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(54) **Title:** TRANSPARENT FLEXIBLE THERMOSET POLYURETHANE FILMS WITH GOOD DIMENSIONAL STABILITY
AND METHOD FOR MANUFACTURING THE SAME

(57) **Abstract:** The present invention provides a polyurethane resin composition and a method for transforming said composition
into thermoset polyurethane films. These films are particularly useful for applications in electronic devices, such as displays.



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Transparent flexible thermoset polyurethane films with good dimensional stability and method for manufacturing the same

This invention relates to polyurethane resin composition and its film which has a high refractive index, good optical and mechanical properties, good dimensional stability at high temperature and
5 good chemical resistance, and a method to produce the same. The said polyurethane films are suitable for use in electronics industry such as flat panel displays and touch panels.

Transparent plastic films have been widely used in liquid crystal display (LCD), flexible electronic devices, and touch screen panel due to its high transparency, light weight, ease of design, impact-resistance, and economic advantage attained from continuous manufacturing such as a roll-to-roll
10 (R2R) process. However, conventional plastic films such as polyesters, polycarbonates and cellulosic derivatives have a relatively low heat resistance and generally need a coating to improve their chemical resistance. On the other hand, urethane resin films may show a good mechanical characteristic, abrasion resistance and chemical resistance.

WO2010/148424, EP2801586 A1 and EP2246378 disclose a polyurethane resin composition
15 including a thiol for an optical lens element of thickness in the millimeter range or a molded optical device of similar dimensions. WO2008/061839 discloses a coating formulation based on similar compositions. None of these documents disclose a method for producing a polyurethane film from selected isocyanates and polythiols.

Thus, it would be desirable for the skilled person concerned with the design of liquid crystal displays,
20 flexible electronic devices and touch screen panels to have a flexible and transparent polymer film which further exhibits good chemical resistance, good optical and mechanical properties and good dimensional stability at higher temperatures.

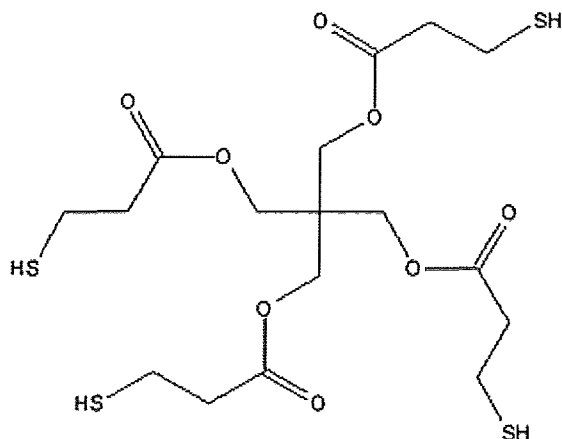
Therefore, the present invention provides a polyurethane resin composition, comprising at least one isocyanate and at least one thiol selected from the group consisting of tetrathiols and/or polythiols.

25 This polyurethane resin composition can be transformed into thermoset polyurethane films, thereby obtaining films having a combination of features such as flexibility, transparency, good chemical resistance, good optical and mechanical properties and good dimensional stability at higher temperatures which makes them very useful for applications in electronic devices, in particular display devices.

30 It is preferred that the at least one thiol is an ester of a polyol, preferably ester of a tetraol, pentaol, or hexanol. As thiol compounds particularly useful for obtaining thermoset polyurethane films, thiols consisting of esters of pentaerythritol or erythritol can be mentioned. Therefore, in a preferred embodiment of the present invention, the at least one thiol is an ester of pentaerythritol or

erythritol Generally, it is understood that if not explicitly stated otherwise, all features and embodiments of the present invention can be combined with each other

It was found that pentaerythritol Tetra-3-mercaptopropionate (PETMP)



5

PETMP

gave particularly good results when forming flexible thermoset polyurethane films having the above-mentioned combination of desirable properties Thus, it is preferred that the at least one thiol in the polyurethane resin composition according to the present invention is pentaerythritol Tetra-3-mercaptopropionate

With regard to the isocyanate used in the polyurethane resin composition according to the present invention, tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2-methylpentamethylene diisocyanate, 2,2,4-trimethyl-hexamethylene diisocyanate, dodecanemethylene diisocyanate, 1,4-diisocyanatocyclohexane, 3-isocyanatomethyl-3,3,5-trimethylcyclohexyl isocyanate, 4,4'-diisocyanatodicyclohexylmethane, 4,4'-diisocyanato-3,3'-dimethyldicyclohexylmethane, 4,4'-diisocyanato-2,2-dicyclohexylpropane and mixtures thereof can be mentioned. Thus, it is preferred that the isocyanate is selected from the group consisting of tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2-methylpentamethylene diisocyanate, 2,2,4-trimethyl-hexamethylene diisocyanate, dodecanemethylene diisocyanate, 1,4-diisocyanatocyclohexane, 3-isocyanatomethyl-3,3,5-trimethylcyclohexyl isocyanate, 4,4'-diisocyanatodicyclohexylmethane, 4,4'-diisocyanato-3,3'-dimethyldicyclohexylmethane, 4,4'-diisocyanato-2,2-dicyclohexylpropane and mixtures thereof In particular, good results have been achieved with mixtures of 1,6-hexamethylen

diisocyanate and 3-isocyanatomethyl-3,3,5-trimethylcyclohexyl isocyanate. Accordingly, mixtures of 1,6-hexamethylene diisocyanate and 3-isocyanatomethyl-3,3,5-trimethylcyclohexyl isocyanate are preferred as isocyanates in the present invention, in particular in combination with PETMP or TMPMP. Furthermore, the at least one isocyanate in the present invention may be present in the form of a trimer, urethane, biuret, allophanate or uretdione.

Furthermore, it was found that good film forming capabilities of the polyurethane resin composition may be achieved when the NCO:SH ratio was kept in certain ranges. Thus, it is preferred that the NCO:SH ratio is in the range of from 10:1 to 1:10, preferably in the range of from 5:1 to 1:5, more preferably in the range of from 2:1 to 1:2. Particularly good results were achieved when the NCO:SH ratio were in the range of from 1.01:1 to 1.2:1. Accordingly, a NCO:SH ration in this range is particularly preferred in the present invention.

The compositions according to the present invention may further contain a solvent, and optionally a defoamer, thermostabilizer and/or wetting agent.

The solvent can be selected from aromatics such as xylol oder toluene, ketone such as acetone, 2-butanone, methyl-isobutylketone, diacetonalkohols, alcohols such as methanol, ethanol, i-propanol, butanol, 1-methoxy-2-propanol, ethers such as 1,4-dioxane, ethylenglykol-n-propylether, or ester such as acetic acid ethylester, acetic acid butylester, 1-methoxy-2-propylacetate or mixtures comprising these solvents. Preferred solvents are ethanol, i-propanol, butanol, acetic acid ethylester, acetic acid butylester, 2-methoxy-propylalcohol, diacetonalkohol, xylol or toluene.

As already mentioned, the polyurethane resin compositions according to the present invention can be readily transformed into flexible, transparent films having a desirable combination of properties useful for applications such as displays in electronic devices. Therefore, another object of the present invention is a method for producing a polyurethane film, comprising casting a polyurethane composition according to the present invention. The term casting as used in the present invention has the meaning as conventionally used in the art of film forming. Generally, casting said film is carried out by coating a certain substrate with the polyurethane resin composition according to the present invention. Since it is very desirable to coat a great number of substrates or a great area of a substrate as quickly as possible for economic reasons, it is preferred that the first coating step is carried out in a continuous process. For example, the coating may be carried out by wet coating, preferably by continuous wet coating. By using a wet coating process, manufacture of coated films according to the present invention is made simpler, easier to implement under a desirable reduction of costs and with uniform and consistent surface quality. Preferably, the wet coating method is selected from kiss coating, roll-to-roll coating, rotogravure coating, extrusion, spraying, air knife and dip/immersion coating. When flexible and transparent polyurethane films are desired (which is preferred for display applications), it was found that solvent casting processes are particularly

useful for casting the films according to the present invention. Thus, it is preferred that the casting step in the method according to the present invention is a solvent casting step. Solvent casting can be carried out as common in the art, for example by means of a bar coater, a doctor blade die, a slot die etc. Generally, solvent casting the polyurethane resin composition according to the present invention involves casting the composition onto a substrate. Said substrate may be part of a belt machine or a drum casting machine and comprise a metal and/or polymeric material. Preferably, the substrate comprises a polymer substrate such as a polyimide substrate since it was found that the polyurethane film may be easily separated from this kind of substrate. It is further preferred that the method according to the present invention involves a drying step, preferably directly after applying the composition according to the present invention onto said substrate. Drying methods may include indirect heating, heating by radiation and air-stream drying. They may be separated or combined in different zones in order to increase the accuracy of control over film formation and film drying at the substrate surface. Furthermore, one or more curing steps may follow after casting the film onto the substrate and drying. Curing may be carried out as thermal curing in a first curing step at a temperature in the range of from 50 to 100 °C and a second curing step at a temperature in the range of from 130 to 200 °C. The thermal curing step may be carried out in a period of time in the range of from 15 to 100 min and involve said first and second curing step or only one curing step with the conditions described for the second curing step. Finally, a cooling step may be follow after the drying and curing steps, if necessary. The cooling step may involve cooling rollers or chilled air or both of them. Optionally, further coatings and/or protective layers, e.g. for protection during transport, may be added after the optional chilling step.

A further object of the present invention is a thermoset polyurethane film, obtained by the method according to the present invention. With regard to its applications e.g. in display devices, it is preferred that the maximum process temperature is at least 140 °C and the glass transition temperature according to ASTM D3418 is at least 80 °C. The maximum process temperature is defined as the temperature beyond which certain properties of the films do not meet the specific requirements when exposed for a period of time. The properties monitored include, curling, transmittance, YI and haze values of the film after the heat treatment. A thermoset polyurethane film according to the present invention having a maximum process temperature and a T_g as described above is particularly useful for applications in electronics and displays. Further advantages are achieved with regard to the processability of the films in continuous processes.

Due to the desirable combination of advantageous features and effects of the thermoset polyurethane films according to the present invention, a further object of the present invention is the use of the film according to the present invention as backlight panel or display panel, preferably of a flat panel display, touch panel display or flexible electronic device.

Examples

Hereinafter, the present invention will be explained in detail with reference to examples, but the present invention is not limited thereto.

Measurements:

Glass transition temperatures (T_g)

- 5 The glass transition temperatures (T_g) of the polyurethane synthesized was measured according to ASTM D3418 using a Differential Scanning Calorimeter (DSC) under nitrogen purge with a heating rate of 10 °C/min. The temperature range was from 30 to 300 °C. The sample was cooled from 300 °C to 30 °C at a cooling rate of 10 °C/min. The transition temperature from the second heating was recorded as the glass transition temperature of the sample.

10 Mechanical Properties

The mechanical properties were measured by using Instron Universal Testing Machine 5569. The grip used was a pneumatic side action grip with rubber face. The test was carried out at ambient conditions (RT: 25 °C, RH 56%). The load capacity was 100 N and the rate was set at 1.00 mm/min.

Optical Properties

- 15 The total transmittance and transmission haze were measured by Hunter Lab Ultrascan PRO spectrophotometer

Pencil Hardness

Pencil hardness was measured using Elcometer3086 Scratch Boy in accordance with ASTM D3363 and the weight was chosen to be 750 g.

20 Maximum Process Temperature

- The dimension of the samples was chosen to be 150x150mm². The properties of the film samples without heat treatment were measured first. The orientation of the sample was noted as Machine Direction (MD) and Transverse Direction (TD). The film samples were then subjected to heat treatment for 2 hours at 150 °C. The maximum process temperature was defined as the temperature
25 when the criteria for above mentioned properties could be met.

Refractive Index

The refractive index of the film was measured using the Metricon 2010/M prism coupler. The index is determined at three different wavelengths, i.e., 402, 594 and 784 nm by changing the source wavelength settings in the equipment.

Example 1:

11.58 g of Desmodur NZ1 isocyanate (Bayer Material Science), 6.42 g of Pentaerythritol Tetra-3-mercaptopropionate (THIOCURE® PETMP from Bruno Bock Chemische Fabrik GmbH & Co.), and 12 g of MEK solvent were mixed together in a PP container. This mixture was homogenized using a Thinky Mixer (ARE 310) at 2000 rpm for 5 minutes followed by a de-foaming step at 2200 rpm for 2 minutes. The solid content was 60 % and the NCO-SH ratio was 1.05 in order to achieve an optimum film forming capability.

After mixing, the solution was cast onto a polyimide film using a bar coater with a wet film thickness of 150 µm. The cast film was then subjected to thermal curing at 80 °C for 15 min and 180 °C for 45 minutes. The obtained film showed excellent optical mechanical properties. The maximum process temperature was 150 °C.

Example 2 (Comparison): 11.23 g of Desmodur NZ1 isocyanate (Bayer Material Science), 6.77 g of Trimethylolpropane Tri (3-mercaptopropionate) (THIOCURE® TMPMP from Bruno Bock Chemische Fabrik GmbH & Co.) and 12 g of MEK solvent were mixed together in a PP container. This mixture was homogenized using a Thinky Mixer (ARE 310) at 2000 rpm for 5 minutes followed by a de-foaming step at 2200 rpm for 2 minutes. The solid content was 60 % and the NCO-SH ratio was 1.05.

After mixing, the solution was cast onto a polyimide film using a bar coater with a wet film thickness of 150 µm. The cast film was then subjected to thermal curing at 80 °C for 15 min and 180 °C for 45 minutes. This resin did not show a film forming capability and gave a flaky appearance instead.

Example 3:

A scale up process was conducted via a roll to roll pilot coating line with a knife blade coater. 386.12 g of Desmodur NZ1 and 213.88 g of PETMP were dissolved in 150 g of BA in a 2 liter metal container and homogenized using an overhead stirrer (300 rpm) for 20 minutes. The solid content was 80 % and the NCO-SH ratio was 1.05. The viscosity immediately after mixing was found to be 100 cP. The components were mixed only 1 hour before the actual run to avoid unnecessary gelling owing to the higher solid content. The resultant film was optically clear and easy to be peeled off from the release substrate (PI). The film was annealed at 180 °C for 1 h before all tests. The results showed excellent mechanical, optical and surface properties and good resistance to chemicals. The results are summarized in table 1 below.

Table 1: Results of Example 3

Item [unit]	Thermoset PUR film
Thickness [μm]	100
Total transmittance [%]	91
Haze [%]	0.2
Refractive Index (594 nm)	1.5460
Glass transition temperature [$^{\circ}\text{C}$]	88
Tensile strength [MPa]	58
Youngs modulus [GPa]	2.6
Tensile strain at break [%]	9.8
Pencil hardness	F-H
Max. process temperature [$^{\circ}\text{C}$]	150
Chemical resistance (RT, 15 min)	Acetone, methanol, isopropyl alcohol, toluene, methyl ethyl ketone, 10 % H_2SO_4 , 10 % NaOH

Claims

1. Method for producing a polyurethane film, comprising casting a polyurethane composition , comprising at least one isocyanate and at least one thiol selected from the group consisting of tetrathiols and/or polythiols.
- 5 2. Method according to claim 1, wherein the at least one thiol is an ester of a polyol.
3. Method according to claim 1 or 2, wherein the at least one thiol is an ester of a tetraol, pentaol, or hexanol.
4. Method according to at least one of the preceding claims, wherein the at least one thiol is an ester of pentaerythritol, or erythritol, .
- 10 5. Method according to at least one of the preceding claims, wherein the at least one thiol is pentaerythritol tetra-3-mercaptopropionate.
6. Method according to at least one of the preceding claims, wherein the at least one isocyanate is selected from the group consisting of tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2-methylpentamethylene diisocyanate, 2,2,4-trimethyl-hexamethylene diisocyanate, 15 dodecanemethylene diisocyanate, 1,4-diisocyanatocyclohexane, 3-isocyanatomethyl-3,3,5-trimethylcyclohexyl isocyanate, 4,4'-diisocyanatodicyclohexylmethane, 4,4'-diisocyanato-3,3'-dimethyldicyclohexylmethane, 4,4'-diisocyanato-2,2-dicyclohexylpropane and mixtures thereof, preferably a mixture of 1,6-hexamethylene diisocyanate and 3-isocyanatomethyl-3,3,5-trimethylcyclohexyl isocyanate.
- 20 7. Method according to claim 6, wherein the at least one isocyanate is a trimer, urethane, biuret, allophanate or uretdione.
8. Method according to at least one of the preceding claims, wherein the NCO:SH ratio is in the range of from 10:1 to 1:10, preferably in the range of from 5:1 to 1:5, more preferably in the range of from 2:1 to 1:2, and even more preferably in the range of from 1.01:1 to 1.2:1.
- 25 9. Method according to at least one the preceding claims, further comprising a solvent, and optionally a defoamer, thermostabilizer and/or wetting agent.
10. Method according to at least one the preceding claims, wherein the casting step is a solvent casting step.
11. Method according to at least one the preceding claims, wherein the casting step comprises a 30 continuous casting on a substrate, preferably a polymer substrate.

12. Polyurethane film, obtainable by a method according to at least one of claims 1 to 11.
13. Polyurethane film according to claim 12, wherein the maximum process temperature is at least 140 °C and the glass transition temperature T_g according to ASTM D3418 is at least 80 °C.
14. Use of the film according to claim 12 or 13 as backlight panel or display panel, preferably of a
5 flat panel display, touch panel display or flexible electronic device.

INTERNATIONAL SEARCH REPORT

International application No

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A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/73 C09D175/04 C08G18/38
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/148424 A1 (CARL ZEISS VISION AU HOLDING [AU]; CHEN FANG [AU]) 29 December 2010 (2010-12-29) claims 1,4,22 -----	1-14
X	EP 2 801 586 A1 (BRUNO BOCK CHEM FAB GMBH & CO KG [DE]) 12 November 2014 (2014-11-12) paragraph [0032]; example V3; table 2 -----	1-14
X	EP 2 246 378 A1 (MITSUI CHEMICALS INC [JP]) 3 November 2010 (2010-11-03) paragraph [0001]; claims 1-4 -----	1-14
A	WO 2008/061839 A1 (AKZO NOBEL COATINGS INT BV [NL]; VAN DER VEN LEENDERT GERARD JA [NL];) 29 May 2008 (2008-05-29) example 1 -----	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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