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(71) Applicant(s)
Huntsman International LLC

(72) Inventor(s)
Luc Ferdinand Leon Colman

(74) Agent/Attorney
CALLINAN LAWRIE, Private Bag 7, KEW VIC 3101

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(71) Applicant: ~~IMPERIAL CHEMICAL INDUSTRIES PLC~~
~~(GB/GB); Imperial Chemical House, Millbank, London~~
~~SW1P 3JF (GB);~~

(72) Inventor: COLMAN, Luc, Ferdinand, Leon; Molendreef 34,
B-9111 Belsele (BE).

(74) Agents: SWINNEN, Anne, Marie et al.; ICI Europe Ltd.,
ICI Polyurethanes, Intellectual Property Dept., Everslaan 45,
B-3078 Everberg (BE).

(71) ~~HUNTSMAN ICI CHEMICALS~~

~~LLC~~

~~The Corporation Trust Company~~

~~1209 Orange Street~~

~~Wilmington New Castle~~

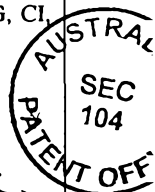
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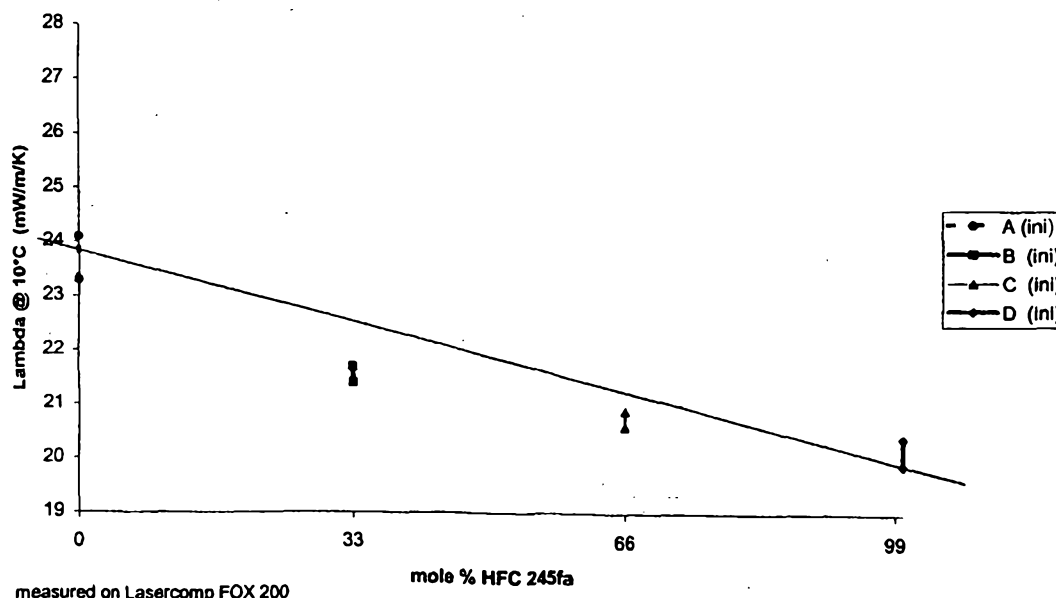
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(71) **Huntsman International LLC,**
500 Huntsman Way, Salt Lake City,
Utah, 84108, (U.S.).



(54) Title: PROCESS FOR RIGID POLYURETHANE FOAMS



(57) Abstract

Process for preparing rigid polyurethane or urethane-modified polyisocyanurate foam using as blowing agent a mixture containing from 1 to 50 mole % 1,1,1,3,3-pentafluoropropane and from 50 to 99 mole % isopentane and/or n-pentane.

DESCRIPTION

PROCESS FOR RIGID POLYURETHANE FOAMS

This invention relates to processes for the preparation of rigid polyurethane or urethane-modified polyisocyanurate foams, to foams prepared thereby, and to novel compositions useful in the process.

Rigid polyurethane and urethane-modified polyisocyanurate foams are in general prepared by reacting the appropriate polyisocyanate and isocyanate-reactive compound (usually a polyol) in the presence of a blowing agent. One use of such foams is as a thermal insulation medium as for example in the construction of refrigerated storage devices. The thermal insulating properties of rigid foams are dependent upon a number of factors including, for closed cell rigid foams, the cell size and the thermal conductivity of the contents of the cells.

A class of materials which has been widely used as blowing agent in the production of polyurethane and urethane-modified polyisocyanurate foams are the fully halogenated chlorofluorocarbons, and in particular trichlorofluoromethane (CFC-11). The exceptionally low thermal conductivity of these blowing agents, and in particular of CFC-11, has enabled the preparation of rigid foams having very effective insulation properties. Recent concern over the potential of chlorofluorocarbons to cause depletion of ozone in the atmosphere has led to an urgent need to develop reaction systems in which chlorofluorocarbon blowing agents are replaced by alternative materials which are environmentally acceptable and which also produce foams having the necessary properties for the many applications in which they are used.

Initially, the most promising alternatives appeared to be hydrogen-containing chlorofluorocarbons (HCFC's). US 4076644, for example, discloses the use of 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123) and 1,1-dichloro-1-fluoroethane (HCFC-141b) as blowing agents for the production of polyurethane foams. However, HCFC's also have some ozone-depletion potential. There is therefore mounting pressure to find substitutes for the HCFC's as well as the CFC's.

Alternative blowing agents which are currently considered promising because they contain no ozone-depleting chlorine are partially fluorinated hydrocarbons (HFC's) and hydrocarbons (HC's).

One of the most viable HFC candidate is 1,1,1,3,3-pentafluoropropane (HFC-245fa) as described in US 5496866 and EP 381986.

In respect of HC's especially five-carbon member hydrocarbons are considered



such as isopentane and n-pentane, as described in WO 90/12841.

Currently a lot of attention is paid to blowing agent mixtures, which could, apart from a possible reduction in cost, also provide additional benefits such as foam density reduction and thermal conductivity.

5 US 5,562,857 describes the use of mixtures containing from 50 to 70 mole % of HFC-245fa and from 30 to 50 mole % isopentane as blowing agent for rigid polyurethane foams.

It is an object of the present invention to ameliorate at least some of the disadvantages of the prior art.

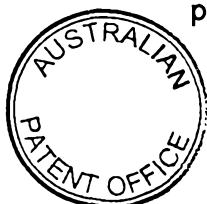
10 Accordingly, the present invention relates to process for preparing rigid polyurethane or urethane-modified polyisocyanurate foams comprising the step of reacting an organic polyisocyanate with a polyfunctional isocyanate-reactive component in the presence of water and a physical blowing agent mixture containing 1,1,1,3,3-pentafluoropropane and isopentane and/or n-pentane characterised in that the mole ratio
15 1,1,1,3,3-pentafluoropropane/iso- and/or n-pentane is between 1/99 and 40/60.

Preferably the mole ratio HFC 245fa/iso- and/or n-pentane is between 10/90 and 40/60.

Preferably on the hydrocarbon side only isopentane or n-pentane is used and most preferably only isopentane. But also mixtures of isopentane and n-pentane can be used;
20 in these mixtures the mole ratio isopentane/n-pentane is preferably between 80/20 and 20/80.

Suitable isocyanate-reactive compounds to be used in the process of the present invention include any of those known in the art for the preparation of rigid polyurethane or urethane-modified polyisocyanurate foams. Of particular importance for the preparation of
25 rigid foams are polyols and polyol mixtures having average hydroxyl numbers of from 300 to 1000, especially from 300 to 700 mg KOH/g, and hydroxyl functionalities of from 2 to 8, especially from 3 to 8. Suitable polyols have been fully described in the prior art and include reaction products of alkylene oxides, for example ethylene oxides and/or propylene oxide, with initiators containing from 2 to 8 active hydrogen atoms per molecule.

30 Suitable initiators include: polyols, for example glycerol, trimethylolpropane, triethanolamine, pentaerythritol, sorbitol and sucrose; polyamines, for example ethylene diamine, tolylene diamine (TDA), diaminodiphenylmethane (DADPM) and polymethylene polyphenylene polyamines; and aminoalcohols, for example ethanolamine and diethanolamine; and mixtures of such initiators. Other suitable polymeric polyols include
35 polyesters obtained by the condensation of appropriate proportions of glycols and higher functionality polyols with dicarboxylic or polycarboxylic acids. Still further suitable polymeric



polyols include hydroxyl terminated polythioethers, polyamides, polyesteramides, polycarbonates, polyacetals, polyolefins and polysiloxanes.

The present blowing agent mixture is especially suitable for use in isocyanate-reactive compositions containing polyether polyols, especially those derived from aliphatic or aromatic amine containing initiators, especially aromatic ones such as TDA and DADPM. A preferred isocyanate-reactive composition contains from 10 to 75 wt% (based on total isocyanate-reactive components) of aromatic amine initiated polyether polyols.

Suitable organic polyisocyanates for use in the process of the present invention include any of those known in the art for the preparation of rigid polyurethane or urethane-modified polyisocyanurate foams, and in particular the aromatic polyisocyanates such as diphenylmethane diisocyanate in the form of its 2,4'-, 2,2'- and 4,4'-isomers and mixtures thereof, the mixtures of diphenylmethane diisocyanates (MDI) and oligomers thereof known in the art as "crude" or polymeric MDI (polymethylene polyphenylene polyisocyanates) having an isocyanate functionality of greater than 2, toluene diisocyanate in the form of its 2,4- and 2,6-isomers and mixtures thereof, 1,5-naphthalene diisocyanate and 1,4-diisocyanatobenzene. Other organic polyisocyanates which may be mentioned include the aliphatic diisocyanates such as isophorone diisocyanate, 1,6-diisocyanatohexane and 4,4'-diisocyanatodicyclohexylmethane.

The quantities of the polyisocyanate compositions and the polyfunctional isocyanate-reactive compositions to be reacted will depend upon the nature of the rigid polyurethane or urethane-modified polyisocyanurate foam to be produced and will be readily determined by those skilled in the art.

Other physical blowing agents known for the production of rigid polyurethane foam can be used in small quantities (up to 30 wt% of the total physical blowing agent mixture) together with the blowing agent mixture of the present invention. Examples of these include dialkyl ethers, cycloalkylene ethers and ketones, (per)fluorinated ethers, chlorofluorocarbons, perfluorinated hydrocarbons, hydrochlorofluorocarbons, other hydrofluorocarbons and other hydrocarbons.

For example a mixture of HFC-245fa, isopentane and cyclopentane can be used.

Analogously to the present invention mixtures of HFC-245fa and other hydrocarbons (preferably linear alkanes) containing from 3 to 7 carbon atoms (such as cyclopentane, isobutane and n-hexane) can be used as blowing agent for rigid polyurethane foams.

Generally water or other carbon dioxide-evolving compounds are used together

with the physical blowing agents. Where water is used as chemical co-blowing agent typical amounts are in the range from 0.2 to 5 %, preferably from 0.5 to 3 % by weight based on the isocyanate-reactive compound.

The total quantity of blowing agent to be used in a reaction system for producing cellular polymeric materials will be readily determined by those skilled in the art, but will typically be from 2 to 25 % by weight based on the total reaction system.

In addition to the polyisocyanate and polyfunctional isocyanate-reactive compositions and the blowing agents, the foam-forming reaction mixture will commonly contain one or more other auxiliaries or additives conventional to formulations for the production of rigid polyurethane and urethane-modified polyisocyanurate foams. Such optional additives include crosslinking agents, for examples low molecular weight polyols such as triethanolamine, foam-stabilising agents or surfactants, for example siloxane-oxyalkylene copolymers, urethane catalysts, for example tin compounds such as stannous octoate or dibutyltin dilaurate or tertiary amines such as dimethylcyclohexylamine or triethylene diamine, isocyanurate catalysts such as quaternary ammonium salts or potassium salts, fire retardants, for example halogenated alkyl phosphates such as tris chloropropyl phosphate, and fillers such as carbon black.

Isocyanate indices of from 70 to 140 will typically be used in operating the process of the present invention but lower indices may be used, if desired. Higher indices, for example 150 to 500 or even up to 3000 may be used in conjunction with trimerisation catalysts to make foams containing isocyanurate linkages. These higher index foams are usually made using polyester polyols as isocyanate-reactive material.

In operating the process for making rigid foams according to the invention, the known one-shot, prepolymer or semi-prepolymer techniques may be used together with conventional mixing methods and the rigid foam may be produced in the form of slabstock, mouldings, cavity fillings, sprayed foam, frothed foam or laminates with other materials such as hardboard, plasterboard, plastics, paper or metal.

It is convenient in many applications to provide the components for polyurethane production in pre-blended formulations based on each of the primary polyisocyanate and isocyanate-reactive components. In particular, many reaction systems employ a polyisocyanate-reactive composition which contains the major additives such as the blowing agent and the catalyst in addition to the polyisocyanate-reactive component or components.

Therefore the present invention also provides polyfunctional isocyanate-reactive composition comprising a polyfunctional isocyanate-reactive component, water and a physical blowing agent mixture containing from 1 to 40 mole % of 1,1,1,3,3-pentafluoropropane and from 60 to 99 mole % of isopentane and/or n-pentane.

The various aspects of this invention are illustrated, but not limited by the following examples.

The following reaction components are referred to in the examples:

Polyol 1: a sucrose initiated polyether polyol of OH value 495 mg KOH/g.

Polyol 2: an aromatic amine initiated polyether polyol of OH value 310 mg KOH/g.

Polyol 3: an aromatic amine initiated polyether polyol of OH value 500 mg KOH/g.

Polyol 4: a glycerol initiated polyether polyol of OH value 55 mg KOH/g.

Arconate 1000: propylene carbonate available from Arco.

L 6900: a silicone surfactant available from Union Carbide.

Polycat 8: an amine catalyst available from Air Products.

Desmorapid PV: an amine catalyst available from Bayer.

isopentane: 99.7 % pure isopentane available from Halterman.

HFC-245fa: 1,1,1,3,3-pentafluoropropane available from PCR.

RUBINATE: polymeric MDI available from Imperial Chemical Industries.

RUBINATE is a trademark of Imperial Chemical Industries.

EXAMPLE

Rigid polyurethane foams were produced at laboratory scale using a Heidolph RZR 50 type mixing device from the ingredients listed below in Table 1.

The following properties were measured on the obtained foam: free rise density measured on cup foams, thermal conductivity (on a sample of core density about 33 kg/m^3) according to standard ISO 2581, initial and after ageing at room temperature or at 70°C and compression strength (in the weakest direction only) (on a sample of core density about 33 kg/m^3) according to standard DIN 53421, initial and after ageing for 5 weeks at room temperature (expressed as stress at 10 % thickness).

The results are also present in Table 1.

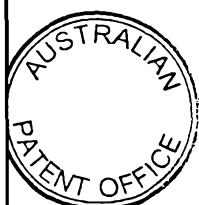


Table 1

Foam		A	B	C	D
Polyol 1	pbw	50.0	50.0	50.0	50.0
Polyol 2	pbw	26.0	26.0	26.0	26.0
Polyol 3	pbw	19.0	19.0	19.0	19.0
Polyol 4	pbw	1.5	1.5	1.5	1.5
Arconate 1000	pbw	1.5	1.5	1.5	1.5
L 6900	pbw	2.5	2.5	2.5	2.5
Polycat 8	pbw	2.5	2.5	2.5	2.5
Desmorapid PV	pbw	0.3	0.3	0.3	0.3
water	pbw	1.4	1.4	1.4	1.4
isopentane	pbw	18.5	12.4	6.2	0.0
HFC-245fa	pbw	0.0	11.47	22.95	34.42
RUBINATE M	pbw	136.0	136.0	136.0	136.0
Index	%	110	110	110	110
Free rise density	kg/m ³	24.5	24.0	24.3	23.9
Lambda value					
Initial at RT	mW/mK	23.2	21.3	20.5	19.8
After 2 weeks at RT	mW/mK	23.7	21.9	21.3	20.5
After 3 weeks at RT	mW/mK	24.3	22.4	21.8	21.3
After 5 weeks at RT	mW/mK	24.7	22.9	22.4	21.8
Initial at 70°C	mW/mK	24.1	21.6	20.8	20.3
After 2 weeks at 70°C	mW/mK	26.3	23.4	22.5	21.9
After 3 weeks at 70°C	mW/mK	27.4	24.8	24.1	23.4
After 5 weeks at 70°C	mW/mK	27.6	25.2	24.6	24.1
Compression strength					
Initial	kPa	190.5	182.3	183.2	175.1
After 5 weeks at RT	kPa	174.3	174.2	165.4	152.0

In figure 1 the initial lambda is set out as a function of the blowing agent mixture composition. In figure 2 the same is set out for the aged lambda (at room temperature).

From figure 1 it is clear that the thermal conductivity of the blowing agent mixture is always lower than the mathematical average between the two extremes (expressed by the straight line in figure 1). The deviation from the mathematical average is larger for the blowing agent mixture according to the invention (Foam B) than for the blowing agent mixture described in US 5562857 (Foam C).

Thus blowing agent mixtures according to the present invention yield foams of comparable thermal insulation value as the foams described in US 5562857 although more isopentane is used which inherently has a higher thermal conductivity than HFC-245fa. Also because isopentane is less expensive than HFC-245fa the same performance is obtained at lower cost. Further other physical properties such as compression strength of the foam are not detrimentally affected.

Where the terms "comprise", "comprises", "comprised" or "comprising" are used in this specification, they are to be interpreted as specifying the presence of the stated features, integers, steps or components referred to, but not to preclude the presence or addition of one or more other feature, integer, step, component or group thereof.



The claims defining the invention are as follows:

1. Process for preparing rigid polyurethane or urethane-modified polyisocyanurate foams comprising the step of reacting an organic polyisocyanate with a polyfunctional isocyanate-reactive component in the presence of water and
5 a physical blowing agent mixture containing 1,1,1,3,3-pentafluoropropane and isopentane and/or n-pentane characterised in that the mole ratio 1,1,1,3,3-pentafluoropropane/iso- and/or n-pentane is between 1/99 and 40/60.
2. Process according to claim 1, wherein the mole ratio 1,1,1,3,3-pentafluoropropane/iso- and/or n-pentane is between 10/90 and 40/60.
- 10 3. Process according to claim 1 or claim 2, wherein the physical blowing agent mixture consists of 1,1,1,3,3-pentafluoropropane and isopentane.
4. Process according to any one of the preceding claims wherein the polyfunctional isocyanate-reactive component comprises polyether polyols.
5. Process according to claim 4, wherein the polyfunctional isocyanate-
15 reactive component contains from 10 to 75 wt% (based on total isocyanate-reactive components) of aromatic amine initiated polyether polyols.
6. Process according to claim 5, wherein the aromatic amine is selected from the group consisting of tolylene diamine, diaminodiphenylmethane and polymethylene polyphenylene polyamine.
- 20 7. Process according to any one of the preceding claims, wherein the amount of water is between 0.2 and 5 % by weight based on total isocyanate-reactive components.
8. Rigid polyurethane or urethane-modified polyisocyanurate foam obtained by the method as defined in any one of the preceding claims.
- 25 9. Polyfunctional isocyanate-reactive composition comprising a polyfunctional isocyanate-reactive component, water and a physical blowing agent mixture containing from 1 to 40 mole % of 1,1,1,3,3-pentafluoropropane and from 60 to 99 mole % of isopentane and/or n-pentane.
10. Polyfunctional isocyanate-reactive composition according to claim 9,
30 wherein the mole ratio 1,1,1,3,3-pentafluoropropane/iso- and/or n-pentane is between 10/90 and 40/60.
11. Process according to claim 1 for preparing rigid polyurethane or urethane-modified polyisocyanurate foams which process is substantially as herein described with reference to the Example and/or accompanying Figures.



12. Polyfunctional isocyanate-reactive composition according to claim 9, substantially as herein described with reference to the Example and/or accompanying Figures.

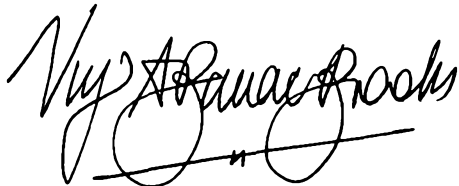
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Dated this 11th day of September, 2001.

HUNTSMAN INTERNATIONAL LLC

By their Patent Attorneys:

10 CALLINAN LAWRIE



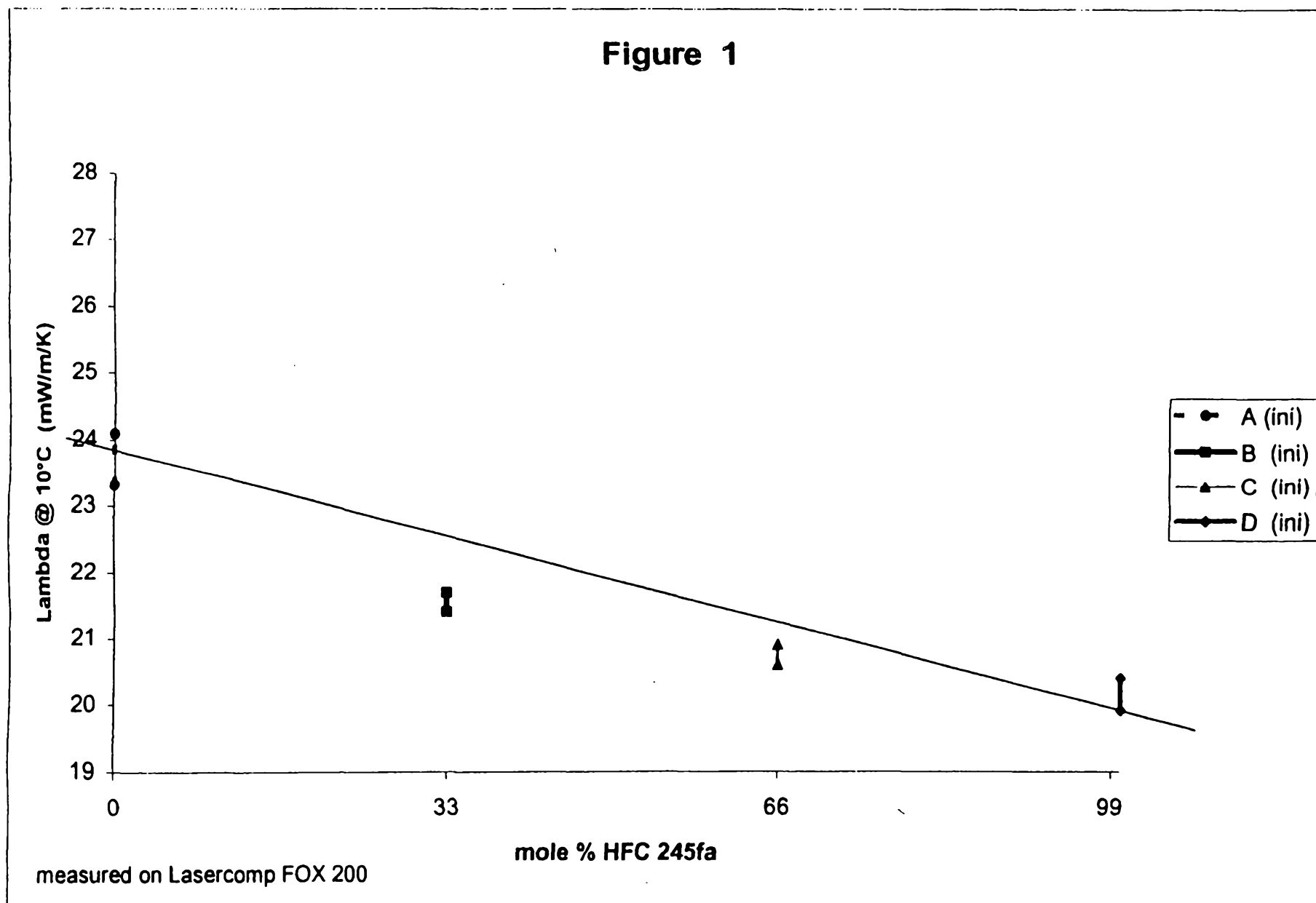
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Figure 1



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Figure 2

