Las acciones de competencia desleal, protección del consumidor, oposiciones u observaciones, cancelación administrativa y judicial, nulidad, medidas cautelares, concesión de licencias, la tutela, la protección de secretos industriales, y en general los juicios civiles, penales, administrativos o contencioso administrativos relacionados con

in due compliance with the terms of paragraph 1st. of article 543 of the Commercial Code, do hereby appoint EMILIO FERRERO, tpa. 31929; GONZALO PERDOMO, tpa. 831; LUZ CLEMENCIA DE PAEZ, tpa. 23555 and GERMAN CAVELIER, tpa. 832, domiciled at Carrera 4a N° 72 35, Bogotá, Colombia, the first as principal and the others as alternates, in the order of their appointment, as our representatives for all industrial property matters with faculty to receive notifications and to appoint attorneys in and out of Court. The first alternate shall replace the principal in case of his absence or of temporal or definitive impediment. The same rule will apply when the second alternate representative is to replace the first one, or when the third is to replace the first or second alternates in their turn, or both of them, second. In such cases, the principal representative, or the first or second alternates in their turn, or both of them, shall state their intention not to act as representatives through a declaration given before a Notary Public in Colombia, or before a Notary or another Public Official or a Colombian Consul abroad; and in case of impediment, the appropriate certificate shall suffice. If any of the appointees were to be definitely absent, the following alternate shall take his place. When the absence or impediment of the principal representative, or of the first or second alternate in their turn ceases, the representation can be taken again in their sequence, by the principal, the first or second alternate depending on case, and the mere fact or its exercise will suffice. The exercise of the representation by the first, second or third alternates is hereby authorized. In addition, we grant a Power of Attorney to the attorneys at law named attorneys at law so that they may obtain the protection of my (our) industrial property and against unfair competition for which purpose I (we) authorize the said attorneys to represent me (us) before any authorities or persons, with or without jurisdiction, especially those administrative, administrative-contencioso and judicial, before Arbitration Court, in all matters concerning the following: a) Obtainment of patents, utility models and industrial designs; the registration of trademarks, collective, defensive and service marks, slogans, commercial names, trade emblems, domain names, vegetal varieties and denominations of origin; its renewal, assignment, change of name or domicile, voluntary cancellation; and the registration of licenses of use of the above rights; b) Actions of unfair competition, protection to the consumer, oppositions or observations, administrative or Court cancellation, nullity, infringement, granting of licenses, the action for writ mandamus, the protection of trade secrets, and in general the civil, penal, and administrative suits relating to those rights; actions and suits

estos derechos; acciones y procesos que promovamos o que nos promuevan. Y para que en todos los asuntos arriba determinados, puedan sustituir este mandato, transigir, conciliar, admitir los hechos del proceso, desistir, cancelar, recibir, renunciar, y ratificar los actos de agentes oficiosos.

instituted by me (us) or against me (us). And that in all cases they may substitute this Power of Attorney, compromise, concede the facts of the case, desist, cancel, receive, resign, and ratify acts done by my representatives without a power of attorney.

Dado y firmado hoy/Given and signed this _____
en/in Midland, Michigan 48674, U.S.A.
por/by GRAHAM E. TAYLOR
Vice President
Firma  Signature



State of Michigan



DEPARTMENT OF STATE

APOSTILLE

(Convention de La Haye du 5 Octobre 1961)

1. Country: **UNITED STATES OF AMERICA**

This public document

2. has been signed by: **Ann Heritier**

3. acting in the capacity of: **Michigan Notary Public**

4. bears the seal of: **Ann Heritier**

Bay County, Michigan

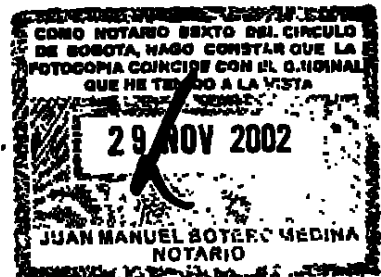
CERTIFIED:

5. at **Lansing, Michigan** 6. the **18th of June, 2002**

7. by **Secretary of State, State of Michigan**

8. NO. **15229F-02**

9. Seal/Stamp:



10. Signature:

Candice S. Miller

Candice S. Miller

This certification attests only to the authenticity of the signature of the official who signed the affixed document, the capacity in which that official acted, and where appropriate, the identity of the seal or stamp which the document bears. This certification is not intended to imply that the contents of the document are correct, nor that they have the approval of the State of Michigan.

CERTIFICADO NOTARIAL (INDIVIDUO)

A los _____ días del mes de _____
de 200__ ante mí, Notario Público o Funcionario Autorizado
de _____
compareció(eron) personalmente _____

a quien(es) doy fe de conocer y me consta que es(son) la(s)
persona(s) firmante(s) del documento que precede, y quien(es)
tiene(n) capacidad legal para otorgarlo

Notario Público o Funcionario Autorizado -- Notary Public or Attesting Official

CERTIFICADO NOTARIAL (SOCIEDAD)

Hoy _____ de _____ de 200__
Compareció(eron) ante mí

Graham E. Taylor

quien(es) conozco personalmente y que firma(n) este
documento en representación de la Sociedad/compañía
denominada DOW GLOBAL TECHNOLOGIES INC.

Significo:

1. Que he visto los siguientes documentos: *
• Artículos de Constitución fechados Abril 6, 1993.
• Político de Autorización de dicha compañía
fechado el 11 de febrero, 2002.
2. Que dichos documentos prueban lo siguiente:

2.1. Que DOW GLOBAL TECHNOLOGIES INC.

es una Sociedad/Compañía legalmente constituida y existente
de acuerdo con las leyes del Estado de Delaware
EE.UU.

2.2. Que el domicilio de dicha Sociedad/Compañía es
1790 Building, Washington Street
Midland, Michigan, 48674. EE.UU.

2.3. Que el objeto u objetos para los cuales se otorga el presente
poder están comprendidos dentro del objeto social de la
mencionada Sociedad/Compañía.

2.4. Que el(los) Sr.(Sres.) Graham E. Taylor
está(n) autorizado(s) para otorgar el presente Poder.

Ciudad Midland

Estado Michigan

Hoy 7 Junio de 2002

Notario Público o Funcionario Autorizado -- Notary Public or Attesting Official

* Los documentos deben identificarse con fecha y origen

CAVELIER ABOGADOS

WPP0DE01-181 (MINUTA N°12.1.1.2.6 USA)

NOTARIAL CERTIFICATE (INDIVIDUAL)

87

On this _____ day of _____
200__ before me, a Notary Public or Attesting Official of _____
personally appeared _____

to me known, and known to me to be the person(s) who
executed that foregoing document, and who has(have) legal
capacity to execute it.

NOTARIAL CERTIFICATE (CORPORATION)

On this _____ day of _____ 200__
appeared before me

GRAHAM E. TAYLOR

who(m) I know personally and who(m) signed this document as
representative(s) of the Corporation/Company named DOW
GLOBAL TECHNOLOGIES INC.

I certify:

1. That I have seen the following documents: *
Articles of Incorporation dated April 6, 1993

Authorization Policy of said Corporation
dated February 11, 2002
2. That the above documents duly prove the following:

2.1. That DOW GLOBAL TECHNOLOGIES INC.

is a Corporation/Company legally constituted and in existence
in accordance with the laws The State of Delaware, U.S.A.

2.2. That the domicile of said Corporation/Company is
1790 Building, Washington Street
Midland, Michigan, 48674. U.S.A.

2.3. That the purpose or purposes for which the present Power
of Attorney is granted are comprised within the corporation
purposes set forth in the charter of the mentioned
Corporation/Company.

2.4. That Mr.(Messrs.) GRAHAM E. TAYLOR
is(are) authorized to grant the present Power of Attorney.

City Midland

State Michigan

This 7 day of June 2002

ANN HERITIER

NOTARY PUBLIC, BAY COUNTY, MICHIGAN

ACTING IN MIDLAND COUNTY, MICHIGAN

MY COMMISSION EXPIRES DECEMBER 3, 2002

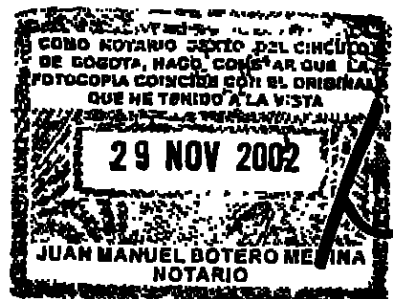
* Documents must be identified with date and origin

APOSTILLE
(Convention de La Haye du 5 octobre 1961)

1. Country:
- . This public document
2. has been signed by
3. acting in the capacity of
4. bears the seal/stamp of

Certified

5. at 6. the
7. by
8. No.
9. Seal/stamp 10. Signature

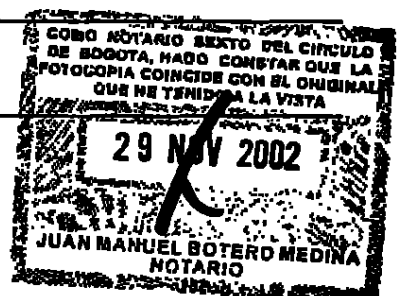


TRADUCCIÓN OFICIAL No. 29.10/02b realizada por Diego Vargas, Traductor Oficial, Resolución No. 0001 de 1999 del Ministerio de Justicia y registrado ante el Ministerio de Relaciones Exteriores de Colombia.

A continuación se traducen los sellos y legalizaciones que de un documento de Representación y Poder escrito en inglés y español por medio del cual DOW GLOBAL TECHNOLOGIES INC., domiciliado en el 1790 Building, Washington Street, Midland, Michigan 48674, Estados Unidos de América otorga derechos de representación y poder a los Doctores EMILIO FERRERO, tpa. 31929; GONZALO PERDOMO, tpa. 831; LUZ CLEMENCIA DE PÁEZ, tpa. 23555 y GERMÁN CAVELIER, tpa. 832.

Dado y firmado hoy _____
en Midland, Michigan 48674, Estados Unidos de América
por GRAHAM E. TAYLOR
Vicepresidente

Firma Firma Ilegible



CERTIFICADO NOTARIAL (SOCIEDAD) del 7 de junio de 2002 donde se certifica la firma anterior del Señor Graham E. Taylor en representación de DOW GLOBAL TECHNOLOGIES INC. Adicionalmente se certifica que la anterior sociedad fue constituida y es actualmente existente de acuerdo con las leyes del Estado de Delaware, que su domicilio es el 1790 Building, Washington Street, Midland, Michigan 48674, Estados Unidos de América y que el Señor Graham E. Taylor está autorizado para otorgar el presente poder.

Diego F. Vargas
DIEGO F. VARGAS
TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL - INGLES - INGLES - ESPAÑOL
RES. 0001 DE ENERO 4 DE 1999
MINISTERIO DE JUSTICIA

Dado y firmado en Midland, Estado de Michigan el 7 de Junio de 2002.

Notario Público o Funcionario Autorizado Firma Ilegible

ANN HERITIER
NOTARIO PÚBLICO, CONDADO DE BAY, MICHIGAN
ACTUANDO EN EL CONDADO DE MIDLAND, MICHIGAN
MÍ COMISIÓN VENCE EL 3 DE DICIEMBRE DE 2002

(RESPALDO)
Formato de Apostille sin diligenciar

ESTADO DE MICHIGAN

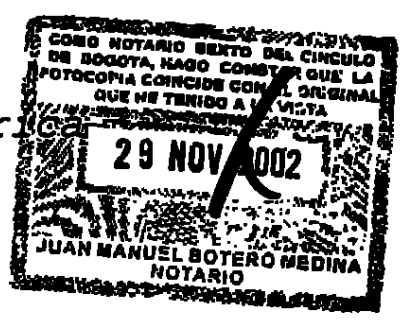
ESCUDO DE ARMAS

DEPARTAMENTO DE ESTADO

APOSTILLA

(Convention de La Haye du 5 Octubre 1961)

1. País: Estados Unidos de América



Este documento público

- 2. ha sido firmado por Ann Heritier
- 3. actuando en capacidad de: Notario Público de Michigan
- 4. lleva el sello/estampilla de: Ann Heritier

Condado de Bay, Michigan

CERTIFICADO:

- 5. en Lansing, Michigan
- 6. el 18 de Junio de 2001
- 7. por el Secretario de Estado, Estado de Michigan

Diego F. Varga
DIEGO F. VARGA
TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL - INGLES - INGLES - ESPAÑOL
RES. 0001 DE ENERO 4 DE 1999
MINISTERIO DE JUSTICIA

8. NO. 15229F-02

9. Sello/estampilla:

10. Firma:



Firma ilegible

Candice S. Miller

Esta certificación solo testifica la autenticidad del oficial que firmó el documento adjunto, la calidad en la cual el funcionario actúa, y en donde sea adecuado, la identidad del sello o estampilla que porta el documento. Esta Certificación no tiene el propósito de dar a entender que el contenido del documento es correcto o que tiene la aprobación del estado de Michigan.

Aparece un sello dorado autoadhesivo en la esquina superior izquierda uniendo las cuatro hojas que componen este documento con la leyenda:

EL GRAN SELLO DEL ESTADO DE MICHIGAN

Es traducción fiel y completa de la cual se deja copia en esta oficina para su confrontación.

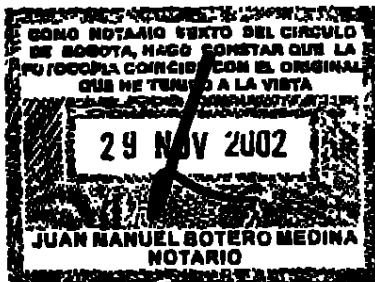
DVZ/ID-3930/WPCL002G/COLO 13518-841-001-7

NO SE ASUME
RESPONSABILIDAD DEL TEXTO

2002 NOV 29 A 11:19

DE LEGALIZACIONES
CENTRO DE BOGOTA D.C.

Diego F. Vargas
DIEGO F. VARGAS
TRADUCTOR E INTERPRETE OFICIAL
ESPAÑOL - INGLES - INGLES - ESPAÑOL
RES. 0001 DE ENERO 4 DE 1999
MINISTERIO DE JUSTICIA



MINISTERIO DE RELACIONES
EXTERIORES

532097

Diego Vargas
CUYA FIRMA APARECE EN EL
DOCUMENTO DESEDE EN
LAS FUNCIONES INDICADAS

3



91

Industria y Comercio

SUPERINTENDENCIA

SUPERINDUSTRIA Y COMERCIO
Radicacion : 02108710 00000000 Folios: 91
Fecha (AMB): 2002-11-29 17:24:01
Tramite : 011 PCT-PATENT 379 FASE NNCI 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 02 - 75,600
FECHA : NOVIEMBRE 13 DE 2002

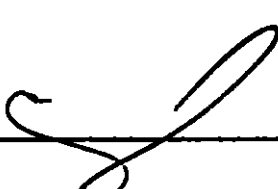
***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PBO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	3136955	13/11/2002	15,849,560.00

***** CONCEPTO *****

CANT. CONTABILITICO	CONCEPTO	TOTAL CONCEPTO
1 50005-01-01 SOLICITUDES	1 TRAMITES DE SOL. DE PATENTE DE IN	378,000.00
	TOTAL :	\$ 378,000.00

SON: TRESCIENTOS SETENTA Y OCHO MIL PESOS

RESPONSABLE : 

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

Cdo 13518-841-001-7

Carrera 13 No. 27-00 Pisos 5, 7 y 10
Conmutador 382 0840
Fax 350 5220
E-mail: info@sic.gov.co
www.sic.gov.co
Bogotá, D.C., Colombia

REQUISITOS NECESARIOS PARA PRESENTACION Y AGILIZACION DEL TRAMITE

	USUARIO	RADICADOR
PATENTE DE INVENCION ✓ MODELO DE UTILIDAD	()	()
- Indicación de que se solicita la concesión de una patente.	()	()
- Datos de identificación del solicitante o de la persona que se presenta la solicitud.	()	()
- Descripción de la invención.	()	()
- Dibujos de ser estos pertinentes.	()	()
- Comprobante de Pago de las tasas establecidas.	()	()

COMPLETA () INCOMPLETA ()

DISEÑO INDUSTRIAL ()

- Indicación de que se solicita el registro de Diseño Industrial	()	()
- Datos de identificación del solicitante o de la persona que presenta la solicitud.	()	()
- Representación gráfica y fotográfica del Diseño Industrial o muestra del Material que incorpora el diseño.	()	()
- Comprobante de pago de las tasas establecidas	()	()

COMPLETA () INCOMPLETA ()

ESQUEMA DE TRAZADO ()

- Indicación de que solicita el registro de un Esquema de trazado.	()	()
- Datos de identificación del solicitante o de la persona que presenta La solicitud.	()	()
- Representación gráfica del esquema de trazado	()	()
- Comprobante de pago de las tasas establecidas.	()	()

COMPLETA () INCOMPLETA ()

Firma Responsable: 

Fecha: