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**Solicitud de registro de patente de invención
denominada "Adición de Iniciadores Orgánicos Durante
la Caída de Presión en la Polimerización de Monómeros
de Cloruro de Vinilo"**

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. **7128**, mediante el cual se presenta el Concepto Técnico No. **1658**, que fue notificado por fijación en lista el 26 de Junio de 2.009.

1. En cuanto a las objeciones de Novedad

Con el fin de superar las objeciones presentadas por parte del señor Examinador respecto a la novedad de la presente invención, consignadas en el numeral **5.1** del citado Oficio No. **7128**, se ha realizado un análisis más detallado de la presente solicitud, así como también de las enseñanzas del documento citado como referencia. Por lo cual, a continuación me permito exponer los hechos y argumentos que demuestran la novedad que reviste el proceso de obtención de resinas de PVC, reivindicado en la presente solicitud.

1.1. Referencia citada

De la simple lectura del concepto técnico No. 1658, es posible determinar que el señor Examinador cita las enseñanzas del documento **WO 00/17245 (D1)** para desvirtuar la novedad de la presente invención.

El documento **WO 00/17245 (D1)** divulga un proceso para la polimerización del cloruro de vinilo en donde por lo menos parte del peróxido se dosifica a la mezcla de polimerización a la temperatura de la reacción, caracterizado porque esencialmente todo el peróxido orgánico usado en el proceso de la polimerización tiene una vida media a partir de 0.05 horas a 1.0 horas a la temperatura de polimerización (ver el resumen y la reivindicación 1). Según la página 4, líneas 9-20, por lo menos el 10% p/p, y preferiblemente 20-40% p/p, del peróxido orgánico está presente durante la fase del calentamiento de la reacción (es decir, mientras se va elevando la temperatura), y el resto del peróxido orgánico se agrega a partir del tiempo en el que la temperatura de la reacción está en el valor deseado (ver página 3, líneas 13-17 de D1 citadas por ese Despacho).

En este punto, vale la pena llamar la atención al hecho de que si bien es cierto que el documento citado por el señor Examinador se desarrolla en el mismo campo industrial de la presente invención, como es el campo de los procesos para la fabricación de resinas de cloruro de vinilo (PVC). Sin embargo, también resulta evidente que las enseñanzas de este documento NO son suficientes para desvirtuar la novedad del proceso objeto de la presente invención, toda vez que el proceso revelado en D1, presenta características técnicas operativas diferentes a las del proceso ahora reivindicado, que no se hubieran podido derivar de las enseñanzas del documento D1, como me permito exponerlo a continuación.

1.2. Argumentos que realzan la Novedad de la presente solicitud

De la lectura del concepto técnico es claro que el señor Examinador intenta desvirtuar la novedad del proceso de la presente invención al afirmar lo siguiente:

"[...]"

No obstante, en D1 se divulga un proceso para polimerizar uno o más monómeros por medio de uno o más peróxidos orgánicos (iniciadores

orgánicos) que se dosifican a la mezcla de polimerización a la temperatura de reacción. El proceso de acuerdo con este invento es adecuado para polimerizar mezclas de monómeros que contengan cloruro de vinilo monómero (VCM) (Página 2, líneas 5, 6, 40-43).

[...]

En D1 también se explica que "Cuando la mezcla de polimerización alcanza la temperatura de polimerización, el resto del peróxido puede dosificarse a la mezcla para controlar el ritmo de polimerización" (Página 3, líneas 22-23) es decir que se dosifica cuando la presión está cayendo.

En D1 se divulga que los iniciadores tienen una vida media de menos de 1,0 hora, por ejemplo, 0,05 a 1 hora (Página 9, Reivindicación 1).

Es importante mencionar que al encontrarse afectada la novedad de la Reivindicación independiente 1, la cual encierra el objeto de patentabilidad; sus correspondientes reivindicaciones dependientes, estarían señalando características particulares de un proceso que no es novedoso, por consiguiente carecen de novedad.

En conclusión, el proceso de la solicitud no es Nuevo y por tanto no cumpliría con el requisito del artículo 16 de la Decisión 486."

Sobre este particular, en primer lugar respetuosamente me permito manifestar a ese Despacho que se deben aclarar algunos aspectos del proceso reivindicado, tales como:

El cloruro de vinilo es un compuesto de bajo punto de ebullición (punto de ebullición: -13.9°C) y es solamente líquido cuando esta a altas presiones. Por lo tanto, cuando está en un recipiente de tapa cerrada, se presenta un equilibrio entre el cloruro de vinilo de la fase líquida y la fase gaseosa. Esto significa que, a una temperatura constante, la presión en el reactor es constante e igual a la presión de vapor del cloruro de vinilo a esa temperatura.

En conexión con lo anterior, y teniendo en cuenta lo que se explica en la enciclopedia del PVC, vol. 1, 1976 (P. 77, Il. 16-24, y P. 83, Il. 5-8), y en los documentos US 5.739.222 (columna. 1, Il. 25-33), y US 4.015.065 (columna. 3, Il. 27-33), de los cuales se anexa una copia simple; sobre el consumo de cloruro de vinilo en una reacción de polimerización, el cual es

alcanzado en un punto de la reacción en el cual el cloruro de vinilo no está más disponible como monómero líquido libre. El único monómero líquido remanente se absorbe en el polímero de PVC formado. Consecuentemente, la cantidad de cloruro de vinilo en fase gaseosa comienza a disminuir y, por lo tanto, la presión en el reactor comienza a caer. Esta caída de presión ocurre cuando la reacción está muy cercana a su terminación, por lo general, cuando cerca del 70 % en peso del monómero de cloruro de vinilo se han convertido en PVC.

En resumen, mientras haya cloruro de vinilo líquido libre, sigue estando la presión del reactor en un valor constante. Solamente cuando no hay monómero líquido libre remanente (lo cual se presenta al final del proceso de polimerización) la presión en el reactor cae. Esta característica es inherente a los procesos de la polimerización de cloruro de vinilo y también es comúnmente conocida por una persona con conocimientos medios en la materia. De hecho, durante el proceso completo de polimerización, se consume el cloruro de vinilo. Sin embargo, debido al equilibrio líquido/gas, la presión sigue siendo constante durante un tiempo y solamente comienza a caer cuando no hay más de cualquier monómero líquido libre disponible en la mezcla de reacción. Es decir, evidentemente, al final de la reacción.

Por lo tanto, es claro que el documento D1 **NO** enseña la dosificación del iniciador cuando la presión está cayendo. Pues el aparte citado por el señor Examinador tan solo indica la adición del resto del iniciador cuando se alcanza la temperatura de polimerización, es decir, cuando se alcanza el equilibrio en el reactor (temperatura de polimerización estable), pero no se puede afirmar que indica la adición de iniciador cuando la presión del reactor cae. Dicha apreciación frente a lo realmente conocido en el estado del arte y a lo que verdaderamente enseña el documento D1, es una interpretación del texto mencionado, lo cual no es válido para objetar la novedad de una invención (ver página 66, quinto párrafo del "Manual para el Examen de Solicitudes de Patentes de Invención en las Oficinas de Propiedad Industrial de los Países de la Comunidad Andina")

En vista de lo anterior, es claro que las consideraciones hechas por parte del señor Examinador en el concepto técnico citado, para objetar la novedad del proceso reclamado son equivocadas, toda vez que como fácilmente se puede notar de una simple lectura de la descripción y las reivindicaciones del documento D1, especialmente, de las enseñanzas contenidas en los ejemplos presentados, se limita dicha invención a enseñar un proceso de polimerización, en el cual lo realmente esencial es que todos y cada uno de los peróxidos que puedan ser empleados cumplan con el requisito de tener una vida media en el intervalo específico de 0.05 a 1.0 hora, pero no se ocupa en ninguno de sus apartes, de la adición de una parte del iniciador o de un segundo iniciador durante la caída de la presión del reactor.

En conexión con lo anterior, me permito llamar la atención de ese despacho al hecho de que solamente en el Ejemplo Comparativo F, el documento WO 00/17245 (D1) muestra el uso de dos iniciadores y la adición de un primer iniciador en la primera parte de la reacción de la polimerización y de un iniciador adicional cuando se alcanza la temperatura de reacción deseada. En dicho ejemplo comparativo F, 0.05% p/p de Trigonox® EHP fue agregado al principio de la reacción y 0.01% p/p de Trigonox® 187 fue dosificado a la reacción 2.5 horas después del comienzo del calentamiento, en alrededor de 1 hora. La adición de peróxido en este ejemplo comparativo fue terminada ya antes de que la presión del reactor comenzara a caer. Por lo tanto, ninguna de las enseñanzas del documento WO 00/17245 divulga o revela exactamente el mismo proceso de la presente invención y mucho menos se enseña ni en forma explícita ni intrínseca la adición de iniciador durante la caída de presión.

En este punto, respetuosamente se llama la atención de ese Despacho al hecho de que no es ni habitual, ni mucho menos aceptado en la práctica de patentes desvirtuar la novedad de una solicitud, a partir de la interpretación de una información técnica, lo cual requeriría de armar a pedazos la invención. Lo realmente aceptado es que se objete la novedad cuando en un mismo documento del estado del arte, se revelen **todas y cada una de las características y condiciones específicas de la invención en cuestión**, lo cual no ocurre en el presente caso.

En vista de lo anterior, es completamente claro que el proceso de D1, presenta diferencias técnicas relevantes, con respecto al proceso de la presente invención, toda vez, que de acuerdo al alcance dado por la reivindicación 1, el proceso ahora reclamado incluye una forma de operar diferente a la forma de operar ya conocida en el estado del arte, específicamente lo revelado en D1, donde no se adiciona una parte del iniciador o un segundo iniciador cuando cae la presión del reactor.

A este respecto, atentamente dirijo la atención de ese Despacho a la lectura de algunos párrafos del profesor Breuer, quien es un estudioso de múltiples temas en el ámbito de las patentes. Pues bien, en cuanto a la novedad de los procesos o procedimientos, el profesor Breuer establece entre otras cosas, lo siguiente:

"La novedad de los procedimientos, es decir, el invento, puede consistir: a) en la agregación de alguna nueva etapa;... d) en tratar materiales en sí conocidos en forma también conocida en sí, pero que no había sido usada para el tratamiento de esos materiales.....En forma general, puede decirse que el nuevo procedimiento puede caracterizarse como invención: a) en la manera de operar; b) por los materiales que son operados, y c) por ambas cosas a la vez. En todos los casos – y como ocurre respecto de todas las demás invenciones – la pauta acerca de si existe o no invención nos la dará el resultado.....El procedimiento químico puede producir un nuevo resultado y ser, por consiguiente, patentable: ...(c) cuando mediante una o más reacciones practicadas en forma conocida, se tratan productos que nunca habían sido empleados para obtener el resultado perseguido." *los del estado de la técnica*"¹ (Resaltado fuera de texto).

En el presente caso, el modo de operar mediante las etapas del proceso de polimerización de la presente invención y especialmente mediante la adición de una parte del iniciador o de un segundo iniciador durante la caída de la presión en el reactor (es decir, hacia el final de la reacción) que

¹ "Breuer, C.M. Tratado de Patentes de Invención. Volumen I. Abeledo-Perrot Editores. Buenos Aires. Argentina. 1957. páginas 158 y 161.

permiten mejorar la eficiencia y eficacia del proceso, así como también se llegan a obtener productos (resinas de PVC) con características mejoradas, esto es, **el resultado**. Por lo tanto, es evidente que el proceso de polimerización con adición de iniciadores durante la caída de presión de la presente invención también es novedoso, toda vez que permiten llegar a un resultado nuevo y mejorado.

En conexión con la anterior argumentación presentada, atentamente me permito dirigir la atención de ese Despacho a lo que se establece con respecto a la evaluación de la novedad de una invención, en dos apartes del *"Manual para el Examen de Solicitudes de Patentes de Invención en las Oficinas de Propiedad Industrial de los Países de la Comunidad Andina"* (en adelante Manual de Patentes), el cual resulta útil para demostrar en forma contundente que la presente invención, se ajusta cabalmente a la Normativa Andina en lo referente al requisito de novedad que deben cumplir todas y cada una de las invenciones para poder gozar del privilegio de patente solicitado. En el acápite 9.4, del citado Manual de Patentes, se establece:

*"Para determinar la novedad de la invención, se debe comprobar si existen anticipaciones del estado de la técnica que contengan explícitamente todas las características técnicas esenciales de la invención. El examen de novedad se efectúa comparando elemento por elemento de la invención tal como está definido por las reivindicaciones con los del estado de la técnica"*² (Resaltado fuera de texto).

Y en otro acápite del mismo Manual de Patentes, se afirma lo siguiente: *"Si todas las características técnicas de la reivindicación independiente se encuentran descritas en un mismo antecedente y además se encuentran íntimamente relacionadas, el objeto de dicha reivindicación carece de novedad. Si una característica, aunque sea banal, no se encuentra contenida en el antecedente, la reivindicación es nueva."*³ (resaltado fuera de texto).

² COMUNIDAD ANDINA, Secretaría General, "Manual para el Examen de Solicitudes de Patentes de Invención en las Oficinas de Propiedad Industrial de los Países de la Comunidad Andina", 2ª Edición, Quito, Ecuador, Junio de 2004, página 65.

³ Op. Cit. Página 66.

De acuerdo con las diferencias técnicas mencionadas anteriormente y teniendo en cuenta las enseñanzas del los apartes citados del Manual de Patentes, es claro que en el análisis de novedad realizado en el presente caso, se cita un documento (D1) en cuyo contenido **NO se enseñan en forma explícita todas y cada una de las características técnicas esenciales del proceso de polimerización ahora reclamado**; en particular, ningún aparte del texto que describe el proceso del documento D1, enseña o anticipa la condición específica de que se deba hacer la adición de parte del iniciador o de un segundo iniciador cuando la presión del sistema cae, es decir, hacia el final de la reacción.

En consecuencia, al llevar a cabo el examen de novedad frente a las enseñanzas del documento D1, teniendo en cuenta las recomendaciones hechas por parte de las oficinas de patentes de los países miembros de la CAN, se encuentra que a pesar de que el documento citado se desarrolla en el mismo campo tecnológico de la presente invención, **no constituye una anticipación relevante de la materia reivindicada**, como ya se ha demostrado. Por lo tanto, es evidente que las enseñanzas del documento citado D1, **NO resultan lo suficientemente relevantes como para desvirtuar la NOVEDAD de la presente invención.**

2. 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. 04-056.932, 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), Australia y Taiwan han sido concedidas como patentes bajo los números **EP 1456257 B1, AU2002361137 y TW270553**, 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), Australia y Taiwan, 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 y aplicación industrial requeridos.

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

- ¿Por qué tres oficinas diferentes conceden una patente para la misma materia objeto de la solicitud Colombiana No. 04-056.932?, 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 han concedido dichas patentes, y a la legislación Andina, para poder establecer si se ciñen 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 los requisitos de patentabilidad, específicamente en la novedad, tal y como se mostrará a continuación.

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)⁴	Convención Europea de Patentes (EPC)⁵
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⁴ www.emercatoria.edu.co/PAGINAS/volumen3/Documentos01/DECISION%20486.doc

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 los 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 como invenciones dentro del significado del párrafo 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	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

	escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida.	cualquier otro medio antes de la fecha de presentación de la solicitud de patente Europea.
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Al hacer una simple comparación de cada uno de los requisitos exigidos por la legislación Colombiana y la Europea, 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 el artículo 16 de la D486 y el artículo 54 de la EPC, que exigen en forma idéntica, que la invención sea novedosa frente a lo conocido en el estado del arte, específicamente frente a lo revelado en el documento D1, el cual también hace parte de los documentos citados por el examinador Europeo.

Entonces, para entender porque tres diferentes oficinas de patentes conceden este privilegio para la misma materia objeto de la solicitud Colombiana en cuestión, no es necesario sino comprender que esto se debe a que la materia objeto de la solicitud Colombiana, resulta completamente NOVEDOSA, 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 que el proceso de polimerización reclamado en las reivindicaciones 1 a 5, reúne los suficientes elementos técnicos que le brindan novedad, altura inventiva y aplicación industrial, por lo que esta invención representa un avance en el estado actual de la técnica.

En vista del resultado de la comparación anterior, resulta fácil entender porque la concesión de dichas patentes por parte de la EPO, la Oficina Australiana y la Oficina de Patentes de Taiwan, **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 vigente en materia de patentes en Colombia.

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 citado artículo 46, claramente le da la facultad a los Examinadores técnicos y legales de las oficinas de patentes de los países miembros de la CAN (de la cual Colombia hace parte) 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 las Oficinas de Australia, Taiwan y la EPO, no obliga a la concesión de dicha patente por parte de 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 más que razonable de que la materia objeto de la solicitud en cuestión, posee efectivamente los suficiente elementos novedosos e inventivos 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 permite que se reconozcan los resultados de exámenes hechos en otros países y/o los títulos obtenidos en otros países para la concesión de una patente, tal y como claramente se aprecia en el citado artículo 46 de la 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 incluya como indicio de patentabilidad el hecho de que ya se han concedido títulos de patente para la misma materia objeto en otros países, corroborando toda la argumentación técnica y legal que se ha aportado en el presente caso para demostrar la patentabilidad del proceso de polimerización de las reivindicaciones 1 a 5 de la presente solicitud de patente.

3. CONCLUSION

Los argumentos expuestos a lo largo del presente escrito, ponen de manifiesto de una manera clara y contundente, que el objeto de la presente invención es el de proveer un proceso de polimerización de monómero de cloruro de vinilo (VCM) con el uso eficiente de la capacidad de enfriamiento, en el cual se lleva a cabo la dosificación de una parte del iniciador o de un segundo iniciador cuando la presión del reactor comienza a caer.

Mientras que el estado del arte representado por el documento citado WO 00/17245 (D1) ni aborda este problema, ni enseña o al menos sugiere la misma solución propuesta por el solicitante. Por lo tanto, las reivindicaciones 1 a 5 de la presente solicitud de patente Colombiana resultan tanto NOVEDOSAS como INVENTIVAS sobre lo revelado en WO 00/17245, como claramente lo evidencia la concesión de patente para la misma materia objeto en otros países.

4. Anexos

- Copia informal de las patentes EP 1456257 B1 y AU2002361137.
- Copia informal de la Enciclopedia del PVC, vol. 1, 1976 (Pag. 77, Il. 16-24, y Pag. 83, Il. 5-8); y de los documentos US 5.739.222 y US 4.015.065.

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

Atentamente,



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(54) **ADDITION OF ORGANIC INITIATORS DURING THE PRESSURE DROP IN VINYL CHLORIDE MONOMER POLYMERIZATION**

ZUGABE VON ORGANISCHEN INITIATOREN WÄHREND DES DRUCKABFALLS IN VINYLCHLORIDPOLYMERISATIONEN

ADDITION D'AMORCEURS ORGANIQUES PENDANT LA CHUTE DE PRESSION DANS DES REACTIONS DE POLYMERISATION DES MONOMERES DE CHLORURE DE VINYLE

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WO-A-00/17245 US-A- 4 015 065
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Description

[0001] The present invention relates to a process wherein one or more initiators are used to polymerize a mixture containing one or more monomers of which one is vinyl chloride monomer (VCM).

[0002] As is known to a person skilled in the art, such a process can be performed in many different ways. It is generally desired to shorten the total polymerization time. This can be achieved by shortening the period of constant pressure in the polymerization reactor, or by reducing the time required to complete the polymerization reaction after the pressure in the reactor starts to drop. An example of a process where the time of pressure drop is reduced is US 5,908,905, wherein a process is described which is completed at a higher temperature than a preset temperature for the polymerization. However, such a temperature increase may result in discolouration of the polymer. Above all, it has the disadvantage of influencing the molecular weight of the polymers formed.

[0003] US 5,739,222 describes another process, wherein when the internal pressure of the reactor declines, further monomer is fed to the reactor. This procedure will significantly affect the physical properties of the polymer particles.

[0004] US 4,015,065 describes a process wherein a polymerization initiator is added at the pressure drop to the polymer formed, while subjecting the polymer to radio frequency dielectric heating. With this process, the aim is to remove or partially remove the abundantly present vinyl halide monomer from the vinyl halide polymer. The use of radio frequency dielectric heating is less desired, since it is energy intensive and affects the properties, such as thermal stability and colour, of the polymer produced.

[0005] It is an object of the present invention to provide an improved process which overcomes the disadvantages of the prior art processes. More specifically, it is intended to provide a process wherein the overall polymerization time is reduced by a reduction of the pressure drop time.

[0006] The process of the present invention is a process as described in the opening paragraph, and wherein one or more initiators are added to a polymerization mixture at the reaction temperature when the pressure in the polymerization reactor is dropping due to the depletion of the vinyl chloride monomer, with the proviso that the polymer formed is not subject to radio frequency dielectric heating in the presence of additional organic initiator.

[0007] During VCM polymerizations, the pressure initially is proportional to the temperature of the reaction mixture. This is because the pressure in the polymerization reactor is predominantly determined by the vapour pressure of the VCM in the polymerization mixture. Towards the end of the polymerization reaction, the VCM is depleted. At a certain moment no liquid VCM phase is present any longer and the pressure in the reactor starts to drop below the pressure otherwise observed at that temperature. After and/or during the pressure drop there still is VCM present in the gas phase, but typically more and more is being adsorbed in the water and polymer phase of the reaction mixture. At that time the polymerization rate conventionally decreases and the cooling capacity of the reactor is not optimally used.

[0008] The inventors have now identified these problems and found that the available cooling capacity of the reactor can be used more efficiently if the polymerization rate is enhanced by the addition of one or more initiators after the initial pressure drop and/or during the pressure drop. Preferably, the initiator is added at or after the moment at which the pressure drops in the reactor. It is less preferred to add said initiator before that moment, as it may lead to an undesirable runaway reaction, which is generally accompanied by an undesirable and dangerous increase in pressure. Apart from more efficient use of the cooling capacity, the total polymerization time is reduced due to a higher pressure drop rate, thereby shortening the period in which the pressure of the reactor is dropping. Also, the reactor space-time yield is improved.

[0009] 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 30 minutes, preferably 20 minutes, more preferably 10 minutes, and most preferably 5 minutes, before the pressure drop is actually observed. Most preferably, the addition of initiator takes place when the pressure becomes lower than the pressure that was observed earlier at the same temperature.

[0010] The initiators can be any kind of organic peroxide suitable for use in the polymerization process, such as peroxydicarbonates and acetyl-cyclohexylsulfonyl-peroxide. Hence, the additional initiator can be the same as or different from the initiator(s) used in the polymerization before the pressure drop. More preferred additional initiators are fast initiators such as organic peroxides having a half-life of from 0.0001 to 1 hour at the polymerization temperature. Even more preferred are peroxides having a half-life ranging from 0.0001 to 0.5 hour at the polymerization temperature. Most preferred are extremely fast peroxides having a half-life of from 0.0001 to 0.05 hour at the polymerization temperature.

[0011] Preferred examples of organic peroxides used in the process of the invention are 1,1,3,3-tetramethylbutylperoxy methoxy acetate, tert.-butylperoxy methoxy acetate, tert.-amylperoxy methoxy acetate, tert.-butylperoxy ethoxy acetate, diisobutanoyl peroxide (Trigonox® 187), hexanoyl pivaloyl peroxide, 2-ethyl-butanoyl-isononanoyl peroxide, isobutanoyl-lauroyl peroxide, isobutanoyl-isononanoyl peroxide, bis(tert-butylperoxy) oxalate, cyclododecyl-tert. butylperoxy oxalate, 2,2-bis-2-ethylhexanoylperoxy-4-methylpentane, 2,2-bis-2-ethylbutanoylperoxy-4-methylpentane, 2,2-bis(2,2-dimethylpropanoylperoxy)-4-methylpentane, 1-(2-ethylhexanoylperoxy)-1,3-dimethylbutyl-1-peroxy-pivalate (Trigonox® 267) or 2,4,4-trimethylpentyl-2-peroxyneodecanoate (Trigonox® 423), tert-amyl peroxyneodecanoate (Trigonox® 123), tert-

butyl peroxyneodecanoate (Trigonox® 23), benzene (m.p)di(2-isopropyl-2-peroxyneodecanoate), 2-methyl-4-hydroxypentane-2-peroxyneodecanoate, α -cumyl peroxyneodecanoate (Trigonox® 99), and peroxydicarbonates such as di-sec-butylperoxydicarbonate (Trigonox® SBP), di(4-tert-butylcyclohexyl) peroxydicarbonate (Perkadox® 16) and di(2-ethylhexyl) peroxydicarbonate (Trigonox® EHP).

[0012] Other organic peroxides having a half-life ranging from 0.0001 to 1 hour at the polymerization temperature can also be used. Whether a peroxide is suitable and has the required half-life can be determined by conventional thermal decomposition studies in monochlorobenzene, as is well-known in the art (see for instance the brochure "Initiators for high polymers" with code 10013921001 available from Akzo Nobel).

[0013] The initiator according to the invention 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.

[0014] The amount of initiator (or initiators) to be used in a process according to the invention after the start of the pressure drop and/or during the pressure drop is within the range conventionally used in polymerization processes. Typically, this range has a lower limit of 0.001 % by weight (% w/w) of additional initiator and more preferably of 0.005% w/w, and an upper limit of 0.3% w/w of additional initiator, preferably of 0.2% w/w; most preferably, 0.05% w/w, based on the weight of VCM monomer, is used.

[0015] The additional initiator is added to the reactor 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 dilute the initiator. Preferably, such solvents are easily removed during the steps where the polymer is worked up 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, as in the case of solvents that are desired plasticizers for the final resin. 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 such a solvent is isododecane. If an initiator dispersion is added, 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 added in a concentration of at least 0.1% w/w, more preferably 0.5% w/w, and most preferably 2% w/w, and at most 75% w/w, more preferably at most 60% w/w, even more preferably at most 50% w/w, more preferably still 25% w/w, and most preferably 15% w/w. The more dilute initiator solutions or dispersions ensure rapid mixing of the initiator and the polymerization mixture, which leads to a more efficient use of the initiator, which is important for the fast initiators that are used.

[0016] The addition after the start of the pressure drop and/or during the pressure drop preferably is the addition of fast initiators having a half-life of less than 1 hour at the polymerization temperature, as 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 peroxides 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.

[0017] During the first part of the polymerization reaction any conventional initiating system can be used. Herein, the initiator can be added intermittently or continuously to the polymerization mixture at the polymerization temperature. All of the initiator can be added to the reactor at once in just one portion. In such case, preferably a relatively slow initiator having a half-life of more than 1 hour is used. The initiator may also be added at at least 2, preferably at least 4, more preferably at least 10, and most preferably at least 20 moments.

[0018] Typically, one or more protective colloids are used in the polymerization 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 at least 60%, and most preferably at least 62%, and a degree of hydrolysis of at most 90%, more preferably at most 85%, and most preferably at most 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. 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. It is also envisaged to employ a combination of two or more of the above protective colloids. The amount and type of colloid that is to be used is well-known and conventional. Optionally, such colloids are also added after the start of the pressure drop and/or during the pressure drop. If used after the start of the pressure drop and/or during the pressure drop, they can be added together with or separately from the initiator which is added in accordance with the invention.

[0019] However, in a preferred embodiment, one or more surfactants are added after the start of the pressure drop and/or during the pressure drop. If used in such a fashion, they can be added together with or separately from the initiator

which is added in accordance with the invention. The addition of such surfactants was found to be very helpful, since it reduces the (excessive) formation of foam in the process. Examples of suitable surfactants are polyvinyl acetates with a degree of hydrolysis of less than 60% and conventional foam reducers (defoamers), as generally known to a person skilled in the art. Preferably, the surfactant is added together with the additional initiator.

[0020] Preferably, the addition of the initiator, of the optional colloid and the optional surfactant, either during the constant pressure time or after and/or during the pressure drop, can be effected at any suitable entry point to the reactor. Such an entry point may be positioned below or above the surface of the reaction mixture, as desired. The addition of these compounds can be separately to the reactor via individual entry points, or they can be pre-mixed and enter the reactor through one entry port, or a combination of such techniques can be used. 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 added to also add the initiator and/or the optional protective colloid and/or surfactant. It is also envisaged that the reactor comprises dedicated piping and a plurality of entry points located in different positions on the periphery of the said reactor, so as to ensure better, faster, and more homogeneous mixing of the initiator, protective colloid, and/or surfactant in the reaction mixture. If the reactor further comprises a reflux condensor, it is contemplated to add these compounds to the reaction mixture via the reflux condensor.

[0021] The process according to the invention is directed to polymerizing monomer mixtures comprising vinyl chloride monomer (VCM). Preferably, the process according to the invention involves the polymerization of monomer mixtures comprising at least 5% w/w of VCM, preferably at least 10 %w/w, more preferably at least 20 %w/w, and most preferably at least 50 %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.

[0022] The polymerization process can be conducted as a mass process wherein the reaction mixture is predominantly monomer, or as a more preferred 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. 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), anti-fouling agent(s), and pH-buffer(s), can be present. Depending on the type of polymer desired, each of the above-mentioned processes may be preferred. The process according to the invention is especially suited for use in suspension processes.

[0023] 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. It is preferred that the resulting resin contains less than 50 ppm of residual initiator, more preferably less than 40 ppm, and most preferably less than 25 ppm of initiator, immediately after drying for 1 hour at 60°C and screening, since such resins exhibit excellent heat stability as measured with a Metrastat® PSD260 testing oven in accordance with 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. Hence the process can comprise an additional process step in which excess initiator is decomposed. Preferably, said process step is taken after the polymerization reaction has finished and before the resin has dried.

[0024] Examples to demonstrate the unexpected effect of the addition of fast peroxides during the pressure drop in PVC suspension polymerization:

Experimental

[0025] In a standard suspension polymerization experiment, a temperature controlled 1-litre stainless steel Büchi reactor provided with one baffle, a three-bladed stirrer, a pressure transducer, a VCM feed line, and a nitrogen purge line was charged with 425 g demineralized water, Alcotex B72 (1000 ppm on VCM) in a 5% w/w solution in demineralized water, and was pressurized to 15 barg, using nitrogen. If no leaks are observed, the reactor is evacuated and pressurized with nitrogen up to 5 barg three times to flush out virtually all air. Next, the reactor was evacuated and charged with 250 g VCM ex Akzo Nobel Salt & Basics, followed by heating up of the reactor to the polymerization temperature in 30-60 min.

[0026] The conventional peroxide, such as Trigonox® EHP (Tx EHP), used to initiate the polymerization is added via a hot-start procedure. The hot-start procedure means that the peroxide is added to the reactor at the polymerization temperature in a very short period, i.e. 1-5 min.

[0027] During the pressure drop period of the polymerization a fast initiator with a half-life at the polymerization temperature of less than 0.1 hr. is added to the reactor until the pressure in the reactor has dropped 3.5 bar. For adding of the (additional) fast initiator, a relatively low-concentration (about 1% w/w) emulsion is used. In the comparative example the addition of the (additional) fast initiator was omitted.

[0028] After reaching the said pressure drop of 3.5 bar the peroxide dosing was stopped and then the reactor was cooled to 20-25°C, evacuated, and freed of virtually all remaining VCM. The polymer was obtained after filtration, washing, and drying (at 60°C for 1 hour using a fluidized bed).

Example 1

[0029] The initiators used (Tx EHP (75% w/w) dissolved in isododecane (25% w/w) and Tx 187 [0.3% w/w aqueous emulsion]), the amount dosed, the dosing procedure, and the polymerization results are presented in Table 1.

[0030] After reaching the polymerization temperature the mentioned amount of Tx EHP (calculated on VCM) in isododecane is added in a period of 1-5 minutes.

Table 1: The results of VCM suspension polymerization with di(2-ethylhexyl) peroxydicarbonate (Tx EHP) at 57°C without (Comparison example) and with (Example 1) adding of diisobutanoyl peroxide (Tx 187) during the pressure drop

	Example 1	Comparison example
Hot-start peroxide and quantity	800 ppm Tx EHP	800 ppm Tx EHP
Adding peroxide during pressure drop	80 ppm Tx 187 during 30 minutes	None
Constant pressure time	182 min	180 min
Pressure drop rate	7 bar/hr	4 bar/hr
Polymerization time until the reactor pressure has dropped 3.5 barg	210 minutes	230 minutes
PVC yield	91%	87%

[0031] From Table 1 it is deduced that the process of Example 1 clearly has a significantly higher pressure drop rate compared to the conventional process of the comparison example. This higher drop rate leads to a shorter polymerization time. The higher pressure drop rate clearly makes for better usage of the cooling capacity of the reactor.

Claims

1. Process wherein one or more initiators are used to polymerize a mixture containing one or more monomers of which one is vinyl chloride monomer, wherein at least part of the initiators is added to the polymerization mixture at the reaction temperature when the pressure in the polymerization reactor is dropping due to the depletion of the vinyl chloride monomer, with the proviso that the polymer formed is not subject to radio frequency dielectric heating in the presence of additional organic initiator.
2. A process according to claim 1 wherein the initiator added after the start of the pressure drop and/or during the pressure drop has a half-life of from 0.0001 hour to 1 hour at the polymerization temperature.
3. A process according to claim 2 wherein the additional organic initiator added after and/or during the pressure drop has a half-life of from 0.0001 hour to 0.05 hour at the polymerization temperature.
4. A process according to any one of claims 1-3 wherein at least part of the initiators is 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 surfactant is also added when the pressure in the polymerization reactor is dropping due to the depletion of the vinyl chloride monomer to reduce the formation of foam.

Patentansprüche

1. Verfahren, bei dem ein oder mehrere Initiatoren verwendet werden, um ein Gemisch, das ein oder mehrere Monomere enthält, von denen eines ein Vinylchlorid-Monomer ist, zu polymerisieren, wobei wenigstens ein Teil der

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Initiatoren bei der Reaktionstemperatur zu dem Polymerisationsgemisch gegeben wird, wenn der Druck im Polymerisationsreaktor aufgrund des Verbrauchs des Vinylchlorid-Monomers abfällt, mit der Maßgabe, dass das gebildete Polymer keiner dielektrischen Erwärmung mit Radiowellen in Gegenwart von zusätzlichem organischem Initiator ausgesetzt wird.

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2. Verfahren gemäß Anspruch 1, wobei der nach Beginn des Druckabfalls und/oder während des Druckabfalls hinzugefügte Initiator bei der Polymerisationstemperatur eine Halbwertszeit von 0,0001 Stunden bis 1 Stunde hat.

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3. Verfahren gemäß Anspruch 2, wobei der nach und/oder während des Druckabfalls hinzugefügte zusätzliche organische Initiator bei der Polymerisationstemperatur eine Halbwertszeit von 0,0001 Stunden bis 0,05 Stunden hat.

4. Verfahren gemäß einem der Ansprüche 1 bis 3, wobei wenigstens ein Teil der Initiatoren nach Beginn des Druckabfalls und/oder während des Druckabfalls portionsweise und/oder kontinuierlich hinzugefügt wird.

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5. Verfahren gemäß einem der Ansprüche 1 bis 4, wobei dann, wenn der Druck im Polymerisationsreaktor aufgrund des Verbrauchs des Vinylchlorid-Monomers abfällt, auch ein Tensid hinzugefügt wird, um die Bildung von Schaum zu reduzieren.

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Revendications

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1. Procédé dans lequel un ou plusieurs amorceurs sont utilisés pour polymériser un mélange contenant un ou plusieurs monomères, l'un d'eux étant un monomère de chlorure de vinyle, dans lequel au moins une partie des amorceurs est ajoutée au mélange de polymérisation à la température de réaction quand la pression dans le réacteur de polymérisation chute, du fait de l'épuisement du monomère de chlorure de vinyle, à condition que le polymère formé ne soit pas soumis à un chauffage diélectrique à radiofréquence en présence d'un amorceur organique additionnel.

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2. Procédé selon la revendication 1, dans lequel l'amorceur ajouté après le début de la chute de pression et/ou pendant la chute de pression a une demi-vie comprise entre 0,0001 heure et 1 heure à la température de polymérisation.

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3. Procédé selon la revendication 2, dans lequel l'amorceur organique additionnel, ajouté après et/ou pendant la chute de pression, a une demi-vie comprise entre 0,0001 heure et 0,05 heure à la température de polymérisation.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel au moins une partie des amorceurs est ajoutée par intermittence et/ou en continu après le début de la chute de pression et/ou pendant la chute de pression.

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5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel un tensioactif est également ajouté quand la pression dans le réacteur de polymérisation chute, du fait de l'épuisement du monomère de chlorure de vinyle afin de réduire la formation de mousse.

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REFERENCES CITED IN THE DESCRIPTION

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- US 5739222 A [0003]
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(19) AUSTRALIAN PATENT OFFICE		(11) Application No. AU 2002361137 B2	
(54) Title Addition of organic initiators during the pressure drop in vinyl chloride monomer polymerization reactions			
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(74) Agent/Attorney Griffith Hack, Level 3 509 St Kilda Road, Melbourne, VIC, 3004			
(56) Related Art W02000/017245			

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5 to polymerize a mixture containing one or more monomers of which one is vinyl chloride monomer (VCM).

The present invention relates to a process wherein one or more initiators are used to polymerize a mixture containing one or more monomers of which one is vinyl chloride monomer (VCM).

As is known to a person skilled in the art, such a process can be performed in many different ways. It is generally desired to shorten the total polymerization time. This can be achieved by shortening the period of constant pressure in the polymerization reactor, or by reducing the time required to complete the polymerization reaction after the pressure in the reactor starts to drop. An example of a process where the time of pressure drop is reduced is US 5,606,805, wherein a process is described which is completed at a higher temperature than a preset temperature for the polymerization. However, such a temperature increase may result in discolouration of the polymer. Above all, it has the disadvantage of influencing the molecular weight of the polymers formed.

US 5,730,222 describes another process, wherein when the internal pressure of the reactor declines, further monomer is fed to the reactor. This procedure will significantly affect the physical properties of the polymer particles.

US 4,015,005 describes a process wherein a polymerization initiator is added at the pressure drop to the polymer formed, while subjecting the polymer to radio frequency dielectric heating. With this process, the aim is to remove or partially remove the abundantly present vinyl halide monomer from the vinyl halide polymer. The use of radio frequency dielectric heating is less desired, since it is energy intensive and affects the properties, such as thermal stability and colour, of the polymer produced.

The present invention provides an improved process which overcomes the
30 disadvantages of the prior art processes. More specifically, it is

intended to provide a process wherein the overall polymerization time is reduced by a reduction of the pressure drop time.

5 In one embodiment the present invention provides a process wherein one or more initiators are used to polymerize a mixture containing one or more monomers of which one is vinyl chloride monomer, wherein at least part of the initiators is added to the polymerization mixture at the reaction temperature when the pressure in the polymerization reactor is dropping due to the depletion of the vinyl chloride monomer, with the proviso that the polymer formed is not subject to radio frequency dielectric heating in the presence of additional organic initiator.

10 The process of the present invention is a process as described in the opening paragraph, and wherein one or more initiators are added to a polymerization mixture at the reaction temperature when the pressure in the polymerization reactor is dropping due to the depletion of the vinyl chloride monomer, with the proviso that the polymer formed is not subject to radio frequency dielectric heating in the presence of additional organic initiator.

15 During VCM polymerizations, the pressure initially is proportional to the temperature of the reaction mixture. This is because the pressure in the polymerization reactor is predominantly determined by the vapour pressure of the VCM in the polymerization mixture. Towards the end of the polymerization reaction, the VCM is depleted. At a certain moment no liquid VCM phase is present any longer and the pressure in the reactor starts to drop below the pressure otherwise observed at that temperature. After and/or during the pressure drop there still is VCM present in the gas phase, but typically more and more is being adsorbed in the water and polymer phase of the reaction mixture. At that time the polymerization rate conventionally decreases and the cooling capacity of the reactor is not optimally used.

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Actual position/positioning of the ship is determined by a set of sensors and a computer system.

shortening the period in which the pressure of the reactor is dropping. Also, the reactor space-time yield is improved.

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 30 minutes, preferably 20 minutes, more preferably 10 minutes, and most preferably 5 minutes, before the pressure drop is actually observed. Most preferably, the addition of initiator takes place when the pressure becomes lower than the pressure that was observed earlier at the same temperature.

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The initiators can be any kind of organic peroxide suitable for use in the polymerization process, such as peroxydicarbonates and acetyl-cyclohexyl-sulfonyl-peroxide. Hence, the additional initiator can be the same as or different from the initiator(s) used in the polymerization before the pressure drop. More preferred additional initiators are fast initiators such as organic peroxides having a half-life of from 0.0001 to 1 hour at the polymerization temperature. Even more preferred are peroxides having a half-life ranging from 0.0001 to 0.5 hour at the polymerization temperature. Most preferred are extremely fast peroxides having a half-life of from 0.0001 to 0.05 hour at the polymerization temperature.

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Preferred examples of organic peroxides used in the process of the invention are 1,1,3,3-tetramethylbutylperoxy methoxy acetate, tert-butylperoxy methoxy acetate, tert-amylperoxy methoxy acetate, tert-butylperoxy ethoxy acetate, diisobutanoyl peroxide (Trigonox® 187), hexanoyl phthaloyl peroxide, 2-ethylbutanoyl-leonanoyl peroxide, isobutanoyl-lauroyl peroxide, isobutanoyl-leonanoyl peroxide, bis(tert-butylperoxy) oxalate, cyclododecyl-tert-butylperoxy oxalate, 2,2-bis-2-ethylhexanoylperoxy-4-methylpentane, 2,2-bis-2-ethylbutanoylperoxy-4-methylpentane, 2,2-bis(2,2-dimethylpropanoylperoxy)-4-methylpentane, 1-(2-ethylhexanoylperoxy)-1,3-dimethylbutyl-1-peroxyphthalate (Trigonox® 287) or 2,4,4-trimethylpentyl-2-peroxyneodecanoate (Trigonox® 423), tert-amyl peroxyneodecanoate (Trigonox® 123), tert-butyl peroxyneodecanoate (Trigonox® 23), benzene (m.p.) di(2-isopropyl-2-peroxy-

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neodecanoate), 2-methyl-4-hydroxypentane-2-peroxyneodecanoate, α -cumyl peroxyneodecanoate (Trigona® 80), and peroxydicarbonates such as di-sec-butylperoxydicarbonate (Trigona® 88P), di(4-tert-butylcyclohexyl) peroxydicarbonate (Perkadox® 10) and di(2-ethylhexyl) peroxydicarbonate (Trigona® EHP).

Other organic peroxides having a half-life ranging from 0.0001 to 1 hour at the polymerization temperature can also be used. Whether a peroxide is suitable and has the required half-life can be determined by conventional thermal decomposition studies in monochlorobenzene, as is well-known in the art (see for instance the brochure "Initiators for high polymers" with code 10013021001 available from Akzo Nobel).

The initiator according to the invention 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 amount of initiator (or initiators) to be used in a process according to the invention after the start of the pressure drop and/or during the pressure drop is within the range conventionally used in polymerization processes. Typically, this range has a lower limit of 0.001% by weight (% w/w) of additional initiator and more preferably of 0.005% w/w, and an upper limit of 0.3% w/w of additional initiator, preferably of 0.2% w/w; most preferably, 0.05% w/w, based on the weight of VCM monomer, is used.

The additional initiator is added to the reactor 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 dilute the initiator. Preferably, such

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solvents are easily removed during the steps where the polymer is worked up 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, as in the case of solvents that are desired plasticizers for the final resin. 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 such a solvent is laurodecane. If an initiator dispersion is added, 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 added in a concentration of at least 0.1% w/w, more preferably 0.5% w/w, and most preferably 2% w/w, and at most 75% w/w, more preferably at most 60% w/w, even more preferably at most 50% w/w, more preferably still 25% w/w, and most preferably 15% w/w. The more dilute initiator solutions or dispersions ensure rapid mixing of the initiator and the polymerization mixture, which leads to a more efficient use of the initiator, which is important for the fast initiators that are used.

The addition after the start of the pressure drop and/or during the pressure drop preferably is the addition of fast initiators having a half-life of less than 1 hour at the polymerization temperature, as 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 peroxides 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.

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During the first part of the polymerization reaction any conventional initiating system can be used. Herein, the initiator can be added intermittently or continuously to the polymerization mixture at the polymerization temperature. All of the initiator can be added to the reactor at once in just one portion. In such case, preferably a relatively slow initiator having a half-life of more than 1 hour is used. The initiator may also be added at at least 2, preferably at least 4, more preferably at least 10, and most preferably at least 20 moments.

Typically, one or more protective colloids are used in the polymerization 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 at least 60%, and most preferably at least 62%, and a degree of hydrolysis of at most 80%, more preferably at most 85%, and most preferably at most 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. 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 celluloses, water-soluble polymers, oil-soluble emulsifying agents or water-soluble emulsifying agents. It is also envisaged to employ a combination of two or more of the above protective colloids. The amount and type of colloid that is to be used is well-known and conventional. Optionally, such colloids are also added after the start of the pressure drop and/or during the pressure drop. If used after the start of the pressure drop and/or during the pressure drop, they can be added together with or separately from the initiator which is added in accordance with the invention.

However, in a preferred embodiment, one or more surfactants are added after the start of the pressure drop and/or during the pressure drop. If used in such a fashion, they can be added together with or separately from the initiator which is

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added in accordance with the invention. The addition of such surfactants was found to be very helpful, since it reduces the (excessive) formation of foam in the process. Examples of suitable surfactants are polyvinyl acetates with a degree of hydrolysis of less than 60% and conventional foam reducers (defoamers), as generally known to a person skilled in the art. Preferably, the surfactant is added together with the additional initiator.

Preferably, the addition of the initiator, of the optional colloid and the optional surfactant, either during the constant pressure time or after and/or during the pressure drop, can be effected at any suitable entry point to the reactor. Such an entry point may be positioned below or above the surface of the reaction mixture, as desired. The addition of these compounds can be separately to the reactor via individual entry points, or they can be pre-mixed and enter the reactor through one entry port, or a combination of such techniques can be used. 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 added to also add the initiator and/or the optional protective colloid and/or surfactant. It is also envisaged that the reactor comprises dedicated piping and a plurality of entry points located in different positions on the periphery of the said reactor, so as to ensure better, faster, and more homogeneous mixing of the initiator, protective colloid, and/or surfactant in the reaction mixture. If the reactor further comprises a reflux condenser, it is contemplated to add these compounds to the reaction mixture via the reflux condenser.

The process according to the invention is directed to polymerizing monomer mixtures comprising vinyl chloride monomer (VCM). Preferably, the process according to the invention involves the polymerization of monomer mixtures comprising at least 5% w/w of VCM, preferably at least 10 %w/w, more preferably at least 20 %w/w, and most preferably at least 50 %w/w of VCM, based on the weight of all monomer. Comonomers that can be used are of the conventional

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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.

The polymerization process can be conducted as a mass process wherein the reaction mixture is predominantly monomer, or as a more preferred 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. 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), anti-fouling agent(s), pH-buffer(s), etc. can be present. Depending on the type of polymer desired, each of the above-mentioned processes may be preferred. The process according to the invention is especially suited for use in suspension processes.

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. It is preferred that the resulting resin contains less than 50 ppm of residual initiator, more preferably less than 40 ppm, and most preferably less than 25 ppm of initiator, immediately after drying for 1 hour at 80°C and screening, since such resins exhibit excellent heat stability as measured with a Mettler® PSD200 testing oven in accordance with 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. Hence the process can comprise an additional process step in which excess initiator is decomposed. Preferably, said process step is taken after the polymerization reaction has finished and before the resin has dried.

Examples to demonstrate the unexpected effect of the addition of fast peroxides during the pressure drop in PVC suspension polymerization:

8 Experimental

10 In a standard suspension polymerization experiment, a temperature controlled 1-litre stainless steel Bichi reactor provided with one baffle, a three-bladed stirrer, a pressure transducer, a VCM feed line, and a nitrogen purge line was charged with 425 g demineralized water, Alcolac B72 (1000 ppm on VCM) in a 5% w/w solution in demineralized water, and was pressurized to 15 barg, using nitrogen. If no leaks are observed, the reactor is evacuated and pressurized with nitrogen up to 5 barg three times to flush out virtually all air. Next, the reactor was evacuated and charged with 250 g VCM ex Alcoa Nobel Salt & Basics, followed by heating up of the reactor to the polymerization temperature in 30-60 min.

15 The conventional peroxide, such as Trigonox® EHP (Tx EHP), used to initiate the polymerization is added via a hot-start procedure. The hot-start procedure means that the peroxide is added to the reactor at the polymerization temperature in a very short period, i.e. 1-5 min.

20 During the pressure drop period of the polymerization a fast initiator with a half-life at the polymerization temperature of less than 0.1 hr. is added to the reactor until the pressure in the reactor has dropped 3.5 bar. For adding of the (additional) fast initiator, a relatively low-concentration (about 1% w/w) emulsion is used. In the comparative example the addition of the (additional) fast initiator was omitted.

25 After reaching the said pressure drop of 3.5 bar the peroxide dosing was stopped and then the reactor was cooled to 20-25°C, evacuated, and freed of virtually all remaining VCM. The polymer was obtained after filtration, washing, and drying (at 60°C for 1 hour using a fluidized bed).

Example 1

The initiators used (Tx EHP (75% w/w) dissolved in isododecane (25% w/w) and Tx 187 (0.3% w/w aqueous emulsion)), the amount dosed, the dosing procedure, and the polymerization results are presented in Table 1.

- 5 After reaching the polymerization temperature the mentioned amount of Tx EHP (calculated on VCM) in isododecane is added in a period of 1-5 minutes.

Table 1: The results of VCM suspension polymerization with di(2-ethylhexyl) peroxycarbonate (Tx EHP) at 57°C without (Comparison example) and with
10 (Example 1) adding of diisobutanoyl peroxide (Tx 187) during the pressure drop

	Example 1	Comparison example
Hot-start peroxide and quantity	800 ppm Tx EHP	800 ppm Tx EHP
Adding peroxide during pressure drop	80 ppm Tx 187 during 30 minutes	None
Constant pressure time	182 min	180 min
Pressure drop rate	7 bar/hr	4 bar/hr
Polymerization time until the reactor pressure has dropped 3,5 barg	210 minutes	230 minutes
PVC yield	91%	87%

- From Table 1 it is deduced that the process of Example 1 clearly has a
significantly higher pressure drop rate compared to the conventional process of
15 the comparison example. This higher drop rate leads to a shorter polymerization
time. The higher pressure drop rate clearly makes for better usage of the cooling
capacity of the reactor.

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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.

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1. Process wherein one or more initiators are used to polymerize a mixture containing one or more monomers of which one is vinyl chloride monomer, wherein at least part of the initiator is added to the polymerization mixture at the reaction temperature when the pressure in the polymerization reactor is dropping due to the depletion of the vinyl chloride monomer, with the proviso that the polymer formed is not subject to radio frequency dielectric heating in the presence of additional organic initiator.
2. A process according to claim 1 wherein the initiator added after the start of the pressure drop and/or during the pressure drop has a half-life of from 0.0001 hour to 1 hour at the polymerization temperature.
3. A process according to claim 2 wherein the additional organic initiator added after and/or during the pressure drop has a half-life of from 0.0001 hour to 0.05 hour at the polymerization temperature.
4. A process according to any one of claims 1-3 wherein at least part of the initiators is 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 surfactant is also added when the pressure in the polymerization reactor is dropping due to the depletion of the vinyl chloride monomer to reduce the formation of foam.
6. A process wherein one or more initiators are used to polymerize a mixture containing one or more monomers of which one is vinyl chloride monomer, substantially as herein described with reference to the example.

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Encyclopedia of PVC

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The older, one-step bulk polymerization produces absorbent particles with a wide distribution of particle sizes. The bulk densities of both the bulk-polymerized resins are on the low side. This is because the particles are essentially fluffy. There has been only a small amount of polyvinyl chloride resin produced by the one-step bulk process. It is not generally considered to be an attractive method of polymerizing vinyl chloride.

B. Suspension Polymerization

In this process, which has been the backbone of the industry for many years, the vinyl chloride monomer, which is a liquid under sufficient pressure, has an oil-soluble, free-radical catalyst dissolved in it and the oil phase is suspended in water as small droplets in which the polymerization takes place. For this to be accomplished, it is necessary to have a suspending agent, or a protective colloid, or some type of surfactant that will allow the beads to be formed and to remain stable. The systems of doing this are indeed varied and in general represent processes peculiar to each specific manufacturer. In fact, many manufacturers regard this as their "secret process."

The equipment used for this type of process is an agitated, glass-lined, pressure vessel of the Pfaudler type. Many reactors have agitators of continuously variable speed. More modern installations are tending toward stainless steel reactors with the more conventional flat-blade, or turbine-type impellers. Because producing polyvinyl chloride polymers has become a very competitive business and the conversion costs are extremely important, it is generally found that these reactors are large. Reactors of less than 1000 gal are uneconomical; the general size found is somewhere between 3000 and 4000 gal, although some manufacturers have reactors as large as 6000 gal. The reactors are cooled by circulating water through a jacket. The jackets are sometimes open at the top and the excess cooling water overflows and is either discharged or recirculated.

Since the cleanliness of the reactor is extremely important (frequently it is necessary to enter the reactor and manually clean the walls), most manufacturers shy away from using coils that would give them a means of obtaining greater heat transfer areas. The amount of water and the cooling surface area control the cycle time because the exothermic reaction must be cooled to maintain the requisite constant temperature. If polymerization is too rapid, the heat involved cannot be removed rapidly enough and a runaway reaction will result. Normally, the pressure in the autoclaves used for making polyvinyl chloride will be in the order of 130 psig to perhaps 180 psig. The temperature of the reaction, of course, controls the pressures that will be experienced. Wider variations are possible for those reactors in which copolymers are made because then the influence of the comonomer is reflected in the pressure that develops.

A typical sequence of reaction events in making polyvinyl chloride is as follows: Water is first charged to a clean reactor and suspending agent may be dusted on the surface or added as a solution. Catalyst is added next and the reactor sealed and evacuated to remove oxygen introduced into the system from the ingredients charged or from the air space. Under ideal conditions, the vessel is evacuated to the vapor pressure of the water. This reduces the oxygen concentration so that

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3. POLYVINYL CHLORIDE: POLYMERIZATION AND MANUFACTURE

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it does not retard the polymerization or introduce an induction or delay time. After this, the monomer is introduced. Some suspending agents can be agitated and the reactor warmed to the reaction temperature immediately, but others may require a period of agitation to achieve a suspension equilibrium before heating is begun.

With some suspending systems (and for special purposes such as particle size control), the monomer is added to cold water and the whole reactor brought up to reaction temperature. In other cases, the monomer is added to warm water and the reactor brought up to temperature. Using warm water when possible helps to reduce the cycle time. The reactor is brought to the desired temperature by passing warm water, or water and steam, through the jacket. The polymerization is exothermic and requires cooling to control the reaction. The cooling water may go through a reactor jacket once or it may be recycled — depending on the type of control system. After the reaction is started, it is maintained at a constant temperature for most of the reaction cycle.

As the monomer is consumed, a point is reached at which the monomer is no longer available as a free monomer and represents only monomer absorbed into the solid phase (concentrated phase). It has been indicated previously that based on the Flory-Huggins χ_1 constant, the volume fraction of polymer in the separated phase is of the order 0.6. On a weight basis, there is approximately 70% of the concentrated phase present as polymer and 30% as monomer. Thus, when the conversion reaches about 70%, there is no free monomer available; and since the monomer is absorbed in the polymer, its partial pressure is reduced. The reactor then begins to show a decline in pressure. It is usual to allow the pressure to drop to about 20-70 psig, depending on reaction temperature, at which point the reaction is terminated by cooling and pumping off the unreacted monomer. The slurry that results is frequently pumped to a stripping tank under vacuum, and the temperature of the water is raised to a relatively high temperature (something on the order of 120-175°F) to flash off residual amounts of monomer and other volatiles. In some cases, the reactor may also be used as the stripper. The slurry is pumped to a holding tank (at atmospheric pressure), where it may be blended with other lots. It is then pumped to a centrifuge, where the bulk of the water is separated, and the semidry material eventually goes to some type of rotary drier. The dried product that leaves the rotary drier is usually passed over a screen to remove coarse materials. In some cases, and for special purposes, the dry powder may be sent to a pulverizer or microatomizer and its particle size somewhat reduced. Normally, this is not necessary with suspension resins because it is expensive and generally the requisite particle size can be obtained by formulation or process changes.

As can be gleaned from this sequence of events, there are a great many variables that must be carefully controlled. Some of these are

- Temperature and temperature control
- Catalyst — type and concentration
- Water-to-monomer ratio
- Water quality
- Suspending agents and surfactants (type and concentration)
- Agitator speed, schedule, and type

Cooling rate
Regulators
Shortstops
Venting techniques
Removing bulk unreacted monomer (recovering)
Stripping
Foam
Dewatering
Drying
Sieving
Grinding

In special cases, there may be other variables of equal importance, but these are the ones that are generally encountered.

The temperature of the reaction and its precise maintenance are essential for controlling the molecular weight or relative viscosity of the resultant product. In most commercial operations, this temperature is controlled within a degree Fahrenheit. A wide variety of control equipment and control loops are used in the industry. The system has to be sufficiently flexible that it can be used to heat the reaction to the polymerization temperature, and also control the temperature by cooling after polymerization starts.

A common system is to have a pump circulate water through a jacket and a control valve of the pneumatic type to introduce warm water or cold water, depending on the requirement of the reactor, to the circulating system. Some systems anticipate demand by having controllers that measure changes in the reactor temperature and changes in the jacket outlet water. A well-organized system will be designed in such a way as to indicate the amount of heat being released and carried away by the cooling system. This is directly related to rate of polymerization and allows observing progress of a reaction.

It occasionally happens that towards the end of the reaction, a sudden increase in reaction rate is encountered. This is referred to as a "heat kick." Generally this has been labeled the Trommsdorff effect; but in view of the discussion of the kinetics of vinyl chloride polymerization, this is questionable. We have already seen how the polymer separates from the monomer and becomes insoluble, and how because of this separation the termination rate is markedly reduced. It therefore seems that this effect (if it takes place at all) would have to occur early in the reaction. A possible explanation for this autoacceleration that generally occurs near the end of the reaction may be the following. As the degree of conversion increases, a point is reached at which the amount of monomer is insufficient to provide adequate thermal conductivity in the concentrated polymerizing phase. Because of poor heat transfer from the inside of the particle to the suspending water, the inside becomes hotter; this heat tends to increase the polymerization rate in the center of the particle, resulting in a further increase in temperature, which in turn results in autoacceleration. In any case, heat kicks are very frequently associated with overpressures, and if they are not controlled, it is possible that the reaction can "run away." This is more likely in reactions that are being pushed for short cycles, reactions that have a low water-to-monomer ratio, or reactors with inadequate cooling.

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If such conditions exist and the reactor gets out of control, it may be necessary to vent off some of the monomer. If this can be done safely, the reactor is cooled because of the latent heat of vaporization of the monomer. If this is not sufficient to control the reaction, then a shortstop of some sort is added to terminate the polymerization abruptly. One of the materials frequently used for this purpose is a small amount of styrene. The styrene radicals that are formed are more stable than vinyl chloride radicals and do not tend to initiate polymerization of additional vinyl chloride monomer, and the reaction is essentially terminated.

The amount and nature of catalyst is of prime importance in vinyl polymerizations. We have seen how the kinetics are affected by the level of the catalyst and also how different catalysts have different half-lives or different rates of decomposition. The temperature of polymerization is determined by the molecular weight to be produced, and for the higher temperatures (that is, the lower molecular weights), it is very common to find lauroyl peroxide used. While this peroxide will also work at the lower temperatures, it tends to produce longer cycles. Because vinyl chloride has limited heat stability, attempts are made to keep the exposure as measured by the product of time and temperature during polymerization to as low a value as possible. Therefore, if catalysts can be found that are more reactive, the cycle time can be shortened, provided that the cooling system is capable of handling the heat generated. Reference to the list of half-lives shows that there are many catalysts that are more active than lauroyl peroxide. Some of them in current use are caproyl peroxide, azobisisobutyronitrile, diisopropyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, acetyl cyclohexane sulfonyl peroxide, and α -halolauroyl peroxide. A system known as the PERMIS system was recently suggested. This produces diethyl peroxydicarbonate by the reaction of ethyl chloroformate with hydrogen peroxide. This reaction takes place in the reactor. A prime consideration in the choice of a catalyst is the ease and safety of handling the particular peroxides or azo compounds. Generally speaking, most of these peroxides, such as the diisopropyl peroxydicarbonate or t-butyl peroxyphthalate, tend to be somewhat unstable and must be stored under refrigeration. While it is wise to store all peroxides under refrigeration, some lose activity rapidly if stored at temperatures above 0°F. For such catalysts, proper venting procedures are required so that the gases that are generated do not cause a pressure explosion. Sensitive peroxides are supplied with an inert carrier at a low enough concentration to prevent detonation. We shall later consider the possibilities of catalysts effecting fisheyes in a resin and their effect on reactor cleanliness.

Rapidly reacting catalysts are more sensitive to the temperature of the water used in preparing the batch and should be charged in cool water.

The quality of the water used is very important. Normally, deionized water is used and attempts are made to keep this water of prime quality. If the water has too much ionic material present, it will affect the particle size or the particle size distribution, or even the reaction kinetics. Another variable that must be carefully controlled is the water-to-monomer ratio. Most of the materials produced are produced with a ratio of water to monomer somewhere between 1.5 and 2.0. In some cases, it is necessary to go even beyond these limits. If, for example, a particle is being made that has a high degree of porosity, a large water-to-monomer ratio is imperative. The particle size is related to the water-to-monomer ratio, and some suspending systems are more sensitive to this ratio

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than others. Bulk density of the resultant powdered resin is also related to the water-to-monomer ratio — in a complex manner, depending on the suspending system. Besides serving to disperse the polymer and monomer particles, the water is a good thermal stabilizing system. It provides a material with a high specific heat, and in requiring a lot of heat to change its temperature, thereby assists the control systems. Small water-to-monomer ratios make reactor control more difficult because there is a larger fraction generating exothermic heat of polymerization and a smaller fraction of water to absorb this heat.

The suspending system is the heart of the process and probably has had more intensive research than any other phase of the polymerization process. Initially, pearl-type particles were made by using a solid dispersed throughout the water. This material accumulated at the monomer-water interface and prevented particles from coalescing. Materials such as magnesium hydroxide were used for this purpose. While this type of suspending system is satisfactory for certain liquid monomers, it does not give the kind of control that is essential for commercial polyvinyl chloride; and it has long since lapsed into obsolescence. The present favorites are hydrophilic large molecules such as methylcellulose, methylcellulose with condensed propylene oxide, ethyl cellulose, polyvinyl alcohol, polyvinyl alcohol acetate copolymers, hydroxymethylcellulose, hydroxyethylcellulose, gelatin, maleic-styrene copolymers, and almost any polymeric material that can be modified to acquire some hydrophilic nature. Likewise, almost all of the common surfactants have been investigated at one time or another. Frequently, systems using both a suspending agent (protective colloid) and a surfactant are used for special purposes. The surfactants have a tendency to produce more porous particles.

The patent literature is replete with numerous specific systems — all of which, it is claimed, have special effects in producing polyvinyl chloride polymers.

One system [36] is based on the use of a bisphenol "A" diglycidyl ether condensed with polyethylene glycol as a suspending agent. This is alleged to give a product that uniformly absorbs plasticizer at room temperature, and the use of polyvinyl alcohol and carboxymethylcellulose is alleged to give a product that uniformly does not absorb plasticizer. Another patent discloses the use of ethyl hydroxyethylcellulose [37] along with α -halolauryl peroxide with an almost 2:1 water-to-monomer ratio and polymerization in the range of 5-35°C. This material is supposed to produce a polyvinyl chloride having an average particle size of one-half a millimeter and a very high viscosity. Yield is said to be 75.5%. Systems based on double suspending agents for both polyvinyl chloride homopolymers and copolymers have been based on copolymers of vinyl acetate and alkyl alcohols used along with alkyl phenol condensates of ethylene oxide. This is alleged to produce a low-fisheye-content dry powder for extrusion [38]. Methylcellulose, hydroxymethylcellulose, and ethylcellulose have been used as suspending agents [39], producing low-fisheye resins of good dry-blend time and excellent clarity.

High-viscosity resins have been produced with polyvinyl alcohol as the suspending agent and α -chlorocaproyl peroxide dissolved in benzene as the catalyst. Polymerizations were made at -25°C to 40°C and high-viscosity products with improved thermal resistance, improved softening point, and resistance to solvent were obtained. Extremely high water-to-monomer ratios were used with this system [40], and undoubtedly some method was required to keep the water from freezing at the lower temperature.

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3. POLYVINYL CHLORIDE: POLYMERIZATION AND MANUFACTURE

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A granular polyvinyl chloride has been made using methylcellulose with a high viscosity and the reaction product of sodium cellulose glycolate ether of ungelatinized starch, along with Spans* and Tweens* and pentaerythritol monooleate [41]. Very porous particles of uniform size are said to result from the use of vinyl acetate and allyl alcohol copolymers, along with polyethylene glycol condensates of nonyl phenol. Venting is also required in this process [42].

Copolymers of vinyl methyl ether and maleic acid have been used as suspending agents, along with various amounts of methanol to control the particle size. Without methanol, the system produced a resin, 18% of which was retained by a 40-mesh screen. When methanol was added to the extent of 0.1 part per 100 of monomer, this amount was reduced to 2.4%; and when 0.15 part per 100 of monomer was used, the amount retained on a 40-mesh screen was reduced to 0.2% [43]. The use of methylcellulose and 0.07 part of stearyl alcohol, along with a caproyl peroxide in a system containing 1.5 parts of water per part of monomer and allowed to react at 56°C for 16 hr, produced a resin that was very low in fisheyes. The same formula used without the stearyl alcohol, or with vinyl alcohol or gelatin or both instead of the stearyl alcohol, produced approximately eight times as many fisheyes [44]. Methylhydroxypropylcellulose and other hydrophilic colloids have been reported to produce resins with good dry-blend times and porosities of 0.29 ml per gram. It was also reported that methyl glucoside dilaurates were useful for this application [45].

Gelatin used at a pH such as to remove it far from the isoelectric point and combined with cold-charging is said to produce a low-fisheye resin. A specific example would be the use of an alkali-refined gelatin at a pH of 2.7 to 3.2 made sufficiently acid with phosphoric acid and a system based on cold-charging [46].

It is obvious from these references that all sorts of suspending systems have been investigated and are being investigated. Generally speaking, gelatin and some form of methylcellulose are probably the most used materials for this purpose in the United States, with modifications of polyvinyl alcohol as a close runner-up. Surfactants are frequently added when it is desired to produce very porous particles; and hydroxyethylcellulose is preferred when a dense, nonporous particle is desired. As has been shown, the pH of the system has an effect. If one approaches the isoelectric point, the protective colloid is associated and may become less effective as a protective colloid. It is not uncommon to buffer the water phase of the polymerization to a pH that will control the particle size in the range desired. No doubt, as time goes on, other additives will gain popularity that will control particle size by some as yet undisclosed mechanism.

Along with a proper suspending system, it is necessary to tailor the agitation to produce the type of particle desired. Specific comments for the agitation must be tied to the system involved; but it is well established that high speeds will frequently favor agglomeration of fresh-formed particles, and insufficient agitation (particularly in the early phase of the reaction) will produce the same general effect by allowing coalescence of particles. Thus, there is an optimum speed.

*Registered trademarks of emulsifiers and wetting agents produced by I. C. I. America, Inc.

This speed, it has been alleged, may change as the conversion changes; and in some sophisticated operations, an agitation schedule will be tied to the conversion so that different rates of agitation will be used at different times. The loading in the reactor will certainly change the effectiveness of the agitation; and probably even more important is the presence, or absence, of baffles in the reaction vessel. Pfandier-type agitators are used frequently and have a tendency to put the entire contents of the reactor in a swirling motion. The presence of baffles breaks up this vortexlike motion and produces a better distribution of particles that vary in density as the conversion progresses. The agitation is also important in controlling the heat transfer from the small floating particles to the continuous-water phase. It is the water phase that carries heat to the wall of the reactor, where it is eventually transferred to the cooling water. Without proper control of agitation, hot spots and heat kicks can develop when the process is run with a short cycle. On the other hand, if the material is being allowed to react slowly and a very long cycle time is tolerated, agitation will be less important in heat transfer.

Controlling heat in the reactor and selecting heating or cooling modes are functions of the jacket and circulating system. In efficient reactors, the circulating system is designed to produce a good heat transfer between the metal of the reactor and the water in the jacket. This requires a high water velocity in the jacket — generally achieved by using a circulation pump. For polymerization to be started, steam or hot water is admitted to the inlet of the circulation pump to raise the temperature of the reactor. So the reactor can be cooled, cold water is admitted to the pump. The amount of tempering water admitted can be controlled by a valve, and an overflow valve downstream keeps the amount of water in the circulating system constant. This type of control can keep the temperature in the reactor within $\pm 1^\circ\text{F}$. Because of the explosive nature of the vinyl chloride monomer, most control systems have to be made with explosion-proof components. It has been easiest for the producers of equipment to devise control systems based on expanding bellows, temperature-sensing elements, and pneumatic controllers and valve positioners. But these controls tend to drift and it is essential that the controller be standardized periodically to maintain the proper temperature. The most reliable systems by far are those based on thermocouples. Unfortunately, the apparatus associated with them is usually electronic, and certain states require that it be kept in a separate pressurized room so that there is no possibility of explosive monomer entering this room. Installing thermocouple equipment would therefore contribute to increasing the original capital investment of the plant. However, the gains made are more than offset by the drift-free, consistent, accurate recording and controlling of temperature that can be achieved with this system. Since the flow of water through the jacket of the reactor is kept constant by the circulating pump, recording the inlet and outlet temperatures can be an effective way of calculating the heat that the reaction has liberated; and since the amount of heat liberated is directly related to the pounds of monomer that have been converted to polymer, the conversion can be readily followed. Recently, laboratory equipment has been described that uses an analog computer in a system of this nature to determine extent of reaction and to automatically plot the conversion [47]. This same type of equipment can readily be applied to the thermocouple outlets from sensing elements placed strategically in the reactor system.

The agitation demands for particle size control may sometimes be different from heat transfer requirements. A Belgian patent [48] describes using a reflux

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condenser to remove heat from the vessel by taking advantage of the latent heat of vaporization of the monomer. Condensing vapors have an excellent heat transfer coefficient; taking advantage of this can to some degree allow choosing the agitation speeds needed for particle size control.

After the reaction has reached approximately 70% conversion, the pressure in the vessel begins to drop. This corresponds to the point at which all of the free monomer particles have disappeared, and the only particles remaining are those that represent the precipitated phase of polymer with absorbed monomer. At this point, industrial practices begin to diverge. Some producers will add a short-stopping agent to terminate polymerization; others will allow reaction for a period until the pressure drops to perhaps 30 or 40 psig. At this point, the reaction is considered completed. Some manufacturers add antioxidants to protect the resin during its subsequent processing, while others [49] find it desirable to have such protection during the entire processing. At any rate, the next step is to remove the unreacted monomer. If the product is to be used as a dry-blend resin (that is, a resin with large amounts of porosity), the porosity can be achieved by rapidly removing the occluded monomer in the particles. This causes an expansion of the particle and makes it puffy. One method of achieving this is to rapidly transfer the contents of the reactor into an evacuated stripping vessel. As the fluids are forced into the stripping vessel, there is a rapid and sudden expansion. It has been pointed out that surfactants are sometimes useful in achieving this type of porous particle, but the combination of surfactants and a sudden vent produces a still more porous particle.

For those particles where porosity is not important, the stripping can be accomplished more slowly, and even in the same vessel. The decision to use a separate stripping vessel vs stripping in the reactor depends on the type of plant that has been designed and whether or not such bottlenecks can be tolerated. The monomer is removed using a schedule of increasing vacuum and temperature. In order to reduce the residual monomer to values acceptable to OSHA, high temperatures (up to 190°F) and high vacuum (frequently greater than 27 in. of vacuum) are required. The time is generally as long as possible without degrading the resin. Stringent residual monomer requirements may compromise the quality of the resin somewhat, particularly with respect to heat stability. After stripping the material is transferred to one of several holding tanks which serve as a supply source for a continuous centrifuge. During the centrifuging operation, most of the water is removed and a damp, solid, white powdery material, containing something of the order of 25% water, is passed to the drier. In the case of blotter resins (that is, resins with large porosity), the water content will be somewhat higher. This poses an added strain on the drying facilities.

The driers normally used are rotary driers very much like a sugar granulator. The resin is admitted to this drier along with heat air, the air and resin concurrently passing through the drier, which is usually installed at an incline varying from 10 to 25 degrees depending on the rate at which it is deemed necessary for the resin to pass through the drier. Usually, these driers have fingerlike projections that tend to hold the resin and drop it through the gas space. The filtered air admitted with the resin is usually heated to 150-210°F. As the resin dries, or as the water is taken up by the air, the air temperature is reduced and the exit air may be as low as 140-160°F. The resin is readily dried because homopolymers of

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vinyl chloride tend to be hydrophobic. Water is eliminated rather rapidly, and the dried product may have volatiles on the order of less than 1% (usually about 0.3-0.4%).

After drying, it is customary to pass the material to a screen to remove the large particles. These particles are sometimes agglomerates that have formed during the drying, or crusted material that has become dislodged from the drier wall or other parts of the equipment. Current practice in the United States is to use a 20- to 60-mesh screen for this so-called scalping operation. Some producers tend toward fine particles; others favor the larger particles.

From the screening operation, the resin may go to a bagging unit and be packaged in 50-lb fiber bags; but since vinyl resins are being used in such large quantities, a growing tendency for bulk shipments has developed and the resin, after screening, is generally blown into a silo, from which it can be removed for shipping as a bulk shipment in a truck or a railroad powder car. It has reached the point where it is difficult to pass a freight yard without seeing at least one of these cars on the siding somewhere.

It has been pointed out previously that the molecular weight, which is usually measured as a relative viscosity, depends on the temperature of the reaction. To achieve low molecular weights, high temperatures must be used. The temperature during processing and the time exposed to this temperature contribute to the heat history of the polymer. Exposure to a high temperature or exposure for a long period detracts from the resin's heat stability. It has therefore become common practice in producing low-molecular-weight materials to use a chain transfer agent that is more powerful than the monomer. As indicated previously, this will reduce the molecular weight of the resin. Therefore, one can process at a temperature considerably lower than what would be required to produce a low-viscosity or low-molecular-weight polymer. Chlorinated compounds are frequently used as a transfer agent — carbon tetrachloride and trichloroethylene are the most common. The latter is used frequently because slightly larger amounts can be tolerated and weighing thus becomes an easier operation. Recently, eugenol was proposed for this purpose [50]. Small concentrations of this material of less than one-half part per 100 of monomer can reduce the molecular weight by approximately one-third.

The attributes of the resin that must generally be controlled by these processes in addition to the molecular weight are bulk density, particle size and particle size distribution, porosity, fisheyes, heat stability, color, clarity, viscosity, contamination, and ability of the powder to flow freely.

It was previously pointed out that bulk density depends on the water-to-monomer ratio, as well as on particle size and particle size distribution. Fluffy, porous particles will generally produce products that are less dense. In fact, if one is making a very fluffy, porous powder (such as "blotter" resin), one must have enough water in the reactor so that there will be water left after the particles take in the large quantity of water they are capable of holding.

In other chapters, methods of characterizing the particle size by screen analysis are described. A plot of the cumulative particle size on normal probability paper will disclose whether the distribution is bimodal. If this undesirable situation exists, it may be traced to sudden changes in agitation or to conditions

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that caused the initiation of a second family of particles. The presence of substantial quantities of fines (material passing a 200-mesh screen) can cause difficulties in the air-conveying systems and these fines may also tend to segregate in the storage silos or in the powder cars or trucks.

Methods of determining pore volumes by porosimeters, plasticizer absorption, and so on are also described; for plant control, however, a quick and useful value is the compacted bulk density. This can readily be obtained by measuring the volume of a known weight of resin after it has been compacted to minimum value with a vibrator. The amount of plasticizer that the resin can absorb can be calculated from this value more reproducibly than it can be measured. This test can also be useful in detecting troubles due to static electric charges on the particles. A low bulk density can be increased if a small amount of graphite or ammonium hydroxide is added to the resin when static charges are the cause. Accumulations of static charges in the plant air-conveying system can cause dangerous electrical sparks and shocks.

We have frequently referred to fisheyes, which are small particles that do not readily fuse, thus remaining as discrete, gel-like particles — even after the resin is processed by extrusion, calendaring, and so on. Although fisheyes may occur during any of the polymerization steps, cleanliness is important in their control, because polymer particles adhering to the wall act as nuclei for fisheyes. High-pressure hydraulic hoses operating in the 1000 to 2000 psi range have been found helpful in removing such particles, but it is often necessary to enter the vessel to clean it mechanically.

Some initiators have a tendency to produce more fisheyes than others. The choice of the suspending system also is important in controlling this quality of the resin.

The control of the resin molecular weight, as measured by relative viscosity or other dilute solution viscosity, is of prime importance in determining end use of the resin. The melt viscosity of the resin, alone or with plasticizer, is directly related to molecular weight, which is controlled by proper selection of polymerization temperature and the level of chain transfer agent.

Heat stability tests are described elsewhere; they evaluate one of the most important resin properties. Poor heat stability can result from overheating the resin, heat kicks, or too high a drier temperature.

The color and the clarity of the fused resin are also important qualities. Poor clarity can result from choosing a suspending agent that is not soluble in the molten resin and shows up as a haze. Poor color, like poor heat stability, may reflect the initiator used or the addition of inhibitors or antioxidants.

Lastly, foreign contamination should be kept at a minimum. This contamination can come from any part of the process. It might be flecks of scale from the reactor, charred particles from the drier, or dust and grit picked up by the air-conveying system; in any case, all foreign matter should be kept to a very minimum. A simple method of determining the amount of contamination is to cause a given quantity of the resin to flow as a thin layer from a vibrator and observe the number of off-color particles for a specific weight of resin. Normally, good processing techniques and good housekeeping can keep contamination within acceptable bounds.

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United States Patent [19]
Kobayashi et al.

[11] **Patent Number:** 5,739,222
[45] **Date of Patent:** Apr. 14, 1998

[54] **PROCESS FOR PREPARING VINYL CHLORIDE POLYMER UNDER SPECIFIED VAPOR PRESSURE**

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[73] **Assignee:** Shin-Etsu Chemical Co., Ltd., Tokyo, Japan

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[30] **Foreign Application Priority Data**

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Oct. 4, 1995 [JP] Japan 7-282604

[51] **Int. Cl.⁶** C08F 2/20; C08F 4/38

[52] **U.S. Cl.** 526/87; 526/79; 526/202; 526/228

[58] **Field of Search** 526/78, 79, 80, 526/227, 228

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Primary Examiner—Christopher Henderson
Attorney, Agent, or Firm—McAulay Fisher Nissen Goldberg & Kiel, LLP

[57] **ABSTRACT**

A vinyl chloride polymer is prepared through suspension polymerization of a vinyl chloride monomer in the presence of a polymerization initiator in a reactor. The reactor is charged with up to 1/3 of the overall monomer charge to initiate polymerization. Polymerization is carried out under a certain saturated vapor pressure of P1 kgf/cm² at a preset polymerization temperature. When the internal pressure of the reactor declines to P2 kgf/cm², the remainder of the overall monomer charge is continuously fed to the reactor so as to maintain the internal pressure within the range of (P1-ΔP) wherein ΔP=P1-P2 ranges from 0.1 to 2.0 kgf/cm². A vinyl chloride polymer having a high degree of polymerization is efficiently produced while alleviating the load of heat removal.

4 Claims, No Drawings

PROCESS FOR PREPARING VINYL CHLORIDE POLYMER UNDER SPECIFIED VAPOR PRESSURE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for preparing a vinyl chloride polymer by suspension polymerization and more particularly, to a process for preparing a vinyl chloride polymer in high yields while reducing the load of heat removal.

2. Prior Art

Suspension polymerization of vinyl chloride monomers is generally effected batchwise. A polymerizing reactor or polymerizer equipped with a jacket for passing a cooling medium is charged with water, a suspending agent, a polymerization initiator, a vinyl chloride monomer, and other additives. With stirring, the mixture charged in the reactor is heated to a preset polymerization temperature by passing heating water through the jacket around the reactor. Since the polymerization reaction of vinyl chloride monomers is exothermic, polymerization then proceeds while the reaction heat is removed by passing cooling water through the jacket such that the mixture charged in the reactor may be maintained at the preset temperature. At a point of time when free vinyl chloride monomer is disappearing from the charged mixture as the yield increases, the vinyl chloride monomer in gas phase starts decreasing and the internal pressure of the reactor starts declining. Polymerization reaction is terminated when a predetermined internal pressure is reached.

Generally speaking, in the polymerization of vinyl chloride monomers, the degree of polymerization of a polymer is governed by a preset polymerization temperature. Thus the preset polymerization temperature is automatically determined in accordance with a target degree of polymerization. If the preset polymerization temperature is low, the resulting polymer would have a higher degree of polymerization. For example, the degree of polymerization is about 800 at a preset polymerization temperature of 63° C. but reaches about 2,000 at a preset polymerization temperature of 43° C.

Accordingly, vinyl chloride polymers having a high degree of polymerization will be obtained if the polymerization temperature is set low. This in turn requires a longer polymerization time. The amount of a polymerization initiator added must be increased in order to shorten the polymerization time. The increased amount of a polymerization initiator, in turn, causes the polymerization reaction to generate more heat. To remove the reaction heat, the temperature of cooling water must be set lower, sometimes surpassing the capacity of a water cooling machine. It is then difficult to shorten the polymerization time. The cooling capacity can be increased to provide for heat removal. Even in such a case, if the amount of a polymerization initiator is further increased in order to shorten the polymerization time, then the resulting polymer will have a lower degree of polymerization. Then the polymerization temperature must be set lower, resulting in a lower polymerization rate. This combined with the increased cooling load is disadvantageous. The series of steps are caught in a vicious circle. The increased amount of polymerization initiator gives rise to the additional problem that parts molded from the resulting polymer have a poor color hue.

One known solution to the problem is to add a crosslinking agent to a charge mixture to be polymerized. Although the resulting polymer has an apparently increased degree of

polymerization, its mechanical properties such as tensile elongation and tensile strength are not as high as those of a genuine polymer having an identical degree of polymerization.

It is therefore desired to have a process of preparing a polymer having a high degree of polymerization without excessively lowering the preset polymerization temperature as in the prior art. More specifically, if the current preset polymerization temperature can be increased for the purpose of producing a polymer having a desired degree of polymerization, then the rate of polymerization reaction is increased, permitting the polymerization time to be shortened and the amount of polymerization initiator to be reduced. Additionally, the temperature of cooling water to be passed through the jacket can be increased so that the load of a water cooling machine may be reduced, resulting in a cost reduction.

Also in connection with the polymerization of vinyl chloride monomers, a polymerization initiator is selected from those commonly used at a certain polymerization temperature. If a target yield and polymerization time are given, the necessary amount of that initiator is automatically determined.

In order to prepare vinyl chloride polymers at a high productivity, it is increasingly demanded to complete the polymerization process within a short time. Under such circumstances, it has been a common practice to select a more active polymerization initiator and increase the amount thereof. As the amount of initiator used is increased, the resulting polymer has a more amount of undecomposed initiator carried thereon, which is detrimental to the color hue of parts molded from the polymer. The increased amount of initiator, in turn, causes the polymerization reaction to generate more heat per unit time. To remove the reaction heat, the temperature of cooling water passed through the jacket around the reactor must be lower, sometimes surpassing the capacity of a water cooling machine. Increasing the capacity of a cooling machine leads to an increased cost. In addition, the increased amount of initiator results in a polymer having a lower degree of polymerization. To increase a degree of polymerization, the polymerization temperature must be set lower, resulting in a lower polymerization rate. This combined with the increased cooling load is caught in a vicious circle.

For solving the problem, it is effective to make uniform the pattern of removal of polymerization heat, that is, to establish a uniform polymerization rate. In Japanese Patent Application Kokai (JP-A) Nos. 14670/1971, 149407/1981, and 105709/1993, for example, it was proposed to combine two or more initiators having different activities. This approach is successful in reducing the amount of initiator required to complete polymerization within an identical time because the reaction rate pattern is converted from a rightward rising triangle to a rectangle to increase an average reaction rate throughout the process. Since this reduction of the amount of initiator required is insufficient, there is a need for a further reduction.

Therefore, a primary object of the invention is to provide a process for preparing a vinyl chloride polymer having a high degree of polymerization at a high productivity while reducing the load of heat removal.

Another object of the invention is to provide a process for preparing a vinyl chloride polymer having a high degree of polymerization and improved colorability upon molding at a high productivity while significantly reducing the necessary amount of initiator and the load of heat removal.

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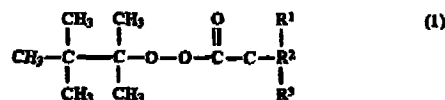
SUMMARY OF THE INVENTION

In conjunction with ordinary batchwise polymerization of a vinyl chloride monomer, there occurs a well-known phenomenon that at a point of time when free vinyl chloride monomer is disappearing from the charge mixture as the yield increases and the rate of polymerization reaction gradually increases, the vinyl chloride monomer in gas phase starts decreasing and the internal pressure of the reactor starts declining, and the rate of polymerization reaction reaches maximum at this point of pressure decline or some time later and thereafter experiences a sudden drop. When the rate of polymerization reaction reaches maximum or nearly maximum at the start of decline of the reactor internal pressure or some time later, the vinyl chloride monomer is added in an additional amount corresponding to the consumption of the vinyl chloride monomer at that rate of polymerization reaction so that the internal pressure of the reactor is maintained substantially at or in proximity to a level enough to ensure the maximum rate of polymerization reaction. Then polymerization reaction proceeds in such a state that this nearly maximum rate of polymerization reaction may be maintained for a relatively long period of time. This is very advantageous for increased productivity. Also, surprisingly, if the amount of the vinyl chloride monomer added in this state is increased to increase the ratio of the additional monomer to the initially charged monomer to such an extent that the additional monomer is at least one fifth of the overall monomer charge, then a vinyl chloride polymer having a high degree of polymerization can be produced.

Therefore, the present invention provides a process for preparing a vinyl chloride polymer by suspension polymerization of a vinyl chloride monomer in a reactor wherein at the instant when the internal pressure of the reactor starts declining in a later stage of polymerization reaction approximately on arrival at maximum of the rate of polymerization reaction or some time later, an additional amount of the vinyl chloride monomer is added whereby a nearly maximum rate of polymerization reaction is maintained for a relatively long period of time, thereby obtaining a polymer having a higher degree of polymerization. More specifically, the reactor is first charged with up to $\frac{1}{2}$ of the overall monomer charge, and the remaining at least $\frac{1}{2}$ of the overall monomer charge is fed to the reactor after the internal pressure of the reactor has started declining.

We have also found that better results are obtained by charging the reactor with up to $\frac{1}{2}$ of the overall monomer charge and carrying out polymerization under a certain saturated vapor pressure of P_1 kgf/cm² at a preset polymerization temperature. When the internal pressure of the reactor declines to P_2 kgf/cm², the remainder of the overall monomer charge is continuously fed to the reactor so as to maintain the internal pressure within the range of ($P_1 - \Delta P$) wherein $\Delta P = P_1 - P_2$ ranges from 0.1 to 2.0 kgf/cm², preferably 0.1 to 1.0 kgf/cm².

We have further found that better results are obtained when a polymerization initiator having a temperature of 30° to 65° C. at which its half life in a 0.1 mol/l benzene solution is 10 hours is used in an amount of 0.01 to 0.3% by weight based on the weight of the overall monomer charge. The polymerization initiator used herein is preferably a 1,1,2,2-tetramethylpropylperoxy ester of the following general formula:



wherein R^1 , R^2 and R^3 are independently selected from normal alkyl groups having 1 to 9 carbon atoms. When suspension polymerization of a vinyl chloride monomer is carried out in the presence of a 1,1,2,2-tetramethylpropylperoxy ester of formula (1) as the polymerization initiator, the vinyl chloride monomer in gas phase starts decreasing and the internal pressure of the reactor starts declining at a point of time when free vinyl chloride monomer is disappearing from the charged mixture. The rate of polymerization reaction rapidly increases from a point of time about 10 to 20 minutes before the start of decline of the internal pressure and a maximum rate of polymerization reaction is reached when the internal pressure declines a little (a decline of about 2 kgf/cm² though it somewhat varies with polymerization conditions). Thereafter, the rate of polymerization reaction is significantly slowed down. This outstanding gel effect is not found with conventional initiators. Based on this discovery, we carried out production of a vinyl chloride polymer.

When the rate of polymerization reaction reaches maximum or nearly maximum due to the outstanding gel effect, the vinyl chloride monomer is added in an additional amount corresponding to the consumption of the vinyl chloride monomer at that rate of polymerization reaction so that the internal pressure of the reactor is maintained substantially at or in proximity to a level enough to ensure the maximum rate of polymerization reaction. Then polymerization reaction proceeds in such a state that this nearly maximum rate of polymerization reaction may be maintained for a relatively long period of time. This procedure permits the initiator to be quite effectively used and advantageously increases productivity. Also, if the amount of the vinyl chloride monomer added in the later stage is increased to increase the ratio of the additional monomer to the initially charged monomer to such an extent that the additional monomer is at least one fifth of the overall monomer charge as previously mentioned, then a vinyl chloride polymer having a high degree of polymerization can be produced. Based on these facts, we have found that when it is desired to produce a polymer having the same degree of polymerization as prior art ones, the polymerization temperature can be set higher, the load of removal of polymerization reaction heat can be alleviated, and the rate of polymerization reaction can be increased. All these factors lead to a favorable cycle in contrast to the prior art. Since the necessary amount of polymerization initiator is significantly reduced, the amount of undecomposed initiator carried on the resulting polymer is reduced, which ensures that parts molded from the polymer are improved in color hue.

Thus we have found that if a 1,1,2,2-tetramethylpropylperoxy ester of formula (1) is used in a reactor for the suspension polymerization of a vinyl chloride monomer as the polymerization initiator in a significantly smaller amount than conventional initiators, and if an additional amount of the vinyl chloride monomer is added at the instant when the internal pressure of the reactor starts declining in a later stage of polymerization reaction approximately on arrival at maximum of the rate of polymerization reaction or some time later, such that the internal pressure of the reactor may fall in the effective range, then a nearly maximum rate of polymerization reaction can be maintained for a relatively long period of time, resulting in a polymer

having a higher degree of polymerization. This is ensured when the reactor is first charged with up to 1/5 of the overall monomer charge, and the remaining at least 4/5 of the overall monomer charge is additionally fed in the later stage.

DETAILED DESCRIPTION OF THE INVENTION

Broadly stated, a process for preparing a vinyl chloride polymer by suspension polymerization of a vinyl chloride monomer in the presence of a polymerization initiator in a reactor is contemplated herein. According to the feature of the invention, the reactor is charged with up to 1/5 of the overall monomer charge to initiate polymerization. After the internal pressure of the reactor has started declining, the remainder of the overall monomer charge is fed to the reactor to continue polymerization.

Suspension polymerization of a vinyl chloride monomer may be carried out in a conventional manner. Usually, a reactor equipped with a jacket through which a heating or cooling medium can be passed for heating or cooling the reactor is charged with water, a suspending agent, a vinyl chloride monomer, and a polymerization initiator. Polymerization is then initiated.

The vinyl chloride monomer used herein encompasses vinyl chloride alone and a mixture of a major proportion, typically more than 50% by weight, preferably more than 70% by weight of vinyl chloride and a minor proportion of another monomer copolymerizable therewith. Examples of the monomer copolymerizable with vinyl chloride include alpha-olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, and 1-tetradecene; vinyl esters such as vinyl acetate; vinyl ethers such as lauryl vinyl ether and isobutyl vinyl ether; maleic acid and maleic anhydride; and vinylidene chloride, alone or in admixture of two or more.

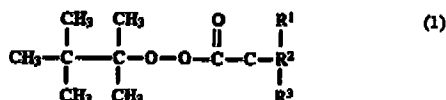
The initial amount of the vinyl chloride monomer charged is up to four fifths, preferably up to two thirds of the overall monomer charge, which is an initial amount of monomer added first plus an additional amount of monomer added later. If the initial charge of the vinyl chloride monomer loaded exceeds 1/5 of the overall monomer charge, then the additional amount of monomer added later is reduced to less than 4/5 of the overall monomer charge. Then the length of time when a nearly maximum rate of polymerization can be maintained is reduced and the degree of polymerization cannot be fully increased, failing to achieve the objects of the invention. If the initial charge of the vinyl chloride monomer is too small, then the absolute quantity of polymerization reaction at the point of time when the additional monomer is fed is reduced, which is detrimental to productivity. For this reason, the initial charge of the vinyl chloride monomer is preferably at least 1/10, especially at least 1/5 of the overall monomer charge.

The suspending agent used for suspension polymerization according to the invention may be selected from those conventionally used in polymerization of vinyl chloride monomers, for example, cellulose derivatives such as methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, and hydroxypropylmethyl cellulose, water or oil-soluble partially saponified polyvinyl alcohol, and water-soluble polymers such as acrylic acid polymers and gelatin. They may be used alone or in admixture of two or more. In combination with the suspending agent, there can be used

propylene oxide block copolymers and anionic emulsifiers such as polyoxyethylene sorbitan monolaurate, polyoxyethylene glycerin oleate, and sodium lauryl sulfate. The suspending agent is preferably added in an amount of about 0.02 to 0.2 part by weight per 100 parts by weight of the overall vinyl chloride monomer charge.

Useful polymerization initiators are those which are effective in the temperature range of 30° to 70° C. which is an ordinary polymerization temperature range of vinyl chloride monomers, that is, polymerization initiators having a temperature of 30° to 65° C. at which its half life in a 0.1 mol/l benzene solution is 10 hours. These polymerization initiators may be used alone while a mixture of two or more polymerization initiators having different 10-hour half-life temperatures may be used for the purpose of providing a constant rate of polymerization reaction until the internal pressure of the reactor starts declining. Examples of the polymerization initiator include diacyl organic peroxides such as isobutyrylperoxide (10-hour half-life temperature 32.5° C.), 3,5,5-trimethylhexanoylperoxide (59.5° C.), and lauroylperoxide (62.0° C.); peroxyester organic peroxides such as cumylperoxyneodecanoate (36.5° C.), tert-butylperoxypivalate (55.0° C.), tert-butylperoxyneodecanoate (49.7° C.), tert-butylperoxyneodecanoate (46.5° C.), and t-hexylperoxyneodecanoate (44.7° C.); peroxydicarbonate organic peroxides such as diallylperoxydicarbonate (38.87° C.), di-sec-butylperoxydicarbonate (45.0° C.), and di-2-ethylhexylperoxydicarbonate (43.5° C.); and azo compounds such as 2,2'-azobisisobutyronitrile (65.0° C.) and 2,2'-azobis-2,4-dimethylvaleronitrile (51.0° C.).

Preferred polymerization initiators are 1,1,2,2-tetramethylpropylperoxy esters of the following general formula:



wherein R¹, R² and R³, which may be the same or different, are independently selected from normal alkyl groups having 1 to 9 carbon atoms.

Preferred examples of the ester of formula (1) which can be used herein include 1,1,2,2-tetramethylpropylperoxyneodecanoate (10-hour half-life temperature in 0.1 mol/l benzene solution: 39.0° C.), 1,1,2,2-tetramethylpropylperoxypivalate (45.7° C.), and 1,1,2,2-tetramethylpropylperoxyneodecanoate (40.6° C.).

The polymerization initiator is preferably added to the polymerization system in an amount of 0.01 to 0.3% by weight, more preferably 0.03 to 0.2% by weight of the overall charge of vinyl chloride monomer. With less than 0.01% of the polymerization initiator, there is a likelihood that the system fails to sustain activity enough for polymerization reaction to proceed. polymerization reaction peaks before the internal pressure of the reactor starts declining, polymerization reaction declines thereafter, there is no chance to add an additional amount of the vinyl chloride monomer in the vicinity of the maximum rate of polymerization reaction, and the polymerization time is prolonged. With more than 0.3% of the polymerization initiator, the rate of polymerization reaction would become so high that the resultant large amount of heat of polymerization cannot be fully removed before the maximum rate of polymerization reaction is reached, inducing runaway reaction.

It is understood that the preferred polymerization initiator is a 1,1,2,2-tetramethylpropylperoxyester compound of for-

mula (1) as mentioned above. It may be used alone or in combination with at least one of other polymerization initiators having a 10-hour half-life temperature in 0.1 mol/l benzene solution of 30° to 60° C. In the latter case, the 1,1,2,2-tetramethylpropylperoxyester compound of formula (1) is desirably used in an amount of at least 1/4, especially at least 1/2 of the total amount of polymerization initiators. If the amount of 1,1,2,2-tetramethylpropylperoxyester compound of formula (1) used is less than 1/4 of the total amount of polymerization initiators, then there would not occur the outstanding gel effect inherent to that compound that the rate of polymerization reaction experiences a rapid leap nearly when the internal pressure of the reactor starts declining. This is against the feature of the invention that polymerization is continued with a smaller amount of initiator and at a high rate of polymerization reaction while adding an additional amount of the vinyl chloride monomer.

Often the entire amount of the polymerization initiator is added at the initial stage although a portion of the polymerization initiator may be continuously or intermittently added during polymerization. Since the point of time when an additional amount of the vinyl chloride monomer is added is critical in the polymerization process of the invention and it is desirable to shorten the length of time passed until the internal pressure of the reactor starts declining, it is recommended to use the polymerization initiator in an amount of at least 0.04%, especially at least 0.06% by weight of the initial monomer charge.

The polymerization initiator may be added to the reaction system in any desired manner, for example, by pumping.

As is conventional, any of optional polymerization aids commonly used in the polymerization of vinyl chloride monomers including a polymerization regulator, chain transfer agent, pH adjusting agent, gelation adjusting agent, anti-static agent, crosslinking agent, filler, and polymer scale inhibitor may be added if necessary.

After the reactor is charged with the reactants, the charge mixture in the reactor is heated by passing a heating medium (typically hot water) through the jacket, thereby initiating polymerization. Once the charge mixture reaches the preset polymerization temperature, heat of polymerization is removed by passing a cooling medium through the jacket, thereby maintaining the preset polymerization temperature. The preset polymerization temperature may be properly selected although a temperature in the range of 30° to 70° C., especially 35° to 65° C. is preferred from the standpoints of a rate of reaction and a degree of polymerization.

While polymerization proceeds in this way, the yield increases and the rate of reaction gradually increases. At a point of time when free vinyl chloride monomer is disappearing from the charge mixture, the vinyl chloride monomer in gas phase starts decreasing and the internal pressure of the reactor starts rapidly dropping. The rate of polymerization reaction rapidly rises from about 10 to 20 minutes before the internal pressure of the reactor starts rapidly dropping, and peaks at a point of time when the internal pressure declines a little (a decline of about 2 kgf/cm² though it somewhat varies with polymerization conditions).

Where the 1,1,2,2-tetramethylpropylperoxyester compound of formula (1) is used as a polymerization initiator, its unique gel effect drives a rapid rise of the rate of polymerization reaction so that the peak rate of polymerization reaction reaches 1.5 times, sometimes 2 or more times the rate before the rise.

At the point of time when the internal pressure of the reactor has declined a little at or in the vicinity of the peak rate of polymerization reaction, the remainder of the overall

monomer charge which has not been fed initially, more specifically at least 1/4, especially at least 1/2 of the overall monomer charge is continuously added to the reaction system to continue polymerization.

It is now assumed that the reaction system has a certain saturated vapor pressure P_1 kgf/cm² at the initial preset polymerization temperature, that is, the reactor has a certain internal pressure P_1 kgf/cm² before the internal pressure starts declining, and that the reactor has an internal pressure P_2 kgf/cm² after the internal pressure has started declining, and $\Delta P = P_1 - P_2$. Supply of an additional amount of the monomer to the reactor is preferably started and continued so as to maintain the internal pressure within the range of $(P_1 - \Delta P)$ wherein $0.1 \text{ kgf/cm}^2 \leq \Delta P \leq 2.0 \text{ kgf/cm}^2$, preferably $0.1 \text{ kgf/cm}^2 \leq \Delta P \leq 1.0 \text{ kgf/cm}^2$. By maintaining ΔP within this range, the rate of polymerization reaction can be maintained maximum or nearly maximum thereafter. If ΔP is outside the range, the rate of polymerization reaction would be lower during supply of the additional vinyl chloride monomer and as a result, the polymerization time would be prolonged, failing to obtain a polymer having a high degree of polymerization. Therefore, by maintaining ΔP within this range, a vinyl chloride polymer having a high degree of polymerization can be produced at high productivity and with the reduced load of heat removal from the reaction system. In order to precisely adjust a degree of polymerization and a polymerization time, it is further preferable that a constant value of ΔP within the above-defined range be maintained. By maintaining ΔP constant, the relationship that the rate of monomer feed is equal to the rate of polymer formation can be maintained.

The vinyl chloride monomer may be supplied to the reactor by various techniques, for example, by pumping or by heating a container of the monomer to create a pressure difference enough to forcibly admit the monomer to the reactor. Any desired technique may be used insofar as it is capable of precise stable supply of the monomer.

After the remainder of the overall monomer charge is completely fed to the reactor, polymerization is terminated in accordance with a conventional polymerization technique.

The process of the invention can produce a vinyl chloride polymer having a high degree of polymerization at a high productivity while reducing the load of heat removal. Where a 1,1,2,2-tetramethylpropylperoxyester compound of formula (1) is used as the polymerization initiator, a vinyl chloride polymer having a high degree of polymerization and improved colorability upon molding can be produced at a high productivity while reducing the necessary amount of initiator and the load of heat removal.

EXAMPLE

Examples of the present invention is described below by way of illustration and not by way of limitation.

Example 1

The reactor used for suspension polymerization of vinyl chloride monomer (VCM) was a stainless steel reactor having an interior volume of 100 liters equipped with a jacket, baffle, and stirrer.

The reactor was charged with 60 kg of deionized water at 22° C. Then 2 kg of an aqueous solution containing 18 grams (0.06% by weight based on the overall vinyl chloride monomer charge) of water-soluble partially saponified polyvinyl alcohol and 12 grams (0.04% by weight based on the overall vinyl chloride monomer charge) of water-soluble

cellulose ether and 100 grams of a mixture of water and methanol (in a weight ratio of 1:1) containing 12 grams (0.04% by weight based on the overall vinyl chloride monomer charge) of oil-soluble partially saponified polyvinyl alcohol as suspending agents were admitted into the reactor and stirred. By passing warm water through the jacket, the reactor contents were heated to 30° C. The reactor interior was evacuated to a vacuum of 120 mmHg. With stirring, the reactor was charged with 14.0 kg of vinyl chloride monomer (VCM) at room temperature (19° C.) to form a mixture. The charge mixture was heated to 30° C. by warm water through the jacket. Thereafter, with the mixture being stirred, 38.57 grams of an isoparaffin solution containing 27.0 grams (0.09% by weight based on the overall vinyl chloride monomer charge) of di-2-ethylhexylperoxydicarbonate as the polymerization initiator was pumped into the reactor to initiate polymerization. At the same time, the charge mixture was heated by warm water through the jacket to a preset polymerization temperature of 54° C. within 30 minutes. Thereafter, coolant water was passed through the jacket to remove heat of polymerization so that the preset temperature was maintained. The internal pressure of the reactor remained constant at 7.9 kgf/cm² for a long while and thereafter, started rapidly declining. When the internal pressure reached 7.4 kgf/cm² (146 minutes after the start of polymerization), the supply of the vinyl chloride monomer (VCM) into the reactor was restarted. The vinyl chloride monomer was continuously pumped to maintain the internal pressure at 7.4 kgf/cm². The flow rate of the vinyl chloride monomer was measured by a mass flow meter in the piping. When the flow rate accumulation reached 16.0 kg (109 minutes after the restart of monomer supply), the supply of the vinyl chloride monomer was interrupted. When the internal pressure of the reactor dropped to 5.5 kgf/cm² (26 minutes after the interruption of monomer supply), 4.5 grams of bisphenol-A was admitted to stop polymerization.

After the polymerization reaction was stopped, the unreacted monomer was recovered from the reactor and the resulting polymer slurry was taken out of the reactor, dewatered, and dried. The weight of the polymer was measured to calculate its yield based on the overall vinyl chloride monomer charge.

Example 2

A vinyl chloride polymer was prepared by the same procedure as in Example 1 except that the initial charge of VCM was 10 kg, the polymerization initiator used was 0.095% by weight based on the overall VCM charge of di-2-ethylhexylperoxydicarbonate, the preset polymerization temperature was 54.5° C., 20 kg of the VCM was continuously pumped to maintain the internal pressure at 7.5 kgf/cm², and polymerization was stopped when the internal pressure dropped to 5.6 kgf/cm².

Example 3

A vinyl chloride polymer was prepared by the same procedure as in Example 1 except that the initial charge of VCM was 20 kg, the polymerization initiators used were 0.045% by weight based on the overall VCM charge of di-2-ethylhexylperoxydicarbonate and 0.05% by weight based on the overall vinyl chloride monomer charge of tert-butylperoxyester, the preset polymerization temperature was 53° C., 10 kg of the VCM was continuously pumped to maintain the internal pressure at 7.2 kgf/cm², and polymerization was stopped when the internal pressure dropped to 5.3 kgf/cm².

Comparative Example 1

A vinyl chloride polymer was prepared by the same procedure as in Example 1 except that the initial charge of VCM was 30 kg, the polymerization initiator used was 0.12% by weight based on the overall VCM charge of di-2-ethylhexylperoxydicarbonate, the preset polymerization temperature was 50.5° C., no additional VCM was fed after the internal pressure of the reactor started declining, and polymerization was stopped when the internal pressure dropped to 4.9 kgf/cm².

Comparative Example 2

A vinyl chloride polymer was prepared by the same procedure as in Example 1 except that the initial charge of VCM was 26 kg, the polymerization initiator used was 0.122% by weight based on the overall VCM charge of di-2-ethylhexylperoxydicarbonate, the preset polymerization temperature was 51° C., 4 kg of the VCM was continuously pumped to maintain the internal pressure at 7.0 kgf/cm², and polymerization was stopped when the internal pressure dropped to 5.0 kgf/cm².

Comparative Example 3

A vinyl chloride polymer was prepared by the same procedure as in Comparative Example 1 except that the polymerization initiator used was 0.092% by weight based on the overall VCM charge of di-2-ethylhexylperoxydicarbonate, 0.037% by weight based on the overall VCM charge of diallyl malate as a crosslinking agent was added at the same time as the polymerization initiator, the preset polymerization temperature was 54° C., and polymerization was stopped when the internal pressure dropped to 5.5 kgf/cm².

The vinyl chloride polymers obtained in Examples 1-3 and Comparative Examples 1-3 were measured for a degree of polymerization and tensile properties. The results are shown in Table 1.

Degree of Polymerization

It was measured according to JIS K6721.

Tensile Test

Tensile strength and elongation were measured by a tensile test according to JIS C3005. Using the tensile tester, Stograph manufactured by Toyo Seiki K.K., a No. 2 dumbbell-shaped specimen having a distance between gage marks of 25 mm and a width of 6 mm was tested at a pulling speed of 200 mm/min. An average of five measurements was reported.

The specimen was prepared by blending 100 parts by weight of the vinyl chloride polymer with 45 parts by weight of dioctyl phthalate, 5 parts by weight of tribasic lead sulfate, 2 parts by weight of dibasic lead phosphite, 10 parts by weight of calcined clay, and 0.5 part by weight of high-melting paraffin, followed by rolling and pressing. The rolling conditions included a 6-inch roll, a milling temperature of 165° C., a milling time of 5 minutes, and a gage of 0.8 mm. The pressing conditions included a 50-t press, a temperature of 170° C., a pressure of 110 kgf/cm², a preheating time of 5 minutes, and a pressing time of 3 minutes.

In Examples 1-3 and Comparative Examples 1-3, the lowest temperature of water passed through the jacket during polymerization was recorded to determine the load of heat removal.

TABLE 1

	E1	E2	E3	CE1	CE2	CE3
Polymerization temperature (°C.)	54.0	54.5	53.0	50.5	51.0	54.0
Initiator						
Type*	EHP	EHP	EHP	EHP	EHP	EHP
Amount (%)	0.090	0.095	0.045	0.120	0.122	0.092
Type*	—	—	BND	—	—	—
Amount (%)	—	—	0.050	—	—	—
Crosslinking agent (%)	—	—	—	—	—	0.037
Initial charge of VCM (kg)	14	10	20	30	26	30
Additional charge of VCM (kg)	16	20	10	0	4	0
VCM supply pressure (kgf/cm ²)	7.4	7.5	7.2	—	7.0	—
Start of VCM supply (min.)	146	117	156	—	230	—
Time of VCM supply (min.)	109	143	90	—	20	—
Pressure dropping time (min.)	26	24	35	38	34	35
Total polymerization time (min.)	281	284	281	283	284	283
Final internal pressure (kgf/cm ²)	5.5	5.6	5.3	4.9	5.0	5.5
Yield (%)	86.0	85.9	86.1	86.2	86.1	86.0
Lowest jacket temperature (°C.)	49.2	49.8	48.4	45.8	46.1	49.6
Degree of polymerization	1300	1310	1300	1300	1310	1300
Tensile test						
Tensile strength (kgf/mm ²)	1.63	1.66	1.61	1.63	1.64	1.25
Tensile elongation (%)	388	380	391	375	382	345

*EHP: di-2-ethylhexylperoxydicarbonate (10-hour half-life temperature in 0.1 mol/l benzene solution: 43.5° C.)
 BND: tert-butylperoxyneodecanoate (46.5° C.)

It is evident from Table 1 that as compared with the prior art, the polymers prepared by the process of the invention within an identical polymerization time had a high degree of polymerization although the amount of initiator used is reduced. The productivity is increased and the preset polymerization temperature can be higher. As a result, the load for heat removal is alleviated. The results of the tensile test on the inventive polymers are superior to those of the polymer whose degree of polymerization was increased by the use of a crosslinking agent (Comparative Example 3).

Example 4

The reactor used for suspension polymerization of vinyl chloride monomer (VCM) was a stainless steel reactor having an interior volume of 100 liters equipped with a jacket, baffle, and stirrer.

The reactor was charged with 60 kg of deionized water at 22° C. Then 2 kg of an aqueous solution containing 18 grams (0.06% by weight based on the overall vinyl chloride monomer charge) of water-soluble partially saponified polyvinyl alcohol and 12 grams (0.04% by weight based on the overall vinyl chloride monomer charge) of water-soluble cellulose ether and 100 grams of a mixture of water and methanol (in a weight ratio of 1:1) containing 12 grams (0.04% by weight based on the overall vinyl chloride monomer charge) of oil-soluble partially saponified polyvinyl alcohol as suspending agents were admitted into the reactor and stirred. By passing warm water through the jacket, the reactor contents were heated to 40° C. The reactor interior was evacuated to a vacuum of 120 mmHg. With stirring, the reactor was charged with 13.0 kg of vinyl chloride monomer (VCM) at room temperature to form a mixture. The charge mixture was heated to 40° C. by warm water through the jacket. Thereafter, 13.7 grams of an isoparaffin solution containing 9.6 grams (0.032% by weight based on the overall vinyl chloride monomer charge) of 1,1,2,2-tetramethylpropylperoxyneodecanoate as the polymerization initiator was pumped into the reactor to initiate polymerization. At the same time, the charge mixture was heated by warm water through the jacket to a preset poly-

merization temperature of 54° C. within 30 minutes. Thereafter, coolant water was passed through the jacket to remove heat of polymerization so that the preset temperature was maintained. The internal pressure of the reactor remained constant at 7.9 kgf/cm² for a long while and thereafter, started rapidly declining. When the internal pressure reached 7.4 kgf/cm² (121 minutes after the start of polymerization), the supply of the vinyl chloride monomer (VCM) into the reactor was restarted. The vinyl chloride monomer was continuously pumped to maintain the internal pressure at 7.4 kgf/cm². The flow rate of VCM was measured by a mass flow meter (model DOO6S-HY-200 by Chiba Oval K.K.) in the piping. When the flow rate accumulation reached 17.0 kg (110 minutes after the restart of monomer supply), the supply of VCM was interrupted. When the internal pressure of the reactor dropped to 5.5 kgf/cm² (36 minutes after the interruption of monomer supply), 4.5 grams of bisphenol-A was admitted to stop polymerization.

After the polymerization reaction was stopped, the unreacted monomer was recovered from the reactor and the resulting polymer slurry was taken out of the reactor, dewatered, and dried. The weight of the polymer was measured to calculate its yield based on the overall vinyl chloride monomer charge.

Example 5

A vinyl chloride polymer was prepared by the same procedure as in Example 4 except that the initial charge of VCM was 10 kg, the polymerization initiator used was 0.037% by weight based on the overall VCM charge of 1,1,2,2-tetramethylpropylperoxyneodecanoate, the preset polymerization temperature was 60° C., 20 kg of the VCM was continuously pumped to maintain the internal pressure at 8.2 kgf/cm², and polymerization was stopped when the internal pressure dropped to 6.5 kgf/cm².

Comparative Example 4

A vinyl chloride polymer was prepared by the same procedure as in Example 4 except that the initial charge of

VCM was 30 kg, the polymerization initiator used was 0.027% by weight based on the overall VCM charge of tert-butylperoxyneodecanoate (equimolar to the 1,1,2,2-tetramethylpropylperoxyneodecanoate in Example 4), no additional VCM was supplied after the internal pressure of the reactor started declining, and polymerization was stopped when the internal pressure dropped to 6.7 kgf/cm².

Comparative Example 5

A vinyl chloride polymer was prepared by the same procedure as in Comparative Example 4 except that the polymerization initiator used was 0.039% by weight based on the overall VCM charge of di-2-ethylhexylperoxydicarbonate (equimolar to the 1,1,2,2-tetramethylpropylperoxyneodecanoate in Example 4), and polymerization was stopped when the internal pressure dropped to 6.0 kgf/cm².

Comparative Example 6

A vinyl chloride polymer was prepared by the same procedure as in Comparative Example 4 except that the polymerization initiator used was 0.032% by weight based on the overall VCM charge of 1,1,2,2-tetramethylpropylperoxyneodecanoate, and polymerization was stopped when the internal pressure dropped to 5.5 kgf/cm².

Comparative Example 7

A vinyl chloride polymer was prepared by the same procedure as in Comparative Example 4 except that the

Degree of Polymerization

It was measured according to JIS K6721.

Initial Coloring Test

With 100 parts by weight of a vinyl chloride polymer were blended 1 part by weight of tin laurate, 0.5 part by weight of a cadmium stabilizer, and 50 parts by weight of dioctyl phthalate. The blend was milled in a twin roll mill at 160° C. for 5 minutes and formed into a sheet of 0.8 mm thick. The sheet was cut into sections which were stacked one on top of the other. The stack was placed in a mold of 4×4×1.5 cm where it was heat compression molded at 160° C. and 65–70 kgf/cm² to form a sample. By analyzing the sample using a photoelectric colorimeter (manufactured by Nihon Denshoku Kogyo K.K.), a lightness index L and values of a and b in Hunter's color difference equation were determined as prescribed in JIS Z8730 (1980).

The samples were rated in four classes of excellent (Exc.), good, fair, and poor.

TABLE 2

	E4	CE4	CE5	CE6	CE7	ES
Polymerization temperature (°C.)	54.0	54.0	54.0	54.0	54.0	60.0
Initiator						
Type*	TMND	BND	EHP	TMND	BND	TMFV
Amount (%)	0.032	0.027	0.039	0.032	0.058	0.037
Type*	—	—	—	—	CND	—
Amount (%)	—	—	—	—	0.030	—
Initial charge of VCM (kg)	13	30	30	30	30	10
Additional charge of VCM (kg)	17	0	0	0	0	20
VCM supply pressure (kgf/cm ²)	7.4	—	—	—	—	8.2
Start of VCM supply (min.)	115	—	—	—	—	93
Time of VCM supply (min.)	120	—	—	—	—	115
Pressure dropping time (min.)	32	70	70	28	45	24
Total polymerization time (min.)	267	585	469	420	269	232
Final internal pressure (kgf/cm ²)	5.5	6.7	6.0	5.5	5.5	6.5
Yield (%)	86.0	81.1	84.1	86.0	86.0	86.1
Degree of polymerization	1310	1150	1140	1150	1150	1030
Initial coloring						
L	71.2	70.6	68.7	70.7	70.1	70.8
a value	-1.5	-1.2	-1.3	-1.2	-1.2	-1.4
b value	10.6	10.8	13.3	10.9	11.8	10.9
Rating	Exc.	Exc.	Poor	Exc.	Good	Exc.

*TMND: 1,1,2,2-tetramethylpropylperoxyneodecanoate (10-hour half-life temperature in 0.1 mol/l benzene solution: 39.0° C.)

TMFV: 1,1,2,2-tetramethylpropylperoxyvalate (45.7° C.)

BND: tert-butylperoxyneodecanoate (46.5° C.)

EHP: di-2-ethylhexylperoxydicarbonate (43.5° C.)

CND: cumylperoxyneodecanoate (36.6° C.)

polymerization initiators used were 0.058% by weight based on the overall VCM charge of tert-butylperoxyneodecanoate and 0.03% by weight based on the overall VCM charge of cumylperoxyneodecanoate, and polymerization was stopped when the internal pressure dropped to 5.5 kgf/cm².

The vinyl chloride polymers obtained in Examples 4–5 and Comparative Examples 4–7 were determined for a degree of polymerization and initial coloring. The results are shown in Table 2.

It is evident from Table 2 that as compared with the prior art, the process of the invention permits a polymer to be produced within a short time of polymerization reaction with a significantly small amount of initiator used. The polymer is improved in colorability upon molding and has a high degree of polymerization. The load of heat removal is reduced.

Japanese Patent Application Nos. 192431/1995 and 282604/1995 are incorporated herein by reference.

5,739,222

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Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

1. A process for preparing a vinyl chloride polymer by suspension polymerization of a vinyl chloride monomer in the presence of a polymerization initiator in a reactor, comprising the steps of:

charging the reactor with $\frac{1}{10}$ to $\frac{1}{4}$ of the overall monomer charge.

initiating polymerization, and

feeding the remainder of the overall monomer charge to the reactor after the internal pressure of the reactor has started declining, thereby continuing polymerization.

and wherein the polymerization is carried out under a certain saturated vapor pressure of P_1 kgf/cm² at a preset polymerization temperature,

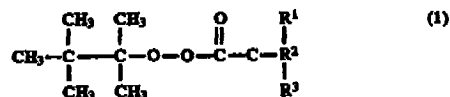
when the internal pressure of the reactor declines to P_2 kgf/cm², the remainder of the overall monomer charge

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is continuously fed to the reactor so as to maintain the internal pressure within the range of $(P_1 - \Delta P)$ wherein $\Delta P = P_1 - P_2$ ranges from 0.1 to 2.0 kgf/cm².

2. The process of claim 1 wherein a polymerization initiator having a temperature of 30° to 65° C. at which its half life in a 0.1 mol/l benzene solution is 10 hours is used in an amount of 0.01 to 0.3% by weight based on the weight of the overall monomer charge.

3. The process of claim 2 wherein the polymerization initiator is a 1,1,2,2-tetramethylpropylperoxy ester of the following general formula:



wherein R^1 , R^2 and R^3 are independently selected from normal alkyl groups having 1 to 9 carbon atoms.

4. The process of claim 1 wherein $\Delta P = P_1 - P_2$ ranges from 0.1 to 1.0 kgf/cm².

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United States Patent [19]

Park et al.

[11] 4,015,065

[45] Mar. 29, 1977

[54] TREATMENT OF VINYL HALIDE POLYMERS

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C08F 6/24; C08F 6/28

[58] Field of Search 450/776; 260/92.8 A,
260/92.8 W, 87.5 R; 204/159.22, 159.17;
528/503

[56] References Cited

FOREIGN PATENTS OR APPLICATIONS

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Delahunty

[57] ABSTRACT

Vinyl halide monomer content of vinyl halide polymer is reduced by subjecting the polymer to radio frequency dielectric heating in the presence of added polymerization initiator.

17 Claims, No Drawings

TREATMENT OF VINYL HALIDE POLYMERS

The present invention relates to a process for the treatment of polymers, and more specifically to a process for the removal or partial removal of vinyl halide monomer from vinyl halide polymers.

Vinyl halide polymers in general contain absorbed monomer. The monomer is removed during recovery of the polymer but it is difficult to produce monomer-free polymer. Moreover, unless special precautions are taken the monomer removed during recovery can present environmental hazards. Recent discoveries have linked vinyl chloride monomer with the rare cancer angio sarcoma of the liver and with other medical problems. It is thus highly desirable to reduce the level of residual vinyl halide monomer in vinyl halide polymers to the lowest possible value.

U.S. Pat. No. 3,434,220 discloses a process for drying polymers containing water or a polar diluent by subjecting the polymer to microwave radiation. In this specification residual material, such as water, in the polymer is removed by evaporation.

According to the present invention the process for treating a vinyl halide polymer containing residual vinyl halide monomer comprises subjecting the polymer to radio frequency dielectric heating in the presence of added free radical polymerisation initiator.

The vinyl halide polymer may be a vinyl halide polymer produced by the polymerisation of monomeric material consisting of vinyl halide and 0 to 30%, by weight of total monomeric material, of comonomers copolymerisable with vinyl halide. Examples of copolymerisable monomers are ethylene, propylene, vinyl acetate, vinyl laurate, vinyl stearate and vinylidene chloride.

The process of the present invention is particularly applicable to vinyl chloride polymer produced from a monomeric material consisting of vinyl chloride and from 0 to 20%, by weight of total monomeric material, of a comonomer copolymerisable with vinyl chloride. Thus, for example, the process is applicable to vinyl chloride homopolymers containing residual vinyl chloride.

The vinyl halide polymer to be subjected to radio frequency dielectric heating is normally a vinyl halide polymer with residual monomer absorbed during polymerisation. Typically the quantity of monomer will not exceed 3% (30,000 ppm.) by weight of polymer, although larger amounts may be present.

The polymer may be subjected to radio frequency dielectric heating directly after polymerisation or at a subsequent stage in its processing. Polymerisation takes place commonly in bulk, in aqueous suspension or micro-suspension or in aqueous emulsion. The process of the present invention is particularly suited for the treatment of vinyl chloride polymer, containing residual monomer, in the form of beads recovered from suspension polymerisation.

The process may, for example, be applied to polymers made by emulsion/suspension process, for example, as described in United Kingdom patent specification Nos. 1,309,582, 1,341,386 and 1,351,461.

The present invention is capable of treating monomer/polymer mixtures produced by any of these processes. As the present method is capable of removing water as well as residual monomer it is not necessary to dry aqueous dispersion polymers before treatment.

Polymers recovered from an aqueous dispersion before drying will often have up to 20% water present, based on weight of dry polymer. Any amount of water may be handled by the process of the present invention however. For example microsuspensions which are commonly spray dried may instead be treated directly by the process of the present invention to remove both water and residual monomer.

Exposure to dielectric heating may be carried out in batch or continuous fashion. To avoid overheating it is preferable to carry out the exposure continuously either by passing the polymer through the treatment area in a layer (e.g. of polymer beads supported on a belt) or to blow polymer particles through the treatment area.

The exposure time may be for periods of 0.1 seconds or less up to 100 minutes, but preferably lies in the range 1 second to 40 minutes, more particularly 1 to 30, for example 1 second to 10 minutes. Times in excess of 1 minute, preferably in excess of 2 minutes are often desirable. The exposure time is preferably chosen in relation to the power applied to the polymer to ensure that the polymer being treated reaches a temperature in the range 70° to 120° C. At higher temperatures the polymer tends to be degraded.

The radio frequency dielectric heating employed in the process of the present invention is well-known to those skilled in the art of electric heating. Dielectric heating is a method of heating poor electrical conductors by subjecting them to an alternating voltage. The electrical power transferred to the material as heat is a function of frequency, the potential across the material and the dielectric properties of the material. In low frequency dielectric heating the material to be heated is placed between electrodes across which an alternating voltage is applied. The voltage applied is controlled so as not to exceed the breakdown voltage of the material to be heated. The frequencies used for low frequency dielectric heating are typically in the range 1 to 150 MHz, for example 20 to 100 MHz. Although higher frequencies can be used in dielectric heating between electrodes the electrodes need to be smaller to avoid high capacitance between the electrodes leading to excessive damping of the alternating voltage, and radiation of stray electromagnetic radiation is increased.

Microwave heating is a special case of radio frequency dielectric heating. In microwave heating the required alternating voltage is provided by the electrical component of microwave electromagnetic radiation to which the material to be treated is subjected within an enclosure of conducting material. The material to be treated may be placed inside a resonant cavity in which a standing microwave field is produced or in a wave guide along which microwave electromagnetic radiation is passed. The design and operation of microwave ovens is well understood by those skilled in the microwave heating art.

Any microwave frequency can be employed, e.g. in the range 600 to 50,000 MHz and suitably in the range 900 to 30,000 MHz. It should be noted that there are legal limitations on the use of microwaves of certain wavelengths in many countries throughout the world.

Suitably the process of the present invention is operated with exposure times and applied power so that there are less than 50 ppm monomer in the treated polymer, preferably less than 25 ppm and most preferably to less than 0.5 ppm.

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It is believed that dielectric heating acts selectively on polar molecules and thus for example acts more strongly on monomers such as vinyl chloride and water than on polyvinyl chloride. Thus as a heating process it has the advantage of selectively heating absorbed monomer inside polymer particles without the need for the heat to transfer to the particle as in a normal heating process.

When polymer is prepared from the monomer it is necessary to introduce an initiator to enable the polymerisation to commence. This initial quantity of initiator required to start polymerisation is not the added initiator required by the process of the present invention. The added initiator is initiator added to polymer and thus is added at a stage at which at least some polymerisation has already taken place. If the initiator is added during polymerisation, the initiator and or the time between starting the polymerisation and addition of the initiator is preferably such that a substantial amount of the initiator (e.g. greater than 50% by weight of the amount added remains at the end of polymerisation. Any initiator added during polymerisation is preferably added after at least 50% conversion of monomer to polymer has taken place, more preferably after 60 to 75% by weight of the monomer has been converted to polymer. Thus it may be convenient to add the added initiator at the "pressure drop". The pressure drop is the drop in pressure within the reactor which takes place when the reaction is nearing completion; i.e. active polymerisation has ceased and in the case of vinyl chloride polymerisation usually takes place when about 70% by weight of the vinyl chloride has been converted to polymer. The initiator added during polymerisation is preferably of the same type as that used to start polymerization. Thus for suspension and microsuspension polymerization it is preferred that any added initiator is monomer soluble while for emulsion polymerisation it is preferred that any added initiator is water-soluble.

Alternatively the added initiator may be brought into contact with the polymer after polymerisation has ended, e.g. by adding the initiator to the polymerisation reactor. The polymer may instead be recovered from the polymerisation reactor before the added initiator is brought into contact with the polymer.

The added initiator, when added after polymerisation has ended need not be of the same type as that used in the polymerisation. Thus a water-soluble initiator may be added in aqueous solution not only to polymer prepared by emulsion polymerisation, but to polymer prepared by bulk, suspension or microsuspension polymerisation using monomer-soluble catalysts. Similarly monomer-soluble initiator dissolved in an organic solvent may be added to polymer prepared by emulsion polymerisation using water-soluble catalysts as well as to polymer prepared using monomer-soluble catalysts, e.g. by suspension, microsuspension or bulk polymerisation.

Where the initiator is added after polymerisation has ended the quantity added may for example be 0.01% to 1%, preferably 0.02% to 0.2%, based on weight of any polymer. Preferably the minimum quantity of initiator present at the beginning of the radio frequency dielectric treatment is 0.1% for suspension polymer and 0.2% for emulsion polymer based on weight of dry polymer.

It may even be advantageous to add additional monomer-soluble initiator dissolved in vinyl halide to the recovered polymer. The amount of vinyl halide em-

ployed to introduce the additional initiator should be kept as small as possible.

The added initiator may be a conventional vinyl halide polymerisation initiator. Examples of suitable initiators are ammonium persulphate, caprylyl peroxide, lauroyl peroxide, benzoyl peroxide, dicyclohexyl peroxy dicarbonate and azo bis isobutyronitrile.

A preferred initiator for use in the process of the present invention is also azo bis diisobutyronitrile which can be used as an aqueous solution but does not have a deleterious effect on electrical properties of the final polymer in the same way as persulphate initiators.

The invention will now be illustrated by reference to the following Examples.

EXAMPLE 1

A conventional polyvinyl chloride suspension homopolymer was prepared using lauroyl peroxide as the initiator and methyl cellulose as the suspending agent.

A 200g sample of the polymer was slurried with 200ml of a 0.2% solution of ammonium persulphate for 10 minutes. The polymer was centrifuged. The moisture content of the centrifuged resin was 18.3% wt/wt and the monomer content was 1.2% wt/wt. A 100g sample of this centrifuged polymer was irradiated in a microwave oven at a frequency of 2450 MHz for 10 minutes. The final moisture content was 2.5% wt/wt and the monomer content was 14 ppm.

TEST A

This is a Comparative Example in which no initiator was added. A 100g sample of the polymer used in Example 1 had a monomer content of about 1% and moisture content of 16% by weight. The resin was not treated with initiator. The resin was irradiated in a microwave oven at a frequency of 2450 MHz for 10 minutes as in Example 1. The final moisture content was 8% by weight and the monomer content was 80 ppm.

EXAMPLE 2

A batch low frequency dielectric heating oven operated at a frequency of 27 MHz and provided with an A.C. generator with a maximum power of 3 kW was used in this experiment. A sample of PVC homopolymer resin in the form of beads recovered from suspension polymerisation was washed with a 0.25% by weight solution of ammonium persulphate. The water from the solution was drained off to give a product with a total solids content of 90% by weight based on the total weight of sample, (i.e. 10% by weight of water).

The vinyl chloride content of the polymer before the radio frequency treatment was 7000 ppm.

A sample of 50g of the wet polymer was placed between the electrodes in the oven and subjected to radio frequency dielectric heating for 3 minutes at a power of about 10 kW. The final vinyl chloride monomer content of the polymer was 531 ppm. and the total solids content of the treated material was about 99% by weight.

EXAMPLE 3

An experiment was carried out as in Example 1 except that the radio frequency dielectric heating was continued for 1½ minutes. The final vinyl chloride monomer content was 1480 ppm.

TEST B

This is a Comparative Example not according to the invention.

An experiment was carried out as in Example 3 except that the polymer was washed with water only instead of ammonium persulphate solution. The heating was for 1½ minutes as in Example 3. The final vinyl chloride monomer content of the polymer was 3400 ppm.

EXAMPLE 4

A 200g sample of wet suspension PVC homopolymer slurry was treated with 200ml of a 0.2% wt/wt solution of azobisisobutyronitrile in ethanol for 10 minutes, and was then centrifuged.

The polymer had a moisture content of 16.1% wt/wt and a monomer content of 3,040 ppm.

A 100g sample of the polymer was irradiated at 2,450 MHz for 10 minutes to give a final moisture content of 1.1% wt/wt and a final vinyl chloride monomer content of less than 3 ppm. (below the limit of detection).

We claim:

1. A process for treating vinyl halide polymer containing residual vinyl halide produced by the polymerization of monomeric material consisting of vinyl halide and 0 to 30% by weight of total monomeric material of comonomers copolymerizable with vinyl halide which comprises subjecting said polymer to radio frequency dielectric heating in the presence of added free radical polymerization initiator.

2. A process according to claim 1 wherein the vinyl halide polymer is polyvinyl chloride, the vinyl halide it contains is vinyl chloride, and the polymer is produced from a monomeric material consisting of vinyl chloride and from 0 to 20% by weight of total monomeric material of comonomer copolymerisable with vinyl chloride.

3. A process according to claim 1 wherein the amount of residual vinyl halide monomer does not exceed 3% by weight of the polymer.

4. A process according to claim 1 wherein the polymer contains up to 20% by water based on weight of dry polymer.

5. A process according to claim 1 wherein the polymer is subjected to radio frequency dielectric heating for a time in the range 0.1 second to 100 minutes.

6. A process according to claim 5 wherein the polymer is subjected to radio frequency dielectric heating for a time in the range 1 second to 40 minutes.

7. A process according to claim 6 wherein the polymer is subjected to radio frequency dielectric heating for a time of at least one minute.

8. A process according to claim 6 wherein the polymer is subjected to radio frequency dielectric heating for a time sufficient to raise the temperature of the polymer to a temperature in the range 70° to 120° C.

9. A process according to claim 1 wherein the polymer is subjected to low frequency dielectric heating between electrodes.

10. A process according to claim 9 wherein the frequency used is in the range 1 to 150 MHz.

11. A process according to claim 1 wherein the polymer is subjected to microwave radiation.

12. A process according to claim 11 wherein the microwave radiation is at a frequency of 600 to 50,000 MHz.

13. A process according to claim 12 wherein the frequency is in the range 900 to 30,000 MHz.

14. A process according to claim 1 wherein initiator is brought into contact with the polymer after polymerisation is ended.

15. A process according to claim 14 wherein from 0.01% to 1% by weight of initiator, based on weight of dry polymer is added to the polymer after polymerisation has ended.

16. The process according to claim 1 wherein the minimum quantity of initiator present at the beginning of the radio frequency dielectric heating of suspension polymer is 0.1% by weight of dry polymer.

17. A process according to claim 2 wherein the polymer subjected to radio frequency dielectric heating is vinyl chloride polymer in the form of beads recovered from suspension polymerization and containing residual monomer.

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