

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO	
RAD: 14-23080- -14	FECHA: 2016-05-12 16:22:31
DEP: 2020 DIRECCION DE NUEVAS CREACIONES	EVE: 1 REGISTRO/DEPOSITO/CONCESION/DEPOSITO
TRA: 2 PATENTES DE INVENCION	FOLIOS: 10
ACT: 519 TRASLADOINFORME	

DIRECCIÓN DE NUEVAS CREACIONES

2020
Bogotá, D.C.,

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

Asunto: Radicación: 14-23080- -14
Trámite: 2
Evento: 1
Actuación: 519
Oficio: 5625
Folios: 10

Patente de Invención	X			Patente de Modelo de Utilidad	
Vía Nacional	X				
Vía PCT (Fase Nacional)		Capítulo I		Capítulo II	
No. Solicitud Internacional					
Fecha de Presentación Internacional					

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° 14-023080-00000-0000	04/febrero/2014
Reivindicaciones:	Rad. N° 14-023080-00008-0000	18/septiembre/2015
Dibujos:	Rad. N° 14-023080-00000-0000	04/febrero/2014

2. 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 sólo se estudiarán las reivindicaciones 1 a 17 del capítulo reivindicatorio (Radicado N°.12-023080-00008-0000, Páginas 15 a 17).

Título de la solicitud: "Proceso de obtención de poliuretanos a partir de aceite de palma y poliuretanos obtenidos" (Pág. 1, radicado N° 14-023080-00000-0000).

El problema planteado en esta solicitud consiste en la necesidad desarrollar métodos alternativos para la obtención de polioles derivados de aceite de palma, utilizados en la preparación de poliuretano, con la combinación de dos métodos para obtener una mayor funcionalidad a la estructura molecular final.

Para resolver este problema técnico, la solicitud en estudio proporciona un método combinado de producción de poliol a partir de aceite de palma y elaboración de espumas de poliuretano rígido a partir de dicho poliol. El primer método de tratamiento del aceite de palma puede realizarse mediante cuatro rutas: maleinización de ácidos grasos, glicerólisis, transesterificación y/o epoxidación de los enlaces insaturados carbono-carbono de dicho aceite de palma.

El objeto de la presente solicitud se relaciona con la Clasificación Internacional de Patentes (CIP): C08G 018/036.

3. De la solicitud de patente

Reivindicaciones (Art 30 D 486, Art 22 PCT)

- En las reivindicaciones 1 los términos y/ frases: *"mezclar", "calentar", "agitar", "adicionar", "solución saturada"*, son escritos de carácter general y sugieren de forma imprecisa que la protección se extiende a otras posibles variaciones o modificaciones, se sugiere realizar las modificaciones respectivas utilizando términos que describan de forma menos general o definir claramente los rangos.
- El método de la reivindicación 1 si bien presenta la secuencia lógica de pasos, no presenta todas las condiciones necesarias por medio de las cuales deba llevarse a cabo dicho método, por tanto, no es clara.
- En la reivindicación 1, se enseña como condición de proceso de la etapa q) las características del poliol obtenido por medio de la ruta 1, método 2, especificando los siguientes rangos: *"... el cual tiene un peso molecular entre 374 y 3366 con un numero de hidroxilo entre 50 y 450 mgKOH/g muestra..."*, sin embargo, dichos rangos no concuerdan con los resultados presentados en la tabla (Pág.20) y en la descripción, en donde presenta para dicha ruta, el rango de KOH está por debajo a los reivindicados, *"2.41 mgKOH/g muestra, 27,13 mgKOH/g muestra"* experimentos 1 y 2 respectivamente; siendo más específicos, los rangos reivindicados de

numero hidroxilo se obtienen por medio de las rutas 5 a 8, combinación de rutas 2 y 8. Por su parte, el rango de peso molecular reivindicado entre 374 y 3366, se obtiene en el ejemplo 9, por medio de las rutas 2 y 4 (epoxidación y glicerólisis) a partir de la fase oleína del refinado blanqueado desodorizado de aceite de palma crudo y empleando óxido de plomo como catalizador, por tanto, se reitera que dichos rangos no son resultado del método reclamado en la reivindicación 1, se sugiere realizar las aclaraciones y modificaciones del caso.

- El rango de la temperatura del paso “h” en la reivindicación 1, no tiene soporte, según lo referido en el ejemplo 2 - Obtención de poliol empleando el segundo método de la ruta 1, en donde se menciona que dicho paso se realiza a una temperatura de 90°C, se sugiere realizar las aclaraciones del caso.
- La reivindicación 5 menciona un proceso en términos de otro proceso, al referir: “...*el glicerol previamente bloqueado del paso g) se obtiene a partir de los siguientes pasos...*”, lo cual no es permitido. Por otro lado, no es claro el paso “b.” de dicha reivindicación, toda vez que menciona que para obtener el glicerol blanqueado, el cual se adiciona al paso “g.” del proceso de obtención de poliuretanos, se calienta la mezcla del paso a) a una temperatura a un tiempo determinados con el fin de obtener el glicerol blanqueado (Ej.2). Lo anterior no tiene relación con lo revelado en la descripción, en donde se explica la obtención de glicerol blanqueado, sin referir al paso a). Se sugiere realizar las aclaraciones y modificaciones del caso.
- Es importante aclarar que las reivindicaciones de productos definidas en términos del proceso de fabricación pueden ser admisibles, siempre y cuando cumpla con los requisitos de patentabilidad y cuando no se pueda definir por sus características estructurales, caso típico de los polímeros, sin embargo, la reivindicación 15 que su objeto es de producto (poliuretano), que en este caso podrían definirse en términos del proceso, no presenta ninguna característica de dicho proceso, ni tampoco ninguna característica estructural o de composición del producto, por tanto, se encuentra mal definida.
- Las reivindicaciones 16 y 17 no son concisas ya que reivindican la misma materia.

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: octubre 3 de 2011 y se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

Ítem	Documento	Título	Fecha de Presentación*
D1	Artículo 1*	"Water-borne and air-drying oil-based resins"	2004
D3	Artículo 3**	"Preparation and characterization of polyurethane foams using a palm oil-based polyol"	14/08/2007

*"Water-borne and air-drying oil-based resins" Gündüz, et al. Progress in organic coatings. 2004. Vol. 49. Págs. 259 a 269

**"Preparation and characterization of polyurethane foams using a palm oil-based polyol". Ryohe Tanaka, Shigeo Hirose, Hyoe Hatakeyma. 2007.

El documento D1¹ divulga un método para la maleinización de triglicéridos y su posterior uso para la formación de barniz de poliuretano (Pág. 260, Col. 2, Párr. 2 y Párr. 3, Pág. 261, Tabla 1, Pág. 261, Col. 2, Párr. 5 a Pág. 262, Párr. 5).

El documento D3² divulga espumas de poliuretano preparadas usando un poliol a base de aceite de palma, en donde la primera etapa dicho aceite se convierte en monoglicéridos como un nuevo tipo de poliol por glicerólisis, en una segunda etapa, se prepara poliuretano a partir de mezclas de poliol y (PEG) o (DEG) y un compuesto de isocianato (resumen).

Examen de Patentabilidad (Art 14 D486)

Nivel Inventivo (Art18 D486)

La reivindicación 1 consiste en "*Proceso para la obtención de poliuretanos a partir de aceite de palma,...*" (Ver página 15 del radicado N° 14-023080-00008-0000).

Comparación de las características técnicas **esenciales**, con las del Estado de la Técnica:

Características Esenciales	D3	D1
Proceso para la obtención de poliuretanos a partir de aceite de palma caracterizado porque consta de los siguientes pasos: a) Mezclar, calentar y agitar aceite de palma con hidróxido de sodio y una solución etanol-agua 1.1.	Preparación de poliuretano usando un poliol a base de aceite de palma (resumen)	Proceso para la obtención de resinas de poliuretano usando monoglicérido maleinizado (MMG) (resumen). Se mezcla aceite de girasol con hidróxido de sodio y una solución etanol-agua 1:1 (Pág. 260, Col. 2, Párr. 5). No menciona que el paso de obtención de PU sea con aceite de palma
b) Adicionar ácido sulfúrico concentrado a la mezcla del paso a) hasta que se observe la separación de las fases.	Glicerólisis del aceite de palma	Se reacciona el jabón obtenido con una cantidad estequiométrica de ácido sulfúrico (Pág. 260, Col. 2, Párr. 5 a Pág. 261, Col. 1, Párr. 1).

1Gündüz, et al. Progress inorganic coatings. 2004. Vol. 49. Págs. 259 a 269

2[https://translate.googleusercontent.com/translate_c?](https://translate.googleusercontent.com/translate_c?depth=1&hl=es&prev=search&rurl=translate.google.com.co&sl=en&u=http://www.sciencedirect.com/science/article/pii/S0960852407005482&usq=ALkJrhiEzaYrz6XxLNx6D9ZMCK9fl2gldg)

[depth=1&hl=es&prev=search&rurl=translate.google.com.co&sl=en&u=http://www.sciencedirect.com/science/article/pii/S0960852407005482&usq=ALkJrhiEzaYrz6XxLNx6D9ZMCK9fl2gldg](https://translate.googleusercontent.com/translate_c?depth=1&hl=es&prev=search&rurl=translate.google.com.co&sl=en&u=http://www.sciencedirect.com/science/article/pii/S0960852407005482&usq=ALkJrhiEzaYrz6XxLNx6D9ZMCK9fl2gldg)

c) Adicionar solución saturada de cloruro de sodio a la mezcla del paso b).	para preparar polioliol: aproximadamente 20 g de glicerol fueron en un matraz de 300ml, se añadió el aceite de palma con un butanol como solvente, se disolvió hidróxido de sodio a la mezcla (...) calentar a una temperatura de aproximadamente 90°C, y se mantuvo por 2 horas con agitación continua, después se dejó enfriar a temperatura ambiente. Se añadió una solución de hidrocroluro para neutralizar el catalizador alcalino. La transesterificación de triglicéridos por glicerólisis se realiza en presencia de un catalizador alcalino a temperatura elevada. En esta etapa, los productos deben ser monoglicéridos y diglicéridos.	Se adiciona cloruro de sodio para separar las fases en la saponificación (Pág. 260, Col. 2, Párr. 5).
d) Descartar la fase acuosa obtenida en el paso c), después de la completa separación de fases		Se separa las fase orgánica de la fase acuosa y la fase orgánica se concentra por filtración descartando la fase acuosa (Pág. 261, Col. 1, Párr. 1).
e) Lavar con agua a una temperatura entre 70°C y 80°C la fase orgánica restante del paso d).		Se lava con agua la fase orgánica varias veces (Pág. 261, Col. 1, Párr. 1).
f) Calentar y agitar la fase orgánica del paso e) y someter a evaporación al vacío obteniéndose los ácidos grasos.		Se remueve el agua por evaporación al vacío (Pág. 261, Col. 1, Párr. 1). En este punto no se observa efecto importante en el orden de adición del ácido sulfúrico y el cloruro de sodio, pues se obtiene con cualquier orden ácidos grasos purificados
g) Mezclar los ácidos grasos obtenidos en el paso f) con glicerol previamente bloqueado y un catalizador, calentar y agitar, en donde el catalizador es ácido toluen sulfónico.	A partir del análisis cuantitativo, la mejor relación de aceite de palma/glicerol se determinó para la preparación del polioliol, que mostro el rendimiento más alto de monoglicéridos. A continuación la mezcla se sometió a un proceso de purificación para eliminar el – BuOH y el glicerol sin reaccionar. En primer lugar el alcohol se elimina por la evaporación al vacío (Págs. 3811 y 3812, Col. 2 y 1, respectivamente).	Se mezclan los ácidos grasos con ácido para toluen sulfónico como catalizador y glicerol bloqueado a 90°C (Pág. 261, Col. 1, Párr. 3). Como materia prima se utiliza ácido toluen sulfónico (Pág.260, Col.1, Párr. 3).
h) Lavar con agua a una temperatura entre 70°C y 80°C la mezcla del paso g)		Se lava con agua varias veces para remover el catalizador (Pág. 261, Col. 1, Párr. 4).
i) Separar la fase acuosa obtenida en el paso h) y descartarla.		Para remover el agua generada en la reacción se emplea tolueno, el cual se separa por destilación retirando así el agua (Pág. 261, Col. 1, Párr. 3).
j) Tratar la fase orgánica restante en el paso i) mediante evaporación al vacío para obtener monoglicérido bloqueado.		El tolueno se separa de la fase orgánica por evaporación al vacío, obteniéndose monoglicérido bloqueado purificado (Pág. 261, Col. 1, Párr. 3 y Párr. 4)
k) Adicionar el monoglicérido bloqueado del paso j) anhídrido maléico, calentar y agitar bajo atmósfera de nitrógeno	No menciona específicamente las etapas finales.	Se tiene en la reacción monoglicérido bloqueado, anhídrido maléico y se somete a 200°C en atmosfera de nitrógeno y con agitación (Pág. 261, Col. 1, Pág. 260, Col. 2, Párr. 1).
l) Enfriar la mezcla del paso k) hasta 100°C		Se enfría a 100°C para que ocurra la reacción con ácido sulfúrico (Pág. 261, Col. 2, Párr. 3).
m) Adicionar ácido sulfúrico al producto de la reacción del paso l)		La decantación es una etapa unitaria usada para separar fases de compuestos hidrofóbicos de los hidrofílicos (Pág. 261, Col. 1, Párr. 1). Aquí Se lava varias veces con agua y se evapora el agua con el metil etil cetona quedando al final el polioliol purificado (Pág. 261, Col. 2, Párr. 3).
n) Lavar con agua a una temperatura entre 70°C y 80°C y decantar el producto de reacción obtenido en el paso separar la fase acuosa obtenida en el paso m).		
o) Separar la fase acuosa obtenida en el paso m).		
p) Lavar la fase orgánica obtenida en el paso m).		
q) Evaporar la fase orgánica del paso n) para obtener el polioliol		
r) Al polioliol obtenido del paso q), se le		

adiciona surfactante y metil etil cetona y hacer reaccionar la mezcla a una temperatura de 50°C durante un periodo de treinta minutos.	La espuma de poliuretano se prepara mezclando el polioli a partir de aceite de palma con PEG o DEG, un catalizador y un surfactante (Pág. 3812, Col.1, Párr. 4).	El polioli se hace reaccionar con MEK (metil etil cetona) y HTPB (hidrox terminal polibutadieno, el cual es un agente un surfactante, propelante) durante 30 minutos a 50°C (Pág. 261. Col. 2. Párr. 6).
En donde el surfactante es un copolimero tipo poliéter.		Los poliuretanos contienen un segmento duro y suave en el esqueleto con poliéster (o poliéter) (...) (Pág.260, Col.1, Párr.1).
s) Adicionar toluen diisocianato con agitación mecánica a una temperatura de 70°C	Posteriormente el polímero isocianato (MDI) fue adicionado a temperatura ambiente con agitación Pág. 3812, Col.1, Párr. 4).	A 70 °C se adiciona el toluen diisocianato (TDI) y se agita por tres horas (Pág. 262, Col. 1, Párr. 2).
t) Enfriar a 50°C	No menciona la etapa final del proceso.	Se enfría a 50°C y se adiciona metil etil cetoxima MEKO por 2 horas (Pág. 262, Col. 1, Párr.3).
u) Adicionar metil etil cetóxima hasta bloquear los grupos NCO libres.		Y los grupos NCO libres del prepolímero se bloquearon con metil etil cetoxima MEKO durante aproximadamente 2 horas (Pág. 262, Col. 1, Párr.3).
v) Adicionar trietilamina en un reactor agitado.		Se adiciona TEA trietilamina y se agita por 30 min a 50°C (Pág. 262, Col. 1, Párr. 4).
w) Adicionar agua, gota a gota, para formar una emulsión en una cantidad de 50% en peso.		Bajo agitación continua y gota a gota se adiciona agua hasta un 50% en peso (Pág. 262, Col. 1, Párr. 5).

El documento D3 se considera el estado de la técnica cercano a la invención definida en la reivindicación 1 porque divulga un método para obtener poliuretano a partir de aceite de palma (resumen).

La diferencia entre la invención definida en la reivindicación 1 y el proceso de D3 consiste en que D3 no menciona específicamente cada etapa del proceso.

No se evidencia un efecto técnico inesperado logrado al especificar las condiciones técnicas en etapas del proceso, toda vez que el documento D3 ya había anticipado el problema técnico que pretende resolver la invención, el cual es buscar métodos alternativos para la obtención de polioles derivados de aceite de palma, utilizados en la preparación de poliuretano, con la combinación de dos métodos.

Por lo tanto, el problema técnico objetivo que pretende resolver esta invención se puede formular así: ¿Cómo obtener un poliuretano de forma alternativa a la revelada en D3?

Sin embargo, a pesar que el documento más cercano no especifica todas las condiciones técnicas del proceso, ya era conocido en el estado de la técnica procesos de obtención de poliuretano a partir de aceites vegetales que involucra la síntesis de monoglicérido maleinizado (MMG), ya que D1 divulga un método para la maleinización de triglicéridos y su posterior uso para la formación de barniz de poliuretano (Pág. 260, Col. 2, Párr. 2 y Párr. 3, Pág. 261, Tabla 1, Pág.

261, Col. 2, Párr. 5 a Pág. 262, Párr. 5), el cual anticipa tanto los reactivos como las condiciones técnicas del proceso.

En consecuencia, una persona normalmente versada en la materia estaría motivada a utilizar tanto los reactivos como las condiciones de proceso conocidos en D1, de forma alternativa a la planteada en D3, para la obtención de poliuretanos a partir de aceite de palma, para así llegar a la materia contenida en la reivindicación 1 de la solicitud, lo cual es considerado obvio y, por lo tanto, sin altura inventiva.

Adicionalmente aunque los documentos D1 y D3 no enseñen que el lavado de los productos intermedios con agua se realice a una temperatura entre 70°C y 80°C, dado que la invención no muestra un efecto técnico sorprendente en relación a dicha característica específica, una persona versada en la materia con el saber general de la técnica (lavado con agua caliente a temperaturas entre 60 y 70°C del poliol obtenido para eliminar acidez (Pág. 276, Col. 2, Párr. 1)³, y con una serie de conocimientos específicos de la invención, estaría motivada a lavar los productos intermedios con agua a una temperatura entre 70°C y 80°C para eliminar acidez en el proceso que se da a conocer en D3, para obtener un poliol libre de impurezas para obtener posteriormente un poliuretano, tal como se encuentra reclamado en la reivindicación 1 de la solicitud, motivo por el cual se considera obvia. Cabe decir, que la solución al anterior problema técnico objetivo se encuentra dentro de un diseño y optimización de procesos⁴, lo cual se encuentra dentro de la práctica habitual de la persona versada en la materia que trabaje en la fabricación de poliuretanos.

Así mismo, el documento D1 divulga las características de las reivindicaciones dependientes así:

Reivindicaciones 2: la temperatura del paso a) a 80°C durante el tiempo necesario para homogenización (Pág. 260, Col. 2, Párr. 5).

Reivindicaciones 5: el glicerol bloqueado viene de a) mezclar glicerol, MEK, ácido toluen sulfónico como catalizador y tolueno; b) calentar la mezcla anterior a 90°C (Pág. 261, Col. 1, Párr. 3).

Reivindicación 9: la reacción de monoglicérido bloqueado con anhídrido maléico se somete a 200°C en atmósfera de nitrógeno y con agitación (Pág. 261, Col. 1, Pág. 260, Col. 2, Párr. 1).

Reivindicación 10: se disminuye la temperatura hasta 100°C antes de la adición del ácido sulfúrico, en donde la agitación durante las reacciones es requerida (Pág. 261, Col. 2, Párr. 3, Pág. 261, Col. 1, Pág. 260, Col. 2, Párr. 1).

Por otra parte la reivindicaciones 3, 4, 6 a 12 son afectadas con el conocimiento

³ Sinadinovic Fiser et al. Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. Journal of the American Oil Chemists' Society. 2001. Vol. 78 (7). Pág. 726, Col. 2. Párr. 1.

⁴ Perry Manual del Ingeniero Químico. Tomo I. Sección 2. Sexta edición. 1992. Págs. 2-81 a 2-85.

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”*⁵, el cual conoce que:

Reivindicación 3: lavados hasta pH neutro de los productos obtenidos de la transformación de aceites y/o ácidos grasos⁶.

Reivindicación 4: la estabilidad de los aceites que contienen ácidos grasos con respecto a la temperatura⁷, por lo que calentar para evaporar como lo realiza la solicitud y evaporar al vacío como se menciona en D1 no produce un efecto técnico inesperado.

Reivindicación 6: la estabilidad de los aceites que contienen ácidos grasos con respecto a la temperatura⁷, por lo que calentar para evaporar durante un tiempo especificado como lo realiza la solicitud y evaporar al vacío como se menciona en D1 no produce un efecto técnico inesperado.

Reivindicación 7: lavados hasta pH neutro de los productos obtenidos de la transformación de aceites y/o ácidos grasos⁶.

Reivindicación 8: la estabilidad de los aceites que contienen ácidos grasos con respecto a la temperatura⁷, por lo que calentar para evaporar durante un tiempo especificado como lo realiza la solicitud y evaporar al vacío como se menciona en D1 no produce un efecto técnico inesperado.

Reivindicación 11: la estabilidad de los polioles obtenidos a partir de aceites naturales con respecto a la temperatura⁸, por lo que lavar con agua caliente durante un tiempo especificado como lo realiza la solicitud no produce un efecto técnico inesperado.

Reivindicación 12: la estabilidad de los polioles obtenidos a partir de aceites naturales con respecto a la temperatura⁸, por lo que calentar para evaporar durante un tiempo especificado como lo realiza la solicitud y evaporar al vacío como se menciona en D1 no produce un efecto técnico inesperado.

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

Reivindicación 13 y 14: El estudio aquí realizado desarrolla un nuevo tipo de espuma de poliuretano usando aceite de palma como materia prima (resumen). Materiales: aceite de palma (AP) de Industrias MALPOM BHD, Malasia, de grado crudo (=CPO, aceite de palma crudo) (Pág.3811, Col.2; Párr.6).

⁵Proceso 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.

⁶Sinadinovic-Fiser et al. Kinetics of in situ epoxidation of soybean oil in bulk catalyzed by ion exchange resin. Journal of the american oil chemists' society. 2001. Vol. 78 (7). Pág. 726, Col. 2. Párr. 1.

⁷Souza et al. A threomalytic and kinetic study of sunflower oil. Brazilian Journal of Chemical Engineering. Vol. 21(2).2000. Pág. 268, Pág. 269, Figs 2 y 3.

⁸Yang, et al. Thermal analysis of soybean oil based polyols. Journal of Thermal Analysis and Calorimetry. 2009. Vol. 95 (3). (Pág. 980, Fig. 3).

Con respecto a las reivindicaciones 15 a 17, que están reivindicando un producto en términos de su proceso, se le recuerda que para cumplir con dicha condición, la materia tiene que ser nueva e inventiva, lo cual no sucede en este caso. Por otra parte, se reitera que dichas reivindicaciones se encuentran mal definidas, ya que no mencionan características técnicas del producto o del proceso. De igual manera, la reivindicación 5 no brinda características técnicas adicionales que le brinden altura inventiva a la reivindicación 1, ya que se encuentra afectada por claridad.

5. Conclusión

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

Ítem	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	Artículo 1	1 a 12	Nivel Inventivo
D3	Artículo 3	1, 13 y 14	Nivel Inventivo

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 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.

Si como respuesta a este requerimiento el solicitante llegara a modificar: i) el capítulo reivindicatorio, ii) la descripción de la invención a proteger, iii) o presente un nuevo capítulo reivindicatorio, y desee que se realice un nuevo examen de patentabilidad a esta modificación, no deberá pagar la tasa de modificación voluntaria pero sí la correspondiente a la tasa de examen de patentabilidad. En todo caso, el número de requerimientos por no patentabilidad estará supeditado a que el término del estudio de patentabilidad no sea superior a 18 meses, contados desde la publicación de la solicitud de patente de invención. Adicionalmente, 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 deberá pagar la tasa 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 2016-05-17

Elaboró: Olga Ximena Benavides Salazar

Revisó: Rachid Ponce Vergel

Water-borne and air-drying oil-based resins

G. Gündüz^{b,*}, A.H. Khalid^a, i.A. Mecidoğlu^c, L. Aras^c

^a Polimer Bilimi ve Teknolojisi Anabilim Dalı, Orta Doğu Teknik Üniversitesi, Ankara 06531, Turkey

^b Kimya Mühendisliği Bölümü, Orta Doğu Teknik Üniversitesi, Ankara 06531, Turkey

^c Kimya Bölümü, Orta Doğu Teknik Üniversitesi, Ankara 06531, Turkey

Received 26 August 2003; accepted 21 September 2003

Abstract

New water-borne polyurethane resins were produced using maleinized monoglyceride (MMG), hydroxyl-terminated polybutadiene (HTPB), toluene di-isocyanate, and ethylene diamine (EDA). Maleinization was performed in order to insert hydrophilic groups in the fatty acid residues, which were then inserted to the backbone of polyurethane. The MMG was mixed with HTPB in different proportions, and the mixture was used as the polyol part of water-borne polyurethane resin. It was then reacted with toluene di-isocyanate, and the isocyanate end groups were blocked with methyl ethyl ketoxime (MEKO). The ratio of MMG to total polyol was changed between 40 and 70 mol%, while the [NCO]/[OH] ratio was kept at 1.5 in all samples. The carboxylic acid groups of MMG were then neutralized with triethyl amine. The formation of ionic groups imparts water dispersibility. Chain extension was performed by adding EDA and baking at 125 °C. Hardness, adhesion, impact resistance, bending, and abrasion resistance tests were applied to the specimens. The samples exhibited good physical and mechanical properties.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Water-borne; Water dispersed; Polyurethane; Maleinization; Monoglyceride; Air-drying

1. Introduction

Polyurethanes exhibit excellent abrasion resistance, toughness, chemical and corrosion resistance and a wide range of mechanical strengths, thus they have found extensive applications in the high performance coatings for the automotive, appliance, and wood industries [1]. In the 1980s, the automakers started to shift from solvent-based to water-based paints to reduce the amount of volatile combustibles. The increasing trend towards water-dispersed paints accelerated the research on the development of new type of polymeric resins for use in paint industry [2,3]. The research on water-borne paints goes down to early fifties, and the work was mostly concentrated on the use of maleinized oils [4].

Most polyurethane paints available in the market are usually made by using polyester polyols to impart sufficient rigidity to the resin. However, polyether polyols are also used as partial substitute to make resins with improved flexibility. Polyethers increase also the dispersion of the resin in water because they have higher number of hydrophilic groups on

the backbone. The use of polyethylene and polybutylene glycol at appropriate ratios may help to balance the hydrophilic and hydrophobic properties at the desired level. Water-borne alkyds drew continuous attention as the availability of raw materials and the superior properties of the product are concerned. The alkyd resins may also be made water dispersible by mixing a normally synthesized resin with a specially synthesized alkyd which contains high acidic groups. The high acidic groups can be achieved by using a chemical with high functionality such as trimellitic anhydride. The styrenated alkyd may be made water-borne by using hydrophilic monomers such as acrylic acid or methacrylic acid [4]. The research on oil containing water-borne resins is still an active subject in paint industry and new patents were introduced using different raw materials and techniques [5–8]. In recent years, water-dispersed epoxy resins also have gained importance [9]. Although water-dispersed paints display excellent performance in many areas of applications they lack abrasion resistance, chemical resistance and general durability [10]. The research work on water-borne resins and paints cover a wide range from synthesis to characterization [11–15].

Water dispersion of polyurethanes is usually achieved by having carboxyl acid residues on the backbone and quaternizing these groups by tertiary amines. The organic salts thus formed become dispersible in water. The most preferred

* Corresponding author. Tel.: +90-312-210-2616;

fax: +90-312-210-1264.

E-mail address: ggunduz@metu.edu (G. Gündüz).

monomer to incorporate hydrophilic group is dimethylol propionic acid though tartaric acid can also be used with some precaution; that is, heavy branching must be prevented during synthesis when tartaric acid is used [14,15]. Polyurethanes contain a soft and a hard segment on the backbone with polyesters (or polyethers) comprising the soft segment, and the urethane group the hard segmental part. Air-drying polyurethane resins can be synthesized by substituting the polyester with monomers containing double bonds on the backbone such as monoglycerides [15]. However, the use of pure monoglyceride results in a thick mixture which is apt to easy gelation. Therefore, it needs to be diluted by using a polyol. The polyol can be of polyester or polyether origin.

The aim of this work was to synthesize water dispersible polyurethane resin containing (i) fatty acid residues to provide air drying and (ii) maleinized fatty acid residues to achieve water dispersion. In other words, the traditionally used dimethylol propionic acid has been substituted by maleinized fatty acids. To improve air drying hydroxyl-terminated polybutadiene (HTPB) was partly used on the backbone. The research work concentrated on synthesizing a maleinized monoglyceride (MMG) derivative from sunflower oil. The monoglyceride derivative contained both fatty acid residues and hydrophilic groups. Two different MMG derivatives were synthesized and the resins made from them were characterized for their properties.

2. Experimental

2.1. Raw materials

The raw materials used were sunflower oil, sodium hydroxide (Merck), sulfuric acid (99.5% pure; Merck), methyl ethyl ketone (99.5% pure; Delta Kimya), toluene sulfonic acid, glycerine (99.5% pure; Birpa Ltd. Ş.), maleic anhydride (Volkan Boya), HTPB (MW = 2700 g/mol; SAGE), toluene diisocyanate (TDI) an isomeric commercial grade mixture (İşbir A.Ş.), methyl ethyl ketoxime (MEKO; Volkan Boya), triethylamine (TEA; ÇBS A.Ş.), ethylene diamine (EDA; Merck), and nitrogen gas (99.999% pure; Habaş).

HTPB was dehydrated by passing nitrogen gas through it for 30 h. MEK and MEKO were dehydrated over molecular sieves. MMG, after its production, was dehydrated under vacuum at 50 °C, for about 2 h, and then magnesium sulfate salt was used to remove any remaining water. Other materials were used as-received.

2.2. Synthesis of MMG derivatives

MMG derivative was produced by two different methods. They are denoted here as Method I and Method II. A number of trials were made to synthesize MMG by direct maleinization of monoglyceride. However, gelation took place in all of these trials because of the reaction of anhydride groups

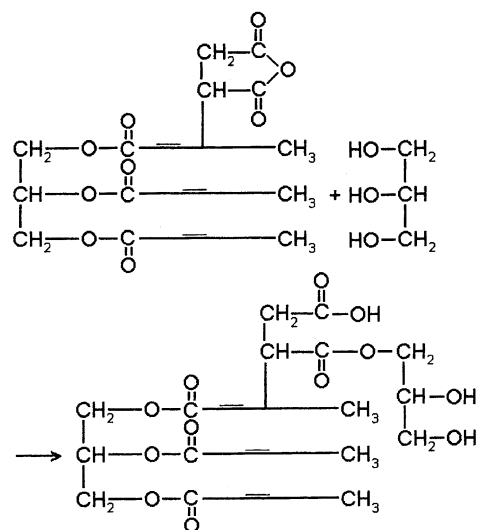
of maleic anhydride and hydroxyl groups of glycerin. In another trial, the oil was maleinized and then reacted with glycerin, but the material gelled in this case too. Therefore, two different methods described below were used to synthesize MMG derivative. The experiments were carried in a 5-necked glass reactor of about 1 l in volume. It is equipped with a stirrer, condenser, thermometer, nitrogen and feed inlet.

2.2.1. Method I

The following steps were performed:

1. The sunflower oil was reacted with maleic anhydride at 200 °C under nitrogen atmosphere for 3 h.
2. The maleinized oil was cooled to 100 °C, and glycerine was added to the reactor. The reaction continued until the acid number came down to a value of 90. As seen in equation the maleinized oil was hydrolyzed with glycerin to yield monoglyceride. It now has two hydroxyl groups to react with a di-isocyanate to make polyurethane, has one carboxylic group that can be used for water dispersion, and two fatty acid residues having double bonds for air drying.

However, this MMG derivative, named MMG-I, resulted in brownish color when used in making polyurethane resin. Therefore, another MMG derivative was synthesized by following another method:



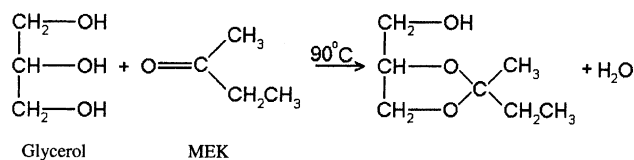
2.2.2. Method II

In this method we needed to use fatty acids in the synthesis of MMG. Therefore, fatty acids were first obtained from the alcoholysis of sunflower oil. The oil was mixed with 1:1 ethanol–water solution, and stoichiometric amount of sodium hydroxide (3 mol per mole of oil) was added. The hydrolysis reaction was carried at 80 °C under reflux until a homogeneous mixture was obtained. The mixture was poured into a saturated solution of sodium chloride in order to precipitate the soap. Then soap was dissolved in water and

reacted with stoichiometric quantity of sulfuric acid. This separates fatty acid phase from water phase. The saturated fatty acids, stearic acid (6 wt.%) and palmitic acid (11 wt.%) with melting points of 69.6 and 63.1 °C, respectively, precipitate at room temperature, and they were filtered out to increase the unsaturation in the final product. The liquid fatty acid phase was washed with water for several times and put under vacuum to remove water.

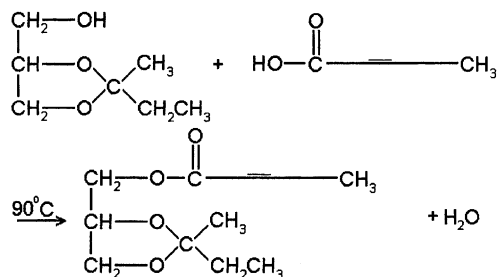
In order to synthesize MMG the following steps were performed:

1. Glycerol was reacted with MEK at 90 °C, using toluene sulfonic acid as a catalyst. Thus two of the hydroxyl groups of glycerine were blocked with MEK:



The reaction water was removed by azeotropic distillation with toluene during reaction.

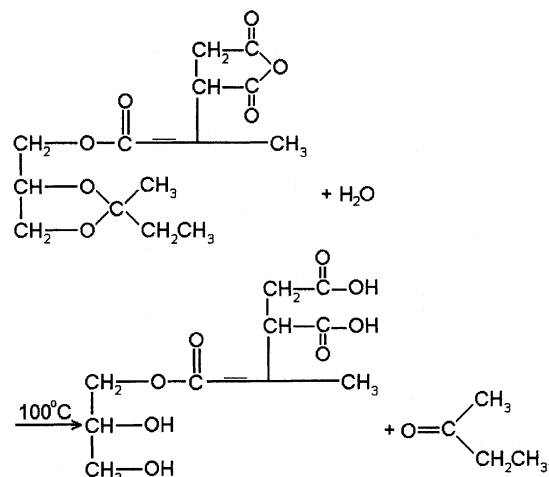
2. The resultant material was reacted with fatty acid mixture using the same catalyst. The fatty acid mixture contains about 35% by weight oleic acid, 62.6% linoleic, and 2.4% linolenic acid. Thus totally unsaturated fatty acid residues are introduced into the structure:



The resulting water was again removed by azeotropic distillation with toluene.

3. The material was washed with water for several times to remove the catalyst. Then, toluene was removed under vacuum.

4. The synthesized chemical was maleinized by reacting it with 30 mol% of maleic anhydride at 200 °C and under nitrogen atmosphere.
5. The maleinized product was hydrolyzed by reacting it with water in the presence of several drops of sulfuric acid, and thus a new maleinized monoglyceride derivative, named MMG-II, was obtained.
6. The MMG derivative was washed with water for several times and then put under vacuum for about 3 h to remove water and MEK produced as a by product:



As the two MMGs are compared, both have two hydroxyl groups, MMG-I has one carboxyl group while MMG-II has two. MMG-I has an additional two more fatty acid residues. The molecular weight of MMG-I is 1053 g/mol, and that of MMG-II is 455 g/mol.

2.3. Water-dispersed polyurethane varnish production

In all experiments, the [NCO]/[OH] ratio was kept at 1.5 in order to assure NCO termination of the prepolymer. The experiments were repeated by changing the ratio of MMG to HTPB. Several formulations of the feed are given in Table 1. The following procedure was carried out in making water-dispersed polyurethane:

1. HTPB and MMG were dissolved in MEK by stirring the mixture for 30 min at 50 °C. This was done in

Table 1
Basic formulations of the resin

Method	Sample	Ratio ^a (%)	MMG (mol)	HTPB (mol)	TDI (mol)	MEKO (mol)	TEA (mol)	EDA (mol)
I	A1	40	0.8	1.2	3.0	2.0	0.8	1.0
I	A2	50	1.0	1.0	3.0	2.0	1.0	1.0
I	A3	60	1.2	0.8	3.0	2.0	1.2	1.0
I	A4	70	1.4	0.6	3.0	2.0	1.4	1.0
II	B1	50	1.0	1.0	3.0	2.0	0.6	1.0
II	B2	55	1.1	0.9	3.0	2.0	0.66	1.0
II	B3	60	1.2	0.8	3.0	2.0	0.72	1.0
II	B4	65	1.3	0.7	3.0	2.0	0.78	1.0
II	B5	70	1.4	0.6	3.0	2.0	0.84	1.0

^a MMG/(MMG + HTPB).

order to have a homogeneous distribution of hydrophilic molecules in the polymer backbone.

2. TDI was added to the mixture and the reaction continued for 3 h with stirring at 70 °C. The reaction time was determined by using di-butylamine back titration method.
3. After the completion of the reaction, the prepolymer was cooled to 50 °C, and the free NCO groups of the prepolymer were blocked with MEKO for approximately 2 h. This step is not necessary. However, it is done to improve the shelf-life of the resin.
4. TEA was added to the solution to neutralize the carboxylic groups, and the mixture was stirred for 30 min, while maintaining the temperature at 50 °C.
5. Water was added to the solution at an amount to make 50% of the total mass from a stop-cock burette by one drop per two or three seconds under continuous stirring.

3. Results and discussion

3.1. Chain extension by baking

Ethylene diamine was used for the chain extension of blocked isocyanate groups. It was added at stoichiometric amounts to all samples prepared. It was added 2–3 h before the application step because it causes gelation at room temperature in 4 days after its addition.

3.2. Preparation of test panels

A standard of 30 μm wet film thickness was applied to test panels. This was done by using film casting knife (Braive-Instruments) on the panels. After casting, the test panels were put in an oven, where the temperature was increased to 125 °C, and maintained at this temperature for 3 h. The varnishes which were produced using MMG produced through Method II required a temperature of 175 °C to form a non-tacky film. The films dried in 1 day at room temperature without using any drier.

3.3. NMR spectroscopy

A Bruker-Spectrospin Avance (DPX 400) Ultra-Shield Nuclear Magnetic Resonance instrument was used to characterize the MMG. The characterization by using ^1H NMR spectroscopy was done only for MMG-II because the process used is a novel one. The characterization was done by comparing the spectroscopy of a mixture of maleic anhydride and monoglyceride in Fig. 1 with that of MMG in Fig. 2.

The results showed that the double bonds of MMG disappeared after the reaction. In Fig. 1, the peak at 6.2 ppm denotes the double bonds of maleic anhydride, and it disappeared after the reaction of maleic anhydride with monoglyceride as shown in Fig. 2. The other peaks appear in both figures because they have similar structure. The peak

at 5.2 ppm denotes the hydrogen atom bonded to the secondary carbon atom in the monoglyceride molecule. This peak covers also carbon–carbon double bond of the fatty acid residue. The peak at 4.1 ppm denotes the carboxylic and ester groups. The peak at 2.6 ppm corresponds to $-\text{CH}_2-$ groups adjacent to double bond in the fatty acid residue, and the one at 2.25 ppm denotes the $-\text{CH}_2-$ groups adjacent to the ester bond and the groups that are not bonded to the carbon atoms in the double bonds. The peak at 2.0 ppm corresponds to the $-\text{CH}_2-$ from maleic anhydride, and the one at 1.3 ppm denotes the $-\text{CH}_2-$ groups adjacent to methyl groups in the fatty acids and methyl ethyl ketone. The peak at 0.9 ppm denotes the $-\text{CH}_3$ group in the fatty acid and methyl ethyl ketone.

3.4. IR spectra

Hitachi (Model: 270-30) Infrared Spectrophotometer was used to characterize the samples. The IR spectrum of MMG-I and of MMG-II are shown in Figs. 3 and 4, respectively.

The peak at 3500 cm^{-1} corresponds to OH stretching, the small shoulder at 3000 cm^{-1} corresponds to unsaturated CH stretching, and the peak at 2900 cm^{-1} corresponds to CH_2 stretching. The peak at 1720 cm^{-1} corresponds to C=O stretching of ester, and the shoulder at 1700 cm^{-1} to C=O stretching of carboxylic group from maleic anhydride. The peak at 1460 cm^{-1} is due to $-\text{CH}_3$ bending and the broadening in the peak is due to *cis* C=C group. The peak due to $-\text{CH}_3$ bending exists at 1380 cm^{-1} , the peak at 1170 cm^{-1} corresponds to C–O–C stretching of ester, and the peak at 720 cm^{-1} is due to multiple CH_2 split from $(\text{CH}_2)_n$.

Both figures look similar, however, it can be noticed that in Fig. 3 the peaks at 3000 cm^{-1} has higher intensity and it is merged into the adjacent peak. This difference is due to the higher concentration of fatty acid residues with unsaturated bonds. The higher intensity of the peak below 1800 cm^{-1} shows the higher concentration of carboxylic groups from maleic anhydride. The higher intensity at 920 cm^{-1} is due to the higher dimer content because of the higher carboxylic acid groups.

Figs. 5 and 6 show the IR spectrum of the polyurethane produced by using MMG-I and MMG-II, respectively. The urethane bond was characterized by the presence of NH group at $3300\text{--}3500\text{ cm}^{-1}$. The peak at 2900 cm^{-1} is due to the CH stretching, and the peak at 1720 cm^{-1} corresponds to C=O stretching from ester groups. The other peaks are from the raw materials used. The absence of peaks in the range $2000\text{--}2300\text{ cm}^{-1}$ shows that all isocyanate groups were involved in the reaction, and that there are no significant isocyanate groups in the resin.

3.5. Color of the dry films

The varnish produced by using MMG-II, gave slightly yellow transparent films. On the other hand, the varnish produced from MMG-I gave brown and semitransparent films.

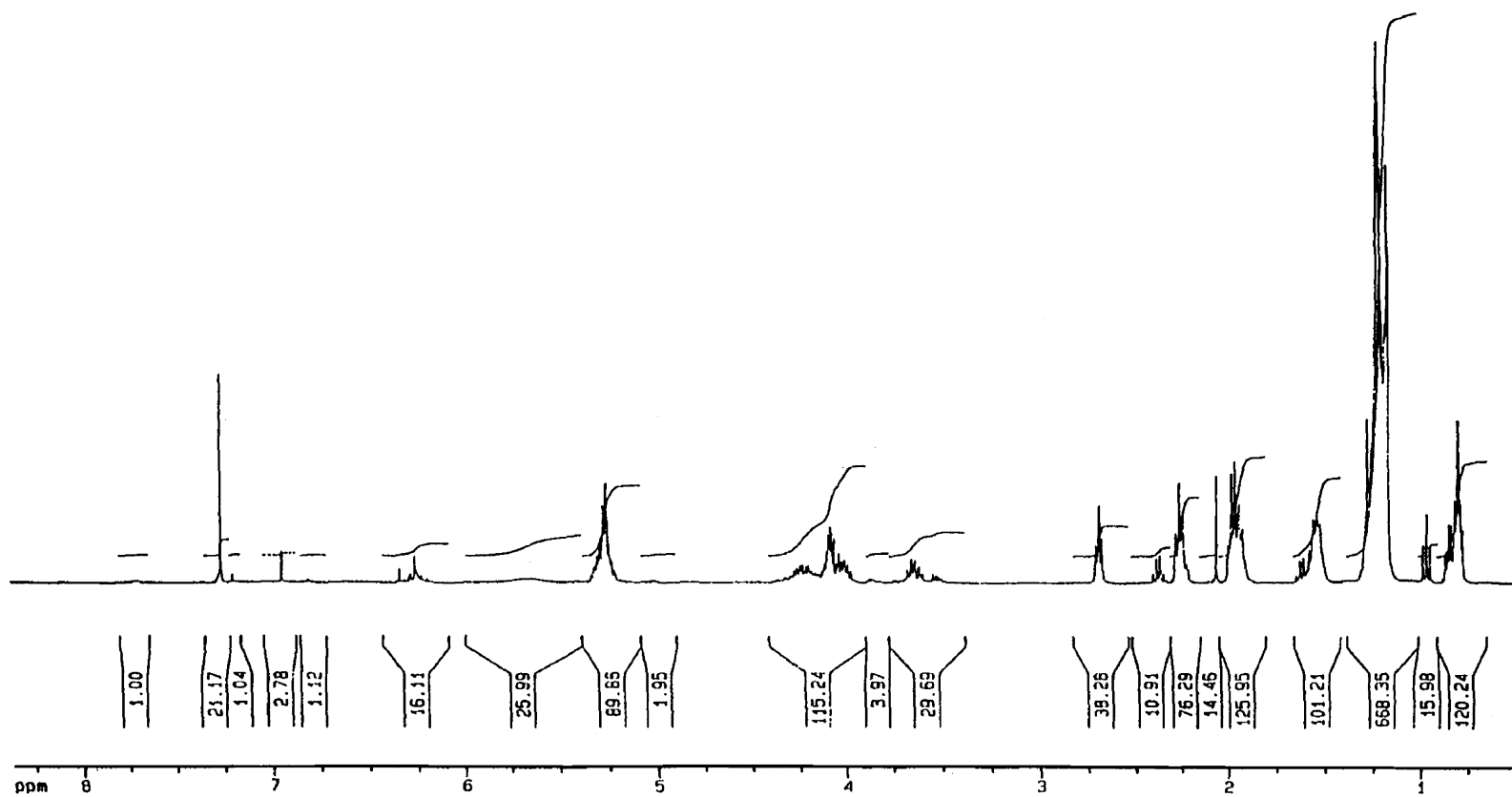


Fig. 1. NMR of monoglyceride and maleic anhydride mixture.

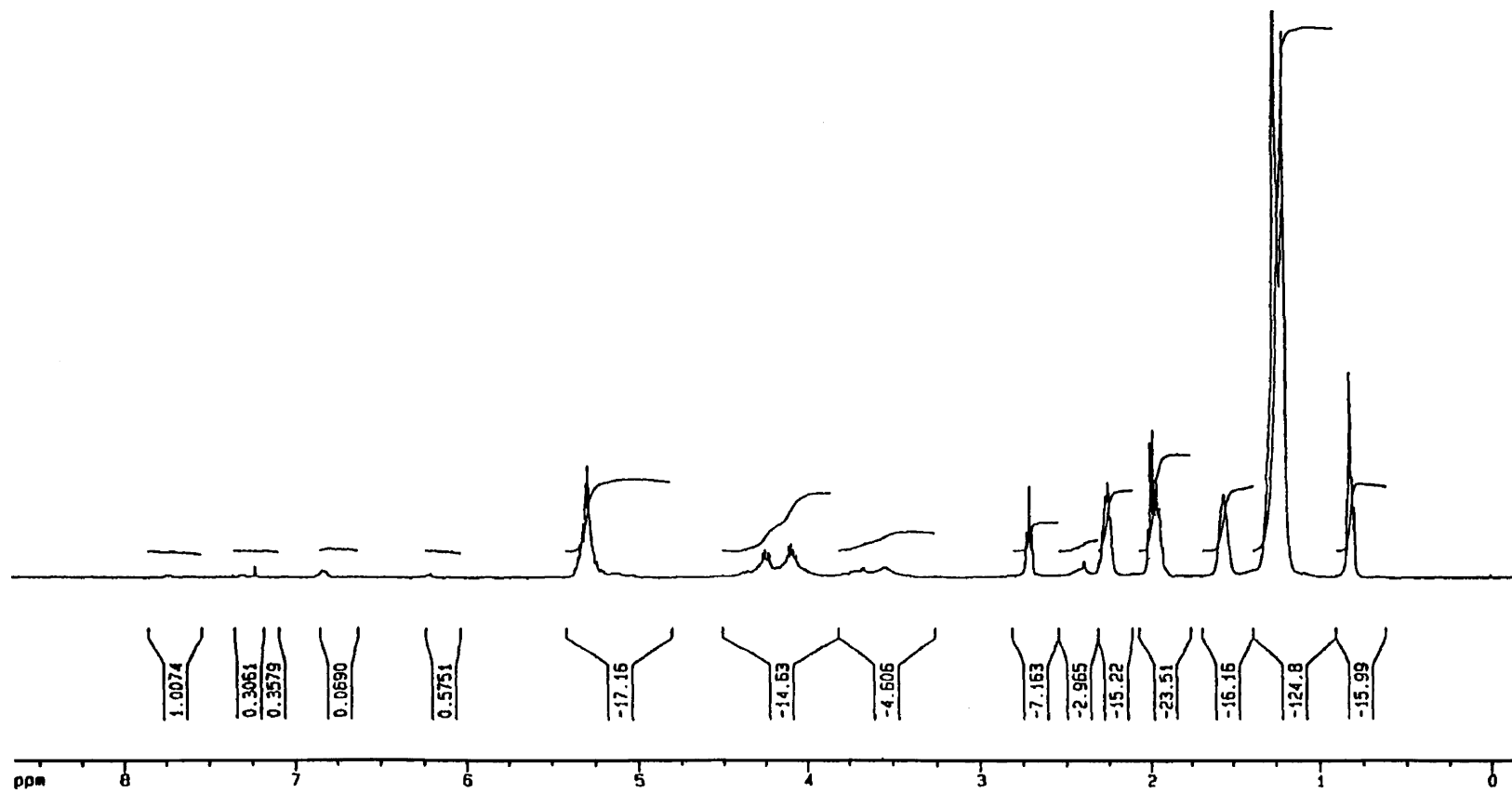


Fig. 2. NMR of MMG.

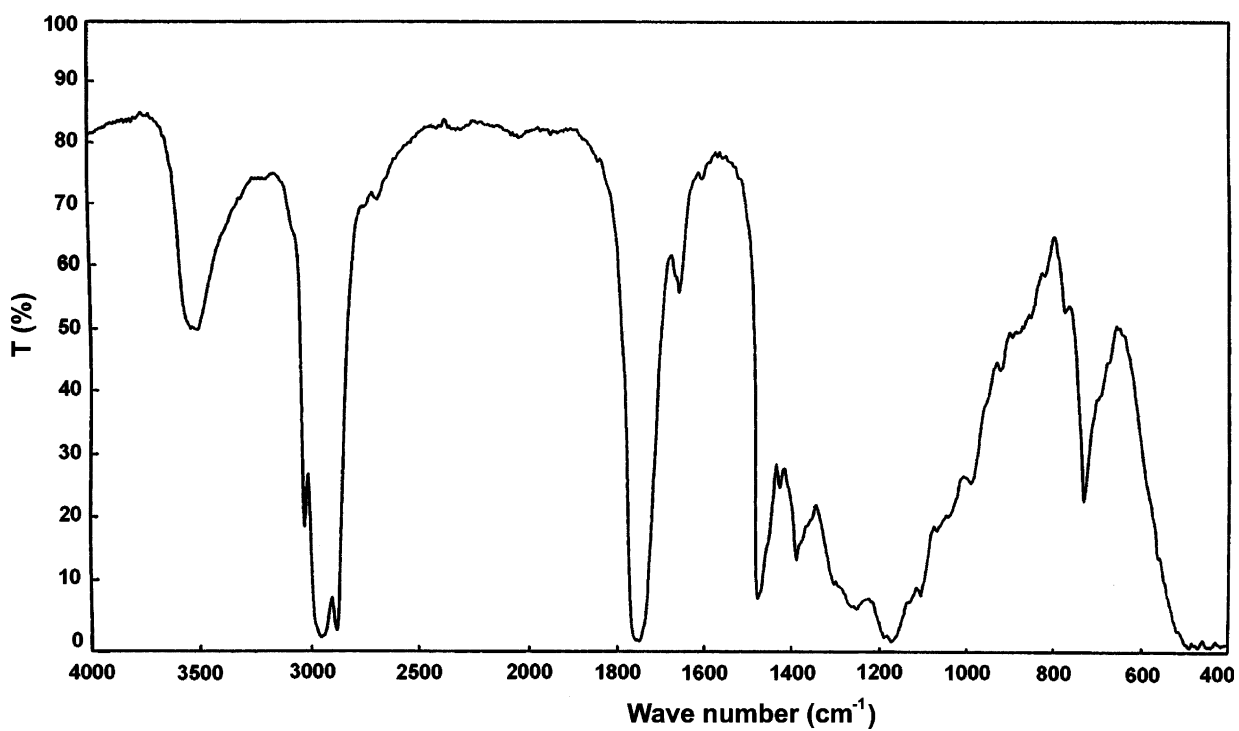


Fig. 3. IR of MMG produced by Method I.

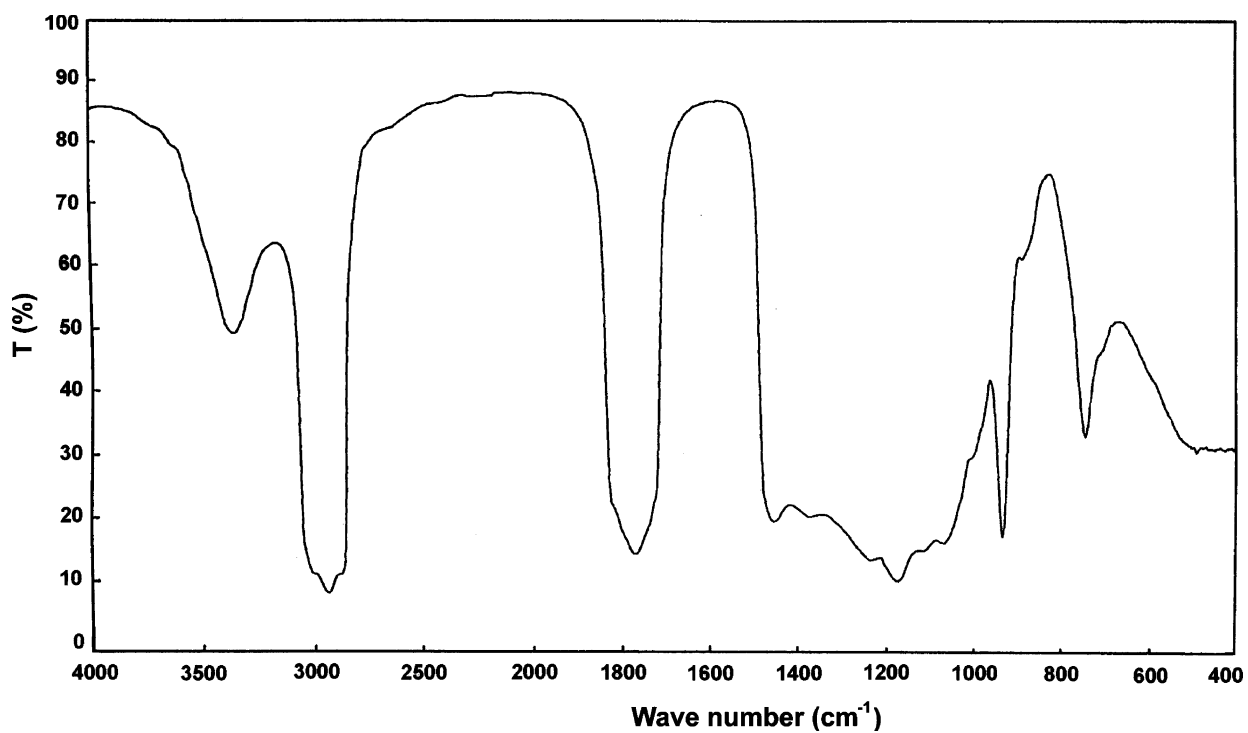


Fig. 4. IR of MMG produced by Method II.

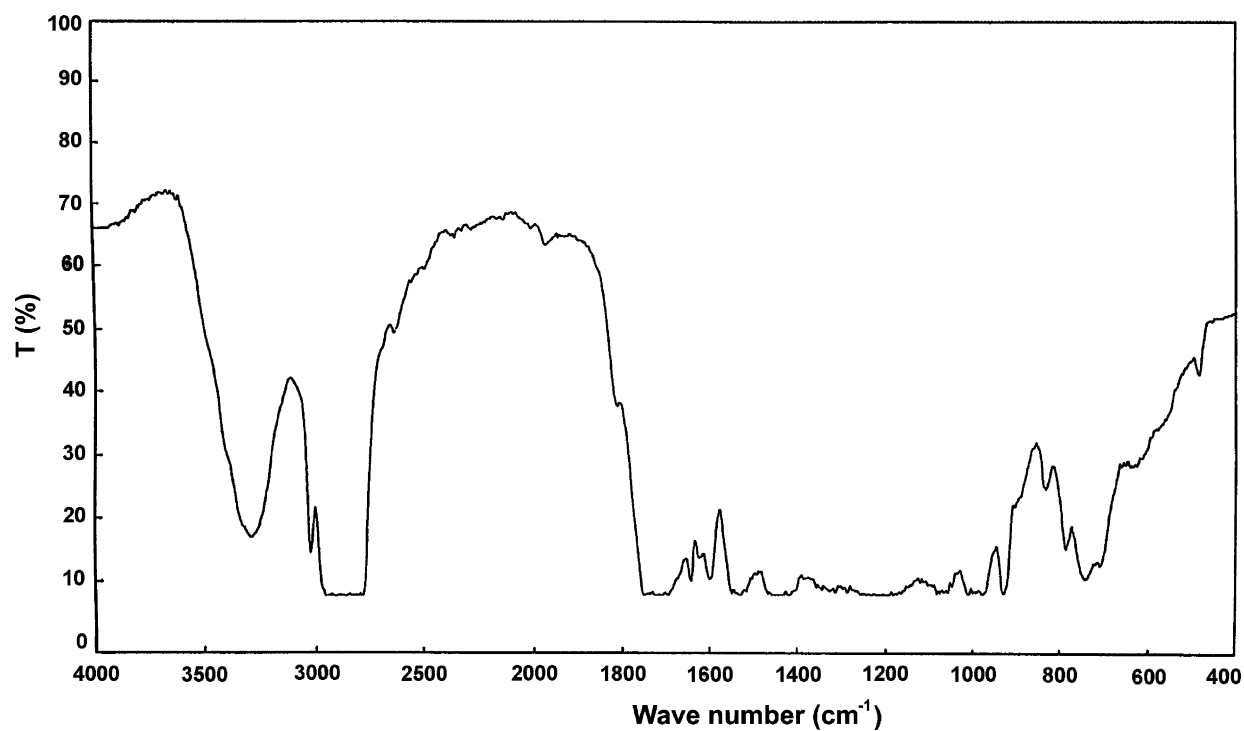


Fig. 5. IR spectrum of dry film of Sample A2.

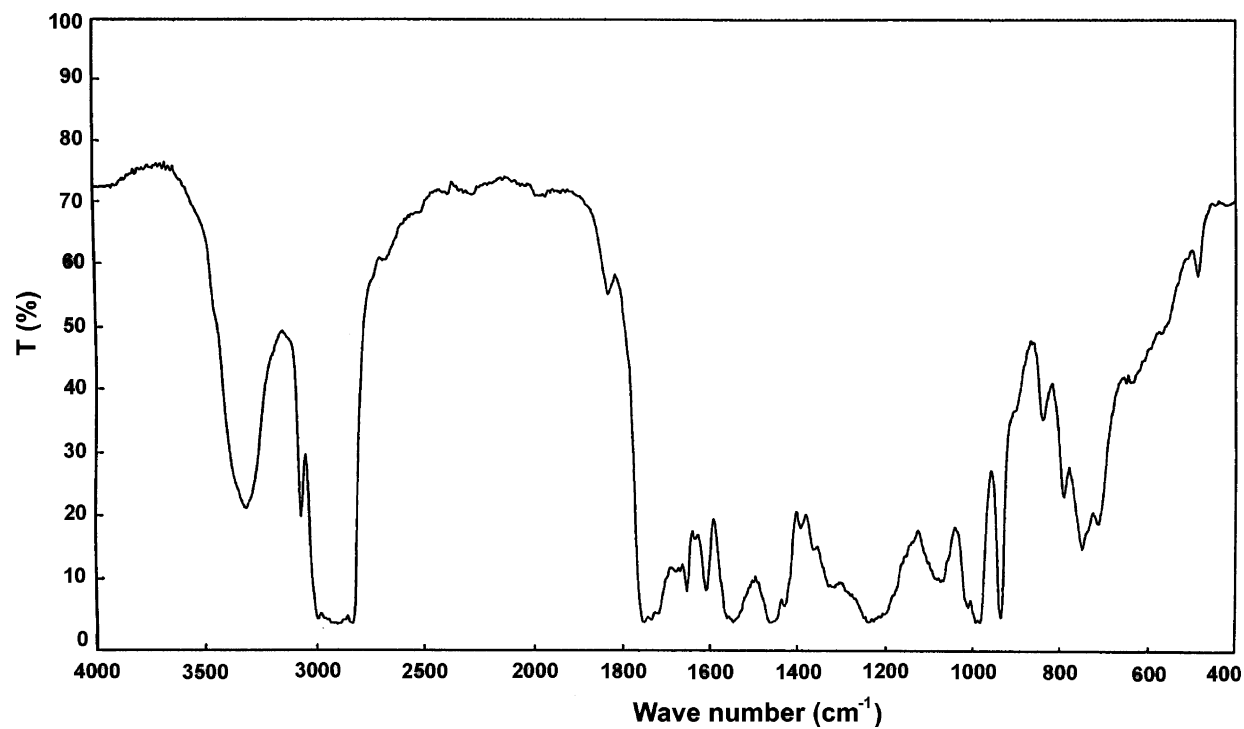


Fig. 6. IR spectrum of dry film of Sample B1.

Table 2
Gloss values for the samples

Method	Sample	Gloss value (%)		
		20°	60°	85°
I	A1	64.5	75.6	35.3
I	A2	21.0	53.2	48.0
I	A3	57.8	87.0	73.5
I	A4	25.5	55.0	49.2
II	B1	97.1	96.7	96.0
II	B2	86.8	90.3	95.0
II	B3	98.8	93.0	92.1
II	B4	78.3	89.0	87.3
II	B5	91.7	98.0	98.2

This difference is apparently due to higher ratio of fatty acid residues in the MMG produced by Method I.

3.6. Gloss test

A Rhopoint-Novoglass glossmeter was used to test the light reflection properties of the specimens. The gloss of dry films was measured at 20°, 60°, and 85°. The results were listed in Table 2. These results show that varnishes produced by using MMG-II had excellent gloss.

3.7. Hardness test

A Braive-Instrument Persoz Pendulum (No. 3034) was used. The principle of this test is based on the fact that the increase of hardness decreases the effect of friction, which increases the number of oscillations of the pendulum swinging on the test panel.

The dependence of hardness on the amount of MMG in the polymer can be seen in Figs. 7 and 8 for the varnishes produced by using MMG-I and MMG-II, respectively. In Fig. 7, the hardness decreases as the amount of MMG increases at all ratios used, while in Fig. 8 it first increases then decreases after 55% of MMG content. The decrease

of the amount of MMG results in a relative increase in the amount of HTPB. The double bond content of monoglyceride is about 1 per 9 carbon atoms and that of HTPB is about 1 per 4 carbon atoms. Therefore, HTPB gives denser cross-linking which results in higher hardness. It is also noticed that the varnish produced by using MMG-II has about twice higher hardness than that produced by using MMG-I. This is because MMG-I contains three fatty acid residues per molecule that makes the resin softer on drying whereas MMG-II contains only one fatty acid residue per molecule.

The decrease of hardness below 55% MMG in Fig. 8 can be due to the fact that hardness decreases with the increased branching. Branching in the polymer is due to the pendant fatty acid residues which come from MMG. The increase in the quantity of fatty acids increases side branches. There are two different cross-linkings which influence hardness: (i) the cross-linking due to double bonds of HTPB on the backbone and (ii) the cross-linking due to double bonds of fatty acid residues which are short branchings. As MMG decreases HTPB increases, so the double bonds on the backbone increase and the double bonds on the side branches decreases, or vice versa. The optimum ratio that balances both sources of hardness is 55% MMG in MMG-II containing varnish.

3.8. Mandrel bending test

A conical mandrel bending tester (Braive-Instruments No. 1510) was used. After coating the panels with the paint at a uniform thickness, they were fastened and bent over, and cracks were observed along the increasing radius of the conical mandrel. All samples passed bending test successfully without any cracks in the bent film. This is mainly due to the flexibility of the film which is a characteristic feature of polyurethanes.

3.9. Impact resistance test

A Gardner Impact tester (Model: 5510) was used for this test. A standard weight of (1+0.9 kg) was dropped on a film

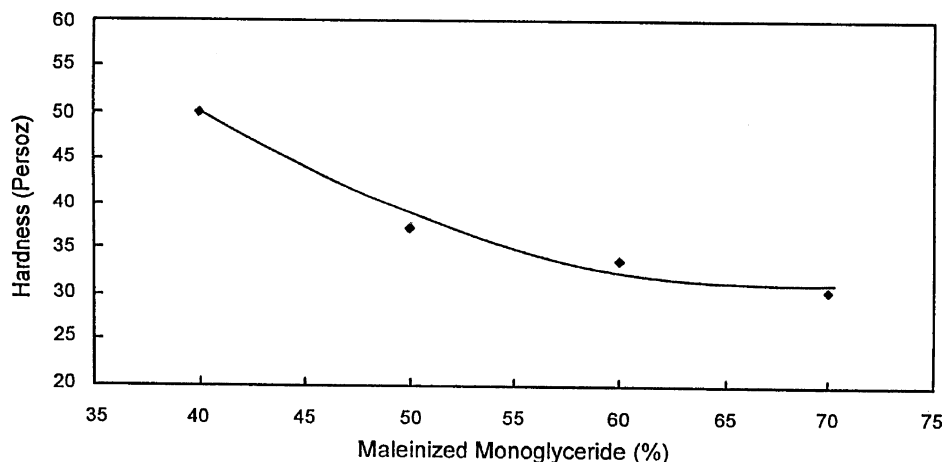


Fig. 7. Change of hardness with the percent of MMG-I in "MMG + HTPB".

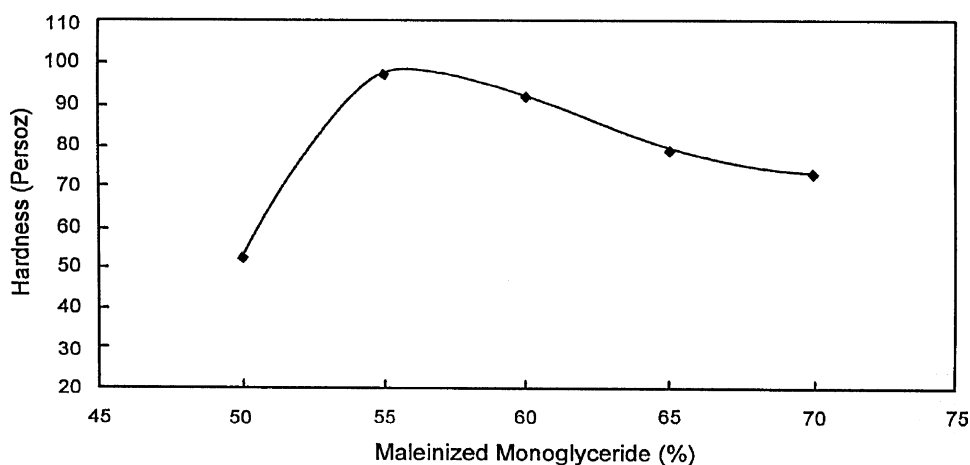


Fig. 8. Change of hardness with the percent of MMG-II in "MMG + HTPB".

coated on a metal plate from different heights. The impact value at which the film cracks is considered as the impact value for that sample. All tested samples showed resistance to impact up to 20 J which is the upper limit used without cracking.

3.10. Adhesion test

A crosshatch cutter was used to cut the film to produce a lattice pattern. After making a cross cut, the coating film was brushed with a soft tissue to remove any detached flakes of coating. Then, the pattern was checked according to ASTM D 3359 B. The maximum number of adhesion is "5" and the minimum is "0". Adhesion was tested on both a metal and a glass surface.

The adhesion test values for the samples are shown in Table 3. These results show that varnishes produced through Method I gives better adhesion than those produced through Method II. This is because MMG produced by Method I contains higher ratio of fatty acid residues, which improves adhesion. Also, it is obvious that Samples B1–B5 have better adhesion on metal plates than on glass plates.

Table 3
Adhesion test

Method	Sample	Adhesion number	
		Metal plate	Glass plate
I	A1	5 B	5 B
I	A2	5 B	5 B
I	A3	5 B	5 B
I	A4	5 B	5 B
II	B1	4 B	3 B
II	B2	5 B	0 B
II	B3	1 B	2 B
II	B4	1 B	1 B
II	B5	4 B	1 B

3.11. Abrasion resistance test

This test determines the resistance of coating film toward a falling abrasive. The abrasive is allowed to fall from a specified height through a guide tube onto a coated panel until the substrate becomes visible. The amount of abrasive per unit film thickness is reported as the abrasion resistance of the coating film. Silica sand was used as abrasive. All samples tested showed very good abrasion resistance and no significant loss in film thickness was observed.

4. Conclusions

1. The MMG-I containing varnish had darker color and lower gloss than the one that contains MMG-II.
2. In general, hardness showed a decreasing trend as the MMG ratio in the polyol increased.
3. The MMG-II-based varnish had higher hardness values than MMG-I-based varnish.
4. The optimum hardness in MMG-II-based varnish was achieved at 55% MMG ratio. This ratio may correspond to the optimum balance between the double bonds of HTPB and fatty acid residues.
5. The samples in which MMG-I was used showed much better adhesion compared to those in which MMG-II was used.
6. All samples tested for impact resistance showed resistance above 20 J.
7. All the tested samples passed conical mandrel bending test without any cracks.
8. No detectable loss in film thickness was observed after the abrasion resistance test.

References

- [1] P. Swaraj, Surface Coatings: Science and Technology, 2nd ed., Wiley, West Sussex, England, 1997, pp. 672–713.

- [2] H. Xiao, H.X. Xiao, B. Suthar, K.C. Frisch, Anionic blocked isocyanate-containing urethane prepolymer for coating applications, *J. Coat. Technol.* 67 (849) (1995) 19–26.
- [3] K.D. Weiss, Paint and coatings: a mature industry in transition, *Prog. Polym. Sci.* 22 (1997) 203–245.
- [4] P.K.T. Oldring, G. Hayward, A Manual for Resins for Surface Coatings, SITA Technology, 1987.
- [5] T. Kuwajima, K. Kida, S. Ishikura, US Patent 4,518,724 (1985).
- [6] P.G. Kooymans, J.J.M.H. Wintraecken, W.T. Raudenbusch, J.M.E. Seelen-Kruijssen, G.C.M. Schreurs, US Patent 4,401,774 (1983).
- [7] D.E. Knox, US Patent 5,093,463; 5,096,960; 5,137,965 (1992).
- [8] F.J. Slama, US Patent 5,883,180 (1999).
- [9] J.D. Elmore, D.S. Kincaid, P.C. Komar, J.E. Nielsen, *J. Coat. Technol.* 74 (931) (2002) 63–72.
- [10] C.L. Rodriguez, J. Weathers, Formulating water-based systems with propylene-oxide-based glycol ethers, *J. Coat. Technol.* 72 (905) (2000) 67–72.
- [11] C. Wang, G. Lin, J.H. Pae, F.N. Jones, Novel synthesis of carboxy-functional soybean acrylic-alkyd resins for water-reducible coatings, *J. Coat. Technol.* 72 (912) (2000) 55–61.
- [12] D.E. Fiori, D.A. Ley, R.J. Quinn, Effect of particle size distribution on the performance of two-component water-reducible acrylic polyurethane coatings using tertiary polyisocyanate crosslinkers, *J. Coat. Technol.* 72 (902) (2000) 63–69.
- [13] B. Zhong, C. Shaw, M. Rahim, J. Massingill, Novel coatings from soybean oil phosphate ester polyols, *J. Coat. Technol.* 73 (915) (2001) 53–57.
- [14] G. Gündüz, M. Gafaroğullari, Highly branched and tartaric acid-based water-borne resins, *J. Appl. Polym. Sci.* 80 (2001) 604–612.
- [15] G. Gündüz, Y. Idlibi, G. Akovali, *J. Coat. Technol.* 74 (931) (2002) 59–62.

Preparation and characterization of polyurethane foams using a palm oil-based polyol

Ryohei Tanaka ^{a,*}, Shigeo Hirose ^b, Hyoe Hatakeyama ^c

^a Department of Biomass Chemistry, Forestry and Forest Products Research Institute, 1, Matsu-no-sato, Tsukuba, Ibaraki 305-8687, Japan

^b Research Institute for Innovation in Sustainable Chemistry, Agency of Industry and Science Technology, Tsukuba, Ibaraki 305-8565, Japan

^c Graduate School of Engineering, Fukui University of Technology, 3-6-1, Gakuen, Fukui 910-8505, Japan

Received 7 February 2007; received in revised form 3 July 2007; accepted 3 July 2007

Available online 14 August 2007

Abstract

Polyurethane (PU) foams were prepared using a palm oil-based polyol (PO-p). At the first stage, palm oil was converted to monoglycerides as a new type of polyol by glycerolysis. A yield of the product reached 70% at reaction temperature of 90 °C by using an alkali catalyst and a solvent. At the second stage, PU foams were prepared from mixtures of the polyol and polyethylene glycol (PEG) or diethylene glycol (DEG) and an isocyanate compound. Characterization of the foams was carried out by thermal and mechanical analyses. The analyses showed that the chain motion of polyurethane becomes more flexible at the higher PO-p content in the whole polymer, which indicates that the monoglyceride molecules work as soft segments. The study here may lead to a development of a new type of polyurethane foams using palm oil as a raw material.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Palm oil; Glycerolysis; Monoglyceride; Polyurethane foam; Thermal analysis

1. Introduction

Palm oil (PO) is one of the most widely used plant oils in the world. It is produced from oil palm (*Elaeis guineensis*), which is grown in mass plantation in tropical countries such as Malaysia, Indonesia and Nigeria. The oil consists of triglycerides (Tri-G) and diglycerides (Di-G) and McNeill and Berger (1993) reported that 95% of the oil is Tri-G and 5% Di-G and carbons of the carboxyls are ranging 10–20 with or without double bonds. Palm oil is mainly used for food applications, but it is also used in some other industries such as soap, detergent and cosmetic production. In recent years, quite a number of research and development works have been carried out for utilizing palm oil in wide range of application, including bio-diesel fuel (Kalam and Masjuki, 2002; Mohamad and Ali, 2002).

Production of bio-based plastics and composites is thought to be one of the most important issues in the research and development for the protection of global environment (Wang et al., 2002; Yang et al., 2004). Research studies on bio-based polyurethanes have great potential in contributing to such development. In general, polyurethanes have been applied in various products such as thermal insulation and medical implants. The polymer is synthesized by a reaction of an isocyanate compound such as diphenylmethane diisocyanate (MDI) and a polyhydroxyl-containing polymer, i.e., polyol, such as polyethylene glycol (PEG). The preparation of various types of polyurethane products has been extensively studied in recent years, especially containing biomass-originated raw materials (Asano et al., 2001; Hatakeyama, 2002; Hatakeyama et al., 1998; Hatakeyama and Hatakeyama, 2004; Kurimoto et al., 2000; Kurimoto et al., 2001). Moreover, it has become clear from previous studies that the biomass-based PUs have biodegradability (Hatakeyama et al., 1995).

* Corresponding author. Tel.: +81 29 8298270; fax: +81 29 8743720.
E-mail address: ryohei@affrc.go.jp (R. Tanaka).

However, polyols for the polyurethane production are mostly derived from petrochemicals in general. Preparation of the polyurethanes from palm oil may expand the application of the oil in various areas as environment-friendly materials, because of its abundance and renewability. Moreover, it may lead to the replacement of petrochemical products by this naturally occurring plant oil.

There are several research studies of using palm oil for PU preparation (Chian and Gan, 1998; Tuan Noor Maznee et al., 2001). PO consists of mainly triglycerides (Tri-Gs), thus it is necessary to introduce hydroxyl groups to a molecule of Tri-G for urethane reaction. Siwayanan et al. (1999) have reported the preparation of polyols from PO by epoxidation for PU production. By their method, Tri-G molecules were converted to polyols by the reaction with epoxides, followed by the reaction with polyhydric alcohols.

Conversion of triglycerides to monoglycerides is an alternative method for introducing hydroxyls for palm oil, which becomes a 'palm oil-based polyols (PO-p)'. Monoglyceride (Mono-G) is a fatty acid ester of glycerol, and three main processes are widely known for its preparation: (1) glycerolysis of fats and oils with glycerol, (2) enzymatic synthesis by using lipase catalysts and (3) direct esterification of fatty acids or their alkyl esters with glycerol (Noureddini and Medikonduru, 1997). McNeill and Berger have reported a study of the enzymatic synthesis for the preparation of Mono-Gs from palm oil (McNeill and Berger, 1993). However, the glycerolysis has not been applied for palm oil to produce Mono-Gs so far.

In this paper, the first part describes the preparation of Mono-Gs from palm oil as a polyol by glycerolysis. Using this polyol (PO-p), polyurethane foams were prepared and their properties were examined in the second part of this paper.

2. Experimental procedures

The following two distinct processes are described in this section: (1) glycerolysis of palm oil for polyol preparation, and (2) preparation of polyurethane foams using the palm oil-based polyol.

2.1. Glycerolysis of palm oil for polyol preparation

2.1.1. Materials

Palm oil (PO) was kindly provided from MALPOM Industries BHD, Malaysia, as a crude grade (=CPO, crude palm oil). Glycerol, sodium hydroxide (NaOH) and *t*-butyl alcohol (*t*-BuOH) were purchased from Wako Pure Chemical Industries, LTD, Japan. Tetradecane (TD), which was used as an internal standard for the quantification, was also purchased from the Wako. PO and the chemicals were used without further purification.

It has been reported by McNeill and Berger (1993) that the carboxyl groups of palm oil consist of 45.6 wt% of $\text{CH}_3(\text{CH}_2)_{14}\text{COO}-$ (C16:0, palmitic), 36.4 wt%

$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}-$ (C18:1, oleic) and 10.3% $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COO}-$ (C18:2, linoleic). Using their precise data for the carboxyls, molecular weights of the PO triglycerides and diglycerides are calculated to be 846.6 and 595.1, respectively, assuming that Tri-G and Di-G have the same carboxyl contents. Moreover, a carboxyl group is expressed as C *x*:*y* in this paper, which *x* is the number of C and *y* the number of double bonds.

2.1.2. Methods

Approximately 20 g of glycerol was placed in a 300 mL three-necked round-bottom flask, equipped with a water-cooling condenser and a thermometer. Accurately weighed PO was added to the flask at the weight ranging 10 ~ 40 g, together with 20 mL of *t*-BuOH as a solvent. Tetradecane (TD) was also accurately weighed to 0.4 g and added to the mixture as an internal standard. 0.2 g of NaOH was then dissolved into the mixture, which works as a catalyst of the glycerolysis.

Placing the flask in a mantle heater, the mixture was heated to approximately 90 °C and was kept for 2 h with continuous stirring. After the reaction completed, the flask was immediately cooled down to the room temperature (*ca.* 20 °C). Ten percent hydrochloride (HCl) (1.8 g) solution was then added to neutralize the alkali catalyst. A homogeneous mixture obtained was dark orange, which was originated from the color of β -carotene naturally contained in PO.

Transesterification of triglyceride (Tri-G) by the glycerolysis undergoes in the presence of an alkali catalyst at an elevated temperature. At this stage, the products must be monoglyceride (Mono-G) and diglyceride (Di-G). Then the Di-G does react with glycerol, resulting in the production of two Mono-Gs. Therefore, one Tri-G can be theoretically converted to 3 Mono-Gs by the glycerolysis.

Quantitative analyses of the Mono-G products were carried out by capillary gas chromatography (GC), according to AOCS (The American Oil Chemists' Society) Official Method Cd 11b-91. A prepared mixture without purification was reacted with bis-trimethylsilyl-trifluoro-acetamide (BSTFA) and trimethylchlorosilane (TMCS) for the conversion of its components to trimethylsilyl (TMS) derivatives. GC analyses of the TMS-derivatized samples were carried out by using a HP6890 GC (Agilent Technologies LTD) equipped with a flame indicator detector (FID) and a capillary column of HP-5 (crosslinked 5% PH ME siloxane).

Prior to the reacted samples, calibration curves were created for two major Mono-G products, i.e., C16:0 and C18:1 Mono-Gs, as C16:0 and C18:1 carboxyls are dominant in the composition of palm oil Tri-Gs. Standard samples of the Mono-Gs were purchased from Sigma Chemical Co. Standard solutions were prepared by dissolving a Mono-G and an internal standard of tetradecane (TD) with various weight ratios in pyridine. The Mono-G in a standard solution was TMS-derivatized as same as the reaction mixture and was analyzed by the GC. Ratios of

the peak area between the Mono-G and TD were calculated and plotted against the weight ratios of the two. Linear relationships were obtained for both C16:0 and C18:1 Mono-Gs, which were used for quantitative analysis of the Mono-Gs in the reacted mixtures.

From the quantitative analysis, the best PO/glycerol ratio was determined for the preparation of a palm oil-based polyol (PO-p), which showed the highest yield of the Mono-Gs. Then the mixture was subjected to the purification process for the removal of *t*-BuOH and unreacted glycerol. At first, the alcohol was removed by the evaporation under vacuum. Then twice a volume of *n*-hexane was added to the remained mixture in a glass container with a screw cap. The container was shaken vigorously to dissolve Mono-G products into the *n*-hexane. After leaving the mixture for overnight, the separation occurred, resulting in an *n*-hexane layer at the top and an unreacted glycerol layer at the bottom. The hexane layer was analyzed by GC and the removal rate of the unreacted glycerol was determined in comparison of the peak areas of glycerol, TD and the Mono-Gs before and after the purification process.

2.2. Preparation of polyurethane foams using the palm oil-based polyol

2.2.1. Materials

A palm oil-based polyol (PO-p) used in this section was prepared by the glycerolysis and the purification process as described in the previous section. Polyethylene glycol (PEG) having molecular weight of 200, diethylene glycol (DEG) and poly (phenylene methane) polyisocyanate (MDI polymer) was commercially obtained.

2.2.2. Methods

A polyurethane (PU) foam was prepared by mixing the PO-p with either PEG or DEG at the beginning. Then 0.1% of dibutyltin dilaurate (DBTDL), a catalyst, was added to the mixture, together with water (1%) and a surfactant (0.2%), forming a 'pre-mixture'. The content of PO-p in each pre-mixture varied between 20 and 80 wt%. Then MDI was added and the reaction was allowed to proceed at room temperature with vigorous stirring. Molecular ratio of isocyanate to hydroxyl groups (NCO/OH ratio) was kept at 1.2 for all samples.

Thermal analyses of thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out for the PU foams. A Seiko TG/DTA 220-SSC6200 and a Seiko DSC 6200 were used for TG and DSC measurements, respectively. For the TG analysis, an accurately weighed sample (approx. 7 mg) was heated from 25 to 600 °C at the rate of 20 °C/min with N₂ gas purging. The DSC measurement was carried out for a sample (accurately weight, approx. 5 mg) at heating rate of 10 °C/min between –120 and 120 °C under N₂ atmosphere.

Mechanical strengths and moduli of PU foams were determined using a Shimadzu Autograph AG-10TB,

according to JIS K7220. A foam sample was cut in a cube of 1 cm × 1 cm × 1 cm. Compressive strength and modulus of each sample were recorded for three replicates from each PU foam sample. Prior to the measurement, an accurate size and a weight were measured for the sample for calculating its density.

3. Results and discussion

3.1. Preparation of palm oil-based polyol by glycerolysis

Quantitative analysis was carried out for detecting C16:0 and C18:1 carboxyl groups converted to Mono-Gs after the reaction of glycerolysis. As mentioned previously, fatty acids of C16:0 and C18:1 carboxyls account for 45.6 and 36.4 wt%, respectively, making total 82% of the whole fatty acids from PO. When glycerolysis occurs, it seems that carboxyl groups at the C1 and C3 positions of Tri-Gs are more likely to be exchanged by OH groups, compared with the C2 position. It has been reported by Deffense that more than 80% of Tri-G has C16:0 and/or C18:1 at the C1 and/or C3 positions (Deffense, 1985). From this aspect, the quantitative analyses of Mono-G with C16:0 and C18:1 carboxyls were considered to represent the total efficiency of conversion from PO to Mono-G by the glycerolysis.

A mixture obtained by the reaction consists of glycerides (mainly Mono-Gs), unreacted glycerol and PO and *t*-BuOH, together with a trace amount of NaCl and water after the neutralization of the catalyst. GC analysis of the mixture was carried out for determining the reaction products. Assuming that there was no effect on the internal standard of TD during the glycerolysis, the amounts of C16:0 and C18:1 monoglyceride products were calculated by using the calibration curves of the standards and the amount of TD added. Results of three reaction mixtures containing different amounts of PO are given in Table 1.

The production percentage shown in the table is simply calculated by dividing total amount of C16:0 and C18:1 Mono-Gs by an initial amount of PO. Theoretically, one molecule of Tri-G reacts with two molecules of glycerol, i.e., 0.5 of (PO/glycerol) ratio, which results in the production of three Mono-Gs. However, Sample 3 in Table 1 had only reacted approximately 1%, whereas the yield was more than 70% when the glycerol added are far much in excess as Sample 1. These results show that the glycerolysis reaction does occur at reaction conditions applied in this study with the reaction efficiency dependent on the PO/glycerol ratio. On the other hand, nearly 90% of glycerol molecules are left unreacted for producing Mono-Gs at the higher yield. This suggests that an optimum condition of glycerolysis should be examined for the Mono-G production with high efficiency.

By more precise calculation, the conversion rates of the monoglycerides have been determined as molecular masses of fatty acids before and after the glycerolysis, which are

Table 1
Percentage and conversion rate of monoglycerides (Mono-Gs) produced at various PO-glycerol ratios

No.	PO used (g)	PO/glycerol molar ratio	Amount of mono-G produced (g)		Production (%)	Conversion rate (%)	
			C16:0	C18:1		C16:0	C18:1
1	10.2	0.05	3.49	3.89	72.4	60.9	86.5
2	20.0	0.1	1.06	0.945	10.0	9.35	10.7
3	40.0	0.2	0.372	0.122	1.24	1.64	0.690

also given in Table 1. The calculation was carried out as follows:

Conversion rate (%)

$$= \frac{W_{\text{Mono-G}}}{M_{\text{Mono-G}}} \times \left(\frac{W_{\text{PO}}(\text{g}) \times 0.95}{846.6} \times 3 + \frac{W_{\text{PO}}(\text{g}) \times 0.05}{595.1} \times 2 \right) \times \text{mol\% of the carboxyl in PO} \times 100 \quad (1)$$

where $W_{\text{Mono-G}}$ is the monoglyceride produced, $M_{\text{Mono-G}}$ is molecular weight of the Mono-G, W_{PO} palm oil added at the beginning. Moreover, mol% of the carboxyl in PO is 48.4 and 35.1 for C16:0 and for C18:1, respectively.

The result shows a significant difference between C16:0 Mono-G and C18:1 Mono-G, especially at a higher yield. It may arise from the difference in the position of carboxyl groups at triglyceride (Tri-G) molecules. According to Defense, 82–90% of Tri-Gs has C16:0 carboxyl group at the C1 and/or C3 and only 14–17% of them has the carboxyl at the C2 position (Defense, 1985). On the other hand, only 38–41% of Tri-Gs has C18:1 carboxyl group at the C1 and/or C3, but 59–65% at the C2. The analyses carried out in this study have determined only Mono-Gs with a carboxyl group at the C1 (or C3) position. Therefore, the higher yield of 1-Mono-G with C18:1 may be produced efficiently by the reaction between the C2-position C18:1 carboxyl groups and glycerol molecules. On the other hand, the C1-position C16:0 carboxyl groups may be slightly less reactive compared to the C18:1 or, possibly, more 2-Mono-G with C16:0 may be produced. It is necessary to have further studies to investigate the details of the glycerolysis reaction.

A monoglyceride mixture prepared at the same condition as Sample 1 in Table 1 was analyzed by GC before and after the purification. The analysis data clearly shows that the peak of glycerol becomes much smaller after the purification when compared with the peaks of tetradecane (=TD, internal standard) and the Mono-Gs. Extraction of Mono-Gs into *n*-hexane was according to the method by Corma et al. for the separation of fatty products from glycerol (Corma et al., 1998). However, the unreacted glycerol seemed to be partially solubilized in the hexane layer, so that the peak of glycerol was still detected after the purification process. Assuming that there was no loss of TD, C16:0 Mono-G and C18:1 Mono-G, unreacted glycerol in the purified product mixture was analyzed from the comparison of the peak areas between glycerol and these substances. Ratios of the peak areas were calculated from the calibration curves as given in Table 2, which Ratio 1

Table 2
Removal rate of unreacted glycerol from monoglyceride products

	Ratio of peak areas		Removal rate (%)
	Before (ratio 1)	After (ratio 2)	
Glycerol/TD	84.0	8.38	90.0
Glycerol/C16:0 Mono-G	9.66	1.02	89.4
Glycerol/C18:1 1Mono-G	8.29	0.846	89.8

TD: tetradecane; Mono-G: monoglyceride.

Removal rate (%) = (1 – Ratio2/Ratio1) × 100.

expresses the ratio of the peak area of glycerol to that of a standard substance before the purification and Ratio 2 expresses the same peak area ratio after the purification. The removal rate of the glycerol was estimated from the Ratio 1 and 2.

It shows that almost 90% of unreacted glycerol has been removed by the purification procedure. There is no difference among the three standard substances, TD and Mono-Gs, which may indicate that there is no loss in the extraction of Mono-Gs and TD during the purification process. Although the removal of unreacted glycerol was not 100%, the purification of Mono-Gs by using *n*-hexane seemed to be quite effective for the production of Mono-Gs studied here. In addition, a larger scale preparation was carried out to produce the Mono-Gs from 200 g of PO and 400 g of glycerol. The removal rate of unreacted glycerol was 83–85%, calculated from the Mono-G standards. This result may indicate that the purification process employed in this study is applicable to a large scale production of Mono-Gs by palm oil glycerolysis.

3.2. Preparation and characterization of palm oil-based polyurethane foams

Polyurethane (PU) foams prepared in this study were semi-rigid type and the foams became more dark and yellowish with increasing PO-p content in the pre-mixture, probably because of the original orange colour of palm oil. Apparent densities of the PEG-contained foams were scattered between 0.05 and 0.13 g/cm³, whereas the DEG-contained foams had almost the same values of 0.06–0.07 g/cm³. It has been reported that good foam samples have the densities of ca. 0.04–0.05 g/cm³ (Hirose et al., 1994). From this viewpoint, it happened that the DEG-contained foams prepared in this study had better shapes than the foams containing PEG.

Thermal decomposition behaviour of PU foams was studied by thermogravimetry (TG). Fig. 1 shows TG curves of PEG- or DEG-contained PU foams. Each curve expresses the change in the percentage of weight residue, $(m_T/m_{20}) \times 100$, where m_T is the sample weight at temperature T and m_{20} at 20 °C (starting temperature). The curves show a multi-step decrease in this temperature range, especially with high PO-p contents. The starting temperature of the thermal decomposition (T_{di}) was determined as the temperature at which samples show a 1% weight loss. Thermal decomposition temperature (T_d) was determined as the temperature of the cross point of extrapolated baseline and tangent line in a TG curve.

T_{di} , T_d and weight residue at 500 °C were plotted against the PO-p content in the pre-mixture for the PU foams as shown in Fig. 2. For all foams, T_d decreased with increasing PO-p content, whereas T_{di} kept almost constant at ca.

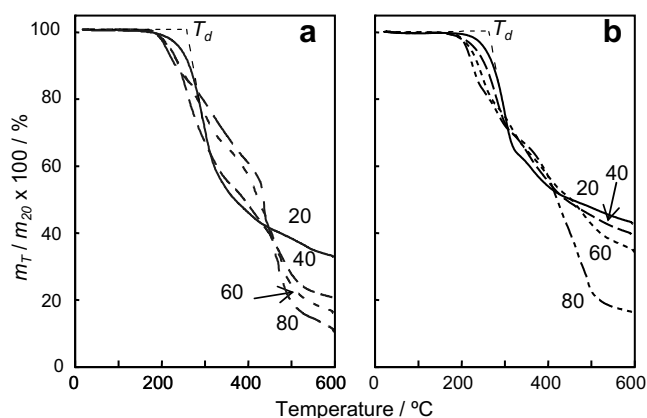


Fig. 1. TG curves of the PEG- or DEG-contained foams having various PO-p contents as indicated on each curve (%): (a) PEG; (b) DEG.

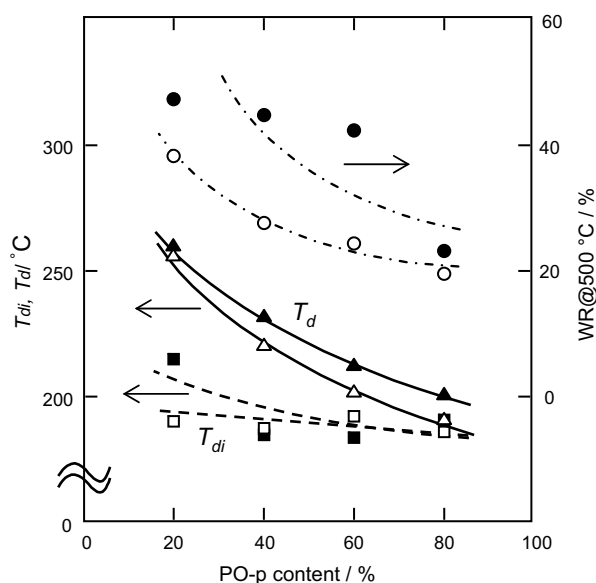


Fig. 2. Starting (T_{di}) and thermal decomposition (T_d) temperatures and weight residues (WR@500 °C) of PU foams having various PO-p content; PEG series: open symbols; DEG series: closed symbols.

200 °C for both PEG and DEG series. From a separate study, thermal degradation of PO-p itself started at very early stage of the TG analysis, i.e., below 100 °C. Kurimoto et al. showed that the degradation of PEG starts at around 200–250 °C (Kurimoto et al., 2001). Moreover, it has been studied that urethane bonds dissociate to form hydroxyl and isocyanate groups at around 250 °C (Hirose et al., 1994). According to these observations, it is considered that the dissociation of urethane bonding starts at T_{di} for all PU foams studied here, irrespective of the PO-p content. The decrease of T_d along the PO-p content, on the other hand, may be due to the introduction of thermally unstable PO-p molecules into PU structure. Therefore, T_d seems to be the decomposition temperature of the polyol molecules, either PO-p or the ethylene glycols.

For weight residue (WR) at 500 °C, the percentage decreased with increasing PO-p content for both PEG and DEG series. As same as the T_d decrease, this indicates that PU structure has become thermally unstable by introducing PO-p segments into ethylene glycol segments of PEG or DEG.

It can also be observed from Fig. 2 that T_d and WR of the DEG series seem to be higher than those of the PEG series, irrespective of PO-p content. Both DEG and PEG have two OH groups in one molecule. Molecular weight of DEG is 106 and that of PEG used in this study is 194, as commercially labelled 200. It means that 100 g of DEG has approximately 2 mols of OH groups, whereas 1 mol for PEG. When the PO-p content is expressed in wt%, total OH content must be higher for a DEG-contained sample than a PEG-contained sample at the same PO-p content. As been mentioned in Section 2.1.2, the molecular ratio of isocyanate groups to hydroxyl groups (NCO/OH) was kept constant at 1.2 for all samples studied here. Therefore, the urethane linkage between OH groups and NCO groups are more in the DEG series and less in the PEG series. Moreover, NCO groups are quite reactive, which may create additional bondings to the urethane linkage. It is also likely to happen in the DEG samples rather than the PEG samples. This may lead to the different behaviour between the both series for the thermal decomposition as shown in Fig. 2.

DSC analysis was carried out to study phase transition of PU foams. Fig. 3 shows stacked DSC curves of PU's containing PEG or DEG. As shown in the figure, two inflectional points were observed by the gap in the baseline due to glass transition (T_{g1} and T_{g2}) for each sample. T_g 's of both series were plotted against the PO-p contents as Fig. 4. The glass transition occurs as a step increase in the heat capacity (C_p) of the sample during heating, which is due to an enhancement of molecular motion in the polymer (Hatakeyama and Quinn, 1994). From each DSC curve, heat capacity difference (ΔC_p) was determined at each transition temperature, ranging 0.02 to 0.07 J/g K for T_{g1} 's and 0.11 to 0.39 for T_{g2} 's. As the ΔC_p at T_{g2} were much larger than the ΔC_p at T_{g1} , it is reasonable to consider that T_{g2} corresponds to relatively large enhancement

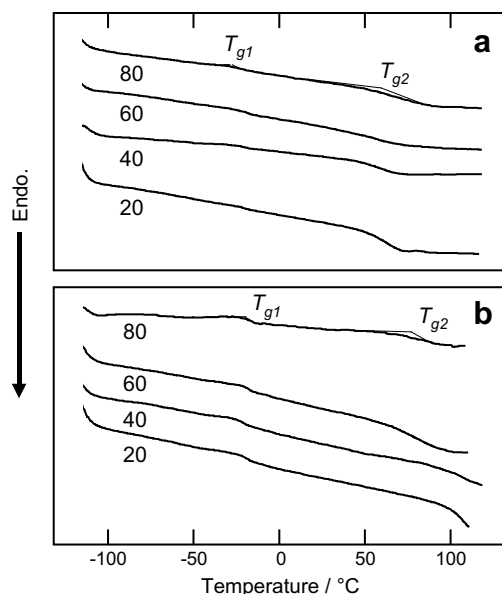


Fig. 3. DSC curves of the PEG- or DEG-containing foams having various PO-p contents as indicated on each curve (%): (a) PEG; (b) DEG.

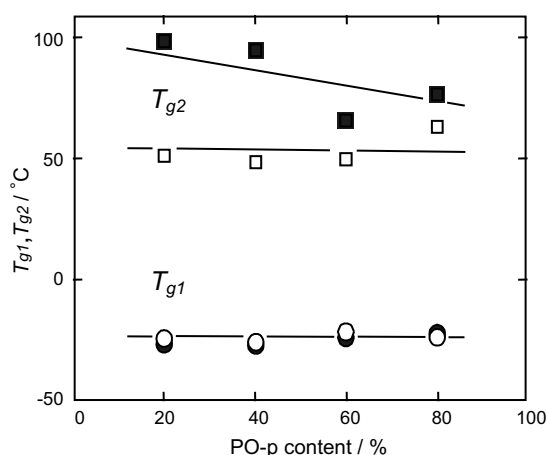


Fig. 4. Relationship between glass transition temperatures (T_{g1} and T_{g2}) and PO-p content; PEG series: open symbols; DEG series: closed symbols.

in molecular motion, whereas T_{g1} is due to rather small movement.

Glass transition at T_{g1} may be attributed to long alkyl carboxyls from the PO-p molecules. The carboxyl groups are assumed to be sticking out from the backbone formed with oxyethylene, glycerol and urethane bonds. Therefore the relaxation of the carboxyls may be independent from the backbone, which leads to constant T_{g1} for all samples.

Enhancement of molecular motion at T_{g2} , on the other hand, may be due to the backbone of PU. As PEG is originally the longer oxyethylene molecule when compared with DEG, the backbone containing PEG is more flexible than that with DEG molecules. This may result in the lower T_{g2} for the PEG series as shown in Fig. 4. However, the dependence of T_{g2} on PO-p content is not clear for both DEG and PEG series. For the DEG series, T_{g2} seems to be decreasing along the PO-p content, whereas it looks almost constant

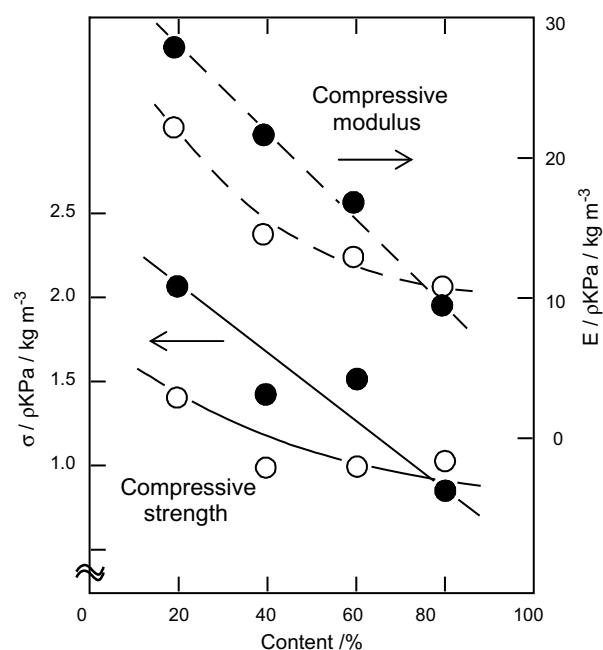


Fig. 5. Changes of compressive strength (σ/ρ) and compressive modulus (E/ρ) along PO-p content; PEG series: open symbols; DEG series: closed symbols.

for the PEG-containing PU. The difference may be related to some complicated alignment and interaction of oxyethylene and PO-p molecules, so that it is necessary to conduct further investigation on the effect of the polyol structure and T_{g2} .

Mechanical properties of the PU foams prepared in this study were also determined as shown in Fig. 5 for compressive strengths (δ) and moduli (E). Each strength or modulus was divided by the sample density (ρ), because these properties are very much dependent on the density and densities of the foam samples were so scattered, especially for the PEG series, as been mentioned previously.

The figure expresses changes of δ/ρ and E/ρ with the PO-p content in the mixtures with DEG or PEG. It is clearly shown that each parameter for both series decreases with increasing the PO-p content. It may be in good agreement with the results of DSC analysis, which suggests that the PO-p molecules work as soft segments in the PU foam. When a pressure is applied, the sample containing more soft segments may be easier to be compressed. Therefore, it reflects in the mechanical properties of the PU foams prepared in this study.

Difference between the DEG series and the PEG series may be the same reason as the phenomena observed at the thermal analyses. The main chain motion in the whole PU is more restricted for the foam containing DEG than that with PEG. So the effect of the PO-p content is the greater for the DEG series.

4. Conclusions

In this study, monoglycerides are derived from palm oil by glycerolysis at the yield of 70%, using an alkali catalyst

and a solvent. After the glycerolysis, 90% of unreacted glycerol is removed by the purification process using *n*-hexane.

Polyurethane foams are prepared using the palm oil-based polyol (PO-p), mixed with polyethlen glycol (PEG) or diethylene glycole (DEG). Chain motion of polyurethane becomes more flexible at the higher PO-p content in the polymer. Monoglyceride molecules, main components of the PO-p, work as soft segments in the whole PU because of the presence of long alkyl chains.

Acknowledgements

The authors are grateful to Dr. Tatsuko Hatakeyama of Lignocel Research Ltd. for her suggestions and critical comments on the manuscript. We also would like to thank Dr. Masahiro Funabashi of Agency of Industry and Science Technology for his help and comments on the mechanical tests.

References

- Asano, Y., Hatakeyama, H., Hirose, S., Hatakeyama, T., 2001. Preparation and physical properties of saccharide-based flexible polyurethane foams. In: Kennedy, J.F., Phillips, G.O., Williams, P.A., Hatakeyama, H. (Eds.), *Recent advances in environmentally compatible polymers*. Woodhead Publishing Ltd., Cambridge, UK, pp. 241–246.
- Chian, K.S., Gan, L.H., 1998. Development of a rigid polyurethane foam from palm oil. *J. Appl. Polym. Sci.* 65, 509–515.
- Corma, A., Iborra, S., Miquel, S., Primo, J., 1998. Catalysts for the production of fine chemicals – Production of food emulsifier, monoglycerides, by glycerolysis of fats with solid base catalysts. *J. Catal.* 173, 315–321.
- Deffense, E., 1985. Fractionation of palm oil. *J. Am. Oil Chem. Soc. (JAOCS)*. 62, 376–385.
- Hatakeyama, H., 2002. Thermal analysis of environmentally compatible polymers containing plant components in the main chain. *J. Therm. Anal. Calor.* 70, 755–795.
- Hatakeyama, T., Hatakeyama, H., 2004. *Thermal Properties of Green Polymers and Biocomposites*. Kluwer Academic Publishers, Dordrecht, the Netherlands.
- Hatakeyama, T., Quinn, F.X., 1994. *Thermal Analysis: Fundamentals and Applications to Polymer Science*. John Wiley & Sons, Chichester, UK.
- Hatakeyama, H., Hirose, S., Hatakeyama, T., Nakamura, K., Kobashigawa, K., Morohoshi, N., 1995. Biodegradable polyurethanes from plant components. *J. Macromol. Sci.: Pure Appl. Chem.* A32, 743–750.
- Hatakeyama, T., Tokashiki, T., Hatakeyama, H., 1998. Thermal properties of polyurethanes derived from molasses before and after biodegradation. *Macromol. Symp.* 130, 139–150.
- Hirose, S., Kobashigawa, K., Hatakeyama, H., 1994. Preparation and physical properties of polyurethanes derived from molasses. *Sen-i Gakkaishi*. 50, 538–542.
- Kalam, M.A., Masjuki, H.H., 2002. Biodiesel from palm oil – an analysis of its properties and potential. *Biomass Bioenergy* 23, 471–479.
- Kurimoto, Y., Takeda, M., Koizumi, A., Yamauchi, S., Doi, S., Tamura, Y., 2000. Mechanical properties of polyurethane films prepared from liquefied wood with polymeric MDI. *Bioresource Technol.* 74, 151–157.
- Kurimoto, Y., Takeda, M., Doi, S., Tamura, Y., Ono, H., 2001. Network structures and thermal properties of polyurethane films prepared from liquefied wood. *Bioresource Technol.* 77, 33–40.
- McNeill, G.P., Berger, R.G., 1993. Enzymatic glycerolysis of palm oil fractions and a palm oil based model mixture: Relationship between fatty acid composition and monoglyceride yield. *Food Biotechnol.* 7, 75–87.
- Mohamad, I.A.I-W., Ali, O.A.I-S., 2002. Experimental evaluation of the transesterification of waste palm oil into Biodiesel. *Bioresource Technology*. 85, 253–256.
- Noureddini, H., Medikonduru, V., 1997. Glycerolysis of fats and methyl esters. *J. Am. Oil Chem. Soc. (JAOCS)*. 74, 419–425.
- Siwayanan, P., Ooi, T.L., Shaari, N.Z.K., Ahmad, S., Wiese, D., Chua, M.C., 1999. Recent development in palm-based polyols. In: *Proceedings of the 1999 PORIM International Palm Oil Congress (Oleochemicals)*. Palm Oil Research Institute Malaysia, Kuala Lumpur, pp. 59–64.
- Tuan Noor Maznee, T.I., Norin, Z.K.S., Ooi, T.L., Salmiah, A., Gan, L.H., 2001. Effect of additives on palm-based polyurethane foams. *J. Oil Palm Res.* 13, 7–15.
- Wang, Q., Narita, J., Xie, W., Ohsumi, Y., Kusano, K., Shirai, Y., Ogawa, H.I., 2002. Effects of anaerobic/aerobic incubation and storage temperature on preservation and deodorization of kitchen garbage. *Bioresource Technology*. 84, 213–220.
- Yang, H.-S., Kim, D.-J., Lee, Y.-K., Kim, H.-J., Jeon, J.-Y., Kang, C.-W., 2004. Possibility of using waste tire composites reinforced with rice straw as construction materials. *Bioresource Technol.* 95, 61–65.

Search history

Search 1: FT=(obtain* and method and (palm oil) and polyol and (sodium hydroxide) and monoglyceride) (Results 568)
Search 2: 1 and (toluenesulfonic acid) (Results 1)
Search 3: 1 and (maleic anhydride) (Results 23)
Search 4: 3 and polyurethane (Results 5)
Search 5: FT=(synthesizing and maleinized and monoglyceride and derivative and (palm oil)) (Results 0)
Search 6: synthesiz* and maleinize* and monoglyceride and (palm oil) (Results 0)
Search 7: synthesis* and maleinized* and monoglyceride and (palm oil) (Results 0)
Search 8: synthesis and maleinized* and monoglyceride and (palm oil) (Results 0)

Title: ADHESIVE PEEL-FORMING FORMULATIONS FOR DERMAL DELIVERY OF DRUGS AND METHODS OF USING THE SAME

Abstract: Source: US2005276842A The present invention is drawn to adhesive peel-forming formulations for dermal delivery of a drug. The formulation can include a drug, a solvent vehicle, and a peel-forming agent. The solvent vehicle can include a volatile solvent system having one or more volatile solvent, and a non-volatile solvent system having one or more non-volatile solvent, wherein the non-volatile solvent system has a solubility for the drug that is within a window of operable solubility for the drug such that the drug can be delivered at therapeutically effective rates over a sustained period of time. The formulation can have a viscosity suitable for application to a skin surface prior to evaporation of the volatile solvents system. When applied to the skin, the formulation can form a solidified peelable layer after at least a portion of the volatile solvent system is evaporated.

Classifications:

International (IPC 8-9): A01N37/12 A01N43/54 A61F13/00 A61F13/02 A61K31/00 A61K31/045 A61K31/07 A61K31/13 A61K31/135 A61K31/137 A61K31/165 A61K31/167 A61K31/19 A61K31/192 A61K31/195 A61K31/196 A61K31/203 A61K31/24 A61K31/245 A61K31/275 A61K31/327 A61K31/4025 A61K31/405 A61K31/415 A61K31/4164 A61K31/4168 A61K31/4174 A61K31/437 A61K31/4439 A61K31/445 A61K31/473 A61K31/4745 A61K31/485 A61K31/505 A61K31/513 A61K31/517 A61K31/52 A61K31/522 A61K31/5415 A61K31/56 A61K31/566 A61K31/567 A61K31/568 A61K31/569 A61K31/57 A61K31/573 A61K31/58 A61K31/59 A61K31/60 A61K31/74 A61K35/64 A61K38/13 A61K38/21 A61K45/00 A61K47/04 A61K47/06 A61K47/08 A61K47/10 A61K47/12 A61K47/14 A61K47/18 A61K47/20 A61K47/22 A61K47/24 A61K47/30 A61K47/32 A61K47/34 A61K47/36 A61K47/38 A61K47/40 A61K47/42 A61K47/44 A61K47/46 A61K8/00 A61K8/02 A61K9/00 A61K9/06 A61K9/08 A61K9/10 A61K9/12 A61K9/14 A61K9/70 A61L15/16 A61L26/00 A61M37/00 A61P17/00 A61P17/06 A61P17/14 A61P21/00 A61P25/00 A61P25/04 A61P25/30 A61P29/00 A61P31/00 A61P31/04 A61P31/10 A61P31/12 A61P31/22 (Advanced/Invention); A61F13/00 A61F13/02 A61K9/70 (Advanced/Non-invention); A01N37/12 A61F13/00 A61F13/02 A61K31/00 A61K31/04 A61K31/045 A61K31/13 A61K31/135 A61K31/165 A61K31/167 A61K31/185 A61K31/21 A61K31/275 A61K31/415 A61K31/4164 A61K31/4427 A61K31/445 A61K31/473 A61K31/4738 A61K31/505 A61K31/513 A61K31/519 A61K31/56 A61K31/568 A61K31/57 A61K31/59 A61K31/60 A61K31/74 A61K35/56 A61K38/12 A61K45/00 A61K47/02 A61K47/06 A61K47/08 A61K47/10 A61K47/12 A61K47/14 A61K47/16 A61K47/20 A61K47/22 A61K47/24 A61K47/30 A61K47/32 A61K47/34 A61K47/36 A61K47/38 A61K47/40 A61K47/42 A61K47/44 A61K47/46 A61K8/02 A61K9/00 A61K9/06 A61K9/08 A61K9/12 A61K9/70 A61L15/16 A61M37/00 A61P17/00 A61P21/00 A61P25/00 A61P29/00 A61P31/00 (Core/Invention); A61F13/00 (Core/Non-invention)

International (IPC 1-7): A61F13/00 A61K9/12 A61K9/12 A61K9/70

CP: A61K31/473 A61K31/513 A61K47/42 A61K47/18 A61K47/12 A61K47/32 A61K47/34 A61K47/06 A61K47/14 A61K47/38 A61K47/44 A61K31/165 A61K31/415 A61K31/445 A61K31/505 A61K31/19 A61K31/275 A61K31/57 A61K31/192 A61K31/195

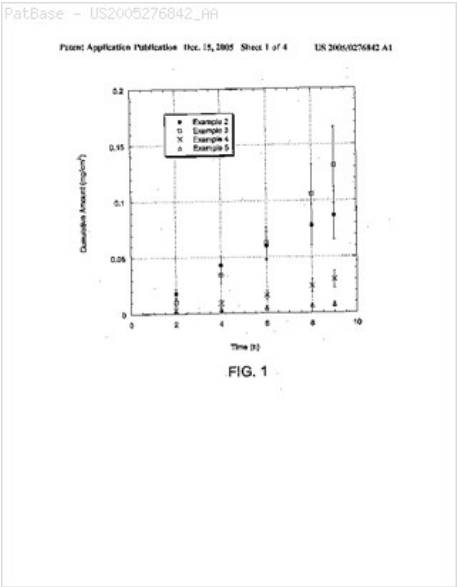
A61K31/24 A61K31/4745 A61K31/568 A61K31/74 A61K31/4174 A61K31/522 A61K9/7007 A61K9/0017 A61L26/0076 A61L26/0066 A61K9/08 A61L2300/402 A61L2300/404 A61L2300/602 A61K31/437 A61K31/196 A61K31/485 A61K9/06 A61K31/07 A61K31/4439 A61K31/56 A61K31/59 A61K47/10 A61K9/7015 A61K31/569 A61K9/0014 A61K31/573 A61K31/167

European: A61K31/07 A61K31/165 A61K31/19 A61K31/192 A61K31/195 A61K31/24 A61K31/275 A61K31/415 A61K31/4174 A61K31/4439 A61K31/445 A61K31/473 A61K31/4745 A61K31/505 A61K31/513 A61K31/522 A61K31/56 A61K31/568 A61K31/57 A61K31/573 A61K31/59 A61K31/74 A61K47/06 A61K47/10 A61K47/12 A61K47/14 A61K47/18 A61K47/32 A61K47/34 A61K47/38 A61K47/44 A61K9/00M3 A61K9/00M3B A61K9/06 A61K9/08 A61K9/70B A61K9/70D A61L26/00H2 K61K47/10 K61K47/18 K61K47/32 K61K47/38 K61K47/42 K61L300/402 K61L300/404 K61L300/602

US: 424/400 424/400P 424/443 424/443P 424/448 424/448P 424/449 424/45 424/45P 424/47 424/47P 424/487 424/539 424/539S 424/59 424/59P 424/61 424/770 424/770S 424/776 424/776S 424/78.02 424/78.02P 424/78.07 424/78.07P 514/11 514/159 514/159S 514/167 514/167S 514/168 514/168S 514/171 514/171S 514/174 514/174S 514/178 514/178S 514/18.7 514/18.700S 514/180 514/180S 514/182 514/182S 514/20.5 514/20.500S 514/226.5 514/226.500S 514/263.31 514/263.310S 514/263.38 514/263.380S 514/266.22 514/266.220S 514/269 514/269S 514/275 514/275S 514/282 514/284 514/284S 514/291 514/291S 514/292 514/292S 514/293 514/293S 514/303 514/330 514/330S 514/343 514/343S 514/383 514/383S 514/399 514/399S 514/401 514/401S 514/420 514/420S 514/422 514/422S 514/524 514/524S 514/536 514/536S 514/559 514/559S 514/563 514/563S 514/567 514/567S 514/568 514/568S 514/569 514/569S 514/570 514/570S 514/617 514/617S 514/626 514/626S 514/647 514/649 514/649S 514/654 514/654S 514/655 514/655S 514/656 514/656S 514/714 514/714S 514/725 514/725S 514/772 514/772.2 514/772.5 514/772.6 514/772S 514/774 514/783 514/783S 514/784 514/784S 514/785 514/785S 514/788 514/788S 514/789 602/48 602/52 602/54 602/57

Family:

Publication number	Publication date	Application number	Application date
AU2005251805 AA	20051222	AU20050251805	20050607
AU2005251805 BB	20120202	AU20050251805	20050607
AU2006326018 AA	20070621	AU20060326018	20061214
AU2006326018 BB	20130418	AU20060326018	20061214
AU2006326033 AA	20070621	AU20060326033	20061214
AU2006326034 AA	20070621	AU20060326034	20061214
AU2006326388 AA	20070621	AU20060326388	20061214
AU2006326388 BB	20130124	AU20060326388	20061214
AU2006339350 AA	20070907	AU20060339350	20061214
CA2569121 AA	20061129	CA20052569121	20050607
CA2569121 C	20130115	CA20052569121	20050607
CA2633464 AA	20080613	CA20062633464	20061214
CA2633466 AA	20080613	CA20062633466	20061214
CA2633472 AA	20080613	CA20062633472	20061214
CA2633489 AA	20080613	CA20062633489	20061214
CA2633489 C	20130924	CA20062633489	20061214
CA2633515 AA	20080613	CA20062633515	20061214
CA2633515 C	20111018	CA20062633515	20061214
CA2747845 AA	20070621	CA20062747845	20061214
CA2747845 C	20121009	CA20062747845	20061214
CN101370453 A	20090218	CN200680052642	20061214
CN101370453 B	20131218	CN200680052642	20061214
CN101374488 A	20090225	CN200680051627	20061214
CN101378729 A	20090304	CN200680052577	20061214
CN101378729 B	20130911	CN200680052577	20061214
CN101442987 A	20090527	CN200680051532	20061214
CN101494976 A	20090729	CN200680051992	20061214
CN101494976 B	20131218	CN200680051992	20061214
CN102670567 A	20120919	CN201210107226	20061214
CN1993092 A	20070704	CN200580026665	20050607
EP1753380 A2	20070221	EP20050760457	20050607
EP1753380 A4	20120718	EP20050760457	20050607
EP1959928 A2	20080827	EP20060845634	20061214
EP1959929 A2	20080827	EP20060847657	20061214
EP1959929 A4	20120815	EP20060847657	20061214
EP1959930 A2	20080827	EP20060847684	20061214



EP1959931 A2	20080827	EP20060848632	20061214
EP1959931 A4	20120822	EP20060848632	20061214
EP1968541 A2	20080917	EP20060849969	20061214
IN01481MN2008 A	20081010	IN2008MN01481	20080714
IN01483MN2008 A	20081010	IN2008MN01483	20080714
IN01484MN2008 A	20081010	IN2008MN01484	20080714
IN01485MN2008 A	20081017	IN2008MN01485	20080714
IN01486MN2008 A	20081010	IN2008MN01486	20080714
JP2008501805 T2	20080124	JP20070527680T	20050607
JP2009519940 T2	20090521	JP20080545816T	20061214
JP2009519956 T2	20090521	JP20080545866T	20061214
JP2009519957 T2	20090521	JP20080545867T	20061214
JP2009519958 T2	20090521	JP20080545868T	20061214
JP2009524586 T2	20090702	JP20080545844T	20061214
JP2014001218 A2	20140109	JP20130155944	20130726
JP5487461 B2	20140507	JP20070527680T	20050607
JP5850889 B2	20160203	JP20130155944	20130726
KR20070027694 A	20070309	KR20077000444	20070108
US2005276842 AA	20051215	US20050146917	20050606
US2007189977 AA	20070816	US20060640132	20061214
US2007189978 AA	20070816	US20060640133	20061214
US2007189980 AA	20070816	US20060640135	20061214
US2007190124 AA	20070816	US20060640444	20061214
US2007196293 AA	20070823	US20060640102	20061214
US2007196323 AA	20070823	US20060640134	20061214
US2007196325 AA	20070823	US20060640101	20061214
US2007196452 AA	20070823	US20060640437	20061214
US2007196453 AA	20070823	US20060640445	20061214
US2007196457 AA	20070823	US20060640117	20061214
US2007196458 AA	20070823	US20060640139	20061214
US2007196459 AA	20070823	US20060640140	20061214
US2007280972 AA	20071206	US20070796145	20070425
US2008019927 AA	20080124	US20070888905	20070801
US2010267678 AA	20101021	US20100761540	20100416
US2012294907 AA	20121122	US20120567289	20120806
US2012294926 AA	20121122	US20120566273	20120803
US2012301517 AA	20121129	US20120566147	20120803
US2013022564 AA	20130124	US20120556089	20120723
US2014314815 AA	20141023	US20140161086	20140122
US2015025051 AA	20150122	US20140293175	20140602
US2015126481 AA	20150507	US20140533419	20141105
US8741332 BB	20140603	US20060640139	20061214
US8741333 BB	20140603	US20060640140	20061214
US8907153 BB	20141209	US20050146917	20050606
WO05120473 A2	20051222	WO2005US20099	20050607
WO05120473 A3	20060511	WO2005US20099	20050607
WO07070643 A2	20070621	WO2006US47747	20061214
WO07070643 A3	20080508	WO2006US47747	20061214
WO07070679 A2	20070621	WO2006US47926	20061214
WO07070679 A3	20090108	WO2006US47926	20061214
WO07070694 A2	20070621	WO2006US48060	20061214
WO07070694 A3	20081224	WO2006US48060	20061214
WO07070695 A2	20070621	WO2006US48061	20061214
WO07070695 A3	20080821	WO2006US48061	20061214
WO07100376 A2	20070907	WO2006US48059	20061214
WO07100376 A3	20080925	WO2006US48059	20061214
WO09017767 A2	20090205	WO2008US09222	20080730
WO09017767 A3	20091230	WO2008US09222	20080730

Priority:

US20040577536P	20040607	US20050146917	20050606	US20050750683P	20051214
WO2005US20099	20050607	JP20070527680	20050607	JP20070527680T	20050607
US20050750524P	20051214	US20050750637	20051214	US20050750523	20051214
US20050750522	20051214	US20050750519	20051214	US20050750521P	20051214
US20050750519P	20051214	US20050750523P	20051214	US20060640132	20061214
US20060640133	20061214	US20060640135	20061214	US20060640444	20061214
US20060640102	20061214	US20060640445	20061214	US20060640117	20061214
US20060640140	20061214	WO2006US48061	20061214	WO2006US48060	20061214
WO2006US47926	20061214	US20050750652P	20051214	US20060795091P	20060425
US20050750637P	20051214	US20050750522P	20051214	US20050750465P	20051214
US20070796145	20070425	US20070888905	20070801	WO2006US47747	20061214
WO2006US48059	20061214	US20060640134	20061214	US20100761540	20100416
CA20062633515	20061214	US20060640139	20061214	US20060640437	20061214
US20120566273	20120803	US20120567289	20120806	US20120566147	20120803
CA20062747845	20061214	US20120556089	20120723	US20060640101	20061214
US20140161086	20140122	US20140293175	20140602	US20140533419	20141105

Probable Assignee: ZARS PHARMA INC

Assignee(s): (std): RIGBY LARRY D ; ZARS INC ; ZHANG JIE ; WARNER KEVIN S ; SHARMA SANJAY ; WAMER KEVIN S ; SHARMA SANJA ; ZARS PHARMA INC ; SANJAY SHARMA ; ASHBURN MICHAEL A ; NIU SUYI ; NUVO RES INC

Assignee(s): NUVO RESEARCH AMERICA INC ; NUVO RESEARCH INC ; PALADIN LABS INC

Inventor(s): (std): ASHBURN MICHAEL A ; JIE ZHANG ; RIGBY LARRY D ; SANJAY SHARMA ; SHARMA SANJA ; SHARMA SANJAY ; NIU SUYI ; SUYI ZHANG JIE WARNER KEVIN S ; WARNER KEVIN S ; ZHANG JIE ; WAMER KEVIN S

Inventor(s): WARNER KEVIN ; ASHBURN MICHAEL ; ZHANG JIE WARNER KEVIN S ; ZHANG JIE WARNER KEVIN S ASHBURN MICHAEL A RIGBY L ; WAMER KEVIN ; RIGBY LARRY ; SUYI NIU ; KEVIN S WARNER ; LARRY D RIGBY ; MICHAEL A ASHBURN

Agent(s): FB RICE; RIDOUT AND MAYBEE LLP; SMART AND BIGGAR; WOMBWELL FRANCIS ET AL; YAMAMOTO OSAMU; TAKEUCHI SHIGEO; ONO SHINJIRO; YAMAGUCHI AKIKO; KOBAYASHI YASUSHI; THORPE NORTH AND WESTERN LLP; OAKESON GARY P ET AL

Designated states: AE AG AL AM AO AT AU AZ BA BB BE BF BG BH BJ BR BW BY BZ CA CF CG CH CI CM CN CO CR CU CY CZ DE DK DM DO DZ EC EE EG ES FI FR GA GB GD GE GH GM GN GQ GR GT GW HN HR HU ID IE IL IN IS IT JP KE KG KM KN KP KR KZ LA LC LI LK LR LS LT LU LV LY MA MC MD ME MG MK ML MN MR MT MW MX MY MZ NA NE NG NI NL NO NZ OM PG PH PL PT RO RS RU SC SD SE SG SI SK SL SM SN ST SV SY SZ TD TG TJ TM TN TR TT TZ UA UG US UZ VC VN YU ZA ZM ZW

Title: COSMETIC COMPOSITION COMPRISING AT LEAST ONE SULPHONIC POLYESTER AND AT LEAST ONE **POLYURETHANE**

Abstract: Source: US2006210507A Disclosed herein is a cosmetic composition comprising, in a cosmetically acceptable medium, at least one water-dispersible sulphonic polyester and at least one high molecular weight **polyurethane**. Also disclosed herein is a **method** for shaping, fixing, and/or holding the hair comprising applying this cosmetic composition to the hair.

Classifications:
International (IPC 8-9): A61K8/85 A61K8/87 A61Q5/06 A61Q5/12 (Advanced/Invention); A61K8/72 A61Q5/06 (Core/Invention)
International (IPC 1-7): A61K7/06 A61K8/85 A61K8/87 A61Q5/06
CPC: A61K8/85 A61K8/87 A61K2800/594 A61Q5/06 A61K8/046
European: A61K8/04F A61K8/85 A61K8/87 A61Q5/06 K61K201/21 K61K800/594
US: 424/70.17 424/70.7

Family:

Publication number	Publication date	Application number	Application date
AT391490 E	20080415	AT20050292219T	20051021
BRPI0506302 A	20060718	BR2005PI06302	20051027
DE602005005917 D1	20080521	DE200560005917T	20051021
DE602005005917 T2	20090520	DE200560005917T	20051021
EP1652510 A1	20060503	EP20050292219	20051021
EP1652510 B1	20080409	EP20050292219	20051021
FR2877215 A1	20060505	FR20040052471	20041028
FR2877215 B1	20061229	FR20040052471	20041028
JP2006124391 A2	20060518	JP20050313327	20051027
MXPA05011571 A1	20060525	MX2005PA11571	20051027
US2006210507 AA	20060921	US20050260440	20051028

Priority:
FR20040052471 20041028 US20050646495P 20050125 US20050260440 20051028

Probable Assignee: L OREAL SA
Assignee(s): (std): BENABDILLAH KATARINA ; LAURENT LUDIVINE ; OREAL
Assignee(s): L'OREAL SA ; L OREAL ; L OREAL SA ; L OREAL SOC ANONYME ; L OREAL SOCIETE ANONYME
Inventor(s): (std): BENABDILLAH KATARINA ; LAURENT LUDIVINE ; LUDIVINE LAURENT ; KATARINA BENABDILLAH
Agent(s): BOURDEAU FRANCOISE; LOREAL; FINNEGAN HENDERSON FARABOW GARRETT AND DUNNER, LLP; FINNEGAN HENDERSON FARABOW GARRETT AND DUNNER LLP
Designated states: AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR

Title: ORAL CARE COMPOSITIONS AND **METHODS**

Abstract: Source: US2011038810A Advantageous oral care composition can include a water insoluble carrier, sweetener, and an additional component selected from the group consisting of flavors, sensates, and combinations thereof, where the composition is configured for use in the oral cavity.

Classifications:

International (IPC 8-9): A61K8/00 A61K8/24 A61K8/30 A61K8/31 A61K8/34 A61K8/46 A61K8/49 A61K8/55 A61K8/81 A61K8/92 A61K8/96 A61K8/97 A61K9/00 A61P23/00 A61P29/00 A61P3/02 A61P31/00 A61P31/10 A61P31/12 A61P39/06 A61Q11/00 A61Q11/02 B65D85/00 (Advanced/Invention)

CPC: A61K8/92 A61K2800/31 A61K8/60 A61K8/922 A61K8/31 A61Q11/00 A61K8/24 A61K8/55 A61K8/556 A61Q11/02

European: A61K8/24 A61K8/31 A61K8/55 A61K8/55F A61K8/60 A61K8/92 A61K8/92C A61Q11/00 A61Q11/02 K61K201/115 K61K201/19 K61K800/31

US: 206/524.1 206/524.100P 424/400 424/400S 424/401 424/401P 424/484 424/49 424/49P 424/49S 424/57 424/57S

Family:

Publication number	Publication date	Application number	Application date
AU2010284339 AA	20110224	AU20100284339	20100817
AU2010284339 BB	20140918	AU20100284339	20100817
AU2010292276 AA	20110317	AU20100292276	20100909
AU2010292276 BB	20140717	AU20100292276	20100909
AU2010319911 AA	20110519	AU20100319911	20101028
AU2010319911 BB	20140717	AU20100319911	20101028
BR112012005327 A2	20160322	BR20121105327	20100909
CA2772119 AA	20110224	CA20102772119	20100817
CA2772119 C	20140715	CA20102772119	20100817
CA2773738 AA	20110317	CA20102773738	20100909
CA2779451 AA	20110519	CA20102779451	20101028
CA2779451 C	20150811	CA20102779451	20101028
CN102625722 A	20120801	CN201080035822	20100817
CN102802732 A	20121128	CN201080038678	20100909
CN103209738 A	20130717	CN201080046996	20101028
EP2467192 A2	20120627	EP20100745706	20100817
EP2475431 A2	20120718	EP20100755274	20100909
EP2493577 A2	20120905	EP20100773808	20101028
IN02213DN2012 A	20150821	IN2012DN02213	20120314
JP2013514275 T2	20130425	JP20120537020T	20101028
MX2012001994 A1	20120229	MX20120001994	20100817
MX2012002962 A1	20120419	MX20120002962	20100909
MX2012004934 A1	20120522	MX20120004934	20101028
RU2012107807 A	20131210	RU20120107807	20101028
US2011038810 AA	20110217	US20100857620	20100817
US2011089073 AA	20110421	US20100879214	20100910
US2011104219 AA	20110505	US20100911112	20101025
US8623388 BB	20140107	US20100911112	20101025
US8747814 BB	20140610	US20100857620	20100817
WO11022343 A2	20110224	WO2010US45677	20100817
WO11022343 A3	20120531	WO2010US45677	20100817
WO11031807 A2	20110317	WO2010US48186	20100909
WO11031807 A3	20130425	WO2010US48186	20100909
WO11059715 A2	20110519	WO2010US54370	20101028
WO11059715 A3	20131017	WO2010US54370	20101028

Priority:			
US20090234512P 20090817	US20090241564P 20090911	US20090255926P 20091029	
US20100857620 20100817	WO2010US45677 20100817	WO2010US48186 20100909	
US20100879214 20100910	US20100911112 20101025	WO2010US54370 20101028	

Probable Assignee: PROCTER AND GAMBLE CO

Assignee(s): (std): BAIG ARIF ALI ; CERDA LUISA NAVARRO ; DECKNER GEORGE ENDEL ; GLANDORF WILLIAM MICHAEL ; LEONARD ROBERT SCOTT ; RAJIAIAH JAYANTH ; PROCTER AND GAMBLE ; WILDER ELIZABETH ANNE ; SMITH STEVEN DARYL ; MEDEIROS FRANCO SILVA

Assignee(s): PROCTER AND GAMBLE COONE PROCTER & GAMBLE PLAZACINNATIONH45202US ; THE PROCTER AND GAMBLE COMPANY ; PROCTER AND GAMBLE CO

Inventor(s): (std): BAIG ARIF ALI ; DECKNER GEORGE ENDEL ; CERDA LUISA NAVARRO ; GLANDORF WILLIAM MICHAEL ; LEONARD ROBERT SCOTT ; JAYANTH RAJIAIAH ; ENDEL DECKNER GEORGE ; RAJIAIAH JAYANTH ; WILDER ELIZABETH ANNE ; SMITH STEVEN DARYL ; MEDEIROS FRANCO SILVA ; ALI BAIG ARIF ; MICHAEL GLANDORF WILLIAM

Inventor(s): RAJIAIAH JAYANTHUS ; ARIF ALI BAIG ; WILLIAM MICHAEL GLANDORF ; STEVEN DARYL SMITH ; ROBERT SCOTT LEONARD ; GEORGE ENDEL DECKNER ; ELIZABETH ANNE WILDER ; LUISA NAVARRO CERDA ; FRANCO SILVA MEDEIROS ; BAIG ARIF ALIUS

Agent(s): PHILLIPS ORMONDE FITZPATRICK; DIMOCK STRATTON LLP; CLEMO NICHOLAS GRAHAM; THE PROCTER AND GAMBLE COMPANY,GLOBAL LEGAL DEPARTMENT - IP; PROCTER AND GAMBLE CO GLOBAL LEGAL DEPARTMENT IP; JAMES E; KATHLEEN Y; ANGELA K; CARRIE A; ARMINA E; THE PROCTER AND GAMBLE COMPANY

Designated states: AE AG AL AM AO AT AU AZ BA BB BE BF BG BH BJ BR BW BY BZ CA CF CG CH CI CL CM CN CO CR CU CY CZ DE DK DM DO DZ EC EE EG ES FI FR GA GB GD GE GH GM GN GQ GR GT GW HN HR HU ID IE IL IN IS IT JP KE KG KM KN KP KR KZ LA LC LI LK LR LS LT LU LV LY MA MC MD ME MG MK ML MN MR MT MW MX MY MZ NA NE NG NI NL NO NZ OM PE PG PH PL PT RO RS RU SC SD SE SG SI SK SL SM SN ST SV SY SZ TD TG TH TJ TM TN TR TT TZ UA UG US UZ VC VN ZA ZM ZW

Title: FUNCTIONALIZED MONOMERS AND POLYMERS

Abstract: Source: US2012245063A This invention relates to a composition, comprising: an unsaturated functionalized monomer of from about 5 to about 30 carbon atoms, which is: (a) polymerized to form a functionalized polymer; (b) copolymerized with a comonomer to form a functionalized copolymer; or (c) reacted with an enophilic reagent to form a polyfunctionalized monomer. The polyfunctionalized monomer may be polymerized to form a polyfunctionalized polymer which may be further reacted with one or more additional reagents. The invention relates to lubricants, functional fluids, fuels, dispersants, detergents and polymeric resins.

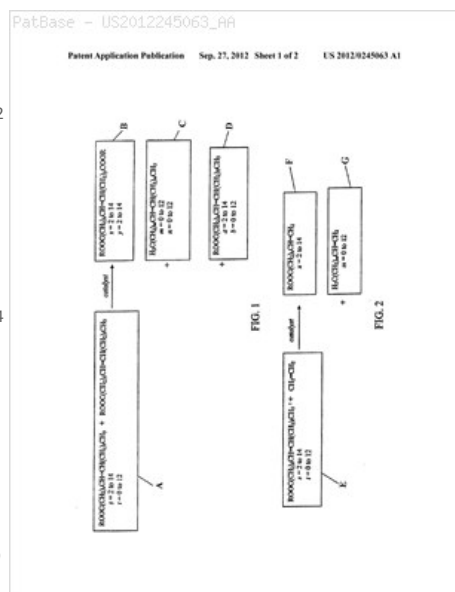
Classifications:

International (IPC 8-9): B21B45/02 C07C229/30 C07C57/02 C07C57/03 C07C57/12 C07C69/34 C07C69/52 C07C69/53 C07C69/58 C07D307/60 C08F10/00 C08F120/04 C08F120/10 C08F122/10 C08F20/14 C08F20/68 C08F210/14 C08F220/04 C08F220/10 C08F36/00 C10L1/00 C10L1/12 C10L1/18 C10L1/182 C10L1/188 C10L1/19 C10L1/22 C10L1/224 C10L1/232 C10M105/34 C10M107/32 C10M125/10 C10M129/70 C10M129/72 C10M133/16 C10M133/40 C10M133/44 C10M133/46 C10M133/48 C10M145/08 C10M145/12 C10M145/14 C10M149/02 C10M159/20 C10M169/04 C10M173/02 C10N10/02 C10N10/04 C10N10/06 C10N10/08 C10N10/10 C10N20/02 C10N30/06 C10N40/25 C11C3/00 C11D3/00 C11D3/37 (Advanced/Invention); C10N10/02 C10N10/04 C10N10/06 C10N10/08 C10N10/10 C10N20/02 C10N30/06 C10N40/25 (Advanced/Non-invention)

CPC: C08F2222/104 C08F220/04 C08F220/10 C08F220/1866 C08F220/64 C08F20/14 C08F20/68 C08F120/04 C08F120/10 C08F122/105 C10L1/1883 C10L1/1905 C10L1/224 C10M133/16 C10M145/08 C10M149/02 C10M159/20 C10M2201/02 C10M2201/062 C10M2203/1006 C10M2203/1025 C10M2205/028 C10M2205/0285 C10M2207/123 C10M2207/282 C10M2209/04 C10M2215/08 C10M2215/28 C10M2217/06 C10M2219/044 C10M2219/046 C10N2210/01 C10N2210/02 C10N2210/03 C10N2210/04 C10N2210/05 C10N2220/021 C10N2220/022 C10N2230/08 C10N2240/10 C10N2250/10 C10N2260/06 C10N2260/09 C10N2270/02 C11C3/00 C11C3/003 C11D3/3746 C10M107/32 C10M2209/1023 C08F210/14 C10M129/72

European: C10M129/72 C10M133/16 C10M145/08 C10M149/02 C10M159/20 M10M201/02 M10M201/062 M10M203/102B M10M203/10B M10M205/028 M10M205/028B M10M207/123 M10M207/282 M10M209/04 M10M215/08 M10M215/28 M10M217/06 M10M219/044 M10M219/046 M10N210/01 M10N210/02 M10N210/03 M10N210/04 M10N210/05 M10N220/021 M10N220/022 M10N230/08 M10N240/10 M10N250/10 M10N260/06 M10N260/09 M10N270/02

US: 44/307 44/314 44/318 44/347 44/348 44/351 44/369 44/385 44/388 44/389 44/392 44/393 44/451 44/457 44/628 508/154 508/178 508/185 508/186 508/207 508/216 508/255 508/277 508/283 508/287 508/290 508/306 508/459 508/463 508/465 508/469 508/470 508/472 508/527 508/583 510/413 526/318.3 526/329 549/255 554/101 554/104 554/122 554/96 560/190 560/205 560/224 562/598

**Family:**

Publication number	Publication date	Application number	Application date
AR083557 AA	20130306	AR2011P103955	20111026
CA2830657 AA	20130918	CA20122830657	20120323
CN103562361 A	20140205	CN201280025047	20120323
CN103562362 A	20140205	CN201280025068	20120323
CN103748122 A	20140423	CN201280025045	20120323
CN103748198 A	20140423	CN201280024990	20120323
EP2688925 A2	20140129	EP20120719510	20120323
EP2688988 A2	20140129	EP20120711540	20120323
EP2688989 A1	20140129	EP20120712492	20120323
EP2688990 A2	20140129	EP20120712493	20120323
MX2013010712 A1	20140131	MX20130010712	20120323
MX2013010713 A1	20140131	MX20130010713	20120323
MX2013010742 A1	20140312	MX20130010742	20120323
MX2013010743 A1	20140312	MX20130010743	20120323
US2012245063 AA	20120927	US20110281108	20111025
US2012264662 AA	20121018	US20120428284	20120323
US2012264664 AA	20121018	US20120428268	20120323
US2012277133 AA	20121101	US20120428458	20120323
US2012283156 AA	20121108	US20120428257	20120323
US2014357539 AA	20141204	US20140464863	20140821
US8846587 BB	20140930	US20110281108	20111025
WO12128788 A1	20120927	WO2011US57713	20111025
WO12129477 A1	20120927	WO2012US30282	20120323
WO12129479 A2	20120927	WO2012US30291	20120323
WO12129479 A3	20121115	WO2012US30291	20120323
WO12129482 A2	20120927	WO2012US30296	20120323
WO12129482 A3	20121115	WO2012US30296	20120323
WO12129490 A2	20120927	WO2012US30316	20120323
WO12129490 A3	20121108	WO2012US30316	20120323

Priority:

US20110467273P 20110324	US20110467275P 20110324	US20110467276P 20110324
US20110467279P 20110324	US20110467292P 20110324	US20110510159P 20110721
US20110281108 20111025	US20120428284 20120323	US20120428268 20120323
US20120428458 20120323	US20120428257 20120323	WO2012US30316 20120323
WO2012US30296 20120323	WO2012US30282 20120323	WO2012US30291 20120323
US20140464863 20140821		

Probable Assignee: ELEVANCE RENEWABLE SCIENCES**Assignee(s):** (std): DIBIASE STEPHEN A ; DIBIASE STEPHEN AUGUSTINE ; HATEGAN GEORGETA ; ELEVANCE RENEWABLE SCIENCES INC ; ELEVANCE RENEWABLE SCIENCES ; RIZVI SYED Q A**Assignee(s):** RIZVI SYED QA ; RIZVI SYED Q**Inventor(s):** (std): DIBIASE STEPHEN A ; DIBIASE STEPHEN AUGUSTINE ; HATEGAN GEORGETA ; RIZVI SYED Q A**Inventor(s):** RIZVI SYED Q ; GEORGETA HATEGAN ; RIZVI SYED QA ; SYED QA RIZVI ; STEPHEN AUGUSTINE DIBIASE**Agent(s):** SMART AND BIGGAR; CARLSSON CARL FREDRIK MUNK; RENNER OTTO BOISSELLE AND SKLAR LLP; DUNCAN JEFFERY M; DUCHEZ NEIL A**Designated states:** AE AG AL AM AO AT AU AZ BA BB BE BF BG BH BJ BR BW BY BZ CA CF CG CH CI CL CM CN CO CR CU CY CZ DE DK DM DO DZ EC EE EG ES FI FR GA GB GD GE GH GM GN GQ GR GT GW HN HR HU ID IE IL IN IS IT JP KE KG KM KN KP KR KZ LA LC LI LK LR LS LT LU LV LY MA MC MD ME MG MK ML MN MR MT MW MX MY MZ NA NE NG NI NL NO NZ OM PE PG PH PL PT QA RO RS RU RW SC SD SE SG SI SK SL SM SN ST SV SY SZ TD TG TH TJ TM TN TR TT TZ UA UG US UZ VC VN ZA ZM ZW

Title: PROCESSES FOR OBTAINING A POLYOL FROM PALM OIL, POLYOLS OBTAINED FROM SAID PROCESSES, PRODUCTS DERIVED FROM SAID POLYOL AND METHOD FOR PREPARING SAME

Abstract: Source: US2014309322A The present invention relates to the process for production of a polyol from palm oil and of rigid polyurethane foams prepared from said polyol derived from palm oil. On the one hand, this invention provides a method for obtaining monomeric polyols from palm oil that have hydroxyl number between 50 450 mgKOH/g sample. The polyols of the present application may be obtained by means of a procedure based on the following four mother routes: Route 1: maleinisation of the fatty acids of palm oil; Route 2: glycerolysis of palm oil; Route 3: transesterification of palm oil; and Route 4: epoxidation of unsaturated carbon-carbon links of palm oil. Additionally, other modalities of the invention permit obtaining polyols from the combination of these mother routes. In other realizations of the invention polyurethanes are prepared from polyols obtained through any of the four routes or by combinations of the same. In a mode of the invention the polyurethanes are produced through the reaction of a mixture of a polyol obtained through the present invention, a commercial polyol, a surfactant, a catalyst and an isocyanate. The polyurethanes may be foams of rigid high density polyurethane.

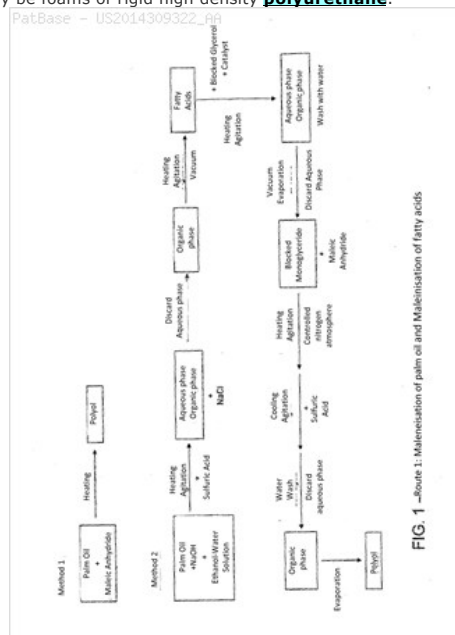
Classifications:

International (IPC 8-9): C07C29/00 C08G18/00 C08G18/34 C08G18/36 C08G18/42 C08G63/78 C11C3/02 (Advanced/Invention)

CPC: C08G18/10 C08G18/3206 C08G18/36 C08G18/8019 C08G2101/0008

C08G2101/0025 C08G2101/0083 C07C29/74 C08G18/348 C11C3/02 C07C29/00

US: 521/157 554/148 554/73

**Family:**

Publication number	Publication date	Application number	Application date
CO6650065 A1	20130415	CO20110130078	20111003
CO6650065 A1	20130415	CO20140023087	20111003
CO6650065 A1	20130415	CO20110130078	20111003
EP2765146 A1	20140813	EP20120837878	20121003
EP2765146 A4	20150624	EP20120837878	20121003
JP2014529002 T2	20141030	JP20140534004T	20121003
MX2014004087 A1	20140922	MX20140004087	20121003
US2014309322 AA	20141016	US20120349029	20121003
WO13050854 A1	20130411	WO20121B01954	20121003

Priority:

CO20110130078 20111003 CO20140023087 20111003 WO20121B01954 20121003

Probable Assignee: INDUSTRIAL AGRARIA LA PALMA LIMITADA INDUPALMA LTDA

Assignee(s): (std): AGUDELO VELASQUEZ DENCY VIVIANA ; BAENA RESTREPO MARGARITA MARIA ; IND AGRARIA LA PALMA LIMITADA INDUPALMA LTDA ; INDUPALMA LTDA ; TORO ALVAREZ DAHIANA

Assignee(s): INDUSTRIAL AGRARIA LA PALMA LIMITADA INDUPALMA LTDA

Inventor(s): (std): AGUDELO VELASQUEZ DENCY VIVIANA ; ALVAREZ DAHIANA TORO ; BAENA RESTREPO MARGARITA MARIA ; RESTREPO MARGARITA MARIA BAENA ; TORO ALVAREZ DAHIANA ; VELASQUEZ DENCY VIVIANA AGUDELO

Inventor(s): DAHIANA TORO ALVAREZ ; DENCY VIVIANA AGUDELO VELASQUEZ ; DENCY VIVIANA AGUDELO VELASQUEZ ; MARGARITA MARIA BAENA RESTREPO

Agent(s): LUZ CLEMENCIA DE PAEZ; HOFFMANN EITTE; OGAWA TOSHIHARU; SENMYO KENJI; CORREA OSCAR

Designated states: AE AG AL AM AO AT AU AZ BA BB BE BF BG BH BJ BN BR BW BY BZ CA CF CG CH CI CL CM CN CO CR CU CY CZ DE DK DM DO DZ EC EE EG ES FI FR GA GB GD GE GH GM GN GQ GR GT GW HN HR HU IE ID IL IN IS IT JP KE KG KM KN KP KR KZ LA LC LI LK LR LS LT LU LV LY MA MC MD ME MG MK ML MN MR MT MW MX MY MZ NA NE NG NI NL NO NZ OM PA PE PG PH PL PT QA RO RS RU RW SC SD SE SG SI SK SL SM SN ST SV SY SZ TD TG TH TJ TM TN TR TT TZ UA UG US UZ VC VN ZA ZM ZW