

OPENED-CELL, LOW-DENSITY POLYURETHANE FOAM

FIELD OF INVENTION

5 The present invention relates to polyol component for the production of
opened-cell, low-density polyurethane foams wherein the polyol component is
a palm oil based dihydroxystearic acids (hereinafter referred to as DHSA).
The invention also relates to a process using palm based DHSA to produce
polyurethane foams for various applications, specifically for packaging
10 application.

BACKGROUND OF THE INVENTION

 Polyurethanes are usually formed by the reactions of two
15 preformulated components, component A and component B in the presence
of blowing agents. Component A typically contains an isocyanate compound
while component B contains the balance of the foam ingredients; namely,
polyol, surfactant and amine catalyst. Common blowing agents used in
polyurethane foam production are water and low-boiling inert liquids or
20 solvents. Water is known as chemical blowing agent because it undergoes
chemical reactions with isocyanates to liberate carbon dioxide gas. There is
no chemical reaction involved between the low-boiling inert liquids or solvents
with any of the foam ingredients. These low-boiling inert liquids or solvents
are classified as physical blowing agents. Occasionally such physical blowing
25 agents are added in association with water. The heat evolved from the
reaction of the component A and B in the presence of blowing agents is more
than sufficient to polymerize the gelling mixture and expand into polyurethane
foam (hereinafter referred to as PUF).

 The great versatility of polyurethanes and the variety of starting
30 materials have resulted in the development of a multitude of products.
Polyols, being a key component for polyurethane production, play a vital role
in determining the characteristics of the final polyurethane polymer. The

structures, molecular weights, functionalities and hydroxyl values of the polyols are the actual basis that contributes in controlling the degree of crosslinking in the polyurethane polymer.

PUF can be classified as opened-cell, closed-cell or the combination of both depending on the blowing mechanism. Besides the closed-cell PUF which is widely known for its numerous applications; opened-cell, low-density PUF also have been used for applications such as packaging foam, as floral foam for flower arrangements, as an energy-absorbing material in the automobile industry and as a sound absorption material. The palm oil based DHSA according to the invention may be used as polyol component for the production of opened-cell, low-density PUF. The DHSA is obtained by hydrolyzing the epoxidized palm based oleic acids and is known from Singapore Patent No. 86353 and Malaysian Patent Application PI 9804456.

U.S. Patent No. 5,512,655 discloses a process for the production of polyurethanes by reacting an isocyanate with a polyol and a dihydroxyfatty acid. The dihydroxyfatty acid was used as an additive (structure element) and not as the main polyol component itself in the preparation of polyurethanes.

In this art, polyurethane was formed by reacting isocyanates with dihydroxystearic acid where the acid itself is used as the polyol. In this process the PU formed was found to exhibit high opened-celled content and low density. The rise time and tack free time of the PU formed are also very fast.

It is known from U.S. Patent No. 6,444,720 that opened-cell rigid foams containing urethane and/or isocyanurate groups and/or urea groups can be prepared using a polyoxyalkylene polyol containing long-chain polyether polyols having low double bond content. The polyoxyalkylene polyols used according to the invention may be prepared, e.g., by polyaddition of alkylene oxides to polyfunctional starter compounds in the presence of caesium, rubidium, strontium or barium hydroxide.

FR-A 1457824 describes the preparation of opened-cell rigid foams using a polyether polyol mixture containing a large proportion of a long-chain polyether polyol having a hydroxyl value from 50 to 200.

EP-A 622 388 describes the preparation of opened-cell rigid foams using a long-chain polyether polyol having an hydroxyl value from 25 to 60, a maximum of 5% of oxyethylene groups and a maximum of 5% of primary terminal hydroxyl groups, in combination with water as the sole blowing agent, and a polyether polyol with an hydroxyl value from 150 to 800 which has a maximum of 5% of primary terminal hydroxyl groups and has a polyfunctional amine as the starter molecule.

U.S. Patent No. 5,538,779 discloses a process to manufacture water-blown methylene diphenylisocyanate-based polyurethane foam from commercially available polyether polyol for use in packaging of shock or vibration sensitive goods. The polyether polyols are obtained by reacting an alkylene oxide, such as for example ethylene oxide, propylene oxide, butylene oxide or mixtures of two or more such oxides, with an active hydrogen-containing initiator.

U.S. Patent No. 4,508,853 and 4,742,087 describes a process for the production of polyols from epoxidized natural oils/fats. These epoxidized oils/fats can be reacted with any polyhydric alcohols in the presence of blowing agents to yield polyurethane foams.

A process for preparing closed-cell PUF, which comprises reacting a polyisocyanate with a polyol composition in the presence of a hydrocarbon-blowing agent is described in U.S. Patent 5,451,615. The polyol composition comprises a polyether or polyester polyol and a castor oil that contains fatty acids. The fatty acids include ricinoleic acid, dihydroxystearic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, eicosanoic acid, or mixtures of two or more thereof.

It is known from U.S. Patent 4,439, 551 that polyol blends comprising aromatic polyester polyol from recycled polyethylene terephthalate and alkylene glycol and dibasic acid waste streams may be used to produce packaging foam.

A process for the production of plastics containing amide groups with elimination of CO₂ by reaction of polyfunctional isocyanate and carboxylic

acids in the presence of tertiary amines is described in U.S. Patent 5,527,876. The carboxylic acids used are derived epoxidized fatty acid esters.

DE1121801 describes a process for the preparation of foamed polyurethane products by the interaction of organic polyisocyanates, water, polyethers and polyesters. Polyesters used in this process are prepared by
 5 condensing polyhydric alcohols with carboxylic acids. The carboxylic acids used in the process include ricinoleic acid, the ricinoleic acidrich mixture obtained by hydrolysis of castor oil, dihydroxystearic acid, hydroxy-acyloxystearic acids, polyhydroxy acids obtained by hydroxylation of
 10 unsaturated fatty acids such as the acids obtained by hydrolysis of soya bean or linseed oils, and polymerised unsaturated fatty acids such as dioleic acid and trilinoleic acid.

GB869988 refers to a process for the manufacture of foamed or non-foamed polyurethanes from diisocyanates (with which may be mixed
 15 triisocyanates) and polyethers, polyesters or polyesteramides. The polyesters can be prepared from succinic, adipic, glutaric, suberic, azelaic, sebacic, alkyladipic, citric, phthalic, isophthalic, terephthalic and trimesic acids, and the polybasic acids obtained by polymerization of unsaturated long-chain fatty acids. Monobasic acids and ricinoleic and dihydroxystearic acids may also be
 20 used

SUMMARY OF THE INVENTION

A process for preparing an opened – celled low density rigid
 25 polyurethane foam which comprises reacting isocyanate with a polyol component in the presence of a blowing agent and additives wherein the polyol component consists of dihydroxystearic acid (DHSA) derived from oleic acids. The oleic acids are derived from palm oil. The DHSA used in this invention is 9, 10-dihydroxystearic acid (9, 10-dihydroxyoctadecanoic acid).
 30 The isocyanate used is an aromatic isocyanate, polymethylene polyphenyl isocyanate having functionality of 3.0. The blowing agent is water. Physical blowing agent such as hydrocarbons can also be used in association with

water to generate the PUF. Examples of the hydrocarbons are HCFC-141b, HCFC-134a, n-pentane, i-pentane and cyclopentane. An opened –cell low density rigid polyurethane foam having an opened –cell content of exceeding 95% is produced in the present invention. A opened –cell low density rigid polyurethane foam produced can be used as packaging material, floral foam for flower arrangements, energy absorbing or acoustical material.

Process of producing opened cell low density rigid polyurethane foam is described below. The starting materials containing effective amounts of DHSA, water, silicone surfactant, amine catalyst, diethanolamine, triethanolamine and flame retardant are mixed in a container normally a plastic cup using a high-speed mechanical stirrer. The DHSA, which in the form of semi-solid at ambient temperature have to be heated first up to 60°C in order to liquefy it before the addition of other ingredients. The mixture is vigorously stirred for about 30 seconds until all the ingredients are thoroughly mixed with the DHSA. The isocyanates are then added into the plastic cup to react with the mixture. The stirring process is stopped when the polyurethane mixture turns creamy. The polyurethane foam is allowed to rise freely in the plastic cup until it is fully cured.

DETAILED DESCRIPTION OF THE INVENTION

It is an object of the invention to provide a process for the production of opened-cell, low-density PUF from palm oil based DHSA.

It is a further object of the present invention to provide an opened-cell, low density PUF as packaging foam produced using palm oil based DHSA and having properties comparable to the commercially available foams made from other types of polyols. In addition, this PUF can also be used for various applications including as floral foam for flower arrangements, as an energy-absorbing material and as a sound absorption material.

The method of producing DHSA from palm oil and its characteristics in terms of iodine value, acid value and the fatty acids composition (hereinafter referred to as FAC) that are suitable to produce PUF in accordance with this

invention is disclosed in Singapore Patent No. 86353 and Malaysian Patent Application PI 9804456. The DHSA are formed by hydrolysis of epoxidized oleic acids. The epoxidized oleic acids are produced from oleic acids having iodine value of 55 to 100 I₂/100g. The oleic acids are derived from palm oil.

- 5 The oleic acids from other oils and fats can be also used to produce epoxidized oleic acids. Examples of other oils are castor oil, soyabean oil, corn oil, sesame oil, olive oil, rapeseed oil, peanut oil, sunflower oil, cottonseed oil and linseed oil. Table 1 illustrates the variation in terms of characteristics of palm oil based oleic acids which may be used to produce
- 10 DHSA. The iodine value, acid value and the FAC of the oleic acids are determined according to their respective AOCS Methods.

Table 1 : Characteristics of Palm Oil Based Oleic Acids

Fatty Acid	Composition (%)
C10:0	0.14
C12:0	0.48
C14:0	2.15
C16:0	32.24
C18:0	8.48
C18:1	49.13
C18:2	7.38
Iodine Value (g I ₂ /100g)	56.8
Acid Value (mg KOH/g)	205.7

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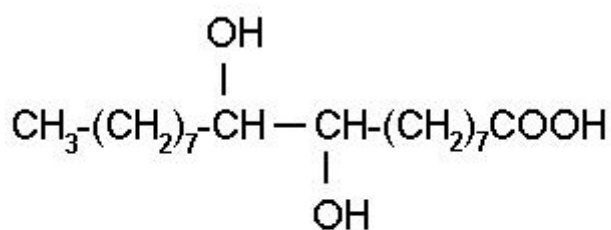
The invention mainly involves a process for making opened-cell, low density PUF by reacting isocyanates with a mixture comprising DHSA, silicone surfactants, water, amine catalyst, diethanolamine, triethanolamine and flame retardant. The preferred characteristics of DHSA used in this

20 invention are tabulated in Table 2.

Table 2 : Characteristics of DHSA

Hydroxyl Number (mg KOH/g))	124.1
pH	3.0
Iodine Value (g I ₂ /100g)	12.32
Acid Value (mg KOH/g)	178.9

- 5 The polyol component used in this invention is 9,10-dihydroxystearic acid (9,10-dihydroxyoctadecanoic acid). The DHSA is produced by hydrolyzing the epoxidized palm oil based oleic acids in an aqueous solution. The oleic acids having iodine value of 55 to 100 g I₂/100g are preferred. This invention is also applicable to oleic acids derived from other types of oils/fats.
- 10 The DHSA corresponding to this invention is used in an amount preferably from 35 – 50 percent of the total ingredient in the polyurethane formulation, and more preferably from 36 – 42 weight percent. The preferable hydroxyl number of DHSA is from 100 to 200 mg KOH/g.



9, 10 - DIHYDROXYSTEARIC ACID

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The isocyanate preferably to be used in this invention is an aromatic isocyanate having functionalities from about 2.5 to 3.0. The preferred isocyanates for PUF production according to this invention are liquid aromatic

mixtures of polymethylene polyphenyl isocyanates containing 4,4' methylene bisphenyl isocyanate (MDI). The polymethylene polyphenyl isocyanate is a mixture consisting of many isocyanate compounds. Each compound has its own functionality. The MDI functionality of 2.5 to 3.0 is normally required to produce rigid foams. The functionality of the polymethylene polyphenyl isocyanate is 3.0. These isocyanates are commercially available. Optionally, other types of isocyanates may be used. The amount of isocyanate preferably to be used in this invention is from 50 - 60 by percent weight. The mass ratio between the isocyanate and DHSA can significantly influence the structure and density of the foams produced. The preferable mass ratio of DHSA to aromatic isocyanate is from 1:1 to 1:1.5.

Water is used as the principal source for blowing in this process. However, physical blowing agent such as hydrocarbons can also be used in association with water to generate the PUF. The blowing agent is selected from a group consisting of HCFC-141b, HCFC-134a, n-pentane, i-pentane and cyclopentane or in any combinations. The water, which acts as the chemical blowing agent, reacts with the isocyanates to produce the carbon dioxide gas thus resulting in the formation of cell structures and foams. The amount of water added influences the structure and density of PUF produced. The preferred amount of water for PUF for this invention is from 0.05 - 6 parts per 100 parts by total weight of polyol component.

Effective amounts of ingredients such as silicone surfactant (e.g. Nixal L6900 from Witco), amine catalyst (Nixal-A33 from Witco), diethanolamine (from BASF), triethanolamine (from BASF) and flame retardant (TCPP from Akzo Nobel) are added in the PUF formulation mainly to enhance the rate of reaction and improve the formation of foam structure. Other conventional auxiliaries such as colouring pigments, tin catalyst, reinforcing fillers may be incorporated during the mixing process in order to modify the properties of the final polymer.

In order that this invention may be readily understood, the whole production process as described in this invention is indicated in the following example:-

Example

5 The starting materials containing effective amounts of DHSA, water, silicone surfactant, amine catalyst, diethanolamine, triethanolamine and flame retardant are mixed in a container normally a plastic cup using a high-speed mechanical stirrer. The DHSA, which in the form of semi-solid at ambient temperature has to be heated first up to 60°C in order to liquefy it before the addition of other ingredients. The mixture is vigorously stirred for about 30
10 seconds until all the ingredients are thoroughly mixed with the DHSA. The isocyanates are then added into the plastic cup to react with the mixture. The stirring process is stopped when the polyurethane mixture turns creamy. The polyurethane foam is allowed to rise freely in the plastic cup until it is fully cured.

15 The foaming characteristics in terms of cream time, gel time, rise time and tack free time are determined at this foaming stage. As the normal practice, the foam is conditioned at room temperature (30°C) for at least 24 hours before testing. The foam is then cut according to the dimension as per the requirement of testing standards. Table 3 shows the density, opened-cell
20 content, compressive stress and the thermal conductivity of the foam are determined by the following test methods:-

Table 3

Properties	Test Methods
Density (kg/m ³)	A foam sample of regular shape and reasonable size is weighed and measured. The density is calculated from the expression : weight (kg) / volume (m ³)
Opened-cell content (%)	Determination using Micromeritics' AccuPyc 1330 Pycnometer. The test is comparable in all respects to the ASTM standard method particularly ASTM D2856.
Compressive Stress (N) at 40% deformation	According to DIN ISO 3386.
Thermal Conductivity, k-value (W/m.K)	Determination using "Kemtherm QTM-D3". The test is based on transient hot wire method.

The PUFs according to this invention is suitable for numerous applications, preferably for packaging application. The typical example of packaging foam formulations used in this invention is given in Table 4. These formulations are expressed in parts (by weight) per hundred parts of polyols, abbreviated as pphp.

Table 4: Packaging Foam Formulations

PU Formation	pphp*	
DHSA	100.0	100.0
Niax-L6900	2.0	2.4
Niax-A33	1.5	1.5
Diethanolamine	2.0	2.0
Triethanolamine	2.0	2.0
TCP	15.0	-
Water	4.0	3.8
MDI	148.0	133.0
Cream time (secs.)	4.0	5.0
Gel time (secs.)	5.0	7.0
Rise time (secs.)	25.0	90.0
Tack free time (secs.)	30.0	180.0
Density (kg/m ³)	17.0	19.4
k-value (W/m.k) @ 29°C	0.0357	0.0387
Open cell content (%)	98.0	89.6
Compressive strength, N (40%)	153.2	113.0

*parts per hundred parts of polyol

- 5 The opened-cell, low-density foams are highly desirable particularly for packaging foam due to its excellent dimensional stability and lightweight, which are in contrast to closed-celled foams. This opened-cell, low-density PUF can be used for the pour- in-place packaging of delicate objects and shock-sensitive goods. The packaging method is known as direct
- 10 encapsulation in which the liquid polyurethane mixture is filled into a carton box whereby the packaged good will be surrounded by foam and thus protected. This packaging technique allows adaptation to any shape of the goods.

Opened-cell foams are also recognized for their superior acoustical insulation properties and are used for applications that require air borne sound absorption. The PUFs of this invention are also well suited for similar applications. This type of opened-cell PUFs may also be used as flora foam in
5 specialized horticulture and in seeding nurseries.

Besides these applications, DHSA derived from palm oil based oleic acids can be mixed with other polyols to produce rigid PUF. Besides using DHSA as polyol component, it also can be used as additives with other polyols to improve foaming reactivity in terms of rise time and tack free time.
10 The incorporation of DHSA in the polyurethane formulation can significantly accelerate the rising time, reduce the density and improve the curing time.

The results presented in Table 4 confirm that when DHSA according to the invention are used, PUF having higher percentage of opened-cell content exceeding 95% and low density can be obtained. These PUFs characteristics
15 are suitable for use for various applications mainly in the packaging industry.

CLAIMS

1. A process for preparing an opened – cell polyurethane foam which comprises reacting isocyanate with a polyol component in the presence of a blowing agent and additives characterised in that:
 - i) the polyol component consists of dihydroxystearic acid (DHSA) derived from oleic acids.
2. A process for preparing an opened – cell polyurethane foam as claimed in claim 1 wherein the DHSA is formed by hydrolysis of epoxidized produced from oleic acids having iodine value of 55 to 100 I₂/100g.
3. A process of preparing an opened - cell polyurethane foam as claimed in claim 1 and 2 wherein the oleic acids are derived from palm oil.
4. A process of preparing an opened - cell polyurethane foam as claimed in claim 1 wherein the DHSA is 9,10-dihydroxystearic acid (9, 10-dihydroxyoctadecanoic acid) and its OH value in the range of 100 to 200 mg KOH/g.
5. A process of preparing an opened – cell polyurethane foam as claimed in claim 1 wherein amount of DHSA used is between 35 and 50 percentage by weight of the total ingredients in the polyurethane formulation.
6. A process of preparing an opened – cell polyurethane foam as claimed in claim 1 wherein amount of DHSA used is between 36 and 42 percentage by weight of the total ingredients in the polyurethane formulation.

7. A process of preparing an opened – cell polyurethane foam as claimed in claim 1 wherein the isocyanate is an aromatic isocyanate having functionalities from about 2.5 to 3.0.
- 5 8. A process of preparing an opened – cell polyurethane foam as claimed in claim 1 wherein the isocyanate is polymethylene polyphenyl isocyanate having functionalities of 3.0.
9. A process of preparing an opened – cell polyurethane foam as claimed
10 in claim 8 wherein amount of polymethylene polyphenyl isocyanate is between 50 and 60 percentage by weight of the total ingredients in the polyurethane formulation.
10. A process of preparing an opened – cell polyurethane foam as claimed
15 in claim 1 wherein mass ratio between isocyanates (polymethylene polyphenyl isocyanate) and DHSA (polyol component) is from 1:1 to 1: 1.5.
11. A process of preparing an opened – cell polyurethane foam as claimed in claim 1 wherein the blowing agent is selected from a group consisting of
20 water, HCFC-141-b, HCFC-134a, n-pentane, i-pentane or cyclopentane or in any combinations.
12. A process of preparing an opened – cell polyurethane foam as claimed in claim 1 wherein the blowing agent is water in an amount from 0.05 to 6
25 pphp.
13. A process of preparing an opened – cell polyurethane as claimed in claim 1 wherein the DHSA are mixed with one or more surfactants, catalysts and other additives.

14. A process of preparing an opened-cell polyurethane foam as claimed in claim 1 wherein the DHSA besides being used as polyol component, it also can be used as additives with other polyols to improve foaming reactivity in terms of rise time and tack free time.

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15. Opened cell, low density rigid polyurethane foam produced according to the process as claimed in claim 1 to 14.

16. Opened-cell, low density rigid polyurethane foam having an opened
10 cell content of exceeding 95%.

17. Opened-cell, low density rigid polyurethane foam produced according to claim 1 to 14 used as packaging material, floral foam for flower arrangements, energy absorbing material or acoustical material.