

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
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DEP: 2020 DIRECCION DE NUEVAS CREACIONES	EVE: 378 FASE NACIONAL INCLUIDO CAPITULO I
TRA: 11 PCT-PATENTE DE INVENCION CAPITULOS I Y II	FOLIOS: 11
ACT: 519 TRASLADOINFORME	

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

Abogado(a)/Señor(a)
LUZ CLEMENCIA DE PÁEZ

Asunto: Radicación: 11-95599- -13
 Trámite: 11
 Evento: 378
 Actuación: 519
 Oficio: 13924
 Folios: 11

Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional					
Vía PCT (Fase Nacional)	X	Capítulo I	X	Capítulo II	
No. Solicitud Internacional	PCT/US2009/069932				
Fecha de Presentación Internacional	31/12/2009				

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

1. Documentos estudiados

Descripción:	Rad. N° 11-095599-00000-0000	29/Julio/2011
Reivindicaciones:	Rad. N° 11-095599-00012-0000	14/Octubre/2015
Dibujos:	Rad. N° 11-095599-00000-0000	29/Julio/2011
Prioridad:	US 61/141,879	31/Diciembre/2008

2. Análisis de la Prioridad

Se acepta la reivindicación de prioridad porque ésta solicitud fue presentada dentro del plazo establecido (Art. 9 D 486) y su contenido técnico corresponde con el de la prioridad reivindicada.

3. Objeto de la invención

De acuerdo con lo establecido en el numeral 1.2.2.2 del Capítulo Primero del Título X de la Circular Única para efectos del examen de patentabilidad, se tendrá en cuenta la tasa pagada por el solicitante al momento de comenzar el examen para las reivindicaciones adicionales; esto es que cuando la solicitud contenga más de diez (10)

reivindicaciones y no se haya pagado la tasa complementaria, sólo se estudiarán las cubiertas por la tasa pagada. Por lo tanto, se estudiarán las reivindicaciones 1 a 15.

Título de la solicitud: “Preparación de esteres y polioles por escisión oxidativa inicial de ácidos grasos, seguida por reacciones de esterificación” (Ver página 1 del radicado N° 11-095599-00000-0000).

El problema planteado en esta solicitud consiste en la necesidad de tener métodos para producir poliol de éster a partir de aceites modificados para hacer mejoras sobre la estructura molecular y acelerar el proceso de producción de revestimientos y espumas.

Para resolver este problema técnico, la solicitud estudiada proporciona métodos para convertir ácidos grasos insaturados derivados de bioaceites en ésteres altamente funcionalizados, polioles de éster, amidas, y polioles de amida. Los productos pueden usarse para fabricar películas y espumas de poliuretano y poliéster.

El objeto de la presente solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): C 07 C 67/003.

4. De la solicitud de patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

Durante la evaluación de claridad y concisión de las reivindicaciones, esta Oficina encontró que:

- Las reivindicaciones 1, 3, 4, 5, 6 y 11 a 15 no son claras porque presentan términos generales “ácido graso libre insaturado”, “poliol”, “monoalcohol”, “alcohol de amina”, “disolvente”, “ácidos grasos insaturados diferentes”, “ácidos de oxidación”, “amida de ácido graso”, “éster de ácido graso”, “alcohol de éster de ácido graso”, “alcohol de amida de éster de ácido graso”, lo cuales, aunque corresponden a términos conocidos, abarcan una extensa gama de posibilidades, de tal manera que sugieren de forma imprecisa que la protección se extiende a otras posibles variaciones o modificaciones. Se sugiere sustituirlas por un término preciso o un rango concreto.
- La reivindicación 1 el término “ácido graso libre” no se encuentra soportado en la descripción, se sugiere realizar las aclaraciones del caso.
- Las reivindicaciones 1 y 5 no son claras porque presentan un término indefinido “*por lo menos*”, utilizado para definir el rango de varias características del método deben eliminarse. Estos términos no permiten establecer un intervalo puntual para cada una de las características técnicas, no siendo estas precisas y por lo tanto no claras, ya que no permiten una comparación con el estado de la técnica.
- Las reivindicaciones 1 y 5 referidas a un proceso se incluyen características funcionales “*de modo que los enlaces dobles carbono-carbono se convierten a grupos ácido carboxílico para formar una mezcla de ácidos de oxidación*”, “*para formar una mezcla de productos de poliol*”, “*para formar una mezcla de ésteres alquílicos de ácido carboxílico*”, “*formando una mezcla de ácidos de oxidación*”, no se tendrán en cuenta para el estudio ya que dichas características si bien se pueden incluir para brindar claridad al objeto a proteger, no le pueden dar novedad ni nivel inventivo a la invención. Las reivindicaciones deben caracterizar el proceso por una secuencia de etapas técnicas con sus condiciones (materias primas, equipos, temperaturas, flujos, presiones, etc.), por medio de las cuales se transforme una materia en un producto o se obtenga un resultado.
- La reivindicación 6 no es clara dado que “...el método incluye además fraccionar la
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mezcla de ácidos de oxidación antes de esterificar el ácido carboxílico.”, sin embargo, en la descripción se divulga que: “Adicionalmente, hemos demostrado que no hay necesidad de fraccionar la mezcla de ácidos de oxidación ...”, lo que “... representa una ventaja técnica y económica significativa de la invención”, por tanto, lo mencionado en dicha reivindicación no tendría relación con el capítulo descriptivo, se solicita hacer las aclaraciones del caso.

- Las reivindicaciones 7 a 9 presentan resultados a obtener al mencionar “concentración de grupos carboxilo está en un rango de 1.01 a 1.1 (...) 1.2 a 1.9 (...) 2 a 12”, por cuanto son resultado del paso de escindir por oxidación el ácido graso insaturado, lo cual no es permitido. Las reivindicaciones deben caracterizar un método por la secuencia de etapas lógicas por las cuales se transforma una materia en un producto y por medio de las condiciones técnicas del método (temperaturas, flujos, presiones, etc.). No se aceptan reivindicaciones que caractericen resultados, usos, ventajas o efectos.

Descripción (Art 28 D 486)

Durante la evaluación de claridad y suficiencia de la descripción, esta Oficina encontró que:

- Una descripción de la invención en términos que permitan la comprensión del problema técnico y de la solución aportada por la invención.
- Una descripción de la mejor manera conocida por el solicitante para ejecutar o llevar a la práctica la invención.
- La información de las características técnicas de la invención no son suficientes para que un técnico experto en la materia pueda realizarla, ya que en los ejemplos no es claro que el ácido graso de partida sea un ácido graso libre insaturado, es decir, se parte de aceite de soya que comprende una mayor porcentaje de ácidos grasos insaturados, pero no hay ninguna evidencia que indique que sean ácidos grasos libres.
- Una descripción que muestre un efecto técnico sorprendente que evidencie el aporte de la invención al estado de la técnica.

4. Determinación del Estado de la Técnica

El estado de la técnica se determinó con base en la fecha de presentación de la solicitud de prioridad, es decir, 31 de diciembre de 2008.

Consultadas las fuentes de información con que se cuenta, se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

Ítem	Documento	Título	Fecha de publicación
D1	WO 2007/027223	“Methods for production of polyols from oils and their use in the production of polyesters and polyurethanes”	8/Marzo/2007
D3	US 4.608.202	“Process for the production of fatty acid esters of short-chain aliphatic alcohols from fats and/or oils containing free fatty acids”	26/Agosto/1986

El documento D1¹ divulga métodos para convertir aceites de base biológica, derivados del petróleo y aceites modificados a ésteres, polioles ésteres, amidas y polioles de amida. Los productos pueden utilizarse para hacer películas y espumas de poliuretano y poliéster (Pág. 1, Resumen).

¹[http://worldwide.espacenet.com/publicationDetails/originalDocument?](http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=WO&NR=2007027223A3&KC=A3&FT=D&ND=&date=20070531&DB=&&locale=en_EP)

[CC=WO&NR=2007027223A3&KC=A3&FT=D&ND=&date=20070531&DB=&&locale=en_EP](http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=WO&NR=2007027223A3&KC=A3&FT=D&ND=&date=20070531&DB=&&locale=en_EP)
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El documento D2² divulga la producción de ésteres de ácidos grasos de cadena corta, alcoholes alifáticos mediante la transesterificación catalítica de grasas y/o aceites naturales que contienen ácidos grasos libres (fase de aceite) con los monoalcoholes correspondientes, la fase de aceite se somete a esterificación preliminar con los monoalcoholes en la presencia de catalizadores de esterificación ácidas a temperaturas no superiores a 120 ° C y bajo presiones no superiores a 5 bares y en presencia de un agente de arrastre de líquido sustancialmente inmiscible con la fase oleosa, después de lo cual el producto de reacción se separa en una agente de arrastre fase que contiene el catalizador ácido y el agua de reacción y la fase de aceite tratado, la fase de aceite se somete a transesterificación mientras que la fase agente de arrastre que contiene el catalizador ácido se devuelve, tras el secado, al menos parcial, a la etapa de esterificación preliminar. Por este proceso, grasas y/o aceites con índices de acidez de hasta 60 pueden ser procesados en la etapa de esterificación preliminar para dar una fase de aceite que tiene un índice de acidez bajo (Resumen).

5. Examen de Patentabilidad (Art 14 D486)

Nivel inventivo (Art18 D486)

La reivindicación 1 consiste en “*Un método para producir un alcohol (...)*” (incluida bajo el radicado N° 11-095599-00012-0000).

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

Características esenciales	D1	D3
Un método para producir un alcohol que comprende:	Un método para producir un éster que comprende: (Reivindicación 1). El alcohol es un poliol, y en donde el éster es un éster de alcohol (Reivindicación 14).	Proceso para la producción de ésteres de ácidos grasos de cadena corta, alcoholes alifáticos a partir de grasas y/o aceites que contienen ácidos grasos libres (Resumen).
Escindir por oxidación un ácido graso libre insaturado de modo que enlaces dobles carbono-carbono se convierten a grupos ácido carboxílico para formar una mezcla de ácidos de oxidación a una temperatura entre -80°C a 80°C; y	Reacción de un aceite de base biológica, derivado de aceite, o aceite modificado con ozono y el exceso de alcohol a una temperatura entre aproximadamente -80°C a aproximadamente 80°C para producir productos intermedios; y (Reivindicación 1). Métodos para convertir los aceites vegetales y / o animales (por ejemplo aceite de soja) a alcoholes altamente funcionalizados en los rendimientos esencialmente cuantitativos mediante un proceso de ozonólisis. Los alcoholes funcionalizados son útiles para una reacción adicional para producir poliésteres y poliuretanos (...) El aceite de soja, que se compone principalmente de ácidos grasos insaturados, es un precursor potencial para la producción de polioles mediante la	No menciona.

2<http://worldwide.espacenet.com/publicationDetails/originalDocument?>

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Superintendencia de Industria y Comercio: Cra 13 No. 27- 00 pisos 1, 3, 4, 5, 6, 7 y 10 - PBX: (571) 5870000
E-mail: contactenos@sic.gov.co - Bogotá D.C., Colombia.

Señor ciudadano la entidad le ofrece los siguientes canales para hacer seguimiento a su solicitud así:
Página web: www.sic.gov.co Línea gratuita a nivel nacional: 018000 910165
Centro de atención telefónica en Bogotá: 5920400 Kiosco Informático Centro Comercial Gran Estación en Bogotá

	adición de funcionalidad hidroxilo a sus numerosos dobles enlaces (Pág. 1, Líneas 3 a 12).	
Ácidos graso libre	No menciona.	Grasas y/o aceites que contienen ácidos grasos libres (Resumen, Reivindicación 1).
Esterificar la mezcla de ácidos de oxidación con un poliol para formar una mezcla de productos de poliol o con un monoalcohol para formar una mezcla de ésteres alquílicos de ácido carboxílico, y	B. reflujo de los productos intermedios o adicionalmente hacerlos reaccionar en una temperatura inferior a la del reflujo, en el que se producen los ésteres a partir de los productos intermedios en los sitios de doble enlace, y sustancialmente todos los ácidos grasos son transesterificados a ésteres en los sitios de glicéridos de ácidos grasos (Reivindicación 1). En el que el alcohol es un poliol (Reivindicación 14). El alcohol es un monoalcohol (Reivindicación 27). En la figura 3 se enseña los pasos esquemáticos del proceso que involucra la conversión de la molécula de aceite de soya por ozonólisis y transesterificación del triglicérido en presencia de glicerina y un catalizador (Fig. 3. Pág.3, Líneas 6 a 9).	Someter las grasas y/o aceites que contienen ácidos grasos libres naturales, como una fase oleosa, que tiene un índice de acidez de más de 1, a esterificación preliminar con un C ₁₋₆ monoalcohol alifático en presencia de al menos un catalizador de esterificación ácido a una elevada temperatura no superior a 120 ° C y bajo una presión no superior a 5 bares (Reivindicación 1).
Por lo menos: amidificar de la mezcla de esteres alquílicos de ácidos carboxílicos con un alcohol de amina; o	Comprende además amidificar los esteres para formar amidas (Reivindicación 21). Amidificar los ésteres para formar amidas comprende hacer reaccionar un alcohol de amina con los esteres para formar el alcohol de amida (Reivindicación 21).	No menciona.
Transesterificar la mezcla de esteres alquílicos de ácidos carboxílicos con un poliol	Característica opcional, no se considera. A) reacción de un aceite de base biológica, derivado de aceite, o aceite modificado con ozono y el exceso de alcohol a una temperatura entre aproximadamente -80 °C a aproximadamente 80 °C para producir productos intermedios; y B) reflujo los productos intermedios o reacción adicional en inferior a la temperatura de reflujo, en ésteres se producen a partir de los productos intermedios en los sitios de doble enlace; y sustancialmente todos los ácidos grasos son transesterificado a ésteres en los sitios de glicéridos de ácidos grasos (Reivindicación 1).	Someter la fase de aceite tratado separado a la transesterificación con un C₁₋₆ monoalcohol alifático bajo condiciones de transesterificación catalizada alcalinos convencionales y la recuperación de dichos ésteres de ácidos grasos de C₁₋₆ monoalcoholes alifáticos (Reivindicación 1). El glicerol es en cualquier caso, lanzado en la siguiente etapa de transesterificación. La elección de glicerol como agente de arrastre para la primera etapa del proceso proporciona así para distintas, más simplificaciones en el proceso Col. 5, Líneas 1 a 5).

	En el que el alcohol es un polio (Reivindicación 14). transesterificación con glicerina o cualquier poliol (Pág. 3, Líneas 19 a 21)	
En donde la mezcla de ácidos de oxidación se esterifica en la presencia de un catalizador de Lewis o ácido de Bronsted, que es seleccionad de ácido sulfúrico, ácido clorhídrico, ácido bromhídrico, trifluoruro de boro, tricloruro de boro, hipofosfito de sodio, hipofosfito de calcio, sales estañosas, sales estancias, o combinaciones de los anteriores.	Figura 4 es un esquema que representa las etapas implicadas en la conversión de una molécula de soja idealizada por ozonólisis y la transesterificación de triglicéridos en la presencia de metanol y trifluoruro de boro a ésteres metílicos escindidos como productos intermedios (Fig. 4, Pág. 3, Líneas 11 a 14). El método de la reivindicación 3 en el que el catalizador de ozonólisis se selecciona de trifluoruro de boro, tricloruro de boro, tribromuro de boro, haluros de estaño, haluros de aluminio, zeolitas, tamices moleculares, ácido sulfúrico, ácido fosfórico, ácido bórico, ácido acético, y ácidos hidrácidos halogenados, o combinaciones de los mismos (Pág. 31, líneas 18 a 21) y el catalizador se selecciona...de ácidos de Lewis y ácidos de Bronsted (Pág. 31, líneas 15 a 16).	En principio, es posible utilizar cualquier, catalizador de esterificación ácida no volátil, es decir, por ejemplo, los correspondientes sistemas basados en ácidos de Lewis, ácidos inorgánicos sustancialmente no volátiles y/o sus ésteres parciales ácidos, heteropolíácidos y similares. Una clase particularmente adecuada de catalizadores ácidos son los ácidos sulfónicos orgánicos que pueden ser descritos, por ejemplo, por la fórmula general RSO_3H donde R es un grupo alquilo, arilo o alcarilo radical. Ejemplos de ácidos sulfónicos adecuados son ácido metano sulfónico, ácido tolueno sulfónico, ácido sulfónico o ácido naftaleno sulfónico. El ácido sulfúrico, por ejemplo, o semiésteres del mismo puede ser utilizado como el ácido inorgánico sustancialmente no volátil. Heteropolíácidos adecuados son, por ejemplo, ácidos fosfotúngstico o fosfomolibdico (Col. 5, Líneas 8 a 22).

Como se dijo anteriormente, los documentos D1 y D2 se consideran el estado de la técnica cercano a la invención definida en la reivindicación 1 porque divulgan un método para producir esteres que incluye los pasos de ozonólisis y transesterificación de ácidos grasos libres insaturados en presencia de glicerina y un catalizador.

La diferencia entre la invención definida en la reivindicación 1 y el método de D1 consiste en que este último, no hacen referencia específicamente que el ácido graso insaturado, sea un ácido graso libre.

No se evidencia un efecto técnico inesperado con el hecho que el material de arranque sea un ácido graso insaturado libre, ya que el documento D1 en la figura 4 de dicho documento presenta los pasos de la conversión de una molécula de soja idealizada por ozonólisis y la transesterificación de triglicéridos en la presencia de metanol y trifluoruro de boro a ésteres metálicos escindidos como productos intermedios (Pág.3, líneas 11 a 14), donde el aceite de soja, se compone principalmente de ácidos grasos insaturados (Pág. 1, Líneas 10 y 11). Igualmente, la descripción aclara que por bioaceites modificados se da a entender los bioaceites que se han modificado mediante transesterificación o amidificación de los ácidos grasos en la cadena principal triglicérido (Pág. 6, Párr. 2).

Por lo tanto, el problema técnico objetivo que pretende resolver esta invención se puede formular así: ¿Cómo obtener un método para producir ésteres de forma alternativa a la revelada en D1?

Sin embargo, la utilización de ácidos grasos libres para obtener polioles y ésteres, ya está divulgada en el documento D3 que se refiere a un procedimiento para la producción de ésteres de ácidos grasos de cadena corta y alcoholes alifáticos por transesterificación catalítica de grasas y/o aceites que contienen ácidos grasos libres que comprende someter las grasas y/o aceites que contienen ácidos grasos libres naturales, como una fase oleosa, que tiene un índice de acidez de más de 1, a esterificación preliminar con un C₁₋₆ monoalcohol alifático en presencia de al menos un catalizador de esterificación ácido a una elevada temperatura no superior a 120°C y bajo una presión no superior a 5 bares (...). Someter la fase de aceite tratado separado a la transesterificación con un C₁₋₆ monoalcohol alifático bajo condiciones de transesterificación catalizada alcalinos convencionales y la recuperación de dichos ésteres de ácidos grasos de C₁₋₆ monoalcoholes alifáticos (Resumen, Reivindicación 1.), donde, el glicerol es en cualquier caso, lanzado en la siguiente etapa de transesterificación. La elección de glicerol como agente de arrastre para la primera etapa del proceso proporciona así para distintas, más simplificaciones en el proceso (Col. 5, Líneas 1 a 5).

En consecuencia, la persona del oficio normalmente versada en la materia, incluiría ácidos grasos insaturados libres de D3 en el método de D1 para llegar así al objeto de la reivindicación 1 de la solicitud. Por lo cual se considera obvia. Cabe decir que el documento D1 enseña que los métodos para convertir los aceites vegetales y /o animales (por ejemplo aceite de soja) a alcoholes altamente funcionalizados con rendimientos esencialmente cuantitativos se realiza mediante un proceso de ozonólisis. Los alcoholes funcionalizados son útiles para una reacción adicional para producir poliésteres y poliuretanos (...) El aceite de soja, que se compone principalmente de ácidos grasos insaturados, es un precursor potencial para la producción de polioles mediante la adición de funcionalidad hidroxilo a sus numerosos dobles enlaces (Pág. 1, Líneas 3 a 12), además la persona versada en la materia conoce que los ácidos grasos insaturados con diferentes longitudes de cadena de alcano también se pueden convertir a diácidos por ozonólisis de los dobles enlaces de los grupos carboxilo. Por ejemplo, la escisión oxidativa del ácido oleico con ozono dio ácido azelaico y ácido pelargónico, mientras que la ozonólisis de ácido petroselinico y ácido erúico genera ácido adípico y ácido brásílico, respectivamente (Pág. 16, Col. 2, Líneas 22 a 27)³, es decir, se forman ácidos de oxidación por ozonólisis de ácidos grasos insaturados, por lo cual, es de esperar que en los productos intermedios en D1 se formen ácidos de oxidación.

Ahora bien, el documento D1 divulga las características de las reivindicaciones dependientes así:

- Reivindicación 2: reacción de un aceite de base biológica, derivado de aceite, o aceite modificado con ozono (Reivindicación 1) La invención proporciona métodos para convertir los aceites vegetales y / o animales (por ejemplo aceite de soja) a alcoholes altamente funcionalizados en los rendimientos esencialmente cuantitativos mediante un proceso de ozonólisis (Pág. 1, Líneas 4 a 6).
- Reivindicación 3 y 4: reacción de un aceite de base biológica, derivado de aceite, o aceite modificado con ozono y el exceso de alcohol (Reivindicación 1) el aceite de base biológica, derivado de aceite, o aceite modificado se hace reaccionar en presencia de un disolvente (Reivindicación 10).

3 J.O. Metzger et al. Lipids as renewable resources: current state of chemical and biotechnological conversion and diversification. Applied Microbiology and Biotechnology. Vol. 71. Junio 2006. Págs. 13-22.

- Reivindicación 10: en la figura 3 se enseña los pasos esquemáticos del proceso que involucra la conversión de la molécula de aceite de soya por ozonólisis y transesterificación del triglicérido en presencia de glicerina y un catalizador (Fig.3. Pág.3, líneas 6 a 9). El poliol se selecciona de glicerina, trimetilolpropano, pentaeritritol, 1,2-propilenglicol, 1,3-propilenglicol, etilenglicol, sorbitol, fructosa glucitol, glucosa, sacarosa, aldosas, cetosas, alditos, o combinaciones de los mismos (Pág. 32, líneas 24 a 27).
- Reivindicación 13: amidificación de los ésteres para formar amidas comprende hacer reaccionar un alcohol amina con los ésteres de los alcoholes para formar amida (Reivindicación 51).
- Reivindicación 14: la transesterificación de los ácidos grasos en el esqueleto de triglicérido para generar alcoholes grasos de éster de ácido (Fig. 8, Párr. 3, Líneas 24 y 25).
- Reivindicación 15: amidificación de los ésteres para formar amidas incluye un proceso seleccionado de calentar la mezcla de alcohol éster/amina, destilar la mezcla de alcohol éster/amina, o a reflujo la mezcla del éster/alcohol de amina (Reivindicación 52).

Asimismo, el documento D3 divulga las características de las reivindicaciones dependientes así:

- Reivindicaciones 11 y 12: en presencia de un agente de arrastre de líquido sustancialmente inmiscible con dicha fase oleosa, dicho el agente de arrastre de líquido es un alcohol, líquido a 50 °C, seleccionado del grupo que consiste en alcanopoliololes que tienen de 2 a 6 átomos de carbono y 2 a 6 grupos hidroxilo, polietilenglicoles, etilenglicol mono-C₁₋₆ éteres de alquilo y el dietilenglicol, el mono-C₁₋₆ éteres de alquilo, para una tiempo suficiente para reducir el contenido de ácido graso libre de dicha fase de aceite a un índice de acidez de 1 o inferior (Reivindicación 1).
- Reivindicación 13: el ácido graso es un éster de ácido graso (Resumen).

La reivindicación 5 se ve afectada con el conocimiento del técnico, “el experto medio deberá poseer experiencia y contar con un saber general en la materia y con una serie de conocimientos en el campo específico de la invención”⁴, el cual conoce que: Los ácidos grasos insaturados con diferentes longitudes de cadena de alcano también se pueden convertir a diácidos por ozonólisis de los dobles enlaces de los grupos carboxilo. Por ejemplo, la escisión oxidativa del ácido oleico con ozono dio ácido azelaico y ácido pelargónico, mientras que la ozonólisis de ácido petroselinico y ácido erúxico genera ácido adípico y ácido brásico, respectivamente (Pág. 16, Col. 2, Líneas 22 a 27)⁵.

Por su parte, la reivindicación dependiente 6 no menciona características técnicas tangibles adicionales que puedan brindarle nivel inventivo al objeto de la reivindicación 1, puesto que esta se encuentra afectada por claridad.

De igual manera, las reivindicaciones dependientes 7 a 9 no mencionan características técnicas tangibles adicionales que puedan brindarle nivel inventivo al objeto de la reivindicación 1, puesto que estas se encuentran redactadas en términos de resultados.

⁴ Proceso 43-IP-2002, publicado en la G.O.A.C. N° 870, de 9 de diciembre de 2002, caso: formulaciones de péptidos hidrosolubles de liberación retardada.

⁵ J.O. Metzger et al. Lipids as renewable resources: current state of chemical and biotechnological conversion and diversification. Applied Microbiology and Biotechnology. Vol. 71. Junio 2006. Págs. 13-22.

Puesto que las reivindicaciones dependientes 2 a 15 no mencionan características inventivas adicionales tampoco se pueden considerar inventivas.

6. Conclusión

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

Ítem	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	WO 2007/027223	1 a 10 y 13 a 15	Nivel Inventivo
D2	US 4608202	1 , 11, 12 y 13	Nivel inventivo

7. Respuesta a los argumentos del señor solicitante

Argumentos con respecto a la claridad de la solicitud

El señor solicitante argumenta que “... en relación con los términos objetados, “ácido graso libre insaturado”, “ácido de oxidación”, “poliol”, “monoalcohol”, “alcohol de amina”, “disolvente”, “éster de ácido graso”, “amida de ácido graso” (...) dichos términos se encuentran definidos en forma clara y precisa en la descripción de la presente solicitud y por lo tanto, el alcance del pliego reivindicatorio también se encuentra claramente definido (...)”. Es importante precisar que la reivindicación independiente 1 no queda claramente definida dado que aunque corresponden a términos conocidos, abarcan una extensa gama de posibilidades, de tal manera que sugieren de forma imprecisa que la protección se extiende a otras posibles variaciones o modificaciones, por lo cual, no se delimita el objeto de la solicitud, y no es claro el alcance de la solicitud.

Por otro lado, es importante mencionar que el método reclamado se encuentra mal definido ya que se caracteriza de forma muy general, dado que se incluyen términos indefinidos y/o imprecisos como lo es: “por lo menos”, el cual no permite establecer un intervalo puntual para cada una de las características técnicas, no siendo estas precisas y por lo tanto no claras. Además, se incluyen términos generales como lo son “ácido graso libre insaturado”, “poliol”, “monoalcohol”, “alcohol de amina”, “disolvente”, “éster de ácido graso”, “amida de ácido graso”, que sugieren de forma imprecisa que la protección se extiende a otras posibles variaciones o modificaciones. Por otro lado, se incluyen características funcionales como los son: “de modo que enlaces dobles carbono-carbono se convierten a grupos ácido carboxílico para formar una mezcla de ácidos de oxidación”, “para formar una mezcla de productos de poliol”, “para formar una mezcla de esteres alquílicos de ácido carboxílico”, lo cual, si bien pueden aparecer, no le puede dar nivel inventivo a la invención. Se reitera que un método se caracteriza por las etapas técnicas o pasos de transformación de la materia, y las condiciones técnicas específicas para llevarlo a cabo, por medio de las cuales se transforme una materia en un producto o se obtenga un resultado.

Como se argumentó oportunamente, los procesos para producir ésteres de un ácido ya están divulgados en el documento D1, que refiere un método en el cual se hace reaccionar un aceite de base biológica, un aceite derivado, o un aceite modificado con ozono y un exceso de alcohol a una temperatura entre -80° C y 80 °C, para producir productos intermedios (Pág. 2, líneas 16 a 18, reivindicación 1), en donde el aceite es un aceite animal y/o vegetal (ej. soya) (Pág.1, líneas 1 y 2).

En la figura 4 de dicho documento se presenta los pasos de la conversión de una molécula de soya idealizada por ozonólisis y la transesterificación de triglicéridos en la presencia de metanol y trifluoruro de boro a ésteres metálicos escindidos como productos intermedios (Pág.3, líneas 11 a 14).

El proceso incluye típicamente el uso de un catalizador de ozonólisis, los cuales incluyen pero no limitan a trifluoruro de boro, tricloruro de boro, tribromuro de boro, haluros de estaño, haluros de aluminio, zeolitas, tamices moleculares, ácido sulfúrico, ácido fosfórico, ácido bórico, ácido acético, y ácido hidrácidos halogenados (Pág.4, líneas 24 a 29), compartiendo dichas características con la invención.

De igual manera, se encuentra que dicho documento contempla la opción de un proceso en el que se involucra la conversión de la molécula de aceite de soya por ozonólisis y transesterificación del triglicérido en presencia de glicerina y un catalizador (Fig.3. Pag.3, líneas 6 a 9). Por tanto, no se presentan evidencias o pruebas técnicas con las cuales se demuestre los beneficios de la invención respecto al arte previo.

Por otra parte, es importante precisar que aún persisten las objeciones por artículo 30, ya que la invención contenida en el capítulo reivindicatorio se encuentra redactada incluyendo términos generales, términos imprecisos, resultados y/o efectos, con lo cual no le permiten diferenciar las características técnicas novedosas o inventivas del estado de la técnica.

Argumentos con respecto al estudio de nivel inventivo

El señor solicitante reitera que "...La principal diferencia que existe es que D1 inicia con un aceite triglicérido y no con un ácido graso libre. La diferencia en los materiales iniciales resulta en que diferentes reacciones se llevan a cabo durante el proceso. En D1, el aceite de triglicérido reacciona directamente con el poliol para producir el éster. En D1, cuando los triglicéridos son escisados, se forman ácidos grasos de ésteres, más no ácidos grasos libres. (...) El mecanismo de reacción de D1 incluye ozonólisis de los dobles enlaces en aceites de base biológica o en procesos de grasas donde los molozónidos formados al inicio son generados en la presencia de polioles o mono-alcoholes. Cuando los molozónidos se disocian en óxidos de carbonilos y en aldehídos, ambos son atrapados por el poliol o el mono-alcohol. En D1, el óxido de carbonilo se convierte en hidroperóxido alcoxi y el aldehído es convertido en un acetal en la presencia de un catalizador ácido (...). Por su parte, D2 también inicia en aceite triglicérido, que es transesterificado para producir éster metílico del ácido graso insaturado y glicerina. El éster metílico del ácido graso insaturado es tratado con ozono para producir acetales y alquenos a través de la reducción electroquímica de ozónidos intermedios".

Es importante señalar que dado que la invención no muestra un efecto técnico que resulte sorprendente e inesperado en relación al estado de la técnica, la invención resulta obvia a la luz de las enseñanzas del documentos D1, sin embargo, dada la respuesta del solicitante donde se especifica que el materia de partida es una ácido graso libre, se traslada el documento D3 y otros documentos que hacen parte de conocimiento de la persona versada en la materia, que afectan el nivel inventivo de la solicitud.

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

Se invita al solicitante se sirva indicar, si así lo considera, su renuncia al término faltante de sesenta (60) días para dar respuesta a este requerimiento y presentarla por escrito.

Finalmente, se le recuerda al solicitante que si como respuesta a este requerimiento llegara a modificar el capítulo reivindicatorio y éste contenga más de diez (10) reivindicaciones, no pagará la tasa de modificación voluntaria pero sí la correspondiente al pago por reivindicación adicional.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única No. 10 de 2001.



JOSÉ LUIS SALAZAR LÓPEZ
Director de Nuevas Creaciones (c)

El anterior requerimiento fue notificado por fijación en lista, de fecha 2015-12-01

Elaboró: Yenny Marcela Campos Borda
Revisó: Olga Ximena Benavides Salazar

Search query (2): [SP]: 1. a method for producing a polyol comprising: oxidatively cleaving an unsaturated biobased free fatty acid so that substantially all carbon-carbon double bonds are converted to carboxylic acid groups to form an oxidation acid and esterifying the oxidation acid with a polyol to form a product polyol. 2. the method of claim 1 further comprising amidifying the product polyol. 3. the method of claim 2 wherein the product polyol is amidified with an amine alcohol. 4. the method of claim 1 further comprising transesterifying the product polyol. 5. the method of claim 1 wherein the fatty acid is oxidatively cleaved by oxidative ozonolysis. 6. the method of claim 1 wherein the fatty acid is oxidatively cleaved in the absence of a solvent. 7. the method of claim 1 wherein the fatty acid is oxidatively cleaved in the presence of a solvent. 8. the method of claim 1 wherein a mixture of at least two different unsaturated fatty acids are oxidatively cleaved forming a mixture of oxidation acids. 9. the method of claim 8 further comprising fractionating the mixture of oxidation acids prior to esterifying the oxidation acid. 10. the method of claim 1 wherein a ratio of a concentration of total hydroxyl groups to a concentration of carboxyl groups in the initial mixture of oxidation acid with the polyol is in a range of about 1.01 to about 1.1. 11. the method of claim 1 wherein a ratio of a concentration of total hydroxyl groups to a concentration of carboxyl groups in the initial mixture of oxidation acid with the polyol is in a range of about 1.2 to about 1.9. 12. the method of claim 1 wherein a ratio of a concentration of total hydroxyl groups to a concentration of carboxyl groups in the initial mixture of oxidation acid with the polyol is in a range of about 2 to about 12. 13. the method of claim 1 wherein the oxidation acid is esterified in the presence of a catalyst. 14. the method of claim 13 wherein the catalyst is sulfuric acid, hydrochloric acid, hydrobromic acid, boron trifluoride, boron trichloride, sodium hypophosphite, calcium hypophosphite, stannous salts, stannic salts, or combinations thereof. 15. the method of claim 1 wherein the oxidation acid is esterified with the polyol and wherein the polyol is an alditol, sorbitol, 1,4-butanediol, glycerin, monoacetin, diacetin, pentaerythritol, trimethylolpropane, neopentyl glycol, 2-methylpropane-1,3-diol, propane-1,2-diol, propane-1,3-diol, ethane-1,2-diol, monosaccharide, disaccharide, or mixtures thereof. 16. the method of claim 1 wherein the oxidation acid is esterified in the presence of a solvent. 17. the method of claim 1 wherein the oxidation acid is esterified in the absence of a solvent. 18. the method of claim 1 wherein the fatty acid is a fatty acid amide. 19. the method of claim 18 wherein the fatty acid is the fatty acid amide and wherein the fatty acid amide is a fatty acid amide alcohol. 20. a method for producing an ester comprising: oxidatively cleaving an unsaturated biobased free fatty acid so that substantially all carbon-carbon double bonds are converted to carboxylic acid groups to form an oxidation acid esterifying the oxidation acid with a polyol to form a product polyol or with a monoalcohol to form a carboxylic acid alkyl ester and either: amidifying the product polyol or the carboxylic acid alkyl ester with an amine alcohol or transesterifying the product polyol or the carboxylic acid alkyl ester with a polyol. 21. a method for producing a polyol comprising: oxidatively cleaving an unsaturated biobased free fatty acid so that substantially all carbon-carbon double bonds are converted to carboxylic acid groups to form a mixture of diacids and monoacids esterifying the mixture of diacids and monoacids with a polyol to form a mixture of product polyols or with a monoalcohol to form a mixture of carboxylic acid alkyl esters and at least one of: amidifying the mixture of carboxylic acid alkyl esters or transesterifying the mixture of carboxylic acid alkyl esters with a polyol. 22. the method of claim 21 further comprising at least one of: amidifying the mixture of product polyols or transesterifying the mixture of product polyols. 23. the method of claim 21 wherein the fatty acid is oxidatively cleaved by oxidative ozonolysis. 24. the method of claim 21 wherein the fatty acid is oxidatively cleaved in the presence of a solvent. 25. the method of claim 21 wherein an initial ratio of a concentration of total hydroxyl groups to a concentration of carboxyl groups is in a range of about 1.01 to about 1.1, or in the range of about 1.2 to about 1.9, or in the range of about 2 to about 12. 26. the method of claim 21 wherein the mixture of diacids and monoacids is esterified in the presence of a catalyst. 27. the method of claim 26 wherein the catalyst is sulfuric acid, hydrochloric acid, hydrobromic acid, boron trifluoride, boron trichloride, sodium hypophosphite, calcium hypophosphite, stannous salts, stannic salts, or combinations thereof. 28. the method of claim 21 wherein the mixture of diacids and monoacids is esterified with the polyol and wherein the polyol is an alditol, sorbitol, 1,4-butanediol, glycerin, monoacetin, diacetin, pentaerythritol, trimethylolpropane, neopentyl glycol, 2-methylpropane-1,3-diol, propane-1,2-diol, propane-1,3-diol, ethane-1,2-diol, monosaccharide, disaccharide, or mixtures thereof. 29. the method of claim 21 wherein the mixture of diacids and monoacids is esterified in the presence of a solvent.

Results: 100

Yenny Campos

Search history

Search 1: TAC=(unsaturated biobased free fatty acid) (Results 1)

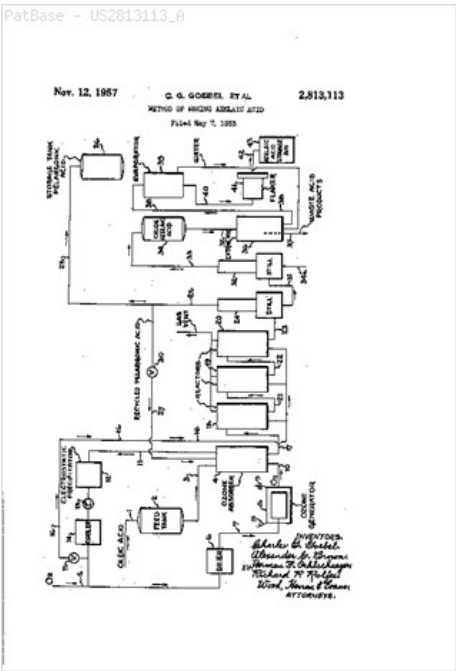
Search 2: [SP]: 1. a method for producing a polyol comprising: oxidatively cleaving an unsaturated biobased free fatty acid so that substantially all carbon-carbon double bonds are converted to carboxylic acid groups to form an oxidation acid and esterifying the oxidation acid with a polyol to form a product polyol. 2. the method of claim 1 further comprising amidifying the product polyol. 3. the method of claim 2 wherein the product polyol is amidified with an amine alcohol. 4. the method of claim 1 further comprising transesterifying the product polyol. 5. the method of claim 1 wherein the fatty acid is oxidatively cleaved by oxidative ozonolysis. 6. the method of claim 1 wherein the fatty acid is oxidatively cleaved in the absence of a solvent. 7. the method of claim 1 wherein the fatty acid is oxidatively cleaved in the presence of a solvent. 8. the method of claim 1 wherein a mixture of at least two different unsaturated fatty acids are oxidatively cleaved forming a mixture of oxidation acids. 9. the method of claim 8 further comprising fractionating the mixture of oxidation acids prior to esterifying the oxidation acid. 10. the method of claim 1 wherein a ratio of a concentration of total hydroxyl groups to a concentration of carboxyl groups in the initial mixture of oxidation acid with the polyol is in a range of about 1.01 to about 1.1. 11. the method of claim 1 wherein a ratio of a concentration of total hydroxyl groups to a concentration of carboxyl groups in the initial mixture of oxidation acid with the polyol is in a range of about 1.2 to about 1.9. 12. the method of claim 1 wherein a ratio of a concentration of total hydroxyl groups to a concentration of carboxyl groups in the initial mixture of oxidation acid with the polyol is in a range of about 2 to about 12. 13. the method of claim 1 wherein the oxidation acid is esterified in the presence of a catalyst. 14. the method of claim 13 wherein the catalyst is sulfuric acid, hydrochloric acid, hydrobromic acid, boron trifluoride, boron trichloride, sodium hypophosphite, calcium hypophosphite, stannous salts, stannic salts, or combinations thereof. 15. the method of claim 1 wherein the oxidation acid is esterified with the polyol and wherein the polyol is an alditol, sorbitol, 1,4-butanediol, glycerin, monoacetin, diacetin, pentaerythritol, trimethylolpropane, neopentyl glycol, 2-methylpropane-1,3-diol, propane-1,2-diol, propane-1,3-diol, ethane-1,2-diol, monosaccharide, disaccharide, or mixtures thereof. 16. the method of claim 1 wherein the oxidation acid is esterified in the presence of a solvent. 17. the method of claim 1 wherein the oxidation acid is esterified in the absence of a solvent. 18. the method of claim 1 wherein the fatty acid is a fatty acid amide. 19. the method of claim 18 wherein the fatty acid is the fatty acid amide and wherein the fatty acid amide is a fatty acid amide alcohol. 20. a method for producing an ester comprising: oxidatively cleaving an unsaturated biobased free fatty acid so that substantially all carbon-carbon double bonds are converted to carboxylic acid groups to form an oxidation acid esterifying the oxidation acid with a polyol to form a product polyol or with a monoalcohol to form a carboxylic acid alkyl ester and either: amidifying the product polyol or the carboxylic acid alkyl ester with an amine alcohol or transesterifying the product polyol or the carboxylic acid alkyl ester with a polyol. 21. a method for producing a polyol comprising: oxidatively cleaving an unsaturated biobased free fatty acid so that substantially all carbon-carbon double bonds are converted to carboxylic acid groups to form a mixture of diacids and monoacids esterifying the mixture of diacids and monoacids with a polyol to form a mixture of product polyols or with a monoalcohol to form a mixture of carboxylic acid alkyl esters and at least one of: amidifying the mixture of carboxylic acid alkyl esters or transesterifying the mixture of carboxylic acid alkyl esters with a polyol. 22. the method of claim 21 further comprising at least one of: amidifying the mixture of product polyols or transesterifying the mixture of product polyols. 23. the method of claim 21 wherein the fatty acid is oxidatively cleaved by oxidative ozonolysis. 24. the method of claim 21 wherein the fatty acid is oxidatively cleaved in the presence of a solvent. 25. the method of claim 21 wherein an initial ratio of a concentration of total hydroxyl groups to a concentration of carboxyl groups is in a range of about 1.01 to about 1.1, or in the range of about 1.2 to about 1.9, or in the range of about 2 to about 12. 26. the method of claim 21 wherein the mixture of diacids and monoacids is esterified in the presence of a catalyst. 27. the method of claim 26 wherein the catalyst is sulfuric acid, hydrochloric acid, hydrobromic acid, boron trifluoride, boron trichloride, sodium hypophosphite, calcium hypophosphite, stannous salts, stannic salts, or combinations thereof. 28. the method of claim 21 wherein the mixture of diacids and monoacids is esterified with the polyol and wherein the polyol is an alditol, sorbitol, 1,4-butanediol, glycerin, monoacetin, diacetin, pentaerythritol, trimethylolpropane, neopentyl glycol, 2-methylpropane-1,3-diol, propane-1,2-diol, propane-1,3-diol, ethane-1,2-diol, monosaccharide, disaccharide, or mixtures thereof. 29. the method of claim 21 wherein the mixture of diacids and monoacids is esterified in the presence of a solvent. (Results 100)

Title: Method of making azelaic acid

Abstract: Source: ES213664A Un metodo de fabricar acidos carboxilicos alifaticos a partir de compuestos grasos insaturados que contienen dobles enlaces, que comprende ozonizar un compuesto graso insaturado que contiene dobles enlaces y oxidar los ozonidos grasos asi formados con oxigeno gaseoso a una temperatura por encima de la de escision de los ozonidos.

Machine translation: A method of manufacturing aliphatic carboxylic acids from unsaturated fatty compounds containing double bonds, comprising ozonate an unsaturated fatty compound containing double bonds and oxidizing fatty ozonides thus formed with oxygen gas at a temperature above that of excision of the ozonides.

Classifications:
International (IPC 8-9): C07C51/34 (Advanced/Invention)
International (IPC 1-7): C07C51/34 C07C55/18
CPC: C07C51/34
European: C07C51/34
US: 422/189 422/606 562/524 562/590



Family:

Publication number	Publication date	Application number	Application date
ES213664 A1	19540701	ES19540213664	19540213
US2813113 A	19571112	US19530353628	19530507

Priority:

US19530353628 19530507

Probable Assignee: EMERY INDUSTRIES INC

Assignee(s): (std): EMERY IND INC ; EMERY INDUSTRIES INC

Inventor(s): (std): ROLFES RICHARD P ; OEHLSCHLAEGER HERMAN F ; GOEBEL CHARLES G ; BROWN ALEXANDER C

Title: Process for the production of fatty hydroxyalkylamides

Abstract: Source: US3024260A (Claim 1) A process for producing hydroxyalkylamides which aminomethane had been initially charged, the analysis of 75 comprises condensing in a first step a fatty carboxylic acid with an alkanol amine containing a labile hydrogen and at a temperature of about 120 degrees to about 180 degrees C., continuing the reaction until the fatty acid content of the reaction product is reduced to below about 5% by weight of said reaction product, forming a reaction product comprised predominantly of a mixture of hydroxyalkylamides and a member of the group consisting of fatty acid esters of the hydroxyalkylamides and fatty acid esters of the hydroxyalkylamines, and thereafter adding to the reaction product a catalyst of the group consisting of alkali metal, alkali amide and alkali alcoholate in an amount in excess of that required to neutralize any free fatty acid remaining in the product and to compensate for moisture present in the reaction product, and thus forming a mixture of said reactants containing free catalyst remaining in said reaction product, reacting said mixture at reduced temperature below about 100 degrees C. in the presence of compounds containing an amine radical containing a labile hydrogen, said amine radical being in excess over the molar concentration of ester carbonyl in the said mixture, converting the major portion of said esters to the corresponding amides, and forming a reaction product consisting essentially of hydroxyalkylamide, and having an ester content not substantially above 5% by weight of the reaction product and a minor amount of free catalyst.

Classifications:

International (IPC 8-9): C07C233/16 (Advanced/Invention)

International (IPC 1-7): C07C103/38

CPC: C07C233/16

European: 124BG12B2F5B2M C07C233/16

US: 554/66

Family:

Publication number	Publication date	Application number	Application date
US3024260 A	19620306	US19590846548	19591015

Priority:

US19590846548 19591015

Probable Assignee: TEXTILANA CORP

Assignee(s): (std): TEXTILANA CORP

Inventor(s): (std): ROBERT ERNST

Inventor(s): ERNST ROBERT

Title: CONTROL OF FOAM FORMATION IN THE SYNTHESIS OF PHOSPHORIC ACID

Abstract: Source: US3437437A ABSTRACT OF THE DISCLOSURE The present invention concerns anti-foaming compositions and their use in the control of foam during the "wet process" synthesis of phosphoric acid. The invention generally comprises adding to the reaction medium of a phosphate rock and mineral acid a composition comprising the reaction product of between 1 to 4 mols of an acid selected from the group consisting iof a saturated fatty acid containing between 4 to 18 carbon atoms and an unsaturated fatty acid containing between 16 to 20 carbon atoms, and 1 mol of a hydroxy amine. The composition is used in an amount of between 0.1 to 5 pounds for every ton of phosphate rock reacted with the mineral acid. B

Classifications:
International (IPC 8-9): B01D19/04 (Advanced/Invention)
International (IPC 1-7): C01B25/22 C07C91/04
CPC: B01D19/0404 C01B25/01 C01B25/18
European: B01D19/04D C01B25/01 C01B25/18
US: 423/319 516/129 562/606

Family:

Publication number	Publication date	Application number	Application date
US3437437 A	19690408	US19660584383	19661005

Priority:
US19660584383 19661005

Probable Assignee: BETZ LABORATORIES
Assignee(s): (std): BETZ LABORATORIES
Assignee(s): BETZ LAB INC
Inventor(s): (std): DORWART GEORGE E
Inventor(s): GEORGE E DORWART

Title: MODIFIED ESTER

Abstract: Esters of type:- (where A = residue of mono- or polyhydric alcohol, and Z correspondingly; $p+q+r+s = 4-14$; R = C5-11 alkyl; and R1,R2,R3,R4 = carboxylic acid residues with 6-12C atoms or H atom linked by ester groups) are prepared by esterifying epoxidised esters (of C12-22 acids, and with epoxy value at least 70 percent and preferably over 80 percent) with saturated C6-12 fatty acids. The esterification is continued to give an oxirane val. of 0 and a hydroxyl val. of 10. The products are useful as lubricants for high and low temperatures, and as cosmetic bases.

Classifications:

International (IPC 8-9): C07C69/34 C10M169/00 (Advanced/Invention);
C07C69/00 C10M169/00 (Core/Invention)

International (IPC 1-7): A61K7/00 C07C69/00 C10M3/00

CPC: C10M3/00 C10M2207/30 C10N2240/08

European: 124B69/66A+B 124B69/66AB C10M3/00

Family:

Publication number	Publication date	Application number	Application date
DE1941522 A1	19710304	DE19691941522	19690814

Priority:

DE19691941522 19690814

Probable Assignee: MIKUSCH BUCHBERG JOHANNES DONA

Assignee(s): (std): MIKUSCH BUCHBERG JOHANNES DONA

Assignee(s): MIKUSCH BUCHBERG JOHANNES DONATUS VON DR

Inventor(s): (std): VON DR MIKUSCH BUCHBERG JOHANN

Inventor(s): VON DR MIKUSCH BUCHBERG JOHANNES DONATUS

Title: Verfahren zur Herstellung von polymeren Esteramiden

Classifications:

International (IPC 8-9): C08G69/44 (Advanced/Invention);
C08G69/00 (Core/Invention)

International (IPC 1-7): C08G20/30 C08G69/44

CPC: C08G69/44

European: C08G69/44

Family:

Publication number	Publication date	Application number	Application date
DE1745448 A1	19710916	DE19671745448	19670509

Priority:

DE1967SC40678 19670509

Probable Assignee: VEBA CHEMIE AG

Assignee(s): (std): VEBA CHEMIE AG

Inventor(s): (std): GUDE FRITZ DIPL CHEM DR ; HUSSEK HERMANN DIPL CHEM DR ; SCHMITT KARL DIPL CHEM DR ; BRANDT SIEGFRIED DIPL CHEM DR

Title: Glass reinforcements and fire retardant glass-resin composites therefrom

Abstract: Source: US4242254A Filamentous glass in which the filaments are sized with non-burning or self-extinguishing polymeric compositions reinforce the physical properties of organic polymeric substances and impart a degree of flame retardance to glass-resin composites greater than that expected from the sizing content. There are provided molding compositions and injection molding granules containing resins and dispersions of such reinforcements and non-burning or self-extinguishing three-dimensional articles comprising resins containing such reinforcements.

Classifications:

International (IPC 8-9): B32B17/02 C03C25/10 C03C25/26 C08J5/08 C08K7/14 C08K9/04 (Advanced/Invention);

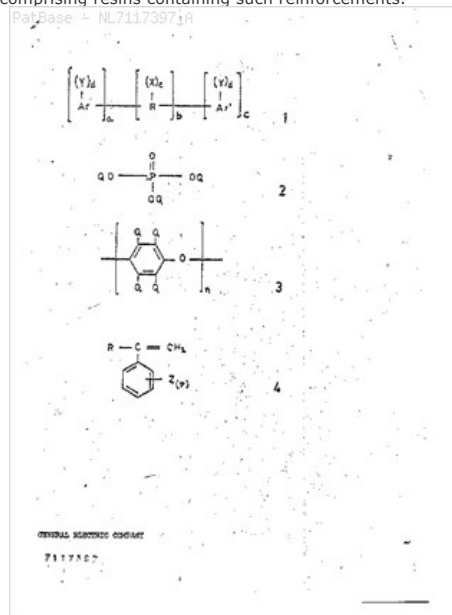
B32B17/02 C03C25/10 C03C25/24 C08J5/04 C08K7/00 C08K9/00 (Core/Invention)

International (IPC 1-7): B29D3/02 B32B17/02 C03C25/02 C08F45/00 C08G37/00 C08G51/10 C08J1/00 C08J5/08 C08K1/00 C08K1/14 C08K1/34 C08K1/84 C08K7/10 C08K9/00 C08K9/04 C08K9/06 C08L25/06 C08L77/00

CPC: C03C25/1005 C08J5/08 C03C25/26 C08K7/14 C08K9/04

European: C03C25/10D C03C25/26 C08J5/08 C08K7/14 C08K9/04

US: 260/40R 523/209 524/411 524/577 524/599 524/606 524/611 524/80



Family:

Publication number	Publication date	Application number	Application date
CA996290 A1	19760831	CA19710128892	19711130
DE2163385 A1	19720713	DE19712163385	19711221
FR2119554 A5	19720804	FR19710045932	19711221
GB1377097 A	19741211	GB19710052463	19711111
IT944075 A	19730420	IT19710032550	19711217
JP55011701 B4	19800327	JP19710099080	19711209
NL7117397 A	19720623	NL19710017397	19711217
US4242254 A	19801230	US19760727349	19760928

Priority:

US19700100441 19701221 US19760727349 19760928

Probable Assignee: GEN ELECTRIC

Assignee(s): (std): GEN ELECTRIC

Assignee(s): GENERAL ELECTRIC ; GENERAL ELECTRIC CO ; GENERAL ELECTRIC COMPANY ; ABOLINS VISVALDIS ; GEC

Inventor(s): (std): ABOLINS VISVALDIS

Title: CROSS-LINKABLE COMPOUNDS

Abstract: Source: US4032565A Crosslinkable polymers, suitable for use in the finishing of keratinous fibres such as wool, have polyoxyalkylene chains in which the alkylene groups consist of unbranched chains of not less than 3 carbon atoms. The polymer molecule contains at least two groupings capable of crosslinking, for example thiol, isocyanate, or thiosulphate groups, and the molecule also contains at least two carboxylic acid residues at least one of which is the residue of a polycarboxylic acid. The polyoxyalkylene chains are themselves linked at both ends to the rest of the molecule by carboxylic ester linkages. Particularly preferred compounds are water soluble and contain one or more solubilizing groups such as thiosulphate or the bi-sulphite adduct of isocyanate or, in the case of compounds with thiol groups, salt forming carboxylic groups. The compounds may be applied to textile fibres as aqueous emulsions or solutions and may be cured by drying in hot air or by steam. The outstanding advantage of the compounds is their improved light stability as compared with previous cross-linkable polymers based on polyalkylene chains. Textiles treated with improved polymers retain their finished properties after exposure to light and offensive smells sometimes generated by thiol polymers on exposure to light are substantially avoided.

Classifications:

International (IPC 8-9): C08G18/42 C08G18/46 C08G63/66 C08G65/334 D06M13/02 D06M13/192 D06M15/53 D06M15/63 (Advanced/Invention); D06M101/00 D06M101/02 D06M101/10 (Advanced/Non-Invention); C08G18/00 C08G63/00 C08G65/00 D06M13/00 D06M15/37 (Core/Invention); C08F D01F (Subclass/Invention)

International (IPC 1-7): C07C149/20 C08F C08G63/02 C08G63/52 C08G65/32 C08G65/48 C08G83/00 C08J3/24 D01F1/06 D06M13/28 D06M15/10 D06M15/30 D06M15/42 D06M15/44 D06M15/48 D06M15/68 D06P3/02 D06P3/14 D06P3/26

CPC: C08G18/4252 C08G18/4661 C08G63/66 C08G65/3342 C08G65/3344 D06M15/63

European: C08G18/42D2K C08G18/46F20N C08G63/66 C08G65/334B C08G65/334D D06M15/63

US: 260/481R 560/147 560/159 560/169 560/182 8/128.3



Family:

Publication number	Publication date	Application number	Application date
AU197471452 A1	19760122	AU19740071452	19740719
BE818153 A1	19741118	BE19740147002	19740726
BR7406198 A0	19750422	BR19740006198	19740726
CA1053255 A1	19790424	CA19740205215	19740719
CH1032474 A4	19760715	CH19740010324D	19740726
CH584796 A3	19770215	CH19740010324	19740726
CH584796 B	19770215	CH19740010324	19740726
DE2436035 A1	19750206	DE19742436035	19740726
DE2436035 C2	19830526	DE19742436035	19740726
ES428682 A1	19770316	ES19740428682	19740727
FI224474 A	19750128	FI19740002244	19740724
FR2238728 A1	19750221	FR19740026124	19740726
FR2238728 B1	19790720	FR19740026124	19740726
GB1480213 A	19770720	GB19730035882	19730727
IE39622 B	19781122	IE19740001514	19740717
IE39622 L	19750127	IE19740001514	19740717
IT1017494 A	19770720	IT19740025633	19740726
JP50100400 A2	19750808	JP19740086527	19740727
NL7410188 A	19750129	NL19740010188	19740729
US4032565 A	19770628	US19740490669	19740722
ZA7404610 A	19750827	ZA19740004610	19740718

Priority:
GB19730035883 19730727 GB19730035882 19730727 GB19730035884 19730727
AU19740071452 19740719

Probable Assignee: IWS NOMINEE CO LTD

Assignee(s): (std): I W S NOMINEE CO LTD ; IWS NOMINEE CO LTD ; I W S NOMINEE LTD ; I W S NOMINEE COMPANY LIMITED TE LONDEN ; I W S NOMINEE LIMITED

Assignee(s): LEWIS DAVID M ; KILPATRICK DAVID J ; SHAW TREVOR ; IWS NOMINEE CY LTD GB ; IWS NOMINEE CY LTD ; I W S NOMINEE CO LTD LONDON ; I W S NOMINEE CO LTD LONDON GB ; I W S NOMINEE COMPANY LIMITED

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Inventor(s): LEWIS DAVID MALCOLM OTLEY YORKSHIRE GB ; LEWIS DAVID MALCOLM OTLEY ; DAVID JOHN KILPATRICK TREVOR SHAW DAVID MALCOLM LEWIS ; DAVID MALCOLM LEWIS ; DAVID JOHN KILPATRICK ; D M LEWIS ; D J KILPATRICK ; KIOPATRICK DAVID JOHN LEEDS ; KILPATRICK DAVID JOHN LEEDS YORKSHIRE GB ; TREVOR SHAW ; T SHAW ; SHAW TREVOR ILKLEY YORKSHIRE GB ; SHAW TREVOR ILKLEY

Title: AMIDIFICATION PRODUCTS OF C' 19 'DICARBOXYLIC ACID AND CYCLICAL DIAMINES

Abstract: Source: US3937687A Polyamids of a C19 diacid and certain cyclical diamine which are excellent engineering plastics.

Classifications:

International (IPC 8-9): C08G69/26 (Advanced/Invention);
C08G69/00 (Core/Invention)

International (IPC 1-7): C08G69/26

CPC: C08G69/26

European: C08G69/26

US: 260/78R 528/336 528/339 528/346 528/349

Family:

Publication number	Publication date	Application number	Application date
US3937687 A	19760210	US19740473968	19740528

Priority:
US19740473968 19740528

Probable Assignee: GEN MILLS CHEM INC

Assignee(s): (std): GEN MILLS CHEM INC

Assignee(s): GENERAL MILLS CHEMICALS INC

Inventor(s): (std): SCHWEBKE GERALD L ; ROGIER EDGAR R ; JEVNE ALLAN H

Title: NOVEL COPOLYESTER-POLYEPOXIDE COMPOSITIONS

Abstract: Source: US4055606A Novel copolyester-polyepoxide compositions possessing a high green strength and tack before curing and characterized by having a single discernible glass transition temperature are produced. The compositions are composed of a copolyester and a polyepoxide mixture containing high, intermediate and low molecular weight components. They are especially useful as gap-filling adhesives and for various other adhesive applications. Methods of preparation are also described.

Classifications:

International (IPC 8-9): C08G59/22 C08G63/181 C08G63/672 C09J163/00 C09J167/02 (Advanced/Invention); C08G59/00 C08G63/00 C09J163/00 C09J167/00 (Core/Invention)

International (IPC 1-7): C08L63/00

CPC: Y10S525/93 C09J163/00 C08G59/226 C08G63/181 C08G63/672 C09J167/02 Y10T428/31522

European: C08G59/22B C08G63/181 C08G63/672 C09J163/00 C09J167/02

US: 428/416 525/438 525/524 525/930

Family:

Publication number	Publication date	Application number	Application date
US4055606 A	19771025	US19760698247	19760621

Priority:

US19760698247 19760621

Probable Assignee: ALLIED CHEM

Assignee(s): (std): ALLIED CHEM

Assignee(s): ALLIED CHEMICAL CORP

Inventor(s): (std): AHARONI SHAUL M ; PREVORSEK DUSAN C

Title: CONTINUOUS PROCESS FOR OZONIZING UNSATURATED COMPOUNDS

Abstract: Source: US4185025A A process and an apparatus for the continuous ozonization of unsaturated organic compounds in the presence of water, wherein (a) the fresh charge mixture of unsaturated compounds to be ozonized is reacted in at least one first reactor in parallel flow with ozonic gas, which was previously used for ozonizing a previously partially ozonized charge mixture, and (b) simultaneously a previously partially ozonized charge mixture is reacted in at least one second reactor in parallel flow with fresh ozonic gas, and wherein, optionally, said at least two reactors contain at least two mixing sections for mixing the charged liquid and gaseous phases with each other where the hydraulic diameter of the mixing elements in the individual mixing section is reduced in the flow direction.

Classifications:

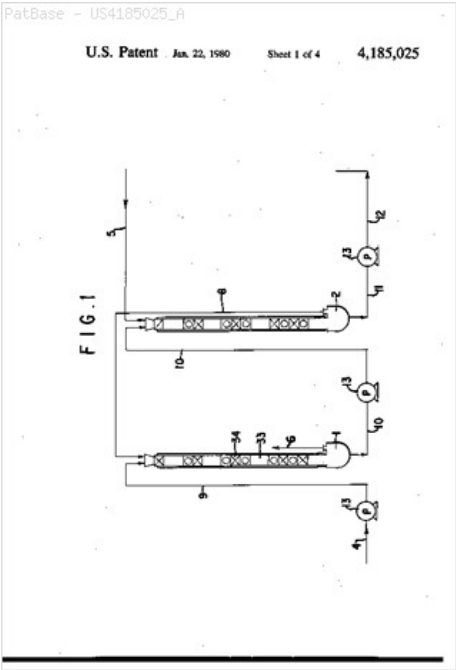
International (IPC 8-9): B01J10/00 B01J19/00 B01J19/24 C07C409/20 C07C45/40 C07C51/34 C07D323/02 (Advanced/Invention); B01J10/00 B01J19/00 B01J19/24 C07C409/00 C07C45/00 C07C51/34 C07D323/00 (Core/Invention)

International (IPC 1-7): B01J1/00 C01B13/11 C07B29/00 C07C51/34 C07C75/00 C07D323/02 C09F7/02 C10G34/00 C11C3/00

CPC: B01J19/242 C07C407/00 B01J2219/00094 B01J2219/00128 C07D323/02 B01J19/245 B01J2208/00176 C07C45/40 C07C51/34 C07C409/20

European: 124AA8Z B01J19/24F C07C409/20 C07C45/40 C07C51/34 C07D323/02 L01J208/00C2D4A L01J219/00B2D4D L01J219/00B2H4

US: 260/406 422/189 422/190 422/191 422/194 422/224 422/606 422/616 422/641 554/133 562/571



Family:

Publication number	Publication date	Application number	Application date
BE865357 A1	19780928	BE19780186302	19780328
BE872556 A1	19790606	BE19780192161	19781206
DE2713863 A1	19781012	DE19772713863	19770329
DE2713863 C2	19890601	DE19772713863	19770329
DE2754366 A1	19790613	DE19772754366	19771207
NL7802549 A	19781003	NL19780002549	19780308
NL7811326 A	19790611	NL19780011326	19781116
US4185025 A	19800122	US19780966948	19781206
US4242309 A	19801230	US19790043619	19790530

Priority:

DE19772713863 19770329 DE19772754366 19771207 US19780966948 19781206
US19780888528 19780321

Probable Assignee: HENKEL KGAA

Assignee(s): (std): HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN TE DUESSEL ; HENKEL KGAA

Assignee(s): HENKEL K G AUF AKTIEN ; HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN TE DUESSELDORF BONDSREPUBLIEK DUTSLAND ; HENKEL AUF AKTIEN KG ; HENKEL AUF AKTIEN TE DUESSELDORF BONDSREPUBLIEK DUTSLAND KG ; HENKEL K G A A ; HENKEL KGAA 4000 DUESSELDORF DE

Inventor(s): (std): WITTHAUS MARTIN DIPL CHEM DR ; WITTHAUS MARTIN ; MAJMUDAR SURESH DIPL CHEM DR ; MAJMUDAR SURESH ; EFFEY GUNTER DIPL ING ; EFFEY GUNTER ; DRAGER AXEL ; DRAEGER AXEL ; CARDUCK FRANZ JOSEF DIPL CHEM ; CARDUCK FRANZ JOSEF

Inventor(s): CARDUCK FRANZ JOSEF DIPL CHEM DR ; CARDUCK FRANZ J ; MAJMUDAR SURESH DIPL CHEMDR ; WITTHAUS MARTIN DIPL CHEMDR ; CARDUCK FRANZ JOSEF DIPL CHEMDR ; DRAEGER AXEL 4000 DUESSELDORF DE

J. O. Metzger · U. Bornscheuer

Lipids as renewable resources: current state of chemical and biotechnological conversion and diversification

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Abstract Oils and fats are the most important renewable raw materials of the chemical industry. They make available fatty acids in such purity that they may be used for chemical conversions and for the synthesis of chemically pure compounds. Oleic acid (1) from “new sunflower,” linoleic acid (2) from soybean, linolenic acid (3) from linseed, erucic acid (4) from rape seed, and ricinoleic acid (5) from castor oil are most important for chemical transformations offering in addition to the carboxy group one or more C-C-double bonds. New plant oils containing fatty acids with new and interesting functionalities such as petroselinic acid (6) from *Coriandrum sativum*, calendic acid (7) from *Calendula officinalis*, α -eleostearic acid (8) from tung oil, santalbic acid (9) from *Santalum album* (Linn.), and vernolic acid (10) from *Vernonia galamensis* are becoming industrially available. The basic oleochemicals are free fatty acids, methyl esters, fatty alcohols, and fatty amines as well as glycerol as a by-product. Their interesting new industrial applications are the usage as environmentally friendly industrial fluids and lubricants, insulating fluid for electric utilities such as transformers and additive to asphalt. Modern methods of synthetic organic chemistry including enzymatic and microbial transformations were applied extensively to fatty compounds for the selective functionalization of the

alkyl chain. Syntheses of long-chain diacids, ω -hydroxy fatty acids, and ω -unsaturated fatty acids as base chemicals derived from vegetable oils were developed. Interesting applications were opened by the epoxidation of C-C-double bonds giving the possibility of photochemically initiated cationic curing and access to polyetherpolyols. Enantiomerically pure fatty acids as part of the chiral pool of nature can be used for the synthesis of nonracemic building blocks.

Introduction

Average annual world oil production in the years 1996 to 2000 amounted to 105.0×10^6 t and will increase in the years 2016 to 2020 to 184.7×10^6 t (ISTA Mielke GmbH Hamburg 2002). Eighty to eighty-one percent of the produced oils and fats are consumed as human food; 5–6% as feed. Approximately 14%, 15–17 million tonnes are used by industry (Gunstone and Hamilton 2001). In contrast, the world consumption of fossil mineral oil was approximately $4,000 \times 10^6$ t in the year 2002. The chemical share was about 11% in the European Union (EU).

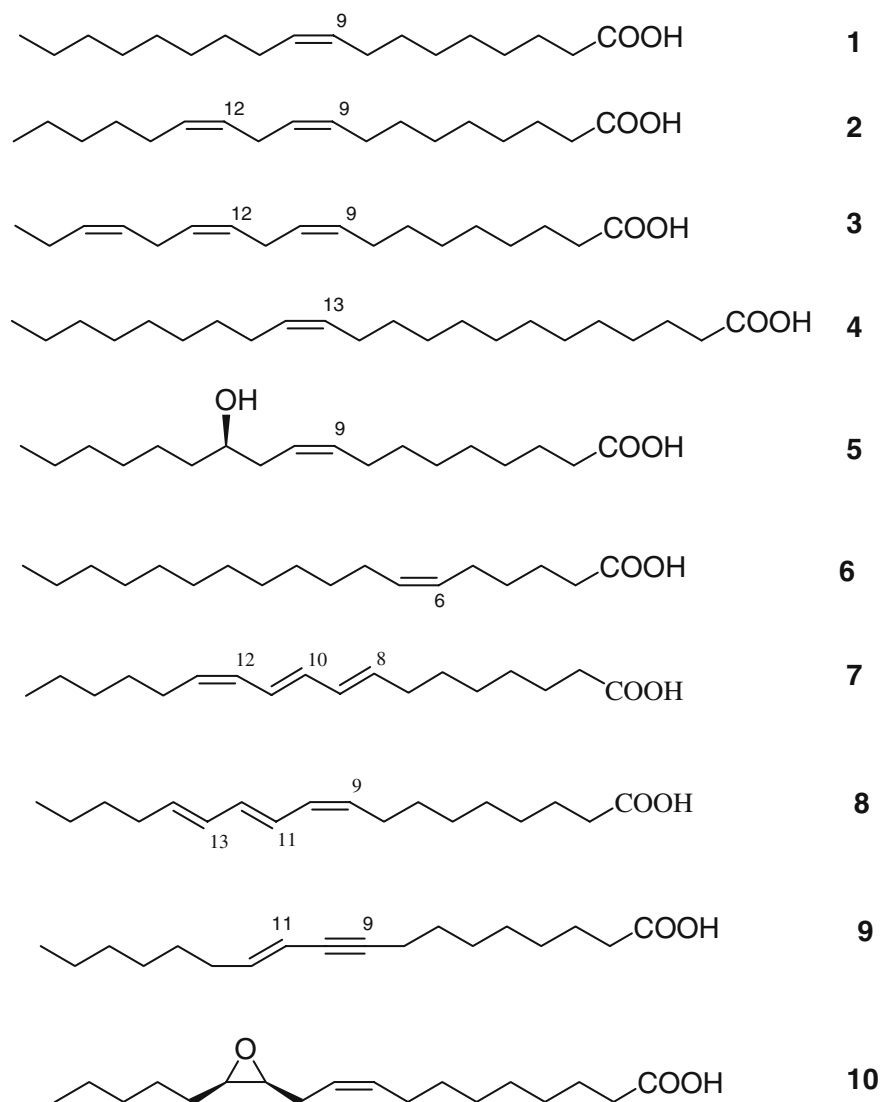
About 80% of the global oil and fat production were vegetable oils and only 20%, with declining tendency, were of animal origin. About one quarter of global production came from soybean, followed by palm oil, rapeseed, and sunflower. Coconut and palm kernel oil (laurics) contain a high percentage of saturated C12 and C14 fatty acids and are most important for the production of surfactants. These commodity oils make available fatty acids in such purity that they may be used for chemical conversions and for the synthesis of chemically pure compounds such as oleic acid (1) from “new sunflower,” linoleic acid (2) from soybean, linolenic acid (3) from linseed, erucic acid (4) from rapeseed, and ricinoleic acid (5) from castor oil (Fig. 1).

Where “nonfood” uses are concerned, genetic engineering approaches can make a special contribution to the expansion in the wealth of raw materials available to oleochemistry such as increasing the content of individual fatty acids or drastically changing the oil quality by the

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Fig. 1 Fatty acids as starting materials for the synthesis of novel fatty compounds:
1 Oleic acid, **2** linoleic acid,
3 linolenic acid, **4** erucic acid,
5 ricinoleic acid, **6** petroselinic acid,
7 calendic acid,
8 α -eleostearic acid, **9** santalbic acid, and **10** vernolic acid



introduction of a new fatty acid, e.g., the development of high lauric rapeseed (Biermann et al. 2000a).

New plant oils

New plant oils containing new and interesting functionalities are becoming industrially available (Baumann et al. 1988; Gunstone 2001). Fatty acids containing the C-C double bond in unusual positions of the alkyl chain and containing conjugated double bonds are most interesting from a chemical view point (Fig. 1). Moreover, fatty acids from the natural chiral pool are exciting substrates for stereoselective transformations to give enantiomerically pure products. We can hope that the increasing usage of renewable feedstocks will also eventually enlarge the agricultural biodiversity. It is to be expected that this is further boosted by the development of genetically engineered plants through metabolic engineering, an area (Biermann et al. 2000a) which is outside of the scope of this article. Significant advances were already made to produce

polyunsaturated fatty acids such as docosahexenoic acid, eicosapentenoic acid, and arachidonic acid in modified oil-seed crops (Singh et al. 2005; Huang et al. 2004).

Petroselinic acid (6) from the seed oil of *C. sativum* is an 18:1 acid with unsaturation at C6 (Meier zu Beerentrop and Röbbelen 1987). Meadowfoam (*Limnanthes alba*) oil contains approximately 65% 20:1 acid with double bond at C5. Both fatty acids show some novel reactivities based on the proximity of the double bond to the carboxyl group. Thus, cyclizations to cyclopentane (Metzger and Mahler 1993) and cyclohexanone (Metzger and Biermann 1993) derivatives were reported (Biermann et al. 2000a).

The seed oil of *C. officinalis* contains up to 60% of calendic acid [(8*E*,10*E*,12*Z*)-octadecatrienoic acid] (7) with a conjugated and stereochemically well-defined hexatriene system (Janssens and Vernooij 2001). α -Eleostearic acid [(9*Z*,11*E*,13*E*)-octadecatrienoic acid] (8) with a conjugated hexatriene as well is obtained from Chinese wood oil (tung oil). Both are drying oils and interesting applications in alkyd resins were reported. Both hexatriene fatty acids allow highly regioselective and stereoselective

Diels–Alder addition of maleic anhydride to the *trans, trans*-conjugated diene system (Metzger and Biermann 2006).

Santalbic acid (9) is the main fatty acid of the seed oil of sandalwood [*S. album* (Linn.)]. It contains a unique conjugated enyne system in the alkyl chain, which could be successfully exploited for highly regioselective additions (Biermann et al. 2000b) and for the selective synthesis of halogenated fatty compounds (Lie Ken Jie et al. 2003).

Vernolic acid (10) can be obtained from the seed oil of *V. galamensis* and of *Euphorbia lagascae*. Vernolic acid [(12*S*,13*R*,9*Z*)-12,13-epoxy-9-octadecenoic acid] is an enantiomerically pure unsaturated epoxy fatty acid with interesting applications as binder in coatings and preferentially in photocuring coatings (Crivello and Carlson 1996). Vernolic acid is an interesting substrate for the stereoselective synthesis of enantiomerically pure compounds.

Basic oleochemicals

With a production of 8.9×10^6 t in 1990, soaps still ranked first in worldwide statistics for industrial use of fats and oils and for surfactants (Schumann and Siekmann 2002). In 2005, the global production of oleochemicals—excluding soaps and biodiesel—was estimated to amount to 6.7×10^6 t/a. The basic oleochemicals—the production in 2000 is given in brackets—are free fatty acids (3.05×10^6 t/a), methyl esters (0.66×10^6 t/a), fatty alcohols (1.44×10^6 t/a), and amines (0.57×10^6 t/a) and glycerol (0.75×10^6 t/a) as a by-product (Gunstone 2001). The free fatty acids are obtained by hydrolysis of triglycerides with water in a continuous process at 20–60 bar and 250°C. The fatty esters are produced by transesterification of the triglycerides with the respective alcohol, mostly methanol. Hydrolysis and transesterification can be performed enzymatically at ambient temperature and normal pressure. However, economics restrict up to now the use of this technology (Bühler and Wandrey 1987). It was claimed that by applying modified technologies for fat splitting and direct transesterification of triglycerides, it would become possible to lower the enzyme concentration dramatically, resulting in an even more economic process compared to the classical methods. In addition, the quality of the products becomes better and even process units of around 2,000 t/a of feed become economic (Noweck et al. 2004).

The production of long-chain fatty alcohols is an important industrial process. Catalytic hydrogenation of fatty acid methyl esters gives long-chain fatty alcohols at approximately 200°C and 250–300 bar. Long-chain fatty alcohols are also produced from petrochemical feedstocks by the Ziegler Alfol process from ethylene and by hydroformylation of olefins (Noweck 2002). It is remarkable to note that the share of natural sources is rising. It is most important that fat alcohols derived from fats and oils as renewable feedstocks show a more favorable life cycle assessment (LCA) than petrochemical alcohols (Hirsinger 2001) and show that they are an important example that base chemicals derived from renewable feedstocks can be

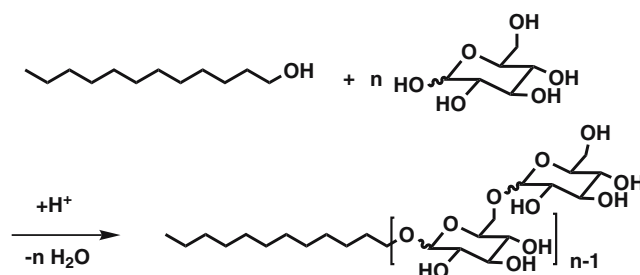


Fig. 2 Synthesis of alkylpolyglycosides by acid catalyzed reaction of lauric alcohol and glucose

commercially competitive. It is possible to perform the hydrogenation of the ester group with retention of the C–C-double bond making oleyl alcohol easily available by hydrogenation of the methyl ester of high oleic sunflower or rapeseed oil.

Fatty amines are produced from fatty acids in a multistep process via nitriles followed by hydrogenation to give the primary amines, which are converted to tertiary amines and to quaternary ammonium compounds (quats) (Franklin et al. 2001).

The production of fatty acids and esters from triglycerides gives as a by-product about 10wt% of glycerol. New uses of glycerol and new chemical transformations to interesting products are of increasing importance. Fortunately, glycerol has a melting point of 20°C and could possibly be a suitable compound to be used as interior render with latent heat stores.

Fatty acid methyl esters have found an important new application as biofuel. The biodiesel production in the EU added up in 2003 to 1.4×10^6 t with steadily increasing tendency. Agenda 21 calls for “criteria and methodologies for the assessment of environmental impacts and resource requirements throughout the full life cycle of products and processes.” A simple metric for the production of biofuels is the overall energy efficiency that is the heating value of biofuel divided by the energy required to produce the biofuel. The biodiesel production in Germany from rapeseed has—without credits for the coproduct glycerol—an overall energy efficiency of 1.9 (Kraus et al. 1999) and the respective from soybean in the USA of about 3 (Sheehan et al. 1998).

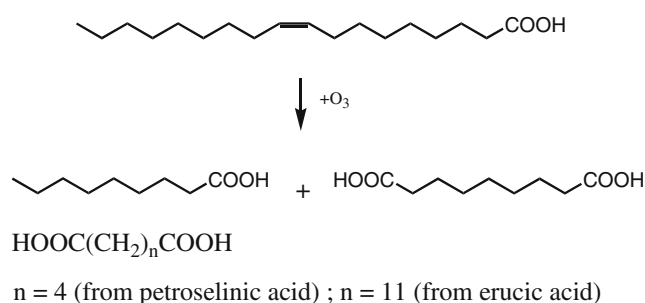
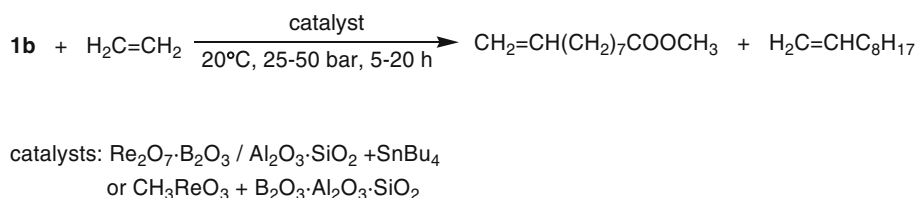


Fig. 3 Oxidative scission of oleic acid with ozone to give azelaic acid and pelargonic acid. Petroselinic acid **6** and erucic acid **4** give adipic acid ($n=4$) and brassylic acid ($n=11$), respectively

Fig. 4 Cometathesis of methyl oleate **1b** and ethylene to methyl 9-decenoate and 1-decene. The ester **1b** used (new sunflower) was 87% pure, the conversions and selectivities each >90%, and the yields were >80%



Vegetable oils are increasingly used as environmentally friendly industrial fluids and lubricants because of their biodegradability and their favorable water pollution class (Erhan and Perez 2002). The usage as insulating fluid for electric utilities such as transformers (Fields 2004; Lewand 2004) and as additive to asphalt to improve the surface properties (Carmen 2004) are interesting new industrial applications.

Current state of chemical conversion of oleochemicals

By means of simple industrial reactions, basic oleochemicals are available from vegetable oils in such purity that they may be used for further chemical conversions and for the synthesis of chemically pure compounds. The basic oleochemicals are chemically converted including enzymatic and microbial transformations (see section below for details) to a great variety of specialties, which are used for the production of cosmetics, lubricants, coatings, surfactants, and many other useful products. Here, chemists make profit from the synthetic input of nature. The chemical structure is essentially retained making the compounds biologically and easily degradable. At present, surfactants are the most important products of oleochemistry. About 430,000 t/a, which is one third of the industrially used fats and oils in Germany, are converted to surfactants. The most recent important innovation in oleochemistry is the production of alkyl polyglycosides by acid catalyzed reaction of lauryl alcohol and of glucose. Glucose is suspended in excess lauryl alcohol (2–6 mol) and the reaction is carried out at a temperature of 100–120°C in the presence of an acidic catalyst, typically a sulfonic acid. After removal of water as by-product (1 equiv relative to glucose) under vacuum, the product mixture comprises alkyl mono-, alkyl oligo-, and alkylpolyglycosides (Fig. 2). The average degree of polymerization for such an alkyl polyglycoside is largely dependent on the ratio of glucose to alcohol in the reaction mixture (von Rybinski and Hill 1998). It may be possible that an enzymatic production method could give well-defined products having improved properties. Alkyl polyglycosides are nonionic surfactants. They show a very good biodegradability and are used in detergents for home care applications and in cosmetics because of the good skin compatibility. They are produced on a scale of 70,000 t/a.

It was said that “more than 90% of oleochemical reactions were those occurring at the fatty acid carboxy group, while less than 10% have involved transformations of the alkyl chain. However, future progress will be along the lines of these latter types of reactions with their potential for considerably extending the range of com-

pounds obtainable from oils and fats” (Baumann et al. 1988). Modern methods of synthetic organic chemistry including enzymatic and microbial transformations were applied extensively to fatty compounds for the selective functionalization of the alkyl chain (Biermann et al. 2000a; Biermann and Metzger 2004b).

Diacids, ω -hydroxy fatty acids, and ω -unsaturated fatty acids

Diacids, ω -hydroxy fatty acids, and ω -unsaturated fatty acids derived from basic oleochemicals are of great interest. Diacids are important intermediates for the production of polyesters and polyamides. At present, the aliphatic dibasic acid with the highest production volume of 2.3×10^6 t/a is globally adipic acid, which is produced industrially by oxidation of a mixture of cyclohexanone and cyclohexanol (obtained by catalytic air oxidation of cyclohexane) with HNO_3 under formation of the coupled product N_2O and different nitrogen oxides (Musser 2000). Adipic acid is a basic chemical with a very high gross energy requirement of about 80 GJ/t, the production of which should be improved to be more sustainable (Eissen et al. 2002). An alternative access to various diacids from renewable feedstocks would be most interesting. Diacids such as azelaic acid (C_9) (Fig. 3) and brassylic acid (C_{13}) can be produced from oleochemical feedstocks by ozonolysis of oleic acid and erucic acid, respectively, giving as by-product nonanoic acid (Baumann et al. 1988). Adipic and lauric acid may be obtained from petroselinic acid. Because ozone is very expensive and the industrial ozonolysis presents some difficulties, an alternative process is required. A catalytic process using peracetic acid and ruthenium catalysts or H_2O_2 and Mo, W, or Re based catalysts was reported yielding only 50–60% diacids (Herrmann et al. 1989; Warwel and Rüschen. Klaas

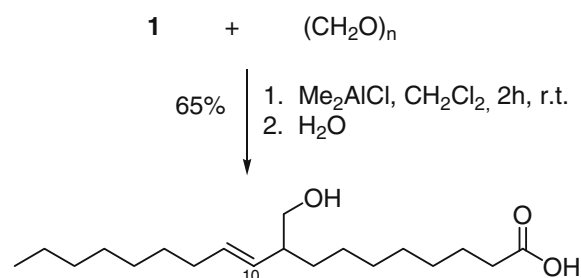


Fig. 5 Me_2AlCl -induced addition of paraformaldehyde to oleic acid (**1**) to give stereoselectively an unsaturated alkyl branched ω -hydroxy fatty acid

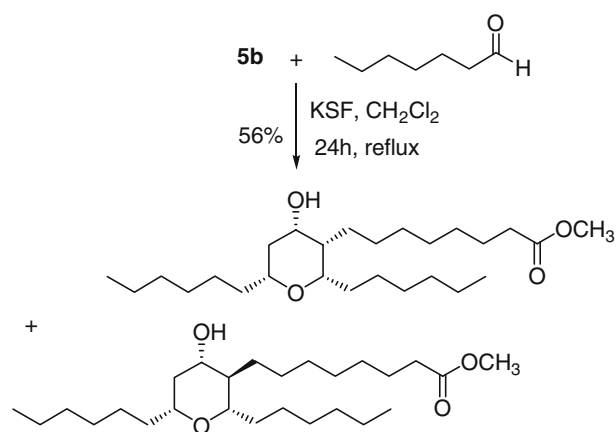


Fig. 8 Addition of heptanal to methyl ricinoleate **5b** in the presence of montmorillonite KSF to give the 4-hydroxytetrahydropyran as two diastereomers in a ratio of 2.7:1

acid or ester is converted into an unsaturated percarboxylic acid by a lipase-catalyzed reaction with H_2O_2 and is then self-epoxidized in an essentially intermolecular reaction (Rüsch gen. Klaas and Warwel 1997).

In the industry, vegetable oil epoxides are currently used mainly as PVC stabilizers. Interesting applications were opened by the possibility of photochemically initiated cationic curing (Crivello and Narayan 1992). The comparison of UV-curable coatings with linseed oil epoxide as binder to a binder produced on a petrochemical basis derived from propylene oxide by LCA showed clear advantages for the renewable raw material linseed oil (Eissen et al. 2002).

The preparation of polyols from epoxides of fatty acids and vegetable oils for polyurethane use was the subject of many studies (Guo et al. 2000, 2002; Petrovic et al. 2000). Recently, polyether polyols were obtained by acid-catalyzed ring-opening polymerization of epoxidized methyl oleate and subsequent partial reduction of ester groups gave primary alcohols (Fig. 7). Depending on the degree of reduction, polyols of different hydroxyl values were obtained, which were reacted with 4,4'-methylenebis (phenyl isocyanate) to yield polyurethanes (Lligadas et al. 2006).

Polyether polyols for polyurethanes are mostly produced from propylene oxide. Propylene oxide is one of the top 50 chemicals in terms of production: in 1997, 1.9×10^6 t were produced in the USA, about 1×10^6 t were produced in Germany, and approximately 4×10^6 t were produced worldwide. It is the top 50 chemical with the highest gross energy requirement of about 105 GJ/t (Eissen et al. 2002). Eventually, polyetherpolyols derived from epoxidized fatty compounds may substitute the petrochemical compounds in various applications.

It is also a challenge to synthesize suitable diisocyanates via diamino compounds derived from vegetable oils, making the production of polyurethanes possible completely from renewables.

Chiral and enantiomerically pure oleochemicals

It seems to be remarkable that enantiomerically pure fatty acids as part of the chiral pool of nature were not used very extensively for the synthesis of nonracemic compounds. In contrast, the stereochemistry is lost in most oleochemical transformations performed with, e.g., ricinoleic acid.

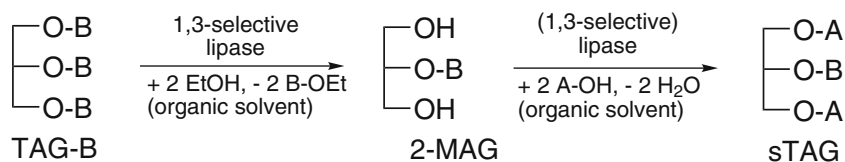
Ricinoleic acid [(12*R*,9*Z*)-12-hydroxyoctadecenoic acid] with a homoallylic alcohol functionality was reacted in a Prins-type reaction with aldehydes mediated by AlCl_3 and the environmentally more benign montmorillonite KSF (Fig. 8) to give with high stereoselectivity 2,3,6-trialkyl-4-chlorotetrahydropyrans, which are interesting building blocks (Biermann and Metzger 2006).

Chemical epoxidation of ricinoleic acid gives, with low diastereoselectivity, two diastereomers of epoxidized ricinoleic acid that were transformed in two steps in the enantiomerically pure hydroxy aziridines. The hydroxy-aziridines were tested for cytostatic/cytotoxic activity with regard to different tumor cell lines. It is interesting to note that the minor diastereomer in all cases showed stronger activity than the major diastereomer. Similar results were obtained for antimicrobial activity tested on different microorganisms. Vernolic acid was reacted quite analogously to give the respective aziridine (Fürmeier and Metzger 2003).

Table 1 Enzymes useful for lipid modification

Enzyme	Applications	Examples
Lipase	Synthesis of structured triglycerides	Cocoa-butter equivalent, Betapol
	Enrichment of specific fatty acids	PUFA from fish oils
	Incorporation of specific fatty acids	PUFA into plant oils
	Synthesis of fatty acid derived products	Emollient esters
Phospholipase	Removal of fatty acids in <i>sn</i> 1- or <i>sn</i> 2-position (PLA ₁ or PLA ₂)	Degumming of oils
	Removal of phosphate group (PLC)	Lyso-phospholipids
	Head group exchange (PLD)	Chiral diglycerides
Monooxygenase	Hydroxylation of fatty acids	Phosphatidylserine
Epoxidase	Epoxidation of double bonds	Precursor for polyesters/lactones
Lipoxygenase	Synthesis of FA-hydroperoxides	–

Fig. 9 Principle of the lipase-catalyzed two-step synthesis to obtain sTAG in high purity. *A* and *B* denote different fatty acids



Current state of enzymatic conversion of fats and oils

A broad range of enzymes can in principle be used for the conversion of fats and oils and their application in lipid modification is well documented in literature (Bornscheuer 2000, 2003; Bornscheuer et al. 2002). Table 1 provides a survey about useful enzymes, their application areas, and selected examples.

By far the most often used biocatalysts are lipases (EC 3.1.1.3, triacylglycerol hydrolases) for which fats and oils are their natural substrates. These enzymes do not require cofactors, many of them are available from commercial suppliers and they exhibit high activity and stability, even in nonaqueous systems. A plethora of publications on the use of lipases has appeared in the last two decades and only the most important and recent examples are highlighted here. Because lipases show chemo-, regio-, and stereo-selectivity, they can be used for the tailoring of natural lipids to meet nutritional properties, especially for humans. The most prominent example is the synthesis of cocoa butter equivalents (Quinlan and Moore 1993). Cocoa butter is predominantly a 1,3-disaturated-2-oleyl-glyceride where palmitic, stearic, and oleic acids account for more than 95% of the total fatty acids. Cocoa butter is crystalline and melts between 25 and 35°C providing the desirable “mouth feel.” Unilever (Coleman and Macrae 1977) and Fuji Oil (Matsuo et al. 1981) filed the first patents for the lipase-catalyzed synthesis of cocoa butter equivalent from palm oil and stearic acid. Both companies currently manufacture it using 1,3-selective lipases to replace palmitic acid with stearic acid at the *sn*1- and *sn*3-positions. Reactions are usually performed as transesterification or acidolysis of cheap oils using tristearin or stearic acid as acyl donors and a 1,3-specific lipase.

Structured triglycerides (sTAG) with a defined distribution of different fatty acids along the glycerol backbone are important compounds for a range of applications in human nutrition. sTAG containing medium-chain fatty acids at the *sn*1- and *sn*3-position and a long preferentially polyunsaturated fatty acid are used to treat patients with pancreatic insufficiency and to give rapid energy supply (i.e., for sports). Another important example is Betapol, which is used for infant nutrition. This sTAG [1,3-dioleoyl-2-palmitoyl glycerol (OPO)] contains oleic acid at the *sn*1- and *sn*3-position and palmitic acid at the *sn*2-position. Currently, Betapol is manufactured by interesterification of tripalmitin with oleic acid using a lipase from *Rhizomucor miehei* (Novozyme RM IM). However, the product contains only 65% palmitic acid in the *sn*2-position. To obtain higher purities and yields, a two-step lipase-catalyzed process was developed (Fig. 9). First, tripalmitin is subjected to alcoholysis with ethanol with a lipase from

Rhizopus delemar immobilized on a polypropylene carrier (EP-100) yielding 95% monopalmitin with a purity >90% after crystallization. Subsequent enzymatic esterification with oleic acid in *n*-hexane proceeded quantitatively within a few hours and the final OPO (yield 70%) contained up to 96% palmitic acid in the *sn*2-position (Schmid et al. 1999).

Another possibility is starting from 1,3-diglycerides (1,3-DAG), which are available on large-scale as cooking and frying oil (see below), 1,3-DAG can be obtained from glycerol and fatty acid vinyl esters (Berger et al. 1992) or via controlled acyl migration from 1,2-diglycerides. These 1,3-DAGs can then be esterified with a lipase exhibiting distinct fatty acid selectivity, i.e., the lipase must not act on the fatty acids present in the *sn*1 and *sn*3-position and solely catalyzes the introduction of the second type of fatty acid (B-OH in Fig. 10) into the *sn*2-position. It could be shown, that commercial lipase from *Pseudomonas cepacia* (Amano PS) and *Candida antarctica* (CAL-B) allow for the synthesis of sTAG. These biocatalysts are not 1,3-regiospecific, but rather show distinct fatty acid specificity (Bornscheuer et al. 2005; Wongsakul et al. 2004). Recently, the first lipase with distinct *sn*2-specificity was created by directed evolution of an esterase (Reyes-Duarte et al. 2005). This enzyme should be very useful for the synthesis of sTAG based on this methodology.

Recent examples for successfully industrialized processes include lipase-catalyzed production of zero-*trans* margarines (ADM and Novozymes) and diglyceride-based cooking and frying oils (Kao Corp. and ADM) (Watanabe et al. 2004). The zero-*trans* and reduced *trans* oils and fats are produced on industrial scale by transesterification using lipase from *Thermomyces lanuginosa* (TL IM) in combination with a cost-effective immobilization technology (Anonymous 2005). Thus, the use of isolated technical enzymes, in contrast to conventional chemical means, provided cost-effective, simple, and straightforward methods to obtain the desired products. In addition, these biocatalytic processes are environmentally friendly and can thus be seen as a result of sustainable developments. The technology developed by ADM and Novozymes received the Presidential Green Chemistry Challenge Award in 2005.

Lipases were also used on industrial scale to produce simple esters, e.g., for cosmetic applications (Fig. 11).

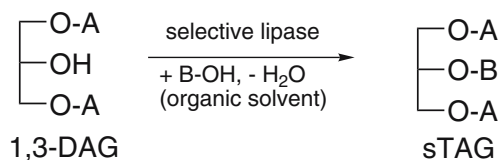
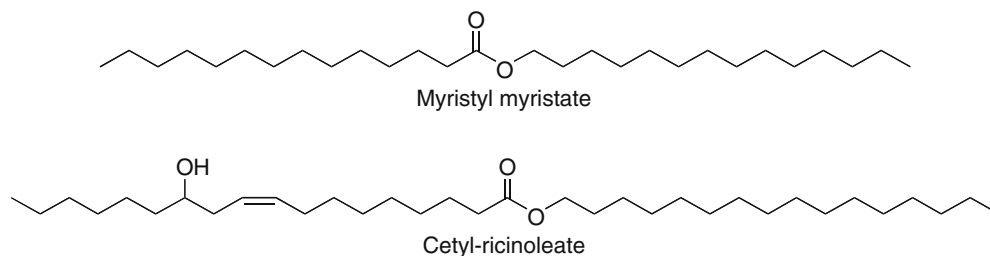


Fig. 10 Principle of the lipase-catalyzed two-step synthesis to obtain sTAG in high purity. *A* and *B* denote different fatty acids

Fig. 11 Myristyl myristate and cetyl ricinoleate are produced by lipase-catalyzed esterification



Prominent examples are cetyl ricinoleate and myristyl myristate (Heinrichs and Thum 2005; Hills 2003). Although both esters were chemically synthesized for a long time, enzyme technology allows higher yields and substantially purer products. The higher costs for the biocatalyst are compensated by savings in energy (ambient temperature instead of 160–180°C) and product purification (i.e., a bleaching and deodorization step can be omitted).

Phospholipase (PLA₁ and PLA₂) are used on large-scale for degumming—the removal of phospholipids—of natural fats and oils. Whereas the earlier process used a mammalian phospholipase from porcine pancreas specific for the *sn*2-position (PLA₂), this method was recently changed to the application of a microbial biocatalyst obtained from *Fusarium oxysporum*, which exhibits *sn*1-selectivity (PLA₁) (Clausen 2001). In both cases, lysophospholipids are formed, which are easily hydratable and therefore allow for the reduction of the phospholipid content below 10 ppm. The microbial enzyme is safer (with respect to enzyme supply and a lowered risk of contamination) and shows better performance in the process, and the products obtained from them are considered kosher and halal.

Whereas phospholipase C has no application in biocatalysis yet, phospholipase D can be used in the head group exchange. This allows for the synthesis of nonnatural phospholipids and the synthesis of compounds bearing natural head groups, i.e., phosphatidyl serine (Skolaut et al. 2005).

To our knowledge, the other enzymes listed in Table 1 do not have large-scale applications yet. One exception is the use of whole-cell systems, i.e., *Candida* yeast for the biohydroxylation to yield dicarboxylic acids as mentioned above. However, the progress made in gene technology, metabolic engineering, and biocatalysis should make the application of these oxidative enzymes feasible in the near future.

Future perspectives of chemical and biotechnological conversion

Most products obtainable from renewable raw materials may at present not be able to compete with the products of the petrochemical industry, but this will change as oil becomes scarcer and oil prices rise. It is very important to note that fat alcohols derived from fats and oils are an example that shows that base chemicals derived from renewable feedstocks can be commercially competitive

with petrochemical products. At present, it can be observed that petrochemical fat alcohols will increasingly be substituted. More examples will come up in the next few years. Middle- and long-chain diacids, ω -hydroxy fatty acids, ω -unsaturated fatty acids, and epoxidized vegetable oils may be the next candidates. The use of modern synthetic methods together with enzymatic and microbiological methods has led to an extraordinary expansion in the potential for the synthesis of novel fatty compounds. With the breeding of new oil plants, numerous fatty compounds of adequate purity are now available, which makes them attractive for chemical synthesis and industrial use. However, numerous synthetic problems have to be solved and solutions have to be found in the coming years.

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References

- Anonymous (2005) Award-winning technology gives healthier fats. Biotimes: Sept. 2005
- Baumann H, Bühler M, Fochem H, Hirsinger F, Zobebelein H, Falbe J (1988) Natural fats and oils—renewable raw materials for the chemical industry. *Angew Chem Int Ed Engl* 27:41–62
- Berger M, Laumen K, Schneider MP (1992) Enzymatic esterification of glycerol I. Lipase-catalyzed synthesis of regioisomerically pure 1,3-*sn*-diacylglycerols. *J Am Oil Chem Soc* 69:955–960
- Biermann U, Metzger JO (1999) Friedel–Crafts alkylation of alkenes: ethylaluminum-sesquichloride induced alkylations with alkyl chloroformates. *Angew Chem Int Ed Engl* 38:3675–3677
- Biermann U, Metzger JO (2004a) Alkylation of alkenes: ethylaluminum sesquichloride mediated hydro-alkyl-additions with alkyl chloroformates and di-*tert*-butylpyrocarbonate. *J Am Chem Soc* 126:10319–10330
- Biermann U, Metzger JO (2004b) Catalytic C,C-bond forming additions to unsaturated fatty compounds. *Top Catal* 27:119–130
- Biermann U, Metzger JO (2006) Synthesis of enantiomerically pure 2,3,4,6-tetrasubstituted tetrahydropyrans by Prins cyclization of methyl ricinoleate and aldehydes. *Eur J Org Chem* (in press)
- Biermann U, Friedt W, Lang S, Lühs W, Machmüller G, Metzger JO, Rüsche gen. Klaas M, Schäfer HJ, Schneider MP (2000a) New syntheses with oils and fats as renewable feedstock for the chemical industry. *Angew Chem Int Ed Engl* 39:2206–2224
- Biermann U, Lützen A, Lie Ken Jie MSF, Metzger JO (2000b) Regioselective cationic 1,2- and 1,4-additions forming carbon-carbon bonds to methyl santalbate, a conjugated enyne. *Eur J Org Chem* 17:3069–3073
- Bornscheuer UT (ed) (2000) *Enzymes in lipid modification*. Wiley-VCH, Weinheim

- Bornscheuer UT (2003) Special issue on enzymes in lipid modification. *Eur J Lipid Sci Technol* 103:561–645
- Bornscheuer UT, Adamczak M, Soumanou MM (2002) Lipase-catalyzed synthesis of modified lipids. In: Gunstone FD (ed) *Lipids as constituents of functional foods*. Barnes, Bridgwater, pp 149–182
- Bornscheuer UT, Weiner DP, Hitchman T, Lyon J, Wongsakul S (2005) Hydrolases, nucleic acids encoding them and methods for making and using them. Diversa Corporation, USA. PCT International Application WO 2005/032496
- Brutting R, Spiteller G (1994) Products of dimerization of unsaturated fatty acids. *Fat Sci Technol* 96:445–451
- Bühler M, Wandrey C (1987) Enzymatic fat splitting. *Fat Sci Technol* 89:156–164
- Carmen (2004) Rapsasphalt. <http://www.carmen-ev.de/dt/industrie/projekte/rapsasphalt.html>
- Clausen K (2001) Enzymatic oil-degumming by a novel microbial phospholipase. *Eur J Lipid Sci Technol* 103:333–340
- Coleman MH, Macrae AR (1977) Rearrangement of fatty acid esters in fat reaction reactants. German Patent DE 2 705 608 (Unilever, N. V.)
- Craft DL, Madduri KM, Eshoo M, Wilson CR (2003) Identification and characterization of the CYP52 family of *Candida tropicalis* ATCC 20336, important for the conversion of fatty acids and alkanes to α,ω -dicarboxylic acids. *Appl Environ Microbiol* 69:5983–5991
- Crivello JV, Carlson KD (1996) Photoinitiated cationic polymerization of naturally occurring epoxidized triglycerides. *J Macromol Sci Pure Appl Chem A33(Suppl 5–6):251–262*
- Crivello JV, Narayan R (1992) Epoxidized triglycerides as renewable monomers in photoinitiated cationic polymerization. *Chem Mater* 4:692–699
- Eissen M, Metzger JO, Schmidt E, Schneidewind U (2002) 10 Years after Rio—concepts on the contribution of chemistry to a sustainable development. *Angew Chem Int Ed Engl* 41:414–436
- Erhan SZ, Perez JM (2002) Biobased industrial fluids and lubricants. AOCs, Champaign, Illinois
- Fell B, Meyer B (1991) Hydroformylation of polyunsaturated fatty acid esters with heterogenized rhodiumcarbonyl phosphane complex catalysts based on organopolysiloxane. *Chem Ztg* 115:19–43
- Fields S (2004) Powering up with biobased oils. *Tribol Lubr Technol* 31–35
- Franklin R, Hoey MD, Zachwieja J (2001) Cationic and amine-based surfactants. In: Gunstone FD, Hamilton RJ (eds) *Oleochemical manufacture and applications*. Academic, Sheffield, pp 23–54
- Fürmeier S, Metzger JO (2003) Fat-derived aziridines and their N-substituted derivatives: biologically active compounds based on renewable raw materials. *Eur J Org Chem* 649–659
- Gunstone FD (2001) Basic oleochemicals, oleochemical products and new industrial oils. In: Gunstone FD, Hamilton RJ (eds) *Oleochemical manufacture and applications*. Academic, Sheffield, pp 1–22
- Gunstone FD, Hamilton RJ (2001) *Oleochemical manufacture and applications*. Academic, Sheffield
- Guo A, Javni I, Petrovic Z (2000) Rigid polyurethane foams based on soybean oil. *J Appl Polym Sci* 77:467–473
- Guo A, Demydov D, Zhang W, Petrovic ZS (2002) Polyols and polyurethanes from hydroformylation of soybean oil. *J Polym Environ* 10:49–52
- Heinrichs V, Thum O (2005) Biocatalysis for the production of care specialties. *Lipid Technol* 17:82–87
- Herrmann WA, Marz D, Kuchler JG, Weichselbaumer G, Fischer RW (1989) Verwendung von rheniumorganischen Verbindungen zur Oxidation von C-C-Mehrfachbindungen, darauf basierende Oxidationsverfahren und neue rheniumorganische Verbindungen. German Patent Application DE-A3902357A1
- Hills G (2003) Industrial use of lipases to produce fatty acid esters. *Eur J Lipid Sci Technol* 105:601–607
- Hirsinger F (2001) Oleochemicals and the environment. In: Gunstone FD, Hamilton RJ (eds) *Oleochemical manufacture and applications*. Academic, Sheffield, pp 300–315
- Huang YS, Pereira SL, Leonard AE (2004) Enzymes for transgenic biosynthesis of long-chain polyunsaturated fatty acids. *Biochimie* 86:793–798
- ISTA Mielke GmbH Hamburg (2002) The revised oil world 2020: supply, demand and prices
- Janssens RJ, Vernooij WP (2001) *Inform* 12:468–477
- Kandamarachchi P, Guo A, Demydov D, Petrovic Z (2002a) Kinetics of the hydroformylation of soybean oil by ligand-modified homogeneous rhodium catalysis. *J Am Oil Chem Soc* 79:1221–1225
- Kandamarachchi P, Guo A, Petrovic Z (2002b) The hydroformylation of vegetable oils and model compounds by ligand modified rhodium catalysis. *J Mol Catal A Chem* 184:65–71
- Kraus K, Niklas G, Tappe M (1999) Aktuelle Bewertung des Einsatzes von Rapsöl/RME im Vergleich zu Dieselmotortreibstoff. Umweltbundesamt
- Lewand LR (2004) Natural ester dielectric liquids. *NETA World* (Fall 2004)
- Lie Ken Jie MSF, Lau MML, Lam CNW, Alam MS, Metzger JO, Biermann U (2003) Novel halo-oxo-allenic fatty ester derivatives from epoxidized methyl santalbate (methyl trans-11-octadecen-9-ynoate). *Chem Phys Lipids* 125:93–101
- Lligadas G, Ronda JC, Galià M, Biermann U, Metzger JO (2006) Synthesis and characterization of polyurethanes from epoxidized methyl oleate-based polyether polyols as renewable resources. *J Polym Sci A* 44:634–645
- Matsuo T, Sawamura N, Hashimoto Y, Hashida W (1981) Method for enzymatic transesterification of lipid and enzyme used therein. European Patent EP 0 035 883 (Fuji Oil Co.)
- Meier zu Beerentrup H, Röbbelen G (1987) New potential oil crops for industrial uses. *Fat Sci Technol* 6:227–230
- Metzger JO, Biermann U (1992) Alkylaluminium chloride catalyzed ene reactions of formaldehyde with unsaturated carboxylic acids, esters and alcohols. *Synthesis* (5):463–465
- Metzger JO, Biermann U (1993) Alkylaluminium dichloride induced Friedel–Crafts acylation of unsaturated carboxylic acids and alcohols. *Liebigs Ann Chem* 645–650
- Metzger JO, Biermann U (2006) Sustainable development and renewable feedstocks for chemical industry. In: Bozell JJ, Patel MK (eds) *Feedstocks for the future renewables for the production of chemicals and materials*. Oxford Univ. Press, Oxford, pp 13–26
- Metzger JO, Mahler R (1993) Free radical cyclization of petroselinic acid. *Liebigs Ann Chem* 203–205
- Musser MT (2000) Adipic acid. In: *Ullmann's encyclopedia of industrial chemistry*. Wiley-VCH Verl, Weinheim
- Anonymous (2005) Award-winning technology gives healthier fats. *Biotimes*. http://www.novozymes.com/library/Publications/Biotimes_Sprog/Biotimes_2005/3-05/GB_adm.pdf. Cited Sept 2005
- Nowack K (2002) Fatty alcohols. In: *Ullmann's encyclopedia of industrial chemistry*. Wiley-VCH Verl, Weinheim
- Nowack K, Frische R, Olbrich-Deussner B (2004) Presented at the 3rd Euro fed lipid congress, Edinburgh, GB, 5–8 September 2004
- Petrovic Z, Guo A, Javni I (2000) Process for the preparation of vegetable oil-based polyols and electroninsulating casting compounds created from vegetable oil-based polyols. US Patent 6,107,433
- Quinlan P, Moore S (1993) Modification of triglycerides by lipases: process technology and its application to the production of nutritionally improved fats. *Inform* 4:580–585
- Reyes-Duarte D, Polaina J, López-Cortés N, Alcalde M, Plou FJ, Elborough K, Ballesteros A, Timmis KN, Golyshin PN, Ferrer M (2005) Conversion of a carboxylesterase into a triacylglycerol lipase by a random mutation. *Angew Chem Int Ed Engl* 44:7553–7557

- Rüsch gen. Klaas M, Warwel S (1997) Lipase-catalyzed preparation of peroxy acids and their use for epoxidation. *J Mol Catal A Chem* 117:311–319
- Schmid U, Bornscheuer UT, Soumanou MM, McNeill GP, Schmid RD (1999) Highly selective synthesis of 1,3-oleoyl-2-palmitoylglycerol by lipase catalysis. *Biotechnol Bioeng* 64:678–684
- Schumann K, Siekmann K (2002) Soaps Ullmann's encyclopedia of industrial chemistry. Wiley-VCH Verl, Weinheim
- Sheehan J, Camobreco V, Duffield J, Graboski M, Shapouri H (1998) Life cycle inventory of biodiesel and petroleum diesel for use in an urban bus. Final Report. US Department of Energy's Office of Fuels Development and US Department of Agriculture's Office of Energy
- Singh SP, Zhou XR, Liu Q, Stymne S, Green AG (2005) Metabolic engineering of new fatty acids in plants. *Curr Opin Plant Biol* 8:197–203
- Skolaut A, Stockfleth R, Buchholz S, Huang S (2005) Enzymic production of phosphatidylserine and purification by extraction. PCT International Application WO 2005/068644
- von Rybinski W, Hill K (1998) Alkyl polyglycosides—properties and applications of a new class of surfactants. *Angew Chem Int Ed Engl* 37:1328–1345
- Warwel S, Jaegers H-G, Thomas S (1992) Metathesis of unsaturated fatty acid esters—a simple approach to long-chain dicarboxylic acids. *Fat Sci Technol* 94:323–328
- Warwel S, Rüsch gen. Klaas M (1997) Oxidative cleavage of unsaturated fatty acids without ozone. *Lipid Technol* 9:10–14
- Warwel S, Büse F, Demes C, Kunz M, Rüsch gen. Klaas M (2000) Polymers and surfactants on the basis of renewable resources. *Chemosphere* 43:39–48
- Watanabe T, Yamaguchi H, Yamada N, Lee I (2004) Manufacturing process for diacylglycerol oil. In: Katsuragi Y, Yasukawa T, Matsuo N, Flickinger BD, Tokimitsu I, Matlock MG (eds) *Diacylglycerol oil*. AOCS, Champaign, pp 253–261
- Wongsakul S, Kittikun A, Bornscheuer UT (2004) Lipase-catalyzed synthesis of structured triglycerides from 1,3-diglycerides. *J Am Oil Chem Soc* 81:151–155