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Superintendencia de Industria y Comercio

División de Nuevas Creaciones

E. S. D.

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 05-111200-00007-0000

Fecha: 2009-09-14 15:18:20 Dep. 2020 NUECREACION
Tra. 11 PATENTEIYII Eve: 379 FASENACIONALI
Act. 444 RESPUESTAREQUE Folios: 52

Ref: Expediente No. 05-111.200

Solicitud de registro de patente de invención
denominada "AUMENTO DEL RENDIMIENTO DEL
REACTOR DE POLIMERIZACIÓN USANDO UN SISTEMA
DE INICIADOR ESPECIFICO"

Solicitante: AKZO NOBEL N.V.

Yo Darío Cárdenas Navas, identificado como aparece al pie de mi firma y obrando en mi condición de apoderado de la sociedad **AKZO NOBEL N.V.**, solicitante de la patente en referencia, a continuación doy respuesta al Oficio No. **5187**, mediante el cual se presenta el Concepto Técnico No. **944**, que fue notificado por fijación en lista el 08 de Mayo de 2.009.

1. Presentación de un capítulo reivindicatorio corregido que permita cumplir con las exigencias del Artículo 30 de la Decisión 486.

En vista de las objeciones presentadas en el numeral 3.1. Reivindicaciones (artículo 30 D 486), en donde se objeta la claridad de algunas expresiones utilizadas dentro de las reivindicaciones 1 y 9, al afirmar que:

- *"En la reivindicación independiente 1 se enuncia un proceso para polimerizar uno o más monómeros, pero la caracterización adolece de graves problemas de definición de la materia de la invención como se detalla a continuación:*

En primer lugar, la expresión "...se usa a lo sumo el 90% en moles de la cantidad que se puede utilizar de manera segura..." no está mencionando tangiblemente cual es esa cantidad del primer iniciador, pues tampoco se define cual es la que se puede utilizar de manera segura. Por lo tanto, se debería incluir la cantidad.

En segundo lugar, se hace mención simplemente de **"...un primer iniciador..."** mas no se define su naturaleza química. Esta expresión es demasiado amplia y prácticamente indefinida pues existen innumerables iniciadores de reacción de monómeros. Lo mismo sucede con la expresión **"...un segundo iniciador..."**. Por lo tanto, se debería definir la naturaleza química de los iniciadores.

En tercer lugar, se dice que el segundo iniciador se dosifica **"...por lo menos parcialmente después del inicio de la polimerización, en una cantidad, y preferiblemente a una tasa variable..."**. Esta expresión no define ni la cantidad ni la variación de la tasa y por lo tanto, la dosificación esta indefinida. Entonces, se debería incluir la cantidad y la tasa.

Por último, se menciona que **"...por lo menos el 92% de la capacidad máxima de enfriamiento se utiliza durante por lo menos un tiempo en donde por lo menos el 10% en peso del monómero se polimeriza."**

Esta expresión enuncia un resultado obtenido y no define la invención. Por lo tanto, debería eliminarse de la reivindicación.

Hasta este momento, se puede observar que existen problemas en la definición del proceso de la reivindicación 1, pues no se menciona las etapas de proceso, tampoco la naturaleza química de los iniciadores, tampoco se define la cantidad de los iniciadores y menos las condiciones de la dosificación. Por ello se le recomienda al señor solicitante modificar la reivindicación 1 de forma que se tengan en cuenta todas las observaciones realizadas en este numeral.

- En la reivindicación 9 se menciona que el reactor de polimerización tiene un volumen de 15 m^3 o más. No obstante, dicha característica corresponde a un aparato y no a una especificación de proceso. Por lo tanto, no es coherente que se plantee un proceso y se especifique un aparato, entonces se debe eliminar dicha reivindicación.

- *En conclusión, las reivindicaciones 1 y 9 no estaría definiendo claramente la materia de la invención y por ello no cumple con el requisito del artículo 30 de la Decisión 486."*

Atentamente, me permito manifestar a ese Despacho, que **es deseo del solicitante** modificar el capítulo reivindicatorio que se encuentra actualmente bajo estudio, con el fin de **superar las objeciones presentadas con respecto a las reivindicaciones 1 y 9, y de realzar las características novedosas e inventivas del proceso de polimerización reivindicado**. Por lo anterior, se han realizado las siguientes modificaciones:

- Con el fin de aclarar el significado de la expresión objetada: **"...se usa a lo sumo el 90% en moles de la cantidad que se puede utilizar de manera segura..."**, se ha incluido en la reivindicación 1, inmediatamente después de la expresión objetada, la siguiente expresión aclaratoria: **"donde la cantidad que se puede utilizar de manera segura es la cantidad máxima de dicho iniciador que puede ser usada en un proceso idéntico que se corre a la máxima capacidad de enfriamiento y donde la temperatura no excede la temperatura puesta o deseada"**. El sustento requerido para esta modificación se encuentra en forma apropiada en la página 4, líneas 22 a 26 de la descripción originalmente presentada ante ese Despacho.
- En segundo lugar, para aclarar las expresiones **"...un primer iniciador..."** y **"...un segundo iniciador..."**, se ha incluido al final de la reivindicación 1 modificada, la expresión: **"...y donde los iniciadores son seleccionados de peróxidos orgánicos e iniciadores azo- convencionales"**. El sustento requerido para esta modificación se encuentra en forma apropiada en la página 8, líneas 6 a 25 de la descripción originalmente presentada ante ese Despacho.
- En tercer lugar, frente a la objeción presentada a la expresión **"...en una cantidad, y preferiblemente a una tasa variable..."**, se ha eliminado de dicha expresión el aparte que dice: **"...y**

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preferiblemente a una tasa variable...”, con lo cual se hace mucho más claro el proceso reclamado en la reivindicación 1 modificada.

- Finalmente, con respecto a la objeción presentada a la materia objeto de la reivindicación 9, me permito manifestar a ese Despacho **que es deseo del solicitante cancelar la materia objeto de dicha reivindicación 9.**

En vista de lo anterior, atentamente me permito manifestar a ese Despacho que las modificaciones realizadas en el capítulo reivindicatorio bajo estudio, **no amplían de ninguna manera el alcance de la invención.** Por el contrario, dichas modificaciones son una limitación adicional al alcance de la invención, que tienen como finalidad aclarar algunos aspectos de la invención para propiciar un mejor entendimiento y puesta en marcha del novedoso proceso reclamado en el nuevo capítulo reivindicatorio presentado.

1.1 ACLARACIONES

De otra parte, también es deseo del solicitante aclarar a ese Despacho, que el empleo de la expresión objetada **“...se usa a lo sumo el 90% en moles de la cantidad que se puede utilizar de manera segura...”**, no le resta de ninguna manera claridad al proceso ahora reclamado, toda vez es del conocimiento normal de una persona que trabaja habitualmente en la producción de polímeros, que la cantidad del primer iniciador depende principalmente de dos variables, que son: a) el tipo de reactor y, b) las condiciones (temperatura, presión, etc.) a las que se llevará a cabo el proceso.

En vista de lo anterior, resulta imposible limitar las reivindicaciones a una cantidad específica de dicho iniciador. Sin embargo, teniendo en cuenta que el objetivo de la descripción es el de describir en forma clara, completa y suficiente la invención y de servir de sustento a las reivindicaciones, se puede encontrar en la descripción original de la presente solicitud, una clara enseñanza que le muestra a una persona medianamente versada en la técnica como se puede calcular dicha cantidad a ser usada del iniciador. Particularmente, en la página 4, líneas 22-26 (ver también, pagina 4, líneas

5 a 16 del documento **WO/2004/096871**), se explica en detalle que la cantidad de iniciador que es adicionado al inicio de la polimerización debe ser a lo sumo el 90% en peso de la cantidad máxima de dicho iniciador que puede ser usado en un proceso idéntico que se corre a la máxima capacidad de enfriamiento y donde la temperatura no excede la temperatura puesta o deseada (es decir, la temperatura de polimerización) debido a un exceso de calor de polimerización.

Entonces, resulta claro que a partir de lo revelado en el citado aparte de la descripción de la invención, una persona medianamente versada en la materia, fácilmente estaría en la capacidad de saber cuál sería la cantidad del primer iniciador, calculándola a partir de su conocimiento de la cantidad total de monómeros a ser polimerizados y de la cantidad máxima de iniciador que se requiere para polimerizar dicha cantidad total de monómeros.

De otra parte, también es deseo del solicitante aclarar a ese despacho, que de acuerdo con lo revelado en la solicitud de patente que se encuentra bajo estudio, no es necesario presentar una lista detallada de los compuestos específicos que pueden actuar como el **"primer iniciador"** y el **"segundo iniciador"**, toda vez que de acuerdo con lo revelado en la reivindicación 1, una persona medianamente versada en la materia estaría en capacidad de entender la naturaleza de los iniciadores que pueden ser empleados.

En efecto, al dirigir la atención a lo que se establece en la reivindicación 1, se puede ver que el segundo iniciador debe tener una vida media a la temperatura de polimerización de 0.0001 a 1.0 horas. Como consecuencia de lo anterior, es evidente que el primer iniciador, que es un iniciador más estable que el segundo, debe tener una vida media más larga que el segundo iniciador. Por lo tanto, es claro que la naturaleza de los iniciadores apropiados depende de la temperatura a la cual se va a realizar la polimerización y la elección de dicha temperatura de polimerización a su vez depende de: a) la naturaleza de los monómeros, y b) de las propiedades deseadas del polímero final que se desea obtener.

En consecuencia, es completamente claro que una persona medianamente versada en la materia estaría en la capacidad de calcular dichas cantidades del primer y segundo iniciadores, con el simple hecho de saber que tipo de polímero final desea, lo cual le indica las cantidades de monómeros a ser utilizadas, y a su vez la temperatura ideal de polimerización, con lo cual podría con la ayuda de la guía que se presenta en la descripción de la presente solicitud, así como en la publicación internacional de la misma solicitud (por ejemplo, pagina 7, líneas 4-27 del documento WO/2004/096871), seleccionar tanto cada uno de los iniciadores apropiados, como la cantidad de de cada uno de dichos iniciadores, para su caso particular.

Por todo lo anterior, la introducción de la expresión aclaratoria que se ha colocado al final de la reivindicación 1, permite superar completamente cualquier duda sobre la naturaleza de los mencionados primer y segundo iniciadores, los cuales se seleccionan de un peróxido orgánico y un iniciador azo - convencional apropiados para la polimerización (dependiendo de la temperatura a la cual se va a realizar dicho proceso, tal y como ya se ha mencionado). Además, de que las cantidades de dichos iniciadores también están perfectamente definidas, tal y como ya se ha mencionado anteriormente, y por lo tanto, de esta forma se superan las objeciones presentadas a la claridad de dichos términos por parte de ese Despacho.

Finalmente, con respecto a la observación de ese Despacho, según la cual la expresión **"...por lo menos el 92% de la capacidad máxima de enfriamiento se utiliza durante por lo menos un tiempo en donde por lo menos el 10% en peso del monómero se polimeriza."**, caracteriza la invención por un resultado a ser obtenido, el solicitante respetuosamente se permite manifestar que dicha caracterización mediante la cantidad de iniciador y el tiempo, corresponde a una característica del proceso y de ninguna manera se puede entender como un resultado a ser obtenido.

En efecto, si se dirige la atención a lo que reclama la reivindicación 1, se podrá notar que se describe que después del inicio de la polimerización se dosifica el segundo iniciador. Pero la dosificación del segundo iniciador no

toma lugar en un punto arbitrario del tiempo después de iniciar la polimerización, sino que dicha dosificación se lleva a cabo al menos parcialmente en un punto del tiempo entre el inicio de la polimerización y el punto en el cual 10% del monómero inicial ha sido polimerizado, de tal forma que en algún momento en el proceso de polimerización, por lo menos el 92% de la capacidad máxima de enfriamiento se utiliza durante por lo menos un tiempo en donde por lo menos el 10% del monómero es usado.

En particular, las ventajas del proceso de la presente invención residen en una forma diferente de operar, seleccionado la cantidad apropiada de un iniciador que es dosificado al comienzo de la polimerización (primer iniciador) y seleccionando las condiciones propias de dosificación para el iniciador adicionado posteriormente (es decir, el segundo iniciador), para obtener un proceso de polimerización que permita un rendimiento espacio-tiempo óptimo, brindando un uso muy eficiente del peróxido y muy bajos niveles de peróxido residual en la resina (polímero final) después de la polimerización (ver por ejemplo, la página 2, líneas 18-29 y los ejemplos 1 y 2 en la descripción de la presente solicitud). En donde la resina con un muy bajo nivel de peróxido residual es verdaderamente el resultado que se desea obtener.

Por lo que, la expresión ***“...por lo menos el 92% de la capacidad máxima de enfriamiento se utiliza durante por lo menos un tiempo en donde por lo menos el 10% en peso del monómero se polimeriza.”***, objetada por ese Despacho, claramente corresponde a una característica particular de la forma de operar el nuevo proceso de polimerización reivindicado, la cual es una característica fundamental que permite que el proceso funcione de tal forma que se obtenga como resultado del mismo una resina (polímero final) con las propiedades deseadas; por lo cual esta expresión de ninguna forma se puede considerar como un resultado a ser alcanzado.

2. Referencia citada

De la lectura del Concepto Técnico No. 944, es posible determinar que el señor Examinador cita las enseñanzas del documento CO 04-056.935 (D1)

como enseñanzas que afectan la NOVEDAD del proceso reclamado en la invención bajo estudio.

El documento citado CO 04-056.935 (D1), se relaciona con un proceso de polimerización, que involucra la dosificación de un iniciador con una vida media a la temperatura de polimerización de 0.0001 a 0.050 horas y opcionalmente, un iniciador convencional (ver resumen y reivindicación 1 del documento D1).

3. Con respecto a la alegada falta de NOVEDAD.

Sobre este particular, atentamente me permito dirigir la atención del señor Examinador a una comparación realizada elemento por elemento entre cada una de las enseñanzas del documento CO 04-056.935 (D1) y el proceso de la presente invención, la cual permite identificar claras diferencias técnicas que hacen que dicho documento citado NO pueda afectar la novedad del proceso reclamado por la solicitud bajo estudio, tal y como a continuación me permito demostrarlo.

En efecto, al llevar a cabo una revisión detenida de lo revelado tanto en el documento D1, como en la presente invención, se encuentra que mientras que en D1 se revela un proceso de polimerización que involucra la dosificación de un iniciador con una vida media a la temperatura de polimerización de 0.0001 a 0.050 horas y opcionalmente, un iniciador convencional. Adicionalmente, en el mismo documento D1 se revela una primera etapa de adición del iniciador de tal forma que la capacidad de enfriamiento deseada, es decir, preferiblemente la máxima capacidad de enfriamiento, es alcanzada al final de este periodo de dosificación y de una segunda etapa de dosificación después de al menos un 40% en peso de conversión del monómero (ver páginas 4 y 5 de la Publicación WO/2003/054040 que corresponde al documento citado D1).

De otra parte, en la solicitud Colombiana bajo estudio, el proceso reivindicado revela la dosificación del iniciador dentro del primer periodo de conversión del 10% y en una cantidad tal que al menos el

92% de la capacidad máxima de enfriamiento es usada durante un tiempo en donde al menos el 10% del monómero es polimerizado; esta forma de operar que se revela en la presente invención, no se menciona explícitamente, y ni siquiera se revela en forma implícita en ninguno de los apartes del documento **CO 04-056.935 (D1)**

De acuerdo con lo anterior, resulta completamente claro y evidente que en el proceso de polimerización revelado en D1 NO se presentan exactamente las mismas características fundamentales del proceso de la presente invención, toda vez que en ninguno de los apartes del documento citado D1, se enseñan exactamente las mismas condiciones y componentes fundamentales para el proceso reclamado, el cual emplea en forma particular un iniciador con una vida media de 0.0001 a 1 hora a la temperatura de polimerización, dosificándolo a la temperatura de polimerización, mientras la dosificación se realiza dentro del primer periodo de conversión del 10% y en una cantidad tal que al menos el 92% de la capacidad máxima de enfriamiento se usa durante dicho periodo de conversión del 10% del monómero.

En este punto, resulta completamente aplicable una de las nociones que contiene el documento titulado ***"Manual para el Examen de Solicitudes de Patentes de Invención en las Oficina de Propiedad Industrial de los Países de la Comunidad Andina"*** (en adelante Manual de Patentes), el cual en las páginas 63 a 66 de dicho documento, hace referencia a la evaluación de la novedad de una invención. Pues bien, en una de las apreciaciones allí consignadas, se establece que la novedad de una invención solo puede ser afectada **si en un mismo documento se revelan todos y cada uno de los elementos y/o condiciones fundamentales en forma idéntica a la reivindicada por la solicitud bajo estudio**. Esta es una apreciación que surgió como fruto del trabajo, del conocimiento y de la práctica habitual de los miembros de las oficinas de propiedad industrial de los países miembros de la CAN, bajo los requerimientos de la Decisión 486, junto con el apoyo de sus colegas de la Oficina Europea (EPO), tal y como se puede constatar en la introducción y los prólogos del mismo Manual de Patentes.

Como se ha mencionado en el presente escrito, al comparar la presente solicitud con lo revelado en el documento citado D1, fácilmente se encuentra que dicho documento citado no enseña en ninguno de sus apartes una forma de operar exactamente idéntica a la forma de operar el proceso ahora reclamado. Por el contrario, lo que realmente se revela en D1 es un proceso en el cual se realiza la polimerización requiriendo que los medios de enfriamiento estén a su máxima capacidad de enfriamiento al finalizar una segunda etapa de polimerización, cuando se llega al 40% de conversión, lo cual es completamente diferente a la presente invención, toda vez que el solicitante ahora reivindica un proceso en el que la dosificación se realiza dentro del primer periodo de conversión del 10% y en una cantidad tal que al menos el 92% de la capacidad máxima de enfriamiento se usa durante dicho periodo de conversión del 10% del monómero, el cual es completamente diferente al revelado en D1.

En vista de lo anterior, la materia objeto de las reivindicaciones 1 a 8 de la presente invención resulta completamente NOVEDOSA sobre las enseñanzas de D1, ya que se ha mostrado con base en las enseñanzas del mismo documento **CO 04-056.935 (D1)** que nada dentro de dicho documento enseña o revela en forma apropiada un proceso idéntico (es decir, un proceso con la misma forma de operar) al proceso específico de la presente invención. Por lo tanto, la enumeración de elementos comunes entre el documento citado y la presente invención, que hace el señor Examinador para sustentar su objeción a la novedad de la invención, no resulta relevante debido a que el conjunto completo del proceso ahora reclamado, no había sido revelado previamente en D1, tal y como ya se ha demostrado.

4. **Argumentos adicionales que demuestran la patentabilidad de la invención.**

Como un indicio que resulta relevante para la evaluación de patentabilidad que se está llevando a cabo sobre la materia objeto de la solicitud de patente Colombiana No. 05-111.200, atentamente me permito llamar la atención de ese despacho al hecho de que las correspondientes solicitudes de patentes que reclaman exactamente la misma materia objeto de la

solicitud en cuestión y que fueron presentadas ante las oficinas de Marcas y Patentes de Europa (EPO) y de Australia han sido concedidas como patentes bajo los números EP 1618137 B1 y AU2004096871, de las cuales me permito anexar una copia informal.

Sobre este particular, me permito llamar la atención del señor Examinador al hecho de que la concesión de patente para la misma materia objeto de la solicitud colombiana, por parte de las Oficinas de Europa (EPO) y Australia, constituye un fuerte indicio que permite demostrar que el proceso de polimerización de la presente solicitud sí cumple con los requisitos técnicos y legales necesarios para gozar del privilegio de patente solicitado, y los cuales al igual que en la Normativa vigente en Colombia (Decisión 486) corresponden a los requisitos de novedad, nivel inventivo requeridos y aplicación industrial.

Ahora bien, frente al hecho de la concesión de las dos patentes citadas anteriormente, podrían surgir algunos interrogantes, como los siguientes:

- ¿Por qué dos oficinas diferentes conceden una patente para la misma materia objeto de la solicitud Colombiana No. 05-111.200?, y
- ¿Por qué la concesión de dichas patentes debe ser considerada como un fuerte indicio de patentabilidad de dicha materia objeto, por parte de otra oficina de patentes, específicamente por parte de la Oficina de Nuevas Creaciones de la SIC?

Para dar respuesta a estos dos interrogantes, se debe recurrir inevitablemente a la legislación vigente en materia de patentes, en cada uno de los países que ya ha concedido dichas patentes, y a la legislación Andina, para poder establecer si se cifan a los mismos principios legales y técnicos para la evaluación de la patentabilidad. En el presente caso, la comparación se realizará con la legislación Europea, la cual guarda una estrecha relación con la Normativa Colombiana en lo referente a la claridad de las reivindicaciones y los requisitos de patentabilidad, específicamente en la novedad, tal y como se mostrará a continuación.

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En conexión con lo anterior, se presentan en las columnas dos y tres del siguiente cuadro comparativo, los artículos propios de cada una de dichas legislaciones, referentes a los requisitos de patentabilidad exigidos.

Cuadro Comparativo:

	Normativa Andina (Decisión 486) ¹	Convención Europea de Patentes (EPC) ²
REQUISITOS DE PATENTABILIDAD	Art 14.- Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento, en todos los campos de la tecnología, <u>siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial.</u>	Art. 52 Invenciones Patentables (1) Las patentes europeas <u>serán concedidas para cualquier invención, en todos lo campos de la tecnología, con la condición de que sean nuevas, involucren un nivel inventivo y sean susceptibles de aplicación industrial.</u> (2) Las siguientes en particular no serán consideradas dentro del significado del parágrafo 1: (a) descubrimientos, teorías científicas y métodos matemáticos; (b) creaciones estéticas; (c) esquemas, reglas y métodos para realizar actos mentales, jugar juegos o hacer negocios, y programas para computadores; (d) presentaciones de información.
NO VEDAD	Artículo 16.- Una invención se considerará nueva cuando no está comprendida en el estado de la técnica. El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o,	Art. 54 1) Una invención se considerara nueva si esta no forma parte del estado de la técnica. (2) El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente Europea.

¹ www.emercatoria.edu.co/PAGINAS/volumen3/Documentos01/DECISION%20486.doc
² [http://documents.epo.org/projects/babylon/eponet.nsf/0/E4F8409B2A99862FC125738B00374CEC/\\$File/EPC_13th_editi on.pdf](http://documents.epo.org/projects/babylon/eponet.nsf/0/E4F8409B2A99862FC125738B00374CEC/$File/EPC_13th_editi on.pdf)

	en su caso, de la prioridad reconocida.	
CLARIDAD DE LAS REIVINDICACIONES	Art 30.- Las reivindicaciones definirán la materia que se desea proteger mediante la patente. <u>Deben ser claras y concisas y estar enteramente sustentadas por la descripción.</u> Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará una reivindicación dependiente múltiple.	Art. 84 Reivindicaciones Las reivindicaciones definirán la materia para la cual se busca protección. <u>Deben ser claras y concisas y estar sustentadas por la descripción.</u>

El cuadro anterior, casi por si solo da respuesta a los interrogantes planteados, toda vez que al hacer una simple comparación de cada uno de los requisitos exigidos por las diferentes legislaciones, se puede ver que son los mismos requisitos tanto legales como técnicos, pues por ejemplo, si tomamos el artículo 14 de la Decisión 486, el cual establece que se otorgaran patentes a las invenciones, siempre y cuando sean novedosas, tengan nivel inventivo y sean susceptibles de aplicación industrial, y lo comparamos con el Artículo 52 de la Convención Europea de Patentes (EPC), encontramos que son exactamente los mismos requisitos técnicos y legales los exigidos en Europa y Colombia, lo mismo ocurre con los artículos 16 y 30 de la D486 y los artículos 54 y 84 de la EPC, que exigen en forma idéntica, que la invención sea novedosa y que las reivindicaciones cumplan con los requisitos de claridad, concisión y que sean debidamente sustentadas por la descripción, respectivamente.

Entonces, para entender porque dos oficinas diferentes conceden una patente para la misma materia objeto de la solicitud Colombiana No. 05-111.200, no es necesario sino comprender que esto se debe a que la materia objeto de la solicitud Colombiana, resulta clara para una persona medianamente versada en la materia, y además, es completamente novedosa e inventiva y con aplicación industrial, pues expertos con los mismos conocimientos técnicos y bajo los mismos requisitos legales que son aplicados por los expertos Colombianos de ese Despacho, han podido encontrar dentro de la materia objeto reclamada, es decir, el proceso de polimerización de las reivindicaciones 1 a 8, los suficientes elementos técnicos que le brindan novedad, altura inventiva y aplicación industrial, a una invención que representa un avance en el estado actual de la técnica.

En vista de las anteriores comparaciones, resulta fácil entender porque la concesión de dichas patentes por parte de la EPO y la Oficina Australiana, debe ser considerada como un fuerte indicio de patentabilidad de la materia objeto de la presente invención, que no debería ser desestimado o pasado por alto por parte de la Oficina de Nuevas Creaciones de la SIC, toda vez que, los conceptos de otras oficinas pueden ser empleados como una muy útil herramienta en la evaluación de la patentabilidad de una solicitud en particular. Esta apreciación, no corresponde a una simple aseveración hecha por el solicitante, sino que es una consideración que tiene su justificación en la misma normativa Andina en materia de patentes. En efecto, el empleo de documentos y estudios provenientes de otras oficinas de patentes, es una práctica reconocida y aceptada por el Artículo 46 de la Decisión 486, el cual en algunos de sus apartes establece lo siguiente:

“Artículo 46.- La oficina nacional competente podrá requerir el informe de expertos o de organismos científicos o tecnológicos que se consideren idóneos, para que emitan opinión sobre la patentabilidad de la invención. Asimismo, cuando lo estime conveniente, podrá requerir informes de otras oficinas de propiedad industrial.

[...]

a) copia de la solicitud extranjera;

- b) copia de los resultados de exámenes de novedad o de patentabilidad efectuados respecto a esa solicitud extranjera;*
- c) copia de la patente u otro título de protección que se hubiese concedido con base en esa solicitud extranjera;*
- d) copia de cualquier resolución o fallo por el cual se hubiese rechazado o denegado la solicitud extranjera; o,*
- e) copia de cualquier resolución o fallo por el cual se hubiese anulado o invalidado la patente u otro título de protección concedido con base en la solicitud extranjera.*

La oficina nacional competente podrá reconocer los resultados de los exámenes referidos en el literal b) como suficientes para acreditar el cumplimiento de las condiciones de patentabilidad de la invención. [...].
(Subrayado fuera de texto).

El artículo 46, claramente faculta a los Examinadores técnicos y legales de las oficinas de patentes de los países miembros de la CAN a considerar como elementos importantes para determinar la patentabilidad de una invención, las opiniones y los resultados de la examinación realizada por parte de los funcionarios de otras oficinas de patentes.

Ahora bien, el solicitante claramente entiende que el hecho de que la misma materia objeto de la solicitud Colombiana en cuestión, haya sido concedida tanto por parte de la Oficina Australiana y de la EPO, no obliga a la concesión de dicha patente por parte otra oficina, específicamente, por parte de la Oficina de Nuevas Creaciones de la SIC, pero lo cierto es que desde el punto de vista técnico, dicha concesión sí constituye un fuerte indicio que resulta mas que razonable de que la materia objeto de la solicitud en cuestión, posee efectivamente los requisitos de novedad, nivel inventivo y aplicación industrial necesarios para gozar del privilegio de patente solicitado, lo cual puede y debe ser tenido en cuenta de acuerdo con la misma legislación Andina (Decisión 486), la cual como ya se mencionó faculta a los señores Examinadores a tener en cuenta dichos conceptos, así como los títulos obtenidos en otros países para la concesión de una patente, tal y como claramente se aprecia en el artículo 46 de la citada Decisión 486.

Por lo tanto, no se está solicitando a ese Despacho que se desconozcan los resultados del examen realizado en Colombia, sino simplemente que se incluyan como indicios de patentabilidad tanto el concepto del examinador internacional, como los títulos obtenidos en otros países los cuales corroboran toda la argumentación técnica y legal que se ha aportado en el presente caso para demostrar la patentabilidad del proceso de las reivindicaciones 1 a 8 de la presente solicitud de patente.

5. CONCLUSION

Las modificaciones realizadas y las aclaraciones presentadas en el capítulo reivindicatorio ahora presentado permiten superar completamente las objeciones presentadas a la claridad del mismo, por lo cual, el nuevo capítulo reivindicatorio cumple a cabalidad las exigencias de claridad establecidas por el artículo 30 de la Decisión 486. De otra parte, los argumentos expuestos al lo largo del presente escrito, ponen de manifiesto de una manera clara y contundente, que el proceso reivindicado en la presente invención es completamente novedoso sobre las enseñanzas del documento D1.

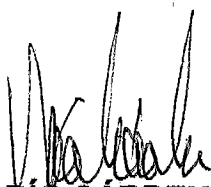
En efecto, como se demostró anteriormente, las enseñanzas contenidas en el documento **CO 04-056.935 (D1)**, no revelan y tampoco llegan a sugerir la posibilidad de disponer de un proceso tan específico, como el de la presente invención, en el cual la dosificación del iniciador se lleva a cabo dentro del primer periodo de conversión del 10% y en una cantidad tal que al menos el 92% de la capacidad máxima de enfriamiento es usada durante un tiempo en donde al menos el 10% del monómero es polimerizado, se logra un proceso mejorado, con características técnicas diferenciables que permiten obtener un producto (resina o polímero final) con características deseadas de bajo contenido de peróxido residual, frente a las resinas obtenidas por los procesos convencionales que hacen parte del estado del arte más cercano, tal y como ha sido reconocido por parte de los expertos técnicos de las oficinas de patentes de Australia y Europa.

Por lo tanto, me permito solicitar a ese Despacho, se sirva llevar nuevamente a cabo el estudio de la presente solicitud a la luz de las modificaciones y de los argumentos aquí presentados, para conceder el privilegio de patente solicitado para el proceso de polimerización reivindicado.

6. **Anexos**

- Recibo oficial de caja No. 09-67.578 correspondiente al pago de la tasa por las modificaciones realizadas.
- Nuevas páginas 21 y 22, que corresponden al nuevo capítulo reivindicatorio modificado, tal y como se describió anteriormente.
- Copia informal de las patentes Nos. EP1618137 y AU2004234056, que cobijan exactamente la misma materia objeto de la presente solicitud de patente.

Atentamente,



DARÍO CÁRDENAS NAVAS

C.C. 17.066.629

T.P. 1.250 *su*

F. P-360

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

NIT : 800176089-2

RECIBO OFICIAL DE CAJA : 09 - 67,578
FECHA : SEPTIEMBRE 10 DE 2009

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



No. 05-111200-00007-0000

Fecha: 2009-09-14 15:16:20 Dep. 2020 NUECREACIONE
Tra. 11 PATENTEIYII Eve: 379 FASENACIONALI
Act. 444 RESPUESTAREQUE Folios: 52

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PAGO	Vr. PAGO
CARDENAS Y CARDENAS P.I. CONSIGNACION		BANCO DE BOGOTA	062754387	17852284	10/09/2009	1,864,040.00

***** CONCEPTO *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-03	CAMBIO DE MODALIDAD Y MODIFICA	
		12 MARCAS Y LEAS COMERCIALES	111,000.00
		TOTAL :	\$ 111,000.00

SON: CIENTO ONCE MIL PESOS

RESPONSABLE :

RECIBO DE CAJA APLICADO AL EXPEDIENTE No.

ADOCADOS

REIVINDICACIONES

1. Un proceso para polimerizar uno o más monómeros en donde se usa a lo sumo 90% en moles de la cantidad que se puede utilizar de manera segura de un primer iniciador, donde la cantidad que se puede utilizar de manera segura es la cantidad máxima de dicho iniciador que puede ser usada en un proceso idéntico que se corre a la máxima capacidad de enfriamiento y donde la temperatura no excede la temperatura puesta o deseada, y un segundo iniciador, que tiene una vida media de 0.0001 horas a 1 hora a la temperatura de polimerización y que es menos estable a la temperatura que dicho primer iniciador, que se dosifica por lo menos parcialmente después del inicio de la polimerización hasta que el 10% del (los) monómero(s) ha(n) sido polimerizado(s), en una cantidad de tal manera que por lo menos 92% de la capacidad máxima de enfriamiento se utiliza durante por lo menos un periodo de tiempo en donde por lo menos 10% en peso del monómero se polimeriza, y donde los iniciadores son seleccionados de peróxidos orgánicos e iniciadores azo- convencionales.
2. Un proceso de acuerdo con la reivindicación 1, en donde los monómeros comprenden cloruro de vinilo.
3. Un proceso de acuerdo con la reivindicación 1 o 2 en donde el proceso es un proceso de polimerización en suspensión, preferiblemente un proceso de polimerización en suspensión por lotes.
4. Un proceso de acuerdo con cualquiera de las reivindicaciones 1-3, en donde el segundo iniciador también se adiciona intermitentemente y/o continuamente después del inicio de la caída de presión y/o durante la caída de presión.

5. Un proceso de acuerdo con cualquiera de las reivindicaciones 1-4, en donde se adiciona un colide protector durante el proceso de polimerización.
6. Un proceso de acuerdo con cualquiera de las reivindicaciones 1-5, en donde dicho primer iniciador tiene una vida media de 0.1 horas a 10 horas a la temperatura de polimerización y el iniciador menos estable a la temperatura tiene una vida media de 0.0001 horas a 1.0 horas a dicha temperatura.
7. Un proceso de acuerdo con cualquiera de las reivindicaciones 1-6, en donde la cantidad del segundo iniciador que se usa es por lo menos 0.01% en peso, con base en el peso del monómero que se polimeriza.
8. Un proceso de acuerdo con cualquiera de las reivindicaciones 1-7, en donde la cantidad total del primero y segundo iniciadores es 0.01% a 1% p/p con base en el peso del monómero que se polimeriza.

212
207



(11) **EP 1 618 137 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
11.06.2006 Bulletin 2006/24

(51) Int. Cl.:
C08F 4/38 (2006.01) C08F 14/06 (2006.01)
C08F 2/18 (2006.01) B01J 19/00 (2006.01)

(21) Application number: 04729652.0

(86) International application number:
PCT/EP2004/004500

(22) Date of filing: 27.04.2004

(87) International publication number:
WO 2004/096871 (11.11.2004 Gazette 2004/46)

(54) **INCREASED POLYMERIZATION REACTOR OUTPUT BY USING A SPECIFIC INITIATOR SYSTEM**

ERHÖHTE POLYMERISATIONSREAKTORAUSBEUTE DURCH VERWENDUNG EINES
SPEZIFISCHEN INITIATORENSYSTEMS

REACTEUR DE POLYMERISATION A RENDEMENT AMELIORE GRACE A L'UTILISATION D'UN
SYSTEME SPECIFIQUE D'INITIATEURS

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PL PT RO SE SI SK TR

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(30) Priority: 01.05.2003 EP 03076390

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(43) Date of publication of application:
25.01.2006 Bulletin 2006/04

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(56) References cited:
EP-A- 0 096 365 WO-A-00/17245
DE-A- 3 029 211 US-A- 3 778 422

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Remarks:

The file contains technical information submitted after
the application was filed and not included in this
specification

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

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Description

[0001] The present invention relates to a process to polymerize one or more monomers in a reactor with a certain cooling capacity, wherein said cooling capacity is limiting the space-time yield of the reactor.

[0002] DE-OS-1 570 963 discloses to dose an initiator, optionally mixed with a solvent, to the mixture to be polymerized via a stream of water. The organic peroxides that are exemplified in this patent application are peroxydicarbonates and acetyl-cyclohexyl-sulfonyl-peroxide (ACSP). This process of DE-OS-1 570 963 was found to solve a number of problems in the industry. However, the process still suffers from insufficient control of the heat peak of the polymerization reaction and a related less than optimal space-time yield of the reactor due to cooling capacity restrictions. Accordingly, a different process not suffering from these drawbacks is desired.

[0003] Similarly, EP-A-0 096 365 discloses how a peroxide is added in three parts during the polymerization. Again, difficulties in controlling the heat that is subsequently generated are reported.

[0004] JP-A-07082304 discloses a process wherein a first peroxide is used at the start of the polymerization. Later in the process, when a reflux condenser is used as an additional cooling device, a second peroxide is dosed to the reactor to more efficiently use the additional cooling capacity of the condenser. Only a limited amount of the second peroxide can be used due to the fact that the first peroxide is still used in a conventional amount. By doing so the polymerization time is reduced from 5 hours and 3 minutes for the conventional process, in which only the first peroxide is used, to 4 hours and 17 minutes for the process wherein additionally the second peroxide is dosed. Although a significant improvement over the prior art, the time gain is still considered less than desired. Even higher time-space yield gains are being looked for.

[0005] Furthermore, the above-mentioned processes of the prior art are not very suitable for increasing the space-time yield of very large polymerization reactors, particularly those of at least 15 m³, more particularly those of at least 20m³, wherein safety margins are maintained to prevent the polymerizing content from "running away", meaning that due to excessive heat development the reactor content is heated to above its set temperature, causing more of the conventional peroxide to decompose, which causes the polymerization rate to further increase, thus auto-acceleration occurs up to the point that the reactor content has to be stopped or dumped or it will rupture the reactor.

[0006] The current invention relates to a new process wherein these problems have largely been solved. More particularly, we have found that by selecting the proper amount of initiator that is dosed at the beginning of the polymerization and the proper dosing conditions for subsequently added initiator, it is possible to obtain a polymerization reaction where the rate of polymerization can be very well controlled and therefore the heat of polymerization can be kept at the maximum cooling capacity, allowing optimum reactor space-time yield, very efficient peroxide usage, and very low residual peroxide levels in the resin after polymerization. Furthermore, the fact that less of a conventional first initiator is dosed at the start of the polymerization, it was found that the distribution of said first initiator over the monomer was improved. Especially for the suspension and emulsion polymerization process this was found to result in polymer particles with less defects, such as fish-eyes, that are considered to be caused by too high peroxide concentration in a monomer droplet. This effect can be further augmented by metering both the initiator and a protective colloid at the same time. Additionally, the porosity of the polymer can be enhanced and better controlled through selection of the appropriate protective colloid and the way in which the protective colloid and/or the peroxide are metered.

[0007] The new process is characterized in that, compared to a process which is run at its maximum rate with all initiator being added at the start of the polymerization, only up to 90 mole% of said initiator (or mixture of initiators) is added at the start of the polymerization and a second initiator, which is less temperature stable than the first initiator that is added at the start, said second initiator having a half-life from 0.0001 hour to 10hour at the polymerization temperature, is dosed to the polymerizing mixture at least partially from the start of the polymerization until 10% of the monomer(s) has been polymerized in an amount and preferably at a varying rate, such that at least 92, preferably at least 96, more preferably at least 98% of the maximum cooling capacity is used during at least a period of time wherein at least 10 % by weight (%w/w), preferably 20%w/w, more preferably at least 30%w/w, most preferably at least 40%w/w of the monomer is polymerized. Preferably the second initiator is dosed in such a way that the maximum cooling capacity is used in a period of time wherein at least 10 % by weight (%w/w), preferably 20%w/w, more preferably at least 30%w/w, most preferably at least 40%w/w of the monomer is polymerized, whereby the actual temperature of the polymerizing mixture is kept at the desired temperature plus or minus 0.2°C, because the more the maximum cooling capacity is being used, the more efficient is the polymerization process. The dosing of the second initiator in conjunction with the use of the first initiator allows for an unprecedented i) accurate control of the polymerization rate and related polymerization heat generation (and, accordingly, also the polymerization temperature) by controlling the peroxide dosing rate, ii) space-time yield of the reactor, and iii) very economic initiator usage.

[0008] If the amount of initiator being added at the start of the polymerization is carefully chosen and the second initiator is dosed according to the invention, then it is furthermore found possible to significantly reduce or remove the run-away safety margins that were necessary in the conventional process and the process can actually run at such a rate that the heat of polymerization is very close to, or it may even temporarily exceed, the cooling capacity, without that

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such a run-away is observed. In this respect, reference is made to JP-A-07082304 (see Example 1) in which conventional safety margins are being maintained of more than 15% of the total cooling capacity. In a process according to the invention the actual temperature of the reacting mixture typically does not reach a temperature that is more than 6°C above the desired polymerization temperature. Preferably, the overshoot of the temperature of the polymerization mixture is less than 4°C, more preferably it is less than 2°C, even more preferably it is less than 1°C. Most preferably, the actual temperature of the polymerizing mixture is kept at the desired temperature plus or minus 0.2°C.

[0009] The amount of initiator being added at the start of the polymerization should be at most 90% by weight (%w/w) of the maximum amount of said initiator that can be used in the identical process that is run at the maximum cooling capacity and whereof the temperature is not exceeding the set temperature due to an excess of polymerization heat. If more than this maximum amount of said initiator is used, the polymerization heat exceeds the heat transfer capacity of the reactor and the reactor content will heat up to a temperature above the maximum allowable polymerization temperature. Since such an overshoot in temperature will cause a more rapid decomposition of the initiator, the temperature may even increase further, up to a point where the reaction runs away and becomes uncontrollable and hazardous. For this reason this maximum amount of initiator is called the safely useable amount. Preferably it is at most 80%w/w of said safely useable amount, more preferably at most 70%w/w, and most preferably at most 65%w/w. The lower the amount of first initiator the better the controlling of the polymerization rate (and, accordingly, the heat of polymerization) during the process. Preferably at least 2%w/w, more preferably at least 5%w/w, most preferably at least 10%w/w of said safely useable amount of first initiator is used.

[0010] It is noted that the term "maximum cooling capacity" as used herein is used in its conventional meaning, being the amount of heat that can be removed from the polymerization reaction mixture when 1) said reaction mixture has a temperature equal to the preset polymerization temperature, and 2) the cooling capacity is at its maximum level under normal polymerization conditions (typically the situation wherein the cooling medium is flowing at its maximum rate at its lowest temperature under normal polymerization conditions).

[0011] The amount of the second initiator that is used is preferably at least 0.01 % by weight (%w/w), more preferably at least 0.015 %w/w, and most preferably more than 0.02 %w/w, all based on the weight of the monomer that is polymerized in the process.

[0012] It is noted that WO 00/17245 discloses a process wherein initiators are dosed to a polymerization reactor at temperatures where essentially all the initiators have a half-life of from 0.05 to 1.0 hour. In non-published application PCT/EP02/14518 extremely fast organic initiators with a half-life from 0.0001 hour to 0.050 hour at the polymerization temperature are used to give an improved control of the polymerization rate, higher polymerization rates, leading to an increased space-time yield of polymerization reactors, and results in the process rendering a polymer with very low residual initiator levels. However, these processes were found to require the use of high amounts of the fast or extremely fast peroxides because the initiator efficiency is below that of a conventional peroxide that is dosed at the start. With the present process, the amount of fast or extremely fast peroxide that is used is lower than the amount as disclosed in WO 00/17245 and PCT/EP02/14518. Also the total amount of active oxygen as needed in the present process, compared to the process of WO 00/17245 and PCT/EP02/14518 with the same polymerization time, was found to be reduced. Therefore, the present process is more economical and yields a polymer with less decomposition products of the initiator, hence a product with improved organoleptic properties, particularly smell. Also, it is known that residual decomposition products typically having a molecular weight of less than 250 Dalton may lead to fogging (the decomposition products evaporate from the resin and condense on another surface), which is undesired. Also, a rework of Example F of WO 00/17245 showed that only after 2.9 hours after the start of the heat-up, and only for an instant, the maximum cooling capacity was used. It was furthermore observed that the present process allows for a better distribution of the initiators over the monomer, which, particularly when the polymerization is a dispersion polymerization, such as an emulsion or suspension polymerization, results in a polymer with improved properties. Particularly the molecular weight and/or the molecular weight distribution of the polymer and/or the number of fish-eyes (resulting from the polymerization of a monomer droplet when a too high peroxide concentration was present) was found to be improved.

[0013] The process according to the invention is pre-eminently suited to polymerize monomer mixtures comprising vinyl chloride monomer (VCM). Preferably, the process according to the invention involves the polymerization of monomer mixtures comprising at least 50% by weight (% w/w) of VCM, based on the weight of all monomer. Comonomers that can be used are of the conventional type and include vinylidene chloride, vinyl acetate, ethylene, propylene, acrylonitrile, styrene, and (meth)acrylates. More preferably, at least 80% w/w of the monomer(s) being polymerized is made up of VCM, while in the most preferred process the monomer consists essentially of VCM. As is known in the art, the polymerization temperature of such processes to a large extent determines the molecular weight of the resulting resin.

[0014] It is to be understood that the word "dosing" is used to describe the step of adding initiator to the polymerizing reaction mixture at polymerization conditions. The dosing can be done intermittently during the polymerization, meaning that at least two portions of initiator are added to the reaction mixture, or it can be continuous, meaning that for a certain period of time the initiator is continuously added to the reaction mixture, or any combination of these techniques. Examples of a combination of such techniques include, for instance, a process wherein the initiator is first added continuously,

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then the addition is stopped, and then again it is added continuously. If an intermittent operation is selected, there are at least 2, preferably at least 4, more preferably at least 10, and most preferably at least 20 moments at the polymerization temperature at which the initiator is dosed. Most preferably, the peroxide is dosed continuously and/or intermittently from the start of the polymerization reaction, preferably after at least 5%, less preferred after at least 10%, even more less preferred after at least 20%, of the monomer(s) has already been polymerized and wherein during the dosing period at least 2, preferably at least 5, more preferably at least 10%, more preferably at least 20%, more preferably at least 40%, and most preferably at least 60%, of all monomer used in the process is polymerized.

[0015] In the process according to the invention, one or more initiators may be used as the second initiator, preferably the initiators are selected from organic peroxides, however, they may also be selected from conventional azo-initiators. Preferred examples of peroxides to be used as a second initiator in the process according to the invention are the following:

- 1,1,3,3-tetramethylbutylperoxy methoxy acetate, or hexanoyl pivaloyl peroxide for polymerization reactions at 35-70°C, preferably 40-65°C.
- diisobutanoylperoxide, bis(tert-butylperoxy) oxalate or 2,2-bis(2,2-dimethylpropanoylperoxy)-4-methyl pentane, for polymerization reactions at 40-85°C, preferably 45-80°C.
- α -cumyl peroxyneodecanoate, 2-(2,2-dimethylpropanoylperoxy)-2-(2-ethylhexanoylperoxy)-4-methyl pentane or 2,4,4-trimethylpentyl-2-peroxyneodecanoate, at polymerization temperatures of 53-99°C, preferably 60-95°C, and
- tert-amyl, tert-butyl peroxyneodecanoate or peroxydicarbonates, at polymerization temperatures of 62-107°C, preferably 75-100°C.

Other peroxides may also be used. Their half-lives can be determined by conventional thermal decomposition studies in monochlorobenzene, as well-known in the art (see for instance the brochure "Initiators for high polymers" with code 10737 obtainable from Akzo Nobel). The term polymerization temperature as used herein is used in its conventional connotation and represent the average temperature in the period in which the majority of the monomer is polymerized. In case of doubt, it is the average temperature in the polymerization period in which not the first and not the last 5% of the monomer is polymerized.

[0016] Preferably, the first initiator that is added at the start of the polymerization, meaning when up to 10% of the monomer has polymerized, preferably when up to 5% of the monomer has polymerized, more preferably when up to 2% of the monomer has polymerized, even more preferably up to 1 % has polymerized, most preferably when essentially no monomer has yet polymerized, has a half-life (when measured in monochlorobenzene at the polymerization temperature) of from 0.1 hour to 10.0 hour. More preferably, essentially all peroxide that is added at the start has a half-life of 0.2 to 5.0 hour, even more preferably 0.4 to 2.0 hour, most preferably 0.5 to 1.0 hour. The first initiator can be a mixture of initiators, provided that the weight average half life of the initiators in the mixture is within the 0.1 - 10 hour range. As said, the first initiator should have a longer half-life than the second initiator (at the polymerization temperature). Preferred first initiators include α -cumyl peroxyneodecanoate, 2-(2,2-dimethylpropanoylperoxy)-2-(2-ethylhexanoylperoxy)-4-methyl pentane, 2,4,4-trimethylpentyl-2-peroxyneodecanoate, 3-hydroxy-1,1-dimethylbutyl peroxyneodecanoate, tert-amyl peroxyneodecanoate, tert-butyl peroxyneodecanoate, peroxydicarbonates (e.g. di-(2-ethylhexyl) peroxydicarbonate and di-(sec butyl)peroxydicarbonate), tert butyl peroxyneodecanoate, tert butyl peroxy pivalate, tert amyl peroxyxpivalate, and dilauroyl peroxide.

[0017] It is noted that when the term "polymerization temperature" is used, that this is the temperature at which the majority of all monomer (i.e. more than 50%w/w, preferably more than 60%w/w, most preferably more than 75%w/w of the monomer being polymerized) is being polymerized. It is known that the polymerization temperature set-point can be varied over time. Known polymerization temperature variations for polymerizations of vinyl chloride include an intentional higher temperature when the polymerization is started and/or a higher temperature upon pressured drop, both used to increase the reactor output. If a variation in the polymerization temperature is applied, then the polymerization temperature is considered to be the average temperature over time from the moment the polymerization temperature is reached until the pressure drop. It is noted that also in the process of the present invention, the polymerization temperature set-point during the start-up and pressure drop stages may be higher than the average polymerization temperature set-point.

[0018] Preferably, the second initiator that is dosed during the polymerization has a half-life (when measured in monochlorobenzene at the polymerization temperature) of from 0.0001 hour to 1.0 hour. More preferably, essentially all second initiator that is used has a half-life of 0.0005 to 0.8 hour, even more preferably 0.001 to 0.5 hour, most preferably 0.005 to 0.35 hour. The second initiator can be a redox initiation system. In such a case the reducing agent, the oxidizing agent, or both can be dosed in accordance with the invention. For such redox systems, the half-life of the redox system is the half-life as measured when all components of the system are present. However, in view of the fact that redox systems typically contain heavy metals and/or undesired reducing agents, the initiators of the present invention preferably are not such redox initiation systems. The second initiator may be a single initiator or a mixture of several initiators. If a mixture is used, all initiators of said mixture should fulfill the half-life requirement. If a mixture of second initiators is used, then preferably all initiator of the mixture is less temperature stable than the first initiator. If the first

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initiator is a mixture of initiators, then it is preferred that the second initiator is less temperature stable than all initiators in said mixture. If both the first and second initiator consists of a mixture of initiators, then it is preferred that the most thermally stable initiator of the second mixture is less stable than the least stable initiator of the first mixture.

5 [0019] In a preferred embodiment, the invention relates to a process wherein the polymerization mixture is formulated at a temperature below the reaction (polymerization) temperature and subsequently heated to reach said desired reaction temperature. In such a cold-start process the first initiator is added at the start as defined above. However, in such a process it can be beneficial to add also some of the more reactive second initiator during the heat-up phase, since it boost the heat up of the reaction mixture. Preferably, from 0 - 60 % by weight (%w/w), more preferably 5 - 40 %w/w, most preferably 5 - 20 %w/w, of the peroxide, based on the total weight of the second initiator used during the polym-
10 erization, is present at the start of the heating-up phase, while the remainder is dosed over a period of at least 1, preferably 2, and more preferably 2-4 hours, depending on the polymerization time. More preferably, the remainder of the peroxide is dosed from the time the reaction mixture temperature is controlled at the desired reaction temperature. The use of a combination of the first initiator and a small amount of the second initiator from the start allows a fast heating up and start of the polymerization, since these initiators will already (partly) decompose during the heating of the polymerization mixture. When the polymerization mixture reaches the polymerization temperature, the remainder of the peroxide can be dosed to the mixture to control the further polymerization rate. Preferably, the dosing is continuous, preferably at a variable rate, since this allows the most accurate control of the polymerization rate and a constant polymerization heat output. The combination of the first and second initiator ensures the highest initiator efficiency and space-time reactor yield. This is particularly important for commercial reactors. Therefore the polymerization process according to the
20 invention is preferably carried out in reactors of 15m³ or more.

[0020] In another preferred embodiment, the reaction mixture is formulated at or near the polymerization temperature. In this process, hereinafter called warm-start process, it is not necessary to add a certain amount of the second initiator at the start while the remainder is dosed over time. However, also in this warm-start process it can be beneficial to add up to 30 %w/w, preferably up to 20%w/w, most preferably up to 10%w/w, of the second initiator immediately after
25 formation of the reaction mixture, the remainder being dosed over time. If this procedure is used, the second initiator preferably is added as the last ingredient. This procedure is particularly preferred if a certain amount of polymerization inhibitor (a radical trapping species) is present in the reaction mixture. If such a radical scavenger is present, for instance because it is introduced with the monomer wherein it is typically used as a stabilizer, the initially dosed peroxide will react with said scavenger, thus preventing a delayed start of the polymerization reaction.

30 [0021] It is furthermore preferred that two steps are present in the process after the polymerization temperature is reached. In a first step with a duration of up to 90 minutes, preferably up to 60 minutes, and more preferably up to 45 minutes, and with a minimum duration of 1 minute, preferably of 5 minutes, more preferably of 10 minutes, from 1 to 60% w/w, preferably from 5 to 40% w/w, of all second initiator is dosed, such that the desired cooling capacity, preferably the maximum one, more preferably the maximum cooling capacity that is acceptable from a safety point of view, is reached at the end of this dosing step. Then, in a second step, the remaining initiator is dosed (added over time) in an amount and at a rate to control the polymerization in such a way that at least 92, preferably at least 96, more preferably at least 98% of the maximum cooling capacity is used during at least a period of time wherein at least 10 % by weight (%w/w), preferably 20%w/w, more preferably at least 30%w/w, most preferably at least 40%w/w of the monomer is
40 polymerized. Typically, this means that a variable dosing rate is used in the second step.

[0022] The total amount of first and second initiator to be used in a process according to the invention is within the range conventionally used in polymerization processes. Typically, from 0.01 to 1 %w/w of initiator, more specifically 0.01-0.5 %w/w, based on the weight of the monomer(s) to be polymerized, is used.

[0023] The part of the second initiator that is dosed to the reactor can be in the pure form or, preferably, in the form of a dilute solution or dispersion (such as a suspension or emulsion). One or more suitable solvents can be used to
45 dilute the initiator. Preferably, such solvents are easily removed during the steps working up the polymer after the polymerization process (such as alcohols), or they are of such a nature that it is acceptable to leave them as a residue in the final polymer. Furthermore, it can be advantageous, but is not necessarily required, that such solvents do not adversely affect the thermal stability of the initiator dissolved therein, as can be verified by analyzing the half-life temperature of the initiator in said solvent. An example of a suitable solvent is isododecane. If an initiator dispersion is dosed, then the dispersion can be of either the initiator itself or of a solution of the initiator, preferably in said suitable solvents. Preferably, the dispersion is an aqueous dispersion. Preferably, the initiator is dosed in a concentration of 0.1 to 60 %w/w, more preferably 0.5 to 25 %w/w, and most preferably 2 to 15 %w/w. The more dilute initiator solutions or dispersions ensure rapid mixing of the peroxide and the polymerization mixture, which leads to a more efficient use of the peroxide.

[0024] It can be beneficial to dose the second initiator together with a protective colloid.

55 [0025] To improve the time-space yield of the polymerization process, it is advantageous to dose at least part of the second initiator during the phase of the process after the start of the pressure drop and/or during the pressure drop, wherein the pressure drops due to depletion of the monomer. By the term "after the start of the pressure drop and/or during the pressure drop" is meant the time during which the pressure in the polymerization reactor drops, including the

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30 minutes, preferably 20 minutes, more preferably 10 minutes, and most preferably 5 minutes, before the pressure drop is actually observed. Typically, the pressure drop is said to have occurred when the pressure is 0.2 bar, preferably 0.1 bar, lower than the (linearly extrapolated) pressure during the earlier part of the polymerization. The second initiator being added after the start of the pressure drop and/or during the pressure drop preferably has a half-life of less than 1 hour at the polymerization temperature, since than a relatively small residual amount of the initiator will remain in the polymer formed. In order to reduce the residual amount even more, it is preferred to add extremely fast second initiators having a half-life of less than 0.05 hour at the polymerization temperature. However, a slower initiator can also be employed. In that case it can be preferred to add a scavenger which is able to neutralize or destroy the residual initiator in any subsequent step to such an extent that the residual amount of the initiator in the polymer is acceptable. It is also contemplated to add a scavenger when fast and/or extremely fast peroxides are used.

[0026] Preferably, the dosing can be effected at any suitable entry point to the reactor. If water is added in the course of the polymerization process, for example to compensate for the shrinkage of the reactor content due to the polymerization reaction, it can be advantageous to use the line through which this water is dosed to also dose the initiator. It is noted that if the formation of the initiator is fast enough, one can dose the raw materials for said initiator into piping or hold-up vessels, from which the initiator is then fed into the polymerization mixture. Alternatively, but less desired, there is the process wherein the raw materials are added to the polymerization mixture. In all instances it can be beneficial to add stirring equipment and/or heat exchangers to the feed lines in order to optimize efficiency.

[0027] It is noted that, due to the use of the more stable first initiator, it is not preferred to conduct the present process such that 80% or more of all monomer is polymerized within a period of 2 hours. With such short polymerization times the amount of residual first initiator would be too high.

[0028] The polymerization process can be conducted either as a mass process wherein the reaction mixture is predominantly monomer or as a suspension process wherein the reaction mixture typically is a suspension of monomer in water, or as an emulsion or micro-emulsion process wherein the monomer typically is emulsified in water. Preferably, the present process is a mass, suspension or emulsion process. More preferably it is a suspension polymerization process. Most preferably it is a batch suspension process. In these processes the usual additives will have to be used. For example, if the monomer is present in the form of a suspension in water, the usual additives like surfactant(s), protective colloid(s), anti-fouling agent(s), pH-buffer(s), etc. may be present. Depending on the type of polymer desired, each of the above-mentioned processes may be preferred.

[0029] One or more protective colloids can be used in the process of the invention. Examples of suitable protective colloids are protective colloids such as polyvinyl alcohols (PVAs), which may, for example, be (partially) saponified polyvinyl acetates with a degree of hydrolysis of at least 40%, more preferably 60%, and most preferably 62%, and a degree of hydrolysis of at most 90%, more preferably 85%, and most preferably 80%. If for example two PVAs are employed, both PVAs may have a similar degree of hydrolysis. It may also be envisaged that the two PVAs have a different degree of hydrolysis. A first PVA may have a degree of hydrolysis as described above. A second PVA may have a degree of hydrolysis of at least 10%, more preferably 20%, and most preferably 30%, and a degree of hydrolysis of at most 80%, more preferably 70%, and most preferably 60%. If more than one PVA is used, the indicated degree of hydrolysis generally is the weight-averaged degree of hydrolysis of the products used. Although said PVAs are the preferred protective colloids for processes according to the invention, it is also possible to use other conventional protective colloids, such as cellulose, water-soluble polymers, oil-soluble emulsifying agents or water-soluble emulsifying agents. Examples of such cellulose are methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, and hydroxypropyl methyl cellulose. Examples of water-soluble polymers are polyacrylic acid, gelatin, styrene maleic acid copolymers, and polyvinyl pyrrolidone. Oil-soluble emulsifying agents are, for example, sorbitan monolaurate, sorbitan trioleate, sorbitan monostearate, glycerin tristearate, and ethylene oxide-propylene oxide block copolymers. Examples of water-soluble emulsifying agents are polyoxyethylene sorbitan monolaurate, polyoxyethylene glycerin oleate, and sodium laurate. It is also envisaged to employ a combination of two or more of the above protective colloids.

[0030] The protective colloid can be in a pure form or be diluted in an appropriate solvent, which in the case of PVA preferably is water or a mixture of water and an alcohol. Aqueous solutions may contain at least 0.05% PVA by weight, more preferably at least 0.5% by weight, and most preferably at least 1 % by weight, and at most 40 % PVA by weight, more preferably at most 20 % by weight, and most preferably at most 10 % by weight. If so desired, the amount of PVA in the solution that is actually mixed into the reaction mixture can be even lower, for instance when an aqueous protective colloid solution as presented above is fed into the reactor together with additional water that is fed to the reaction mixture.

[0031] The amount of protective colloid to be used in the process according to the invention is within the lower ranges as conventionally used in polymerization processes. Typically, this range has a lower limit of 0.01 % w/w of protective colloid and more preferably 0.02% w/w, and an upper limit of 1 % w/w of protective colloid, preferably 0.3% w/w, and most preferably 0.15% w/w, based on the weight of the monomer(s) to be polymerized, is used. When it is said that protective colloid and initiator are added at the same time, it is meant to include not only processes wherein initiator and protective colloid are added simultaneously or together, but also processes wherein initiator and protective colloid are added or dosed in an alternating way or sequentially in random order at the polymerization temperature (each being

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dosed at least twice). Also it is encompassed in the process of the present invention to dose at least part of the colloid just prior to the pressure drop.

[0032] After the polymerization, the resulting (co)polymer (or resin) will be worked up as is usual in the art. Polymers obtained by a suspension polymerization according to the invention, for example, will be submitted to the usual drying and screening steps. The resulting resin preferably is characterized in that it contains less than 50 ppm of residual peroxide, more preferably less than 40 ppm, and most preferably, less than 25 ppm of peroxide, immediately after drying for 1 hour at 60°C and screening. The resin was found to exhibit excellent heat stability as measured with a Metrastat® PSD260 testing oven according to method ISO 182-2 (1990E). The improved heat stability proved that the resin hardly discoloured when submitted to melt-processing steps, e.g., to form shaped articles.

Experimental

[0033] Experiments are carried out according a standard suspension polymerisation process, using a 10 l Buchi reactor provided with one baffle; three flat-bladed stirrers at three levels, a pressure transducer, a vinyl chloride (VCM) feed line, a nitrogen purge line, a peroxide feed line and a peroxide injection point. The reactor is charged with 4700 g of demineralized water; 40.2 g of a 5 % solution of Alcotex ® B72 (polyvinyl acetate/alcohol) in demineralized water; and pressurized with nitrogen to 15 bars. If no leaks are observed, the reactor is evacuated for 5 min at 75 mbars (while stirred) to remove the air, and subsequently charged with 2870 g of VCM (ex Akzo Nobel Salt & Base), followed by heating up the reactor to the desired polymerisation temperature of 57 °C in 30-60 minutes. After reaching a stable temperature, the initial peroxide is dosed either by the injecting point within 1 minute, the peroxide feed line during the polymerisation process or both, whatever is required. Dosing of the (very) fast peroxide through the feed line was done in such a way that the maximum rate (i.e 33 %/h) was reached in 0.5-0.65 hours. The cooling capacity was limited to a value corresponding a maximum polymerization rate of about 33 %/h (the maximum of the reference experiment). The polymerisation was stopped when a pressure drop of 2 bars was reached, by cooling the reactor and degassing the reactor. After removal of the residual VCM by evacuation, the polymer was obtained by filtration, washing and drying. When an aqueous dispersion of the second initiator is dosed during the process, the expected volume dosed is subtracted from the amount of water added in the beginning, so the total amount of water will be (more or less) the same at the end of the reaction.

Experiments 1 and 2 and Comparative Example A and B

[0034] Using the experimental set-up as described, a conventional initiator (Trigonox® EHP ex Akzo Nobel) was used as the first initiator. In Comparative Example A this initiator was used as the sole initiator and it was found that the use of 656 ppm was the maximum amount that could be used whereby the reaction mixture maintained the desired reaction temperature of 57°C. In Comparative Example B this maximum amount of the initial initiator was combined with an additional amount of the second initiator.

In Examples 1 and 2, less than the maximum amount of the first initiator was used in combination with an aqueous dispersion of a second initiator, Trigonox® 187 ex Akzo Nobel. The difference of the maximum temperature that was observed and the preset temperature of 57°C was reported in the table as T incr.

[0035] The amount of polymer as obtained is presented as the yield on monomer (yield). The table furthermore presents some properties of the resulting polymer. Psd is the average polymer particle size, and DOP is a measure for the porosity of the polymer. The time till pressure drop (CPT) as well as the time till the pressure had dropped to a value two bars below the pressure at the start of the pressure drop is also reported as a measure of the polymerization rate.

Experiment	Tx EHP (ppm)	Tx 187 (ppm)	T Incr (°C)	Yield (%)	Psd (µm)	DOP (%)	CPT (min)	Time to -2 bar (min)
A	656	0	0	83.4	155.3	25.9	197	226
B	656	310	6.0	89.1	154.8	24.8	139	170
1	500	410	0.8	86	153.6	25.5	146	177
2	400	450	0	86.3	161.1	25.5	154	184

From these results it follows that much faster polymerization rates are attainable without that a run away of the reaction mixture temperature is observed, when compared to conventional processes. The PVC resulting from Experiments 1 and 2 had good organoleptic properties.

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Claims

1. A process to polymerize one or more monomers wherein at most 90 percent by weight of the safely useable amount of a first initiator is used and a second initiator, having a half-life from 0.0001 hour to 1.0 hour at the polymerization temperature and that is less temperature stable than said first initiator, is being dosed at least partially from the start of the polymerization until 10% of the monomer(s) has been polymerized, in an amount, and preferably at a variable rate, such that at least 92% of the maximum cooling capacity is used during at least a period of time wherein at least 10 percent by weight of the monomer is polymerized.
2. A process according to claim 1 wherein the monomers comprise vinyl chloride.
3. A process according to claim 1 or 2 wherein the process is a suspension polymerization process, preferably a batch suspension polymerization process.
4. A process according to any one of claims 1-3 wherein the second initiator is also added intermittently and/or continuously after the start of the pressure drop and/or during the pressure drop.
5. A process according to any one of claims 1-4 wherein a protective colloid is added during the polymerization process.
6. A process according to any one of claims 1-5 wherein said first initiator has a half-life of 0.1 hour to 10 hours at the polymerization temperature and the less temperature stable initiator has a half-life of 0.0001 hour to 1.0 hour at said temperature.
7. A process according to any one of claims 1-6 wherein the amount of the second initiator that is used is at least 0.01% by weight, based on the weight of the monomer that is polymerized.
8. A process according to any one of claims 1-7 wherein the total amount of first and second initiator is 0.01 to 1 %w/w, based on the weight of the monomer that is polymerized.
9. A process according to any one of claims 1-7 wherein the polymerization reactor has a volume of 15 m³ or more.

Patentansprüche

1. Verfahren zum Polymerisieren von einem oder mehreren Monomeren, wobei höchstens 90 Gew.-% der sicher verwendbaren Menge eines ersten Initiators verwendet werden und ein zweiter Initiator, der eine Halbwertszeit von 0,0001 Stunden bis 1,0 Stunden bei der Polymerisationstemperatur aufweist und weniger temperaturstabil als der erste Initiator ist, von Beginn der Polymerisation an wenigstens partiell zudosiert wird, bis 10% des oder der Monomere polymerisiert sind, und zwar in einer solchen Menge und vorzugsweise in einer variablen Geschwindigkeit, dass während wenigstens der Zeitspanne, in der wenigstens 10 Gew.-% des Monomers polymerisiert werden, wenigstens 92% der maximalen Kühlkapazität verwendet werden.
2. Verfahren gemäß Anspruch 1, wobei die Monomere Vinylchlorid umfassen.
3. Verfahren gemäß Anspruch 1 oder 2, wobei das Verfahren ein Suspensionspolymerisationsverfahren, vorzugsweise ein diskontinuierliches Suspensionspolymerisationsverfahren, ist.
4. Verfahren gemäß einem der Ansprüche 1-3, wobei der zweite Initiator nach Beginn des Druckabfalls und/oder während dem Druckabfall auch portionsweise und/oder kontinuierlich hinzugefügt wird.
5. Verfahren gemäß einem der Ansprüche 1-4, wobei während des Polymerisationsverfahrens ein Schutzkolloid hinzugefügt wird.
6. Verfahren gemäß einem der Ansprüche 1-5, wobei der erste Initiator eine Halbwertszeit von 0,1 Stunde bis 10 Stunden bei der Polymerisationstemperatur aufweist und der weniger temperaturstabile Initiator eine Halbwertszeit von 0,0001 Stunde bis 1,0 Stunden bei dieser Temperatur aufweist.
7. Verfahren gemäß einem der Ansprüche 1-6, wobei die Menge des zweiten Initiators, die verwendet wird, wenigstens

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0,01 Gew.-% beträgt, bezogen auf das Gewicht des Monomers, das polymerisiert wird.

8. Verfahren gemäß einem der Ansprüche 1-7, wobei die Gesamtmenge des ersten und des zweiten Initiators 0,01 bis 1 Gew.-% beträgt, bezogen auf das Gewicht des Monomers, das polymerisiert wird.

9. Verfahren gemäß einem der Ansprüche 1-7, wobei der Polymerisationsreaktor ein Volumen von 15 m³ oder mehr hat.

Revendications

1. Procédé de polymérisation d'un ou de plusieurs monomères, dans lequel au plus 90 % en poids de la quantité utilisable en toute sécurité d'un premier initiateur est utilisée et un second initiateur, ayant une demi-vie de 0,0001 à 1,0 0 heure à la température de polymérisation, et qui est moins stable en température que ledit premier initiateur, est dosé au moins partiellement dès le début de la polymérisation jusqu'à ce que 10% du ou des monomères aient été polymérisés, en une quantité, et de préférence, à un débit variable, pour qu'au moins 92% de la capacité de refroidissement maximale soit utilisée durant au moins une période de temps pendant laquelle au moins 10% en poids du monomère est polymérisé.

2. Procédé selon la revendication 1, dans lequel les monomères comprennent du chlorure de vinyle.

3. Procédé selon la revendication 1 ou 2, dans lequel le procédé est un procédé de polymérisation en suspension, de préférence, un procédé de polymérisation en suspension discontinu.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le second initiateur est également ajouté de manière intermittente et/ou continue après le début de la chute de pression et/ou pendant la chute de pression.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel un colloïde de protection est ajouté pendant le procédé de polymérisation.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel ledit premier initiateur a une demi-vie de 0,1 à 10 heures à la température de polymérisation et l'initiateur moins stable en température a une demi-vie de 0,0001 à 1,0 heure à ladite température.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la quantité du second initiateur qui est utilisé est d'au moins 0,01% en poids, sur la base du poids du monomère qui est polymérisé.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel la quantité totale du premier et du second initiateurs est de 0,01 à 1% p/p, sur la base du poids du monomère qui est polymérisé.

9. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel le réacteur de polymérisation un volume de 15 m³ ou plus.

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(11) Application No. AU 2004234056 B2

(19) AUSTRALIAN PATENT OFFICE

(54) Title
 Increased polymerization reactor output by using a specific initiator system

(51)⁶ International Patent Classification(s)
C08F 2/18 (2006.01) **4/38**
C08F 4/38 (2006.01) 20060101ALI2005100
C08F 14/06 (2006.01) 8BMEP **C08F**
 C08F 2/18 14/06
 20060101AFI2006052 20060101ALI2006072
 1BWWO **C08F** 2BMEP
 PCT/EP2004/004500

(21) Application No: 2004234056

(22) Application Date: 2004.04.27

(87) WIPO No: W004/096871

(30) Priority Data

(31) Number
 03076390.8

(32) Date
 2003.05.01

(33) Country
 EP

(43) Publication Date: 2004.11.11

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 DE 3029211 A
 EP 0096365 A
 WO 2000/017245
 US 3778422 A

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
11 November 2004 (11.11.2004)

PCT

(10) International Publication Number
WO 2004/096871 A1

- (51) International Patent Classification: C08F 4/38, 14/06, 2/18, B01J 19/00 (74) Agent: SCHALKWIJK, Pieter, Cornelis; Akzo Nobel N.V., Intellectual Property Department (Dept. ATP), P.O. Box 9300, NL-6800 SB Arnhem (NL).
- (21) International Application Number: PCT/EP2004/004500 (81) Designated States (unless otherwise indicated, for every kind of national protection available): AI, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CU, CR, CZ, DE, DK, DM, DZ, EC, EG, ES, FI, GB, GD, GE, GH, GM, GR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 27 April 2004 (27.04.2004) (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BI, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 03076390.8 1 May 2003 (01.05.2003) EP
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- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/096871 A1

(54) Title: INCREASED POLYMERIZATION REACTOR OUTPUT BY USING A SPECIFIC INITIATOR SYSTEM

(57) Abstract: The invention pertains to a process to polymerize one or more monomers wherein at most 90%w/w of a safely useable amount of a first initiator is used and a second initiator is added at least after the start of the polymerization, in an amount such that essentially the full cooling capacity of the polymerization reactor is used, resulting in a cost efficient process to make polymers, particularly polymers comprising polymerized vinyl chloride.

INCREASED POLYMERIZATION REACTOR OUTPUT BY USING A SPECIFIC INITIATOR SYSTEM

The present invention relates to a process to polymerize one or more monomers
5 in a reactor with a certain cooling capacity, wherein said cooling capacity is
limiting the space-time yield of the reactor.

DE-OS-1 570 963 discloses to dose an initiator, optionally mixed with a solvent,
to the mixture to be polymerized via a stream of water. The organic peroxides
10 that are exemplified in this patent application are peroxydicarbonates and acetyl-
cyclohexyl-sulfonyl-peroxide (ACSP). This process of DE-OS-1 570 963 was
found to solve a number of problems in the industry. However, the process still
suffers from insufficient control of the heat peak of the polymerization reaction
and a related less than optimal space-time yield of the reactor due to cooling
15 capacity restrictions. Accordingly, a different process not suffering from these
drawbacks is desired.

Similarly, EP-A-0 096 365 discloses how a peroxide is added in three parts during
the polymerization. Again, difficulties in controlling the heat that is subsequently
20 generated are reported.

JP-A-07082304 discloses a process wherein a first peroxide is used at the start
of the polymerization. Later in the process, when a reflux condenser is used as
an additional cooling device, a second peroxide is dosed to the reactor to more
25 efficiently use the additional cooling capacity of the condenser. Only a limited
amount of the second peroxide can be used due to the fact that the first peroxide
is still used in a conventional amount. By doing so the polymerization time is
reduced from 5 hours and 3 minutes for the conventional process, in which only
the first peroxide is used, to 4 hours and 17 minutes for the process wherein
30 additionally the second peroxide is dosed. Although a significant improvement
over the prior art, the time gain is still considered less than desired. Even higher
time-space yield gains are being looked for.

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Furthermore, the above-mentioned processes of the prior art are not very suitable for increasing the space-time yield of very large polymerization reactors, particularly those of at least 15m³, more particularly those of at least 20m³, wherein safety margins are maintained to prevent the polymerizing content from "running away", meaning that due to excessive heat development the reactor content is heated to above its set temperature, causing more of the conventional peroxide to decompose, which causes the polymerization rate to further increase, thus auto-acceleration occurs up to the point that the reactor content has to be stopped or dumped or it will rupture the reactor.

The current invention relates to a new process wherein these problems have largely been solved. More particularly, we have found that by selecting the proper amount of initiator that is dosed at the beginning of the polymerization and the proper dosing conditions for subsequently added initiator, it is possible to obtain a polymerization reaction where the rate of polymerization can be very well controlled and therefore the heat of polymerization can be kept at the maximum cooling capacity, allowing optimum reactor space-time yield, very efficient peroxide usage, and very low residual peroxide levels in the resin after polymerization. Furthermore, the fact that less of a conventional first initiator is dosed at the start of the polymerization, it was found that the distribution of said first initiator over the monomer was improved. Especially for the suspension and emulsion polymerization process this was found to result in polymer particles with less defects, such as fish-eyes, that are considered to be caused by too high peroxide concentration in a monomer droplet. This effect can be further augmented by metering both the initiator and a protective colloid at the same time. Additionally, the porosity of the polymer can be enhanced and better controlled through selection of the appropriate protective colloid and the way in which the protective colloid and/or the peroxide are metered.

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The present invention provides a process to polymerize one or more monomers wherein at most 90 percent by weight of the safely useable amount of a first initiator is used and a second initiator, having a half-life from 0.0001 hour to 1.0 hour at the polymerization temperature and that is less temperature stable than said first initiator, is being dosed at least partially from the start of the polymerization until 10% of the monomer(s) has been polymerized, in an amount, and preferably at a variable rate, such that at least 92% of the maximum cooling capacity is used during at least a period of time wherein at least 10 percent by weight of the monomer is polymerized.

The new process is characterized in that, compared to a process which is run at its maximum rate with all initiator being added at the start of the polymerization, only up to 90 mole% of said initiator (or mixture of initiators) is added at the start of

of the polymerization and a second initiator, which is less temperature stable than the first initiator that is added at the start, said second initiator having a half-life from 0.0001 hour to 1.0 hour at the polymerization temperature, is dosed to the polymerizing mixture in an amount, and preferably at a varying rate, such that at

5 least 92, preferably at least 96, more preferably at least 98% of the maximum cooling capacity is used during at least a period of time wherein at least 10 % by weight (%w/w), preferably 20%w/w, more preferably at least 30%w/w, most preferably at least 40%w/w of the monomer is polymerized. Preferably the second initiator is dosed in such a way that the maximum cooling capacity is used

10 in a period of time wherein at least 10 % by weight (%w/w), preferably 20%w/w, more preferably at least 30%w/w, most preferably at least 40%w/w of the monomer is polymerized, whereby the actual temperature of the polymerizing mixture is kept at the desired temperature plus or minus 0.2°C, because the more the maximum cooling capacity is being used, the more efficient is the polymerization process. The dosing of the second initiator in conjunction with the

15 use of the first initiator allows for an unprecedented i) accurate control of the polymerization rate and related polymerization heat generation (and, accordingly, also the polymerization temperature) by controlling the peroxide dosing rate, ii) space-time yield of the reactor, and iii) very economic initiator usage.

20

If the amount of initiator being added at the start of the polymerization is carefully chosen and the second initiator is dosed according to the invention, then it is furthermore found possible to significantly reduce or remove the run-away safety margins that were necessary in the conventional process and the process can

25 actually run at such a rate that the heat of polymerization is very close to, or it may even temporarily exceed, the cooling capacity, without that such a run-away is observed. In this respect, reference is made to JP-A-07082304 (see Example 1) in which conventional safety margins are being maintained of more than 15% of the total cooling capacity. In a process according to the invention the actual

30 temperature of the reacting mixture typically does not reach a temperature that is more than 6°C above the desired polymerization temperature. Preferably, the overshoot of the temperature of the polymerization mixture is less than 4°C, more

preferably it is less than 2°C, even more preferably it is less than 1°C. Most preferably, the actual temperature of the polymerizing mixture is kept at the desired temperature plus or minus 0.2°C.

- 5 The amount of initiator being added at the start of the polymerization should be at most 90% by weight (%w/w) of the maximum amount of said initiator that can be used in the identical process that is run at the maximum cooling capacity and whereof the temperature is not exceeding the set temperature due to an excess of polymerization heat. If more than this maximum amount of said initiator is
- 10 used, the polymerization heat exceeds the heat transfer capacity of the reactor and the reactor content will heat up to a temperature above the maximum allowable polymerization temperature. Since such an overshoot in temperature will cause a more rapid decomposition of the initiator, the temperature may even increase further, up to a point where the reaction runs away and becomes
- 15 uncontrollable and hazardous. For this reason this maximum amount of initiator is called the safely useable amount. Preferably it is at most 80%w/w of said safely useable amount, more preferably at most 70%w/w, and most preferably at most 65%w/w. The lower the amount of first initiator the better the controlling of the polymerization rate (and, accordingly, the heat of polymerization) during the
- 20 process. Preferably at least 2%w/w, more preferably at least 5%w/w, most preferably at least 10%w/w of said safely useable amount of first initiator is used.

It is noted that the term "maximum cooling capacity" as used herein is used in its conventional meaning, being the amount of heat that can be removed from the

25 polymerization reaction mixture when 1) said reaction mixture has a temperature equal to the preset polymerization temperature, and 2) the cooling capacity is at its maximum level under normal polymerization conditions (typically the situation wherein the cooling medium is flowing at its maximum rate at its lowest temperature under normal polymerization conditions).

30 The amount of the second initiator that is used is preferably at least 0.01% by weight (%w/w), more preferably at least 0.015 %w/w, and most preferably more

than 0.02 %w/w, all based on the weight of the monomer that is polymerized in the process.

It is noted that WO 00/17245 discloses a process wherein initiators are dosed to a polymerization reactor at temperatures where essentially all the initiators have a half-life of from 0.05 to 1.0 hour. In non-prepublished application PCT/EP02/14518 extremely fast organic initiators with a half-life from 0.0001 hour to 0.050 hour at the polymerization temperature are used to give an improved control of the polymerization rate, higher polymerization rates, leading to an increased space-time yield of polymerization reactors, and results in the process rendering a polymer with very low residual initiator levels. However, these processes were found to require the use of high amounts of the fast or extremely fast peroxides because the initiator efficiency is below that of a conventional peroxide that is dosed at the start. With the present process, the amount of fast or extremely fast peroxide that is used is lower than the amount as disclosed in WO 00/17245 and PCT/EP02/14518. Also the total amount of active oxygen as needed in the present process, compared to the process of WO 00/17245 and PCT/EP02/14518 with the same polymerization time, was found to be reduced. Therefore, the present process is more economical and yields a polymer with less decomposition products of the initiator, hence a product with improved organoleptic properties, particularly smell. Also, it is known that residual decomposition products typically having a molecular weight of less than 250 Dalton may lead to fogging (the decomposition products evaporate from the resin and condense on another surface), which is undesired. Also, a rework of Example F of WO 00/17245 showed that only after 2.9 hours after the start of the heat-up, and only for an instant, the maximum cooling capacity was used. It was furthermore observed that the present process allows for a better distribution of the initiators over the monomer, which, particularly when the polymerization is a dispersion polymerization, such as an emulsion or suspension polymerization, results in a polymer with improved properties. Particularly the molecular weight and/or the molecular weight distribution of the polymer and/or the number of fish-

eyes (resulting from the polymerization of a monomer droplet when a too high peroxide concentration was present) was found to be improved.

The process according to the invention is pre-eminently suited to polymerize
5 monomer mixtures comprising vinyl chloride monomer (VCM). Preferably, the
process according to the invention involves the polymerization of monomer
mixtures comprising at least 50% by weight (% w/w) of VCM, based on the weight
of all monomer. Comonomers that can be used are of the conventional type and
include vinylidene chloride, vinyl acetate, ethylene, propylene, acrylonitrile,
10 styrene, and (meth)acrylates. More preferably, at least 80% w/w of the
monomer(s) being polymerized is made up of VCM, while in the most preferred
process the monomer consists essentially of VCM. As is known in the art, the
polymerization temperature of such processes to a large extent determines the
molecular weight of the resulting resin.

15 It is to be understood that the word "dosing" is used to describe the step of
adding initiator to the polymerizing reaction mixture at polymerization conditions.
The dosing can be done intermittently during the polymerization, meaning that at
least two portions of initiator are added to the reaction mixture, or it can be
20 continuous, meaning that for a certain period of time the initiator is continuously
added to the reaction mixture, or any combination of these techniques. Examples
of a combination of such techniques include, for instance, a process wherein the
initiator is first added continuously, then the addition is stopped, and then again it
is added continuously. If an intermittent operation is selected, there are at least 2,
25 preferably at least 4, more preferably at least 10, and most preferably at least 20
moments at the polymerization temperature at which the initiator is dosed. Most
preferably, the peroxide is dosed continuously and/or intermittently from the start
of the polymerization reaction, preferably after at least 5%, less preferred after at
least 10%, even more less preferred after at least 20%, of the monomer(s) has
30 already been polymerized and wherein during the dosing period at least 2,
preferably at least 5, more preferably at least 10%, more preferably at least 20%,

more preferably at least 40%, and most preferably at least 60%, of all monomer used in the process is polymerized.

In the process according to the invention, one or more initiators may be used as the second initiator, preferably the initiators are selected from organic peroxides, however, they may also be selected from conventional azo-initiators. Preferred examples of peroxides to be used as a second initiator in the process according to the invention are the following:

- 1,1,3,3-tetramethylbutylperoxy methoxy acetate, or hexanoyl pivaloyl peroxide for polymerization reactions at 35-70°C, preferably 40-65°C.
 - diisobutanoylperoxide, bis(tert-butylperoxy) oxalate or 2,2-bis(2,2-dimethylpropanoylperoxy)-4-methyl pentane, for polymerization reactions at 40-85°C, preferably 45-80°C.
 - α -cumyl peroxyneodecanoate, 2-(2,2-dimethylpropanoylperoxy)-2-(2-ethylhexanoylperoxy)-4-methyl pentane or 2,4,4-trimethylpentyl-2-peroxyneodecanoate, at polymerization temperatures of 53-99°C, preferably 60-95°C, and
 - tert-amyl, tert-butyl peroxyneodecanoate or peroxydicarbonates, at polymerization temperatures of 62 -107°C, preferably 75-100°C.
- Other peroxides may also be used. Their half-lives can be determined by conventional thermal decomposition studies in monochlorobenzene, as well-known in the art (see for instance the brochure "Initiators for high polymers" with code 10737 obtainable from Akzo Nobel). The term polymerization temperature as used herein is used in its conventional connotation and represent the average temperature in the period in which the majority of the monomer is polymerized. In case of doubt, it is the average temperature in the polymerization period in which not the first and not the last 5% of the monomer is polymerized.

Preferably, the first initiator that is added at the start of the polymerization, meaning when up to 10% of the monomer has polymerized, preferably when up to 5% of the monomer has polymerized, more preferably when up to 2% of the

monomer has polymerized, even more preferably up to 1% has polymerized, most preferably when essentially no monomer has yet polymerized, has a half-life (when measured in monochlorobenzene at the polymerization temperature) of from 0.1 hour to 10.0 hour. More preferably, essentially all peroxide that is added at the start has a half-life of 0.2 to 5.0 hour, even more preferably 0.4 to 2.0 hour, most preferably 0.5 to 1.0 hour. The first initiator can be a mixture of initiators, provided that the weight average half life of the initiators in the mixture is within the 0.1 - 10 hour range. As said, the first initiator should have a longer half-life than the second initiator (at the polymerization temperature). Preferred first initiators include α -cumyl peroxyneodecanoate, 2-(2,2-dimethylpropanoylperoxy)-2-(2-ethylhexanoylperoxy)-4-methyl pentane, 2,4,4-trimethylpentyl-2-peroxyneodecanoate, 3-hydroxy-1,1-dimethylbutyl peroxyneodecanoate, tert-amyl peroxyneodecanoate, tert-butyl peroxyneodecanoate, peroxydicarbonates (e.g. di-(2-ethylhexyl) peroxydicarbonate and di-(sec butyl)peroxydicarbonate), tert butyl peroxyneohexanoate, tert butyl peroxy pivalate, tert amyl peroxy pivalate, and dilauroyl peroxide.

It is noted that when the term "polymerization temperature" is used, that this is the temperature at which the majority of all monomer (i.e. more than 50%w/w, preferably more than 60%w/w, most preferably more than 75%w/w of the monomer being polymerized) is being polymerized. It is known that the polymerization temperature set-point can be varied over time. Known polymerization temperature variations for polymerizations of vinyl chloride include an intentional higher temperature when the polymerization is started and/or a higher temperature upon pressured drop, both used to increase the reactor output. If a variation in the polymerization temperature is applied, then the polymerization temperature is considered to be the average temperature over time from the moment the polymerization temperature is reached until the pressure drop. It is noted that also in the process of the present invention, the polymerization temperature set-point during the start-up and pressure drop stages may be higher than the average polymerization temperature set-point.

Preferably, the second initiator that is dosed during the polymerization has a half-life (when measured in monochlorobenzene at the polymerization temperature) of from 0.0001 hour to 1.0 hour. More preferably, essentially all second initiator that is used has a half-life of 0.0005 to 0.8 hour, even more preferably 0.001 to 0.5 hour, most preferably 0.005 to 0.35 hour. The second initiator can be a redox initiation system. In such a case the reducing agent, the oxidizing agent, or both can be dosed in accordance with the invention. For such redox systems, the half-life of the redox system is the half-life as measured when all components of the system are present. However, in view of the fact that redox systems typically contain heavy metals and/or undesired reducing agents, the initiators of the present invention preferably are not such redox initiation systems. The second initiator may be a single initiator or a mixture of several initiators. If a mixture is used, all initiators of said mixture should fulfill the half-life requirement. If a mixture of second initiators is used, then preferably all initiator of the mixture is less temperature stable than the first initiator. If the first initiator is a mixture of initiators, then it is preferred that the second initiator is less temperature stable than all initiators in said mixture. If both the first and second initiator consists of a mixture of initiators, then it is preferred that the most thermally stable initiator of the second mixture is less stable than the least stable initiator of the first mixture.

In a preferred embodiment, the invention relates to a process wherein the polymerization mixture is formulated at a temperature below the reaction (polymerization) temperature and subsequently heated to reach said desired reaction temperature. In such a cold-start process the first initiator is added at the start as defined above. However, in such a process it can be beneficial to add also some of the more reactive second initiator during the heat-up phase, since it boost the heat up of the reaction mixture. Preferably, from 0 - 60 % by weight (%w/w), more preferably 5 - 40 %w/w, most preferably 5 - 20 %w/w, of the peroxide, based on the total weight of the second initiator used during the polymerization, is present at the start of the heating-up phase, while the remainder is dosed over a period of at least 1, preferably 2, and more preferably 2-4 hours, depending on the polymerization time. More preferably, the remainder

of the peroxide is dosed from the time the reaction mixture temperature is controlled at the desired reaction temperature. The use of a combination of the first initiator and a small amount of the second initiator from the start allows a fast heating up and start of the polymerization, since these initiators will already
5 (partly) decompose during the heating of the polymerization mixture. When the polymerization mixture reaches the polymerization temperature, the remainder of the peroxide can be dosed to the mixture to control the further polymerization rate. Preferably, the dosing is continuous, preferably at a variable rate, since this allows the most accurate control of the polymerization rate and a constant
10 polymerization heat output. The combination of the first and second initiator ensures the highest initiator efficiency and space-time reactor yield. This is particularly important for commercial reactors. Therefore the polymerization process according to the invention is preferably carried out in reactors of 15m³ or more.

15 In another preferred embodiment, the reaction mixture is formulated at or near the polymerization temperature. In this process, hereinafter called warm-start process, it is not necessary to add a certain amount of the second initiator at the start while the remainder is dosed over time. However, also in this warm-start
20 process it can be beneficial to add up to 30 %w/w, preferably up to 20%w/w, most preferably up to 10%w/w, of the second initiator immediately after formation of the reaction mixture, the remainder being dosed over time. If this procedure is used, the second initiator preferably is added as the last ingredient. This procedure is particularly preferred if a certain amount of polymerization inhibitor
25 (a radical trapping species) is present in the reaction mixture. If such a radical scavenger is present, for instance because it is introduced with the monomer wherein it is typically used as a stabilizer, the initially dosed peroxide will react with said scavenger, thus preventing a delayed start of the polymerization reaction.

30 It is furthermore preferred that two steps are present in the process after the polymerization temperature is reached. In a first step with a duration of up to 90

reaction, it can be advantageous to use the line through which this water is dosed to also dose the initiator. It is noted that if the formation of the initiator is fast enough, one can dose the raw materials for said initiator into piping or hold-up vessels, from which the initiator is then fed into the polymerization mixture.

5 Alternatively, but less desired, there is the process wherein the raw materials are added to the polymerization mixture. In all instances it can be beneficial to add stirring equipment and/or heat exchangers to the feed lines in order to optimize efficiency.

10 It is noted that, due to the use of the more stable first initiator, it is not preferred to conduct the present process such that 80% or more of all monomer is polymerized within a period of 2 hours. With such short polymerization times the amount of residual first initiator would be too high.

15 The polymerization process can be conducted either as a mass process wherein the reaction mixture is predominantly monomer or as a suspension process wherein the reaction mixture typically is a suspension of monomer in water, or as an emulsion or micro-emulsion process wherein the monomer typically is emulsified in water. Preferably, the present process is a mass, suspension or

20 emulsion process. More preferably it is a suspension polymerization process. Most preferably it is a batch suspension process. In these processes the usual additives will have to be used. For example, if the monomer is present in the form of a suspension in water, the usual additives like surfactant(s), protective colloid(s), anti-fouling agent(s), pH-buffer(s), etc. may be present. Depending on

25 the type of polymer desired, each of the above-mentioned processes may be preferred.

One or more protective colloids can be used in the process of the invention. Examples of suitable protective colloids are protective colloids such as polyvinyl

30 alcohols (PVAs), which may, for example, be (partially) saponified polyvinyl acetates with a degree of hydrolysis of at least 40%, more preferably 60%, and most preferably 62%, and a degree of hydrolysis of at most 90%, more

preferably 85%, and most preferably 80%. If for example two PVAs are employed, both PVAs may have a similar degree of hydrolysis. It may also be envisaged that the two PVAs have a different degree of hydrolysis. A first PVA may have a degree of hydrolysis as described above. A second PVA may have
5 a degree of hydrolysis of at least 10%, more preferably 20%, and most preferably 30%, and a degree of hydrolysis of at most 80%, more preferably 70%, and most preferably 60%. If more than one PVA is used, the indicated degree of hydrolysis generally is the weight-averaged degree of hydrolysis of the products used. Although said PVAs are the preferred protective colloids for
10 processes according to the invention, it is also possible to use other conventional protective colloids, such as cellulosics, water-soluble polymers, oil-soluble emulsifying agents or water-soluble emulsifying agents. Examples of such cellulosics are methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, and hydroxypropyl methyl cellulose. Examples of
15 water-soluble polymers are polyacrylic acid, gelatin, styrene maleic acid copolymers, and polyvinyl pyrrolidone. Oil-soluble emulsifying agents are, for example, sorbitan monolaurate, sorbitan trioleate, sorbitan monostearate, glycerin tristearate, and ethylene oxide-propylene oxide block copolymers. Examples of water-soluble emulsifying agents are polyoxyethylene sorbitan
20 monolaurate, polyoxyethylene glycerin oleate, and sodium laurate. It is also envisaged to employ a combination of two or more of the above protective colloids.

The protective colloid can be in a pure form or be diluted in an appropriate
25 solvent, which in the case of PVA preferably is water or a mixture of water and an alcohol. Aqueous solutions may contain at least 0.05% PVA by weight, more preferably at least 0.5% by weight, and most preferably at least 1% by weight, and at most 40 % PVA by weight, more preferably at most 20 % by weight, and most preferably at most 10 % by weight. If so desired, the amount of PVA in the
30 solution that is actually mixed into the reaction mixture can be even lower, for instance when an aqueous protective colloid solution as presented above is fed into the reactor together with additional water that is fed to the reaction mixture.

The amount of protective colloid to be used in the process according to the invention is within the lower ranges as conventionally used in polymerization processes. Typically, this range has a lower limit of 0.01% w/w of protective colloid and more preferably 0.02% w/w, and an upper limit of 1% w/w of protective colloid, preferably 0.3% w/w, and most preferably 0.15% w/w, based on the weight of the monomer(s) to be polymerized, is used. When it is said that protective colloid and initiator are added at the same time, it is meant to include not only processes wherein initiator and protective colloid are added simultaneously or together, but also processes wherein initiator and protective colloid are added or dosed in an alternating way or sequentially in random order at the polymerization temperature (each being dosed at least twice). Also it is encompassed in the process of the present invention to dose at least part of the colloid just prior to the pressure drop.

After the polymerization, the resulting (co)polymer (or resin) will be worked up as is usual in the art. Polymers obtained by a suspension polymerization according to the invention, for example, will be submitted to the usual drying and screening steps. The resulting resin preferably is characterized in that it contains less than 50 ppm of residual peroxide, more preferably less than 40 ppm, and most preferably, less than 25 ppm of peroxide, immediately after drying for 1 hour at 60°C and screening. The resin was found to exhibit excellent heat stability as measured with a Metrastat® PSD260 testing oven according to method ISO 182-2 (1990E). The improved heat stability proved that the resin hardly discoloured when submitted to melt-processing steps, e.g., to form shaped articles.

Experimental

Experiments are carried out according a standard suspension polymerisation process, using a 10 l Buchi reactor provided with one baffle; three flat-bladed stirrers at three levels, a pressure transducer, a vinyl chloride (VCM) feed line, a nitrogen purge line, a peroxide feed line and a peroxide injection point. The reactor is charged with 4700 g of demineralized water; 40.2 g of a 5 % solution of

Alcotex ® B72 (polyvinyl acetate/alcohol) in demineralized water, and pressurized with nitrogen to 15 bars. If no leaks are observed, the reactor is evacuated for 5 min at 75 mbars (while stirred) to remove the air, and subsequently charged with 2870 g of VCM (ex Akzo Nobel Salt & Base), followed by heating up the reactor to the desired polymerisation temperature of 57 °C in 30-60 minutes. After reaching a stable temperature, the initial peroxide is dosed either by the injecting point within 1 minute, the peroxide feed line during the polymerisation process or both, whatever is required. Dosing of the (very) fast peroxide through the feed line was done in such a way that the maximum rate (i.e 33 %/h) was reached in 0.5-0.65 hours. The cooling capacity was limited to a value corresponding a maximum polymerization rate of about 33 %/h (the maximum of the reference experiment). The polymerisation was stopped when a pressure drop of 2 bars was reached, by cooling the reactor and degassing the reactor. After removal of the residual VCM by evacuation, the polymer was obtained by filtration, washing and drying. When an aqueous dispersion of the second initiator is dosed during the process, the expected volume dosed is subtracted from the amount of water added in the beginning, so the total amount of water will be (more or less) the same at the end of the reaction.

Experiments 1 and 2 and Comparative Example A and B

Using the experimental set-up as described, a conventional initiator (Trigonox® EHP ex Akzo Nobel) was used as the first initiator. In Comparative Example A this initiator was used as the sole initiator and it was found that the use of 656 ppm was the maximum amount that could be used whereby the reaction mixture maintained the desired reaction temperature of 57°C. In Comparative Example B this maximum amount of the initial initiator was combined with an additional amount of the second initiator.

In Examples 1 and 2, less than the maximum amount of the first initiator was used in combination with an aqueous dispersion of a second initiator, Trigonox® 187 ex Akzo Nobel. The difference of the maximum temperature that was observed and the preset temperature of 57°C was reported in the table as T incr.

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The amount of polymer as obtained is presented as the yield on monomer (yield). The table furthermore presents some properties of the resulting polymer. P_{sd} is the average polymer particle size, and DOP is a measure for the porosity of the polymer. The time till pressure drop (CPT) as well as the time till the pressure had dropped to a value two bars below the pressure at the start of the pressure drop is also reported as a measure of the polymerization rate.

Experiment	T _x EHP (ppm)	T _x 187 (ppm)	T incr (°C)	Yield (%)	P _{sd} (µm)	DOP (%)	CPT (min)	Time to -2 bar (min)
A	656	0	0	83.4	155.3	25.9	197	226
B	656	310	6.0	89.1	154.8	24.8	139	170
1	500	410	0.8	86	153.6	25.5	146	177
2	400	450	0	86.3	161.1	25.5	154	184

- 10 From these results it follows that much faster polymerization rates are attainable without that a run away of the reaction mixture temperature is observed, when compared to conventional processes.
- 15 The PVC resulting from Experiments 1 and 2 had good organoleptic properties.
- 20 It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process to polymerize one or more monomers using a first initiator having a safely useable amount and a second initiator to form a polymerization mixture, and comprising the steps of:
- (i) adding at most 90 percent by weight of the safely useable amount of the first initiator; and
 - (ii) adding the second initiator; the second initiator being dosed at least partially from the start of the polymerization until 10% of the monomer(s) has been polymerized, in an amount such that at least 92% of the maximum cooling capacity of the polymerization mixture is used during at least a period of time wherein at least 10 percent by weight of the monomer is polymerized;
- wherein the second initiator has a half-life from 0.0001 hour to 1.0 hour at the polymerization temperature and is less temperature stable than the first initiator.
2. The process according to claim 1 wherein the second initiator is dosed at a variable rate.
3. The process according to claim 1 or 2 wherein the monomers comprise vinyl chloride.
4. The process according to claim 1-3 wherein the process is a suspension polymerization process.
5. The process according to any one of claims 1-4 wherein the process is a batch suspension polymerization process.
6. The process according to any one of claims 1-5 wherein the second initiator is also added intermittently and/or continuously after the start of the pressure drop and/or during the pressure drop.

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7. The process according to any one of claims 1-6 wherein a protective colloid is added during the polymerization process.
8. The process according to any one of claims 1-7 wherein said first initiator has a half-life of 0.1 hour to 10 hours at the polymerization temperature and the less temperature stable initiator has a half-life of 0.0001 hour to 1.0 hour at said temperature.
9. The process according to any one of claims 1-8 wherein the amount of the second initiator that is used is at least 0.01% by weight, based on the weight of the monomer that is polymerized.
10. The process according to any one of claims 1-9 wherein the total amount of first and second initiator is 0.01 to 1% w/w, based on the weight of the monomer that is polymerized.
11. The process according to any one of claims 1-10 wherein the polymerization reactor has a volume of 15 m³ or more.
12. A process to polymerize one or more monomers substantially as herein described with reference to the accompanying examples.

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