Espacenet



# Bibhiographic datax CN1308150 (A) -2001-08-15 

| In my patents list | Previous | * | $2 / 2$ | Next | 2 | (3) Pagater | 邅! Report data error | Print |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |

## Multifunctional wetness and adhersion resisting cloth producs

| Page bookmark | CN1308150 (A) - Multifunctionat wetness and adhersion resisting cloth product |
| :---: | :---: |
| Inventor(s): | GUO YUCHENG [CN]; GUO QIANG [CN] $\pm$ |
| Applicant(s): | GUO YUCHENG [CN] $\pm$ |
| Classification: | - international: D01F2/28; D03D1/00; (IPC1-7): D01F2/28; D03D1/00 |
|  | - cooperative: |
| Application number: | CN2001106570 20010319 |
| Priority number(s): | CN2001106570 20010319 |

## Abstract of CN1308150 (A)

Translate this text into :-
Albanan

The present invention relates to a kind of wet-resisting anti-sticking multifunction fabric and its products. Said invention uses diacetate short fibre as raw material and adopts textile process to obtain crammed stripe fabric, knitted fabric, knitgoods and hydro-entangled nori-woven fabric. These fabrics possess several functions of dry-refreshing, resisting wet, anti-sticking, resisting bacteriaand static resisting. and these fabrics are soft, do not irritate skin, possess good air permeability and water absorbatility, can reduce exudation of secretion, may be used for making various underclothes, protective clothes and various health-care textiles, and can prevent tinae corporis and dermatitis, so that it is a kind of fibre fabrics with health-care function.

[^0]［19］中华人民共和国国家知识产衩局
341511／42（2006．01）


## ［12］发 明 专 利 说 明 书

专利号 ZL 200410006092.0
［45］授权公告日 2007 年 4 月4日
［11］授权公告号 CN 1308150C
［22］※请日 2004．2．27
［21］中境号 200410006092.0
［30］侯先权
［32］2003． 2.28 ［33］］P［31］052977／2003
［73］专利权人 㮏能榤式会社
地址 日本辌京都
［72］发朋人 相困㩐赫
［56］参考文献

$$
\begin{array}{ll}
J P-8-73117 \mathrm{~A} & 1996.3 .19 \\
J P-7-48050 \mathrm{~A} & 1995.2 .21 \\
J P-5-51166 \mathrm{~A} & 1993.3 .2 \\
J P-8-248710 \mathrm{~A} & 1996.9 .27 \\
J P-4-356070 \mathrm{~A} & 1992.12 .9
\end{array}
$$

审㡍绻 正文静

代理人 禁向冈
［54］发明名称
图像形成装㯰
［57］樀緀

状材料（2）的有无的信息，劷断片状材料（2）的输送不定（S202），并判断输送不良是多种的输送不良中的啡……种，将有关输送不家谄信息发送绘图像控制器（23）－另外，图像揬制器（23），在从引警控制器（21）接收到的关于输送不良的信息悬表示发生了供纸延迟卜紙的信意时，向甸警控制器（21）发送表



1．一种在记录纸上形成图像的图像形成装置，包括：图像处理控制单元，处理来自外部装置的图像信息；
图像形成控制单元，基于来自上述图像处理控制单元的控制信号，控制上述图像形成装置；

输送单元，输送记录纸；
输送路径，用于引导由上述输送单元输送的记录纸；
检测单元，输出关于上述输送路径中有无要输送的记录纸的信息；

其中，上述图像形成控制单元基于上述检测单元输出的关于上述记录纸的有无的信息，判断上述记录纸的输送不良的种类，将判断出的关于输送不良的种类的信息发送给上述图像处理控制单元；

上述图像处理控制单元，在从上述图像形成控制单元接收的关于上述输送不良的种类的信息表示被检测出上述输送不良的记录纸能自动排纸时，将表示应解除上述输送不良的输送不良解除信号发送给上述图像形成控制单元。

2．根据权利要求 1 中所述的图像形成装置，其特征在于：
上述图像形成控制单元，在判断上述记录纸的输送不良后，停止由上述输送单元进行的记录纸的输送，并且，当从上述图像处理控制单元接收到上述输送不良解除信号时，开始由上述输送单元进行的记录纸的输送。

3．根据权利要求 1 中所述的图像形成装置，其特征在于：
还具有输入单元，为了将上述输送不良解除信号从上述图像处理控制单元发送给图像形成控制单元，向上述图像处理控制单元输入预定的指示信号；

上述图像处理控制单元响应由上述输入单元输入的上述预定的指示信号，将上述输送不良解除信号从上述图像处理控制单元发送给上述图像形成控制单元。

4．根据权利要求 3 中所述的图像形成装置，其特征在于：
还具有显示单元，显示从上述图像形成控制单元发送给上述图像处理控制单元的关于上述输送不良的种类的信息。

5．根据权利要求 1 中所述的图像形成装置，其特征在于：
还具有堆放上述记录纸的堆放单元；
上述输送单元提供堆放在上述堆放单元中的上述记录纸，
上述图像形成控制单元，在从上述堆放单元开始上述记录纸的供纸之后经过了预定的时间上述检测单元也没有检测到上述记录纸时，将上述输送不良判断为由供纸延迟引起的输送不良，将表示是由上述供纸延迟引起的输送不良的信息发送给上述图像处理控制单元。

6．根据权利要求 2 中所述的图像形成装置，其特征在于：
上述图像形成控制单元控制上述输送单元，使得在从上述图像处理控制单元接收到上述输送不良解除信号开始上述记录纸的输送后预定初始动作期间结束之前上述检测单元检测到关于上述输送不良的记录纸时，排出上述记录纸。

7．一种图像形成系统，包括在记录纸上形成图像的图像形成装置，和向上述图像形成装置发送图像信息的输入装置，还包括：

图像处理控制单元，处理来自上述输入装置的图像信息；
图像形成控制单元，基于来自上述图像处理控制单元的控制信号，控制上述图像形成装置；

输送单元，输送记录纸；
输送路径，用于引导由上述输送单无输送的记录纸；检测单元，输出关于上述输送路径中有无要输送的记录纸的信息；

其中，上述图像形成控制单元基于上述检测单元输出的关于上述记录纸的有无的信息，判断上述记录纸的输送不良的种类，将判断出的关于输送不良的种类的信息发送给上述图像处理控制单元；

上述图像处理控制单元，在从上述图像形成控制单元接收的关于上述输送不良的种类的信息表示被检测出上述输送不良的记录纸能自动排纸时，当从上述输入装置接收到表示应解除上述输送不良的指示

信号时，将表示应解除上述输送不良的输送不良解除信号发送给上述图像形成控制单元。

8．根据权利要求7中所述的图像形成系统，其特征在于：
上述图像形成控制单元，在判断上述记录纸的输送不良的种类后，停止由上述输送单元进行的记录纸的输送，并且，当从上述图像处理控制单元接收到上述输送不良解除信号时，开始由上述输送单元进行的记录纸的输送。

9．根据权利要求 7 中所述的图像形成系统，其特征在于：
上述输入装置具有显示单元，显示从上述图像形成控制单元经由上述图像处理控制单元传送来的关于上述输送不良的种类的信息。

10．根据权利要求7中所述的图像形成系统，其特征在于：
上述图像形成装置还具有堆放上述记录纸的堆放单元；
上述输送单元提供堆放在上述堆放单元中的上述记录纸，
上述图像形成控制单元，在从上述堆放单元开始上述记录纸的供纸之后经过了预定的时间上述检测单元也没有检测到上述记录纸时，将上述输送不良判断为由供纸延迟引起的输送不良，将表示是由上述供纸延迟引起的输送不良的信息发送给上述图像处理控制单元。

11．根据权利要求 8 中所述的图像形成系统，其特征在于：
上述图像形成控制单元控制上述输送单元，使得在从上述图像处理控制单元接收到上述输送不良解除信号开始上述记录纸的输送后预定初始动作期间结束之前，上述检测单元检测到表示是上述可自动排纸的情况的上述记录纸时，排出上述记录纸。

12．一种在记录纸上形成图像的图像形成装置的控制器，包括：
判断单元，判断在图像形成装置中发生的记录纸的输送不良的种类；

输入单元，输入用于解除图像形成装置所发生的上述输送不良的输入信号；

生成单元，在由上述输入单元输入了上述输入信号时，当上述判断单元的判断结果为被检测出上述输送不良的记录纸能自动排纸时，

生成用于解除上述输送不良的解除信号。

## 图像形成装置

技术领域
本发明涉及图像形成装置。

## 背景技术

在将图像形成于片状材料上的图像形成装置中，在图像形成装置内输送从供纸盘等提供的片状材料时，有时会出现由塞纸，片状材料打滑所引起的输送不良等（以下称为卡纸）的情况。并且，在发生卡纸的时，因为无法正常向片状材料上形成图像，所以使图像形成装置的动作停止。

为了使发生卡纸的图像形成装置的动作再次开始，就必须清除图像形成装置内成为卡纸的原因而残留的片状材料，但在清除这种卡纸状态时，用户必须打开图像形成装置所具有的盖子，清除造成卡纸的片状材料，并在图像形成装犆内不残留有片状材料的状态下关上盖子 （例如，日本特开平 2－182645号公报）。即，图像形成装置所具有的盖子被关上时，认为图像形成装置内造成卡纸的片状材料被清除，再次开始图像形成装犆的动作。

但是，取决于卡纸的种类，用户有时未必要打开盖子清除纸。
例如，用于从供纸盘—张一张地提供片状材料的供纸暂打滑，不能正常地提供片状材料，由供纸辊开始供纸后，会出现在预定时间后片状材料没有到达检测有无片状材料的传感器的异常（以下称供纸延迟卡纸）情况等，尽管用户不特意开闭图像形成装犆的盖子，也能使片状材料输送并向图像形成装置外排出，但是为了清除卡纸状态虽然较麻烦用户也必须开闭盖子。

发明内容
本发明是鉴于上述问题点而完成的，其目的在于提供一种在卡纸

处理中能降低劳烦用户手动的机会的图像形成装置。
本发明的目的在于，提供一种在记录纸上形成图像的图像形成装置，包括：图像处理控制单元，处理来自外部装置的图像信息；图像形成控制单元，基于来自上述图像处理控制单元的控制信号，控制上述图像形成装置；输送单元，输送记录纸；输送路径，用于引导由上述输送单元输送的记录纸；检测单元，输出关于上述输送路径中有无要输送的记录纸的信息；其中，上述图像形成控制单元基于上述检测单元输出的关于上述记录纸的有无的信息，判断上述记录纸的输送不良的种类，将判断出的关于输送不良的种类的信息发送给上述图像处理控制单元；上述图像处理控制单元，在从上述图像形成控制单元接收的关于上述输送不良的种类的信息表示被检测出上述输送不良的记录纸能自动排纸时，将表示应解除上述输送不良的输送不良解除信号发送给上述图像形成控制单元。

本发明的目的还在于，提供一种图像形成系统，包括：在记录纸上形成图像的图像形成装置，和向上述图像形成装置发送图像信息的输入装置，还包括：图像处理控制单元，处理来自上述输入装置的图像信息；图像形成控制单元，基于来自上述图像处理控制单元的控制信号，控制上述图像形成装置；输送单元，输送记录纸；输送路径，用于引导由上述输送单元输送的记录纸；检测单元，输出关于上述输送路径中有无要输送的记录纸的信息；其中，上述图像形成控制单元基于上述检测单元输出的关于上述记录纸的有无的信息，判断上述记录纸的输送不良的种类，将判断出的关于输送不良的种类的信息发送给上述图像处理控制单元；上述图像处理控制单元，在从上述图像形成控制单元接收的关于上述输送不良的种类的信息表示被检测出上述输送不良的记录纸能自动排纸时，当从上述输入装置接收到表示应解除上述输送不良的指示信号时，将表示应解除上述输送不良的输送不良解除信号发送给上述图像形成控制单元。

本发明的目的还在于，提供一种在记录纸上形成图像的图像形成装置的控制器，包括：判断单元，判断在图像形成装置中发生的记录

纸的输送不良的种类；输入单元，输入用于解除图像形成装置所发生的上述输送不良的输入信号；生成单元，在由上述输入单元输入了上述输入信号时，当上述判断单元的判断结果为被检测出上述输送不良的记录纸能自动排纸时，生成用于解除上述输送不良的解除信号。

本发明的其它特征和优点，通过以下的结合附图的说明将得以明确。在这些附图中，相同的参照标号表示相同或相似的部分。

附图说明
图1是表示打印机的概略结构的剖面图。
图2是表示打印机的控制结构的框图。
图3是表示发生记录纸卡纸时的控制动作的流程图。
图4是表示在发生供纸延迟卡纸时，主机的画面上所显示的消息的图。

图5是表示在发生供纸延迟卡纸以外的卡纸时，主机的画面上所显示的消息的图。

图6是表示在盒式供纸辊和定位辊之间存在被停止的片状材料的情况的图。

图7是表示在开始初始化动作之后经过一定时间之前，由 TOP 传感器检测片状材料的前端时的图。

具体实施方式

## （第1实施形式）

使用图1～图5说明本发明的第1实施例。
图 1 是说明本发明的第 1 实施例的图，是表示作为图像形成装置的打印机 20 的概略结构的剖面图。

1 是供纸盘， 2 是片状材料， 3 是盒式供纸辊， 4 是输送辊， 5 是片状材料输送路径， 6 是定位辊， 7 是作为检测有无片状材料 2 的检测传感器之一的 TOP 传感器， 8 是转印辊， 9 是感光鼓， 10 是加压辊， 11 是定影胶片， 11 a 是陶瓷加热器， 11 b 是热敏电阻， 12 是排纸辊， 13 是作为判断装置的 CPU， 14 是加热器驱动电路， 15 是扫描器电机， 16 是主电机， 17 是检测装置之一的排纸传感器， 20 是作为图像形成装置的打印机。

另外，图1所示的打印机20是采用电摄影方式的装置，在后述那样的动作中在片状材料 2 上形成调色剂像。

图2是表示第1实施例的打印机的概略结构的框图。
图 2 中，除了构成打印机的各单元之外，还一并记载有作为发送打印机 20 应打印的图像信号等的外部装置的主机 30 。

在图2中， 21 是引㢣控制器，是控制构成打印机 20 的各单元的装置。

第1实施例中的打印机20，在引攀控制器 21 内部备有 CPU13。
22 是高电压输出电路，用于向：用于使感光鼓 9 的表面带有预定电位的带电辊（无图示），用于用调色剂使形成于感光鼓 9 上的静电潜像显影的显影锟（无图示），用于将形成于感光鼓9上的调色剂像转印到片状材料 2 上的转印辊 8 等，施加高电压。

23 是图像控制器，接收从主机传来的图像信息和打印命令，并将上述图像信息进行展开处理等，使之成为适合于打印机 20 进行图像形成的位数据，并将进行展开处理后的位数据与表示根据图像信号应打印的控制信号的打印开始命令发送给引擎控制器 21 。

24 是用于打印机 20 对操作者（用户）显示消息的显示面板。另外，作为用于对操作者（用户）显示消息的装置，除了上述的

显示面板 24 之外，也可以在与图像控制器 23 连接的主机 30 的显示器等显示画面中显示消息。此时，由打印机 20 和主机 30 构成图像形成系统（参照图4，图5）。

在图 4，图5中， 25 是连接在图像控制器 23 上的卡纸清除按钮， 30 是具有显示画面 31，控制该显示画面 31 的显示的主机。另外， 32是用于在主机 30 和打印机 20 的图像控制器 23 之间进行通信的通信线， 33 是设置在主机 30 的画面上的卡纸清除按钮。另外，主机 30 上的卡纸清除按钮也可以这样构成：将显示画面设计成触摸屏式，操作者（用户）直接按压显示画面上的按钮部分；也可以这样构成：通过主机 30 具备的鼠标等指示设备，操作者（用户）间接地按压显示画面上的按钮部分。

如以上说明的那样，打印机 20 具有显示面板 24 和卡纸清除按钮 25 ，主机 30 具有卡纸清除按钮 33 。

由操作者（用户）按压打印机 20 的卡纸清除按钮后，向图像控制器 23 输入卡纸清除按钮 25 被按压这一情况。并且，根据卡纸清除按钮被按压这一情况，图像控制器 23 向 CPU13或引擎控制器 21 ，发送作为指示应解除输送不良（卡纸）的意思的命令的卡纸清除命令。

另外，主机 30 的显示画面 31 上的卡纸清除按钮 33 被按下后，主机 30 经由通信线 32 ，向图像控制器 23 发送卡纸清除命令。并且，根据卡纸清除按钮被按下这一情况，图像控制器 23 进一步向 CPU13或引擎控制器 21 发送作为指示应该解除输送不良（卡纸）的意思的命令的卡纸清除命令。

另外， 35 是门开关，是用于检测为了访问打印机 20 的内部而可开闭的门的开闭状态的开关。

接下来，说明打印机 20 在片状材料 2 上形成调色剂图像，并使其进行热定影，排出到打印机 20 的外部的一系列的打印动作。另外，井印机 20 的打印动作主要由后述的引擎控制器 21 实施。

首先，图像控制器 23 从主机 30 —并接收作为应打印的意思的命令的打印命令，和应打印的图像信息。并且，图像控制器 23 将图像

信息展开处理成适于进行图像形成的位数据，并将展开处理后的位数据和根据图像信号的表示应打印的意思的控制信号的打印开始命令，传送给引擎控制器 21 。

从图像控制器 23 接收到打印开始命令的引擎控制器 21 ，通过盒式供纸緄 3，使堆放在供纸盘1中的片状材料2供纸，进而，由输送辊4向打印机20内的片状材料输送路径 5 上供纸。

接着，引蔡控制器 21 的 CPU13 判断是态用 TOP 传感器 7 检测到片状材料 2 的前端。

并且，引擎控制器 21 根据 TOP 传感器 7 检测到片状材料 2 的前端这一情况，开始向感光鼓 9 形成静电潜俥，使得安定位辊 6 输送的片状材料 2 的前端与被转印到片状材料 2 上的调色剂像的前端位佔，成为所希望的位置关系。

另外，引㢣控制器 21 ，通过由扫描器单元 15 用激光使感光鼓 9上曝光，从而开始向感光鼓 9 上形成静电潜像，并且，用调色剂将静电潜像显影在显影辊（元图示）上。并且，引㢣控制器 21 通过从高电压输出电路 22 向转印緄 8 施加转印电压，从而将感光鼓 9 上的调色剂像转印到片状材料2上。

并且，引擎控制器 21 使片状祆料 2 输送到用于将调色剂定影到片状材料 2 的加压辊 10，定影胶片11，陶瓷加热器 11a，将调色剂加压定影到片状材料 2 上之后，利用排纸鼣 12 向打印机 20 的外部排纸。

另外，排纸传感器 17 检测片状材料 2 是否被排出。
这里，热敏电阻 11 b 检测陶瓷加热器 11 a 的温度，通知给 CPU13，CPU13 控制加热器驱动电路14，进行陶瓷加热器 11 a 的温度控制。

CPU13 进行控制，使得在片状材料 2 通过陶瓷加热器 11a期间，增加施加的电力，增加的量相当于给子用纸的热量，进行控制使得陶瓷加热器11a保持温度恒定。

主电机 16 驱动转印辊 8，感光鼓9，加压辊 10 。
接下来，使用图 3 的流程图说明在本发明的第 1 实施例中发生记

录纸苗纸时的控制动作。
另外，图3的流程图是主要由打印机20具备的图像控制器 23 和引擎控制器 21 执行的动作。

在图 3 中，引擎控制器 21 通过从图像控制器 23 接收打印开始命令而开始打印（S201）。

接着，引擎控制器 21 的 CPU13监视由供纸辊 3 从堆放在供纸盘 1 的片状材料 2 中提供来的片状材料 2，是否发生输送不良（卡纸） （S202）。

引擎控制器 21 的 CPU13 在步骤 S202 判断多种输送不良（卡纸）。首先，由盒式供纸辊 3 提供片状材料 2 后，如果在一定时间内，用TOP 传感器 7 没有检测到片状材料 2 的前端，则假定被提供的片状材料 2 到达 TOP 传感器 7 发生延迟，判断为＂供纸延迟卡纸＂，进入 S204。

另外，引擎控制器 21 的 CPU13，如果在步骤 S202，TOP 传感器 7 检测到片状材料 2 的前端，而到一定时间后TOP 传感器 7 没有检测到片状材料 2 的后端，则假定片状材料 2 滞留在TOP 传感器 7 所检测的位置，判断为＂TOP 传感器滞留卡纸＂，进入 S204。

另外，引擎控制器 21 的 CPU13，如果在步骤 S202，TOP 传感器 7 检测到片状材料 2 的前端，而到一定时间后（比用于判断 TOP 传感器滞留卡纸的一定时间更长的时间），排纸传感器 17 没有检测到片状 2 的前端，则假定片状材料 2 到达排纸传感器 17 发生延迟，判断为＂排纸传感器前端延迟卡纸＂，进入 S204。

另外，引擎控制器 21 的 CPU13，如果在 S 202 中，排纸传感器 17检测到片状材料 2 的前端，而到一定时间后排纸传感器 17 没有检测到片状材料 2 的后端，则假定片状材料 2 滞留在排纸传感器 17 所检测的位置，判断为＂排纸传感器滞留卡纸＂，进入 S204。

另外，引擎控制器 21 的 CPU13，如果在 S 202 中，判断为＂供纸延迟卡纸＂，＂TOP 传感器滞留卡纸＂，＂排纸传感器前端延迟卡纸＂，＂排纸传感器滞留卡纸＂都没发生，则直至打印结束
（S203）。
在 S204 中，收到 CPU13 的判断，引㢣控制器 21 经由扫描器单元 15，主电机 16，高电压输出电路 22 ，使电机的旋转即片状材料 2 的输送，高电压的输出，用于冷却打印机 20 内部的风扇的旋转，旋转驱动扫描单元 15 内的多面镜电机的扫描器电机的旋转，扫描单元 15内的激光的发光等立即停止。

并且，CPU13 向图像控制器 23 以及经由图像控制器 23 连接的主机 30 进行通信，将此时检测到的卡纸的种类（＂供纸延迟卡纸＂，
＂TOP 传感器滞留卡纸＂，＂排纸传感器前端延迟卡纸＂，＂排纸传感器滞留卡纸＂的某一种）作为状态信息来进行通知。并且，根据各自被通知的卡纸的种类（S205），图像控制器 23 将消息显示在显示面板 24 中，主机 30 将消息显示在主机 30 具有的 CRT 等的显示画面 31 中。

具体地讲，在 S205，图像控制器 23 ，基于从 CUP13通知的表示卡纸的种类的状态信息，判断打印机 20 中发生的卡纸是否为特定的卡纸（这里为供纸延迟卡纸）。

从 CPU13 通知给图像控制器 23 的状态信息所表示的卡纸的种类是＂供纸延迟卡纸＂时，进入S206，图像控制器 23 使主机 30 的显示画面 31 上显示通过自动排纸进行卡纸清除的选择画面（参照图4）。另外，图像控制器 23 使显示面板 24 显示询问是否通过自动排纸进行卡纸清除的画面。而且，向显示面板 24 的显示与在主机 30 的显示可都进行，也可某一方进行。

另一方面，从 CPU13 通知给图像控制器 23 的卡纸的种类为＂供纸延迟卡纸＂以外的＂TOP 传感器滞留卡纸＂，＂排纸传感器前端延迟卡纸＂，＂排纸传感器滞留卡纸＂时，进入 S209，图像控制器 23在主机 30 的显示画面 31 上显示令操作者（用户）通过手动排纸进行卡纸处理的消息（参照图5）。另外，图像控制器 23 在显示面板 24中显示令操作者（用户）通过手动排纸进行卡纸处理的消息。而且，向显示面板 24 的显示与主机 30 中的显示可都进行，也可某一方进

行。
并且，在 S 206中，图像控制器 23 在卡纸清除按钮 25 或 33 被按下，由操作者（用户）进行与输送不良（卡纸）有关的片状材料 2 的自动排纸的意思的选择时，向图像控制器 23 输入表示卡纸清除按钮 25 或 33 被按下这一情况的输入信号。

并且，图像控制器 23 被输入输入信号后，发生用于使 CPU13或者引擎控制器 21 解除由输送不良（卡纸）引起的主电机 16 的旋转停止，和由高压输出电路 22 进行的高电压的输出停止等的卡纸清除命令，并且，发送卡纸清除命令，进入 S 207。

另外，通过操作者的操作，是在任意的时间从卡纸清除按钮 25 输入给图像控制器 23 输入信号的，但是从图像控制器 23 向 CPU13或引擎控制器 21 发送卡纸清除命令，却只是图像控制器 23 在打印机中发生特定的输送不良（这里为供纸延迟卡纸）的情况下才进行的。

在 S 206 中，如果选择不进行自动排纸则进入 S 209。
在 S206中，如果什么都不选择，则待机（也可以这样构成，即一直待机经过一定时间后，假定某一个被选择而继续。）。

并且，在 S207 中，CPU13 判断在打印机 20 内是否没有残留的片状材料 2 或者是否能够自动排纸。

如果详细叙述 S 207 ，则 CPU13 通过从图像控制器 23 接收卡纸清除命令，而开始初始化动作，该初始化动作为，开始主电机 16 的旋转和由高压输出电路 22 产生的高电压的输出。在初始化动作中，由主电机 16 给予输送辊4，定位辊 6 驱动力而旋转片状材料2。在 S204中，如果有停止在盒式供纸辊 3 与定位辊 6 之间的片状材料 2 （图 6），则 TOP 传感器 7 开始初始化动作之后，在经过一定时间之前，检测片状材料 2 的前端（图7）。

如以上那样，TOP 传感器 7 开始初始化动作之后，如果在经过—定时间前，检测到片状材料 2 的前端，则判断为成为供纸延迟卡纸的原因的片状材料 2 能够自动排纸。

并且，TOP 传感器 7 以及排纸传感器 17 开始初始化动作之后，

如果在经过一定时间后，没有检测到片状材料 2，则判断为没有残留在打印机 20 内的片状材料。

CPU13 判断为没有残留在打印机 20 内的片状材料 2 时，或者判断为成为供纸延迟卡纸的原因的片状材料 2 可以自动排纸时，进入 S208。

另一方面，CPU13 判断为有残留在打印机 20 内的片状材料时，或者判断为成为供纸延迟卡纸的原因的片状材料 2 不能自动排纸时，进入 S209。

在 S208中，打印机 20 中所发生的卡纸是可自动排纸的卡纸时，结束自动排纸后进入 S211。

另一方面，在 S209 中，显示令用户用手动打开图像形成装置的盖子进行卡纸处理的消息，进入 S210。

这里，首先说明卡纸的种类为＂排纸延迟卡纸＂的情况。
此时，表示是＂排纸延迟卡纸＂的状态信息被传送到图像控制器 23 时，图像控制器 23 在图 3 的流程图中的 S206中，将卡纸的种类假定为供纸延迟卡纸以外的卡纸，进入步骤 S 209 ，所以，在打印机 20所具备的显示面板 24 中，不显示询问是否通过自动排纸进行卡纸清除的画面。所以，不用从图像控制器 23 向引擎控制器 21 发送卡纸清除命令，不进行自动排纸。

另外，表示是＂排纸延迟卡纸＂的状态信息，经由图像控制器 23，被传送到主机 30 时，图像控制器 23 在图 3 的流程图中的 S206中，假定卡纸的种类为供纸延迟卡纸以外的卡纸，进入步骤 S 209 ，所以，在主机 30 的显示画面 31 中，不显示通过自动排纸进行卡纸清除的选择画面。所以，不用从主机 30 经由图像控制器 23 ，向引擎控制器 21 发送卡纸清除命令，不进行自动排纸。

其理由是因为，如果用户不进行卡纸处理，CPU13 或者引㢣控制器 21 接受来自图像控制器 23 和／或主机 30 的卡纸清除命令，要进行自动排纸，则可能产生以下问题。
＂排纸延迟供纸＂是TOP 传感器 7 检测到片状材料 2 的前端，而

到一定的时间为止，排纸传感器 17 没检测到片状材料 2 的前端的情况时的输送不良，所以作为其特征，可以考虑片状材料 2 的前端卷缠在定影器（定影胶片11或加压辊10）上的情况。并且，以这种状态开始自动排纸后，片状材料 2 可能会进一步卷缠在定影器上，从而成为打开打印机 20 的盖子，操作者（用户）也不能除去成为卡纸的片状材料 2 的卡纸（以下称不可清除卡纸（unclearable jam））的问题。

所以，在是＂排纸延迟卡纸＂时，判断为不能进行自动排纸，不进行自动排纸，操作者（用户）通过手动打开打印机 20 的盖子，除去成为卡纸的片状材料2，根据关闭盖子这一情况，引擎控制器 21 进行卡纸清除。

另外，在以上的说明中说明了＂排纸延迟卡纸＂，但是＂排纸传感器滞留卡纸＂。＂TOP 传感器滞留卡纸＂的情况也与＂排纸延迟卡纸＂一样，可能成为不可清除卡纸。所以，即使因通信儤误等，图像控制器 23 向 CPU13发送卡纸清除命令，CPU13 也不进行自动排纸。

在 S 210 中，CPU13 通过检测门开关 35 的开闭状态，检查手动排纸是否结束，门开关的开闭状态从开状态切换到闭状态，就能确认手动排纸结束，此时进入 S211。

在 S 211 中，假定 S 202 中发生的卡纸已被解除，进行卡纸清除。
进行卡纸清除后，打印机 20 的引擎控制器 21 的控制状态成为就绪状态（S212），成为能够再次开始打印的状态。

通过进行该控制，在称为＂供纸延迟卡纸＂的，即使不开闭图像形成装置的盖子，也能输送片状材料并排出到图像形成装置外的特定的卡纸的情况下，操作者（用户）只通过按下显示面板 24 和／或主机 30 画面上的卡纸清除按钮 $25, ~ 33$ ，就能进行卡纸清除。

所以，能向用户提供用户友好的图像形成装置，图像形成系统，图像形成装置的控制方法以及图像形成系统的控制方法。

另外，即使在＂供纸延迟卡纸＂的情况下，如果用户在程序 （sequence）过程中打开／关闭门（例如用手动取除片状材料 2 的情况

等），则也能进入 S207或 \＄210。

## （第2实施例）

下面说明第 2 实施例。
在第1实施例中，从 CPU13 将＂供纸延迟卡纸＂通知给显示面板 24 和／或主机 30 时，取代用户按下显示面板 24 和／或主机 30 上的卡纸清除按钮 25,33 （在 S 206 中为 YES），而是显示面板 24 和／或主机 30 上的设备（打印机设备等）自动地判断是＂供纸延迟卡纸＂状态，发送卡纸清除命令。

另外，在第1实施例中，CPU13 判断为＂供纸延迟卡纸＂状态 （在 S205 中为 YES）时，也可以省略用户按下显示面板 24 和／或主机 30画面上的卡纸清除按啥25，33的步骤（S206），CPU13或者引擎控制器 21 自动地判断是否没有机内残留纸或者是否可自动排纸 （S207）。

通过进行这样的控制，能提供一种在＂供纸延迟卡纸＂这种特定的卡纸时，不用劳烦用户手动就能自动地进行卡纸清除的用户友好的图像形成装置，图像形成系统，图像形成装置的控制方法以及图像形成系统的控制方法。

另外，在实施例1，2中，说明了在＂供纸延迟卡纸＂时省略用户的操作的例子，但是，本发明不限于此，对于不需要用户手动进行卡纸处理的其他的卡纸的种类，当然也能同样自动地进行处理。

如以上那样，能提供一种可减少卡纸处理中劳烦用户手动的机会的用户友好的图像形成装置，图像形成系统，图像形成装置的控制方法以及图像形成系统的控制方法。

即，能提供一种在特定的卡纸的情况下，用户只通过按下卡纸清除按睩就能进行卡纸清除的图像形成装置，图像形成系统，图像形成装置的控制方法以及图像形成系统的控制方法。

而且，能提供一种在特定的卡纸的情况下，取代用户按下卡纸清除按钮，而是通过显示面板和／或主机上的设备自动地发送卡纸清除命

令，不用劳烦用户手动，能自动地进行卡纸清除的图像形成装置，图像形成系统，图像形成装置的控制方法以及图像形成系统的控制方法。

而且，能提供—种在特定的卡纸情况下，通过 CPU 或者引擎控制器的判断而自动地进行卡纸清除，从而不用劳烦用户手动的图像形成装置，图像形成系统，图像形成装犆的控制方法以及图像形成系统的控制方法。

另外，本发明不限于上述实施例，显然在附加的权利要求书的范围内可进行各种变形。


图 1


图2


图 3



图6

图7

## Espacenet

Bibliographic data: JPH08256891 (A) - -1996 -10-08

FUNCTIONAL BEDDING

| Inventor(s): | ITO NAOMI; IKEI KIYOAKI $\pm$ (ITO NAOMI, ; IKEI KIYOAKI) |
| :--- | :--- |
| Applicant(s): | MITSUBISHI RAYON CO $\pm$ (MITSUBISHI RAYON CO LTD) |
| Classification: - international:A47C27/12; A47G9/02; (IPC1-7): A47C27/12; <br>  - cooperative: <br> Application <br> number: JP19950068393 19950327 |  |

Priority number(s): JP19950068393 19950327

Abstract of JPho8256893(A)

PURPOSE: To provide a functional bedding capable of partially exchanging a pari to restore the function arbitrarily or to endow another function by composing it of mutually attachable/detachable dividable pleces and imparing the pleces with respective functions.
CONSTTUTION: A bedding is divided, for instance, in five pleces so that the first divided piece corresponds to a head and the fifth divided plece to feet. On the side faces of each divided plece 1 PRG 5 , a desired connector such as snap, hook, button, Herkule's fastener, ribbon, eto., is delachably atached to each other. Water absorptivity is given by blending a hydrophllic substance such as polyethylene glycol, etc, forming a hydrophilic layer on the fiber surface, forming the fiber cross section in a polygon, or forming a large number of micropores on the fiber surface, and the divided piece imparted with hydrophilic

propery is placed in the positions of divided pieces 2 and 3 to be in contact with the back, arms, hands, elc. This bedding can be comfortably used in summer by increasing the number of divided plece with the given hydrophilic property.

（54）【発明の名称】 機能性寝具
（57）【要約】
【目的】その一部を部分的に取り替えて，任意に機能性を回復したり別の機能性を付与したりすることのでき る寝具を提供する。
【構成】相互に着脱自在の複数の分割片で構成され，少なくとも一つの分割片に機能性が付与されている機能性䨖具。

| 1 |
| :---: |
| 2 |
| 3 |
| 4 |
| 5 |

## 【特許請求の範囲】

【請求項1】相互に着脱自在の複数の分割片で構成さ れ，少なくとも一つの分割片に機能性が付与されている ことを特徴とする機能性寝具。
【発明の詳細な説明】
【 0001 －
【産業上の利用分野】本発明は，少なくともその一部に任意に機能性を付与し得る寝具に関するものである。
【 000 2】
【従来の技術】従来から，寝具への機能性の付与は，そ の殆どが保温性蟣維や吸水性䋐維等，織維自体が持つ固有の特性を利用する物理的な手法によっていたが，特殊 なケースとして化学的な処理を施したものを使用してい る場合もあった。
【0003】
【発明が解決しようとする課題】しかしながら，何れの場合も，寝具への機能性の付与は，カバーあるいは中綿 の全体に施されており，特に化学的な処理による機能性付与は繰り返し洗灌等によって機能が低下し，初期の機能を維持しようとすれば，カバーや中綿の損傷が殆どな いにもかかかかわらずそれらの全体を取り替えなければ ならないといら問題があった。また別の機能を付与した い場合は，物理的な手法で機能を付与したものであって もカバーや中綿全体を取り替えねぼならなかった。本発明は，かかる従来の問題点を解消し，その一部を部分的 に取り替えて，任意に機能性を回復したり別の機能性を付与したりすることのできる寝具を提供するものであ る。

## 【0 004 】

【課題を解決するための手段】本発明は，相互に着脱自在の複数の分割片で構成され，少なくとも一つの分割片 に機能性が付与されていることを特徵とする機能性寝具 によって，上記課題を解決するものである。
【0005】本発明の寝具を構成する分割片の数は特に限定されないが， $5 \sim 15$ であることが望ましい。 5 未満では経済的ではあるが，人体において，機能性を必要 とする部位に分割片を配置できない場合がある。反対に 15 を越えると，必要とする部位に分割片を配置できる が，寝具形成上コスト高になり，また細分化されること により凹凸部分が多く発生し，快適な睡眠も得られにく くなる。
【 0006 】尚，本発明でいう寝具とは，掛け布団，敷布団，毛布，ソファー，クッション，寝袋，車両用シー ト等就寝時に使用するものの総称である。また本発明で いら機能性とは，吸水性，消臭性，抗菌性，芳香性，清涼感，保温性等，寝具に要求される各種の機能性であ り，これらの機能性は通常寝具のカバーまたは中綿部分 に付与されている。
【0007】図1は，敷き布団を5分割した分割片で構成した本発明の機能性寝具の一例を示す平面図であり，

分割片 1 が頭部，分割片 5 が足部に該当する。この場合各分割片を相互に着脱自在とするには，各分割片 $1 \sim 5$ の側面にスナップ，ホック，ボタン，面状テープ，リボ ン等所望の連結具を設ければよい。
【 0 0 0 0 8 】 吸水性の付与は，ポリエチレングリコール などの親水性化合物をブレンドしたり，繊維表面に親水性層を形成させたり，織維断面を多角形にしたり，瀻維表面に多数の微細孔を形成させたりするなどの方法で行 ら。吸水性を付与した分割片は背中，腕，手等が接する部位（図1 の分割片2，3）に配置することが望まし い。夏期においては吸水性付与の分割片の配置箇所を増加させることにより快適な寝具として用いることが可能 である。
【 O O O 9 】 消臭性に関しては，ゼオライトの酸性基に よる中和反応を使用する等既知の方法で消臭性を付与し た繊維を分割片のカバーまたは中綿に用い，必要とする部位に適宜配置する。
【 00101 】 抗菌性も第 4 級アンモニウム塩等といった既知の抗菌剤を付与して抗菌性能をもつ綫維を使用し，必要部位に適宜配置する。
【0 0 1 1 】 芳香性は，鎮静効果や催眠作用等の効用の ある香りをマイクロカプセル等に封じ込め適当なバイン ターで付着させ洗䍜にも数回程耐えられるような形態で付与する。芳香性の付与は，予め絨維に付与したものを用いてカバーや中綿としてもよく，カバーや中綿を形成後付与しても差し支えない。芳香性を付与した分割片は頭部（図1 の分割片1）への配置が望ましい。
【O O 1 2 】 清涼感は，例えば麻様の形態をもつ織物や听感のある表面をもつ布地を分割片のカバーに用いる ことで付与できる。吸水性と同様に夏期には寝具の大部分に配置するとより快適な稿具となる。
【o 0 1 3 〕 】 保温性は分割片のカバーに起毛織編物を用 いたり，極細繊維や中空系を使用して空気層を保持し，熱伝導を抑えた織編物を活用するなどして付与する。ま た，中綿にセラミックスの微粉末を練り込んだ綫維を用 いてもよい。保温性付与の分割片は適宜必要とされる部位に配置し，特に冬期には手，腰，背中，足をはじめ多 くの部位（図 1 の分割片 $2 \sim 5$ ）に配置することで安眠 が得られる。
【 0014 】図1においては各種の機能性材料への対応及び経済的な要素を加味して寝具の縦方向に5分割とし た例を示しているが，使用する機能材の種類によって寝具の横方向とし分割数も 6 以上とすることも可能であ る。また分割片は必ずしもそれぞれ均等である必要はな く，適宜分割片の大きさを替えることも可能である。ま た，同一の機能性分割片を複数箇所に配置するだけでな く，異なる機能性を有する複数の分割片をそれぞれ適当 な部位に配置してもよい。例えば芳香性を頭部の分割片 1 に付与し，抗菌性を足元の下端部の分割片 5 に付与す る等である。また機能性分割片としては，他の分割片と

比較して軽量なもの，例えば布団に毛布を機能性分割片
として用いてもよい。
【0 0 1 5 】
【発明の効果】本発明の機能性寝具は，相互に着脱自在 の複数の分割片で構成されているので，機能性を付与し た分割片を部分的に取り替えて，任意に機能性を回復し たり別の機能性を付与したりすることが可能である。

## 【図面の簡単な説明】

【図1】本発明の機能性寝具の一例を示す平面図であ る。
【符号の説明】
1 頭部に位置する分割片
5 足部に位置する分割片

【図1】

| 1 |
| :---: |
| 2 |
| 3 |
| 4 |
| 6 |

(19) World Intellectual Property Organization International Bureau
(43) International Publication Date 17 August 2006 (17.08.2006)


PCT
(10) International Publication Number WO 2006/086715 A2
(51) International Patent Classification:

C08G 18/12 (2006.01) C08G 18/48 (2006.01)
C08G 18/08 (2006.01) C08G 18/76 (2006.01)
(21) International Application Number:

PCT/US2006/004894
(22) International Filing Date:

10 February 2006 (10.02.2006)
(25) Filing Language: English
(26) Publication Language:

English
(30) Priority Data:

11/056,067
11 February 2005 (11.02.2005)
US
11/253,927
19 October 2005 (19.10.2005)
US
11/300,229 13 December 2005 (13.12.2005) US
(71) Applicant (for all designated States except US): INVISTA TECHNOLOGIES S.A R.L. [CH/US]; Talstrasse 80, CH-8001 Zurich (CH).
(72) Inventors; and
(75) Inventors/Applicants (for US only): LIU, Hong [US/US]; 174 Abner Lane, Waynesboro, VA 22980 (US). COVELLI, Carmen, A. [US/US]; 2302 Century Lane, Chadds Ford, PA 19317 (US). FARMER, Douglas, K. [US/US]; 4998 Heritage Woods Drive, Greensboro, NC 27407 (US).
(74) Agent: FURR, Robert, B., JR; Three Little Falls Centre, 2801 Centerville Road, Wilmington, DE 19808 (US).
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

## Published:

- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
(54) Title: SOLVENT FREE AQUEOUS POLYURETHANE DISPERSIONS AND SHAPED ARTICLES THEREFROM

(57) Abstract: An article comprising an adhesive, a stretch member and a substrate wherein the adhesive is used to attach the stretch member to the fabric in a folded hem arrangement. The adhesive can be a tape made from an aqueous polyurethane dispersion and the stretch member can be a spandex fiber.

## SOLVENT FREE AQUEOUS POLYURETHANE DISPERSIONS AND SHAPED ARTICLES THEREFROM

## CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This Application claims priority to U. S. applications serial numbers 11/253927 filed on October 19, 2005, 11/056067 filed on February 11, 2005, and $11 / 300229$ filed on December 13, 2005, now pending.

## FIELD OF THE INVENTION

[0002] The present invention relates to novel aqueous polyurethane dispersions and shaped articles made therefrom. Specifically, the present invention relates to solvent-free, stable dispersions, which comprise fully formed polyurethaneurea with blocked isocyanate end groups. The dispersions can be formed by prepolymer mixing processes. The present invention additionally relates to shaped articles and coated articles formed from such aqueous dispersions, which can be heat and /or pressure activated for bonding, lamination and adhesion to substrates. The shaped articles may remain flexible and elastomeric after bonding, lamination or adhesion.

## BACKGROUND OF THE INVENTION

[0003] Polyurethanes (including polyurethaneureas) can be used as adhesives for various substrates, including textile fabrics. Typically, such polyurethanes are either fully formed non-reactive polymers or reactive isocyanate-terminated prepolymers. Such reactive polyurethane adhesives often require extended curing time to develop adequate bonding strength, which can be a disadvantage in manufacturing processes. In addition, the isocyanate groups of the polyurethanes are known to be sensitive to moisture, which limits the storage stability and reduces the shelf life of the product incorporating such polyurethanes.
[0004] Typically, such polymers, when fully formed, are either dissolved in a solvent (solvent borne), dispersed in water (water borne), or processed as thermoplastic solid materials (hot melt). Notably, solvent-based adhesives face ever-tightening health and environmental legislation aimed at reducing volatile
organic compound (VOC) and hazardous air pollutant (HAP) emissions. Accordingly, alternatives to conventional solvent-based products are needed.
[0005] Hot-melt adhesives, although environmentally safe and easily applied as films, generally have high set and poor recovery when subject to repeated stretch cycles. Therefore, improvements are needed.
[0006] Many attempts have been made to develop water borne polyurethane adhesives to overcome these deficiencies.
[0007] U.S. Patent No. 5,270,433 discloses an "adhesive composition comprising a substantially clear and solvent-free, aqueous, one-component polyurethane dispersion containing the reaction products of (a) a polyol mixture comprising polypropylene glycol, (b) a mixture of polyfunctional isocyanates comprising $\alpha, \alpha$, $\alpha^{1}, \alpha^{1}$-tetramethyl xylene diisocyanate (TMXDI), (c) a functional component capable of salt formation in aqueous solution, and (d) optionally, a chainextending agent." The adhesive films from this composition have low recovery power and poor heat resistance in view of the unsymmetrical structure and steric hindrance of isocyanate groups on TMXDI, preventing the formation of strong inter-chain urea hydrogen bonds in the hard segments of the polymer.
[0008] U.S. Patent Application Publication No. 2004/0014880 A1 discloses an aqueous polyurethane dispersion for adhesive bonding in wet and dry laminations stated to have superior coatability, adhesive strength and heat resistance. This dispersion contains a substantial amount of organic solvent methyl ethyl ketone (MEK).
[0009] U.S. Patent Application Publication No. 2003/0220463 A1 discloses a method for making a polyurethane dispersion that is free of organic solvent such as N-methylpyrrolidone (NMP). However, the composition is limited to a prepolymer having low free diisocyanate species, such as methylene bis(4phenylisocyanate) ( $\left.4,4^{\prime}-\mathrm{MDI}\right)$. The process to produce such a prepolymer with low free diisocyanate is complicated (as disclosed in US Patent $5,703,193$ ). Such
processing also requires short path distillation of the free diisocyanate and is thus not economical in producing a prepolymer for making a polyurethane dispersion.

## [00010] U.S. Patent No. 4,387,181 discloses a stable aqueous polyurethane

 dispersion, containing N-methylpyrrolidone (NMP) solvent, prepared by reaction of carboxylic group-containing oxime-blocked, isocyanate-terminated prepolymer and polyamine. The prepolymer is made by reaction of aromatic diisocyanates, such as 4,4'-diphenylmethanediisocyanate (MDI) or toluene diisocyanate (TDI), with polyether or polyester polyols and a dihydroxy alkanoic acid. The oximeblocked isocyanate groups are capable of reacting with polyamine at 60 to $80^{\circ} \mathrm{C}$ within 6 to 18 hours. The dispersion is stable in storage, and the film formed from the dispersion has good tensile properties. However, this dispersion still has organic solvent present and the longer curing time needed is unsuitable for fabric bonding and lamination in practice.[0001] U.S. Patent No. 5,563,208 describes an acetone process to prepare an essentially solvent-free aqueous polyurethane dispersion, comprising urethane prepolymers with blocked isocyanate groups and polyamines within the molecular weight range of 60 to 400 in a molar ratio of blocked isocyanate groups to primary and/or secondary amino groups of from 1:0.9 to $1: 1.5$. This dispersion is stable in storage at room temperatures and gives a heat-resistant binder in coating. It requires long curing time (up to 30 minutes), which is still not suitable for fabric bonding and adhesion. Furthermore, the acetone process requires an additional distillation step to remove the acetone from the dispersion, which makes this process less economical.
[00011] U.S. Patent No. 6,586,523 describes an acetone process for preparing a self-crosslinking polyurethane dispersion for sizing agents, comprising a prepolymer with isocyanate groups partially blocked and partially extended, and excess polyfunctional compounds having molecular weights from 32 to 500 with primary or secondary amino and/or hydroxyl groups. This dispersion composition reduces the curing time to some degree, but still has
deficiencies because an additional distillation step to remove the acetone is required.
[00012] U.S. Patent No. 6,555,613 describes a solvent-free aqueous dispersion of a reactive polyurethane having a number average molecular weight $(\mathrm{Mn})$ of from 800 to 14,000 , a degree of branching of from 0.0 to $3.0 \mathrm{~mol} / \mathrm{kg}$, and an isocyanate functionality from 2.0 to 6.0 per mole. The polyurethane is made from a polyester polyol, a polyisocyanate and polyisocyanate adduct, with low molecular weight polyol and anion-forming units after neutralizing incorporated in the polymer chains, and with blocked isocyanate groups capable of further reactions for crosslinking. The result of such dispersion is a coating material that is hard, glossy and elastic, but such coating material does not have the elastomeric features and stretch/recovery properties required for an adhesive to be used with stretch fabrics.
[00013] Thus, it would be desirable to provide an improved aqueous polyurethane dispersion, which overcomes one or more of the deficiencies of the prior art.

## SUMMARY OF THE INVENTION

[00014] The invention may comprise in a first aspect, a prepolymer for use in an aqueous polyurethane dispersion comprising
at least one polyether (including copolyethers), polycarbonate or polyester polyol component having a number average molecular weight of about 600 to about 3,500, for example, a poly(tetramethylene ether) glycol having a number average molecular weight of about 1,400 to about 2,400 ;
a polyisocyanate, which is a mixture of 4,4'- and 2,4'-methylene bis(phenyl isocyanate) (MDI) isomers, with the ratio of the 4,4'-MDI to $2,4^{\prime}-\mathrm{MDI}$ isomers from about 65:35 to about 35:65; and
at least one diol compound with: (i) hydroxy groups capable of reacting with the mixture of MDI isomers of component b) and (ii) at least one carboxylic acid group capable of forming a salt upon neutralization, wherein the at least one carboxylic acid group is incapable of reacting with the mixture of MDI isomers of component b).
[00015] The invention may comprise in another aspect, a process for making a prepolymer for use in an aqueous polyurethane dispersion, wherein the prepolymer comprises:
at least one polyether (including copolyethers), polycarbonate or polyester polyol component having a number average molecular weight of about 600 to about 3,500 , preferably, a poly(tetramethylene ether) glycol having a number average molecular weight of about 600 to about 3,500 ;
a polyisocyanate, which is a mixture of 4,4' and 2,4'-methylene bis(phenyl isocyanate) (MDI) isomers, with the ratio of the 4, $4^{\prime}-\mathrm{MDI}$ to $2,4^{\prime}-\mathrm{MDI}$ isomers frorr about 65:35 to about 35:65; and
at least one diol compound with: (i) hydroxy groups capable of reacting with the mixture of MDI isomers of component b) and (ii) at least one carboxylic acid
group capable of forming a salt upon neutralization, wherein the at least one carboxylic acid group is incapable of reacting with the mixture of MDI isomers of component b)
and the process comprises combining $a$ ), b), and c) in a substantially solvent-free system.
[00016] The invention may comprise, in another aspect, an aqueous polyurethane dispersion, comprising a prepolymer which comprises components a), b), and c), wherein the aqueous polyurethane dispersion is a substantially solvent-free system that further comprises:
at least one neutralizing agent to form an ionic salt with the component c);
at least one monofunctional dialkyl amine compound as a blocking agent for isocyanate groups;
optionally, at least one diamine chain extension component; and
optionally, at least one polymeric component having a molecular weight of greater than about 500, with at least three or more primary and/or secondary amino groups per mole of the polymer.
[00017] The invention may comprise in a further aspect, a process for making an aqueous polyurethane dispersion, wherein the aqueous polyurethane dispersion comprises: the prepolymer wherein the aqueous polyurethane dispersion is a substantially solvent-free system that further comprises:
at least one neutralizing agent to form an ionic salt with the component c );
at least one monofunctional dialkyl amine compound as a blocking agent for isocyanate groups;
and where the process comprises dispersing the prepolymer in an aqueous medium, wherein the at least one neutralizing agent is added to either the
prepolymer or aqueous medium prior to dispersing the prepolymer in the aqueous medium and the at least one blocking agent is added to the aqueous medium either during or after dispersing the prepolymer in the aqueous medium.
[00018] When the aqueous dispersion is coated on a release paper and converted to a shaped article, the dialkylamine component e) is selected so that (i) the blocked isocyanate groups are essentially stable in both the coating and drying processes, as well as in ambient storage conditions, while, concurrently, (ii) the adhesive film containing the blocked isocyanate groups is capable of being heat and/or pressure activated for fabric bonding and lamination.
[00019] The invention may comprise in a further aspect a shaped article derived from the substantially solvent-free aqueous polyurethane dispersion. The invention may also comprise a garment comprising the shaped article. The invention also may comprise the article comprising the at least one shaped article and a substrate to which said shaped article is applied. The invention further comprises an article wherein the article comprises a substrate coated with the aqueous dispersion. The invention comprises molded articles which comprise shaped articles. The invention comprises molded articles which comprise substrates coated with the aqueous polyurethane dispersion. The invention further comprises garments made from the aforementioned articles.
[00020] The invention may comprise in a further aspect an article comprising the shaped article and a substrate wherein the shaped article and the substrate are attached to form a laminate whereby coefficient of friction of the elastic laminate is greater than that of the substrate alone. Another aspect of the invention is an article comprising a shaped article and a substrate wherein the modulus of the shaped article varies along the length, or alternately the width, of the article.
[00021] The invention may further comprise a shaped article which may may have the following properties: set after elongation of from about 0 to $10 \%$, for example from about 0 to $5 \%$, typically from about 0 to about $3 \%$, elongation of about 400 to about $800 \%$, and tenacity of about 0.5 to about 3 Mpa . The invention may further comprise laminates prepared from articles and substrates
which may have the following properties: peel strength after 50 washes wherein at least $50 \%$ of the strength is maintained from the same before washing, air permeability of at least about 0 to about 0.5 cfm , and moisture vapor permeability of at least about 0 to about $300 \mathrm{~g} / \mathrm{m} 2$ over 24 h .

## BRIEF DESCRIPTION OF THE DRAWINGS

[00022] The present invention will be described in the following detailed description with reference to the following drawings:
[00023] FIG. 1 is a flowchart showing processing steps that may be used to apply dispersions or films according to the invention using a spreading method;
[00024] FIG. 2 is a flowchart showing processing steps that may be used to apply dispersions or films according to the invention using a dipping method;
[00025] FIG. 3 is a flowchart showing processing steps that may be used to apply dispersions or films according to the invention using a painting or spraying method;
[00026] FIG. 4 is a schematic diagram of a process using a flat bed lamination machine to form a laminated article;
[00027] FIG. 5 is a cross-sectional view showing application of dispersions or films according to the invention onto substrates using a spreading method;
[00028] FIG. 6 is a cross-sectional view showing application of dispersions or films according to the invention onto substrates using a dipping method;
[00029] FIG. 7 is a cross-sectional view showing application of dispersions or films according to the invention onto substrates using a painting or spraying method;
[00030] FIG. 8 is an illustration of a knife blade that can be used to distribute dispersions or films according to the invention;
[00031] FIG. 9 is an exploded view of a portion of the knife blade of FIG. 8;
[00032] FIG. 10 is a front view of a woman's brassiere incorporating dispersions or shaped articles according to the invention;
[00033] FIG. 11 is a cross sectional view taken along line $11-11$ of FIG. 10 showing a brassiere cup;
[00034] FIG. 12 is a partial exploded view taken from FIG. 11 showing the brassiere cup and film interface at the peripheral region surrounding the cup;
[00035] FIG. 13 is a front view of a woman's panty incorporating dispersions or shaped articles according to the invention;
[00036] FIG. 14 is a flowchart showing processing steps that may be used to make a stretch article according to one embodiment of the invention;
[00037] FIG. 15 is a flowchart showing processing steps that may be used to make a stretch article according to one embodiment of the invention; and
[00038] FIG. 16 is cross-sectional view showing a substrate fabric hemmed using an adhesive and a stretch member according to one embodiment of the invention.
[00039] FIG. 17 is top view showing a substrate fabric combined with an adhesive tape and an additional adhesive according to one embodiment of the invention.

## DETAILED DESCRIPTION OF THE INVENTION

[00040] Aqueous polyurethane dispersions falling within the scope of the present invention are provided from particular urethane prepolymers, which also form an aspect of the present invention.
[00041] Urethane prepolymers, or capped glycols, can generally be conceptualized as the reaction product of a polyol, a polyisocyanate, and a compound capable of salt-forming upon neutralization, before the prepolymer is dispersed in water and is chain-extended. Such prepolymers can typically be made in one or more steps, with or without solvents. Depending on whether the prepolymer is dissolved in a less volatile solvent (such as MEK, or NMP) which will remain in the dispersion; dissolved in a volatile solvent such as acetone, which can be later removed; or is dispersed in water without any solvent; the dispersion process can be classified in practice as the solvent process, acetone process, or prepolymer mixing process. The prepolymer mixing process has environmental and economical advantages, and therefore is preferred as the basic process for making the solvent-free aqueous dispersions in the present invention.
[00042] In the prepolymer mixing process, it is important that the viscosity of the prepolymer is adequately low enough, without dilution by a solvent, to be transported and dispersed in water. The present invention in one embodiment, relates to polyurethane dispersions derived from such a prepolymer, which meet this viscosity requirement and do not have any organic solvent in the prepolymer or in the dispersion. In accordance with the invention, the prepolymer is the reaction product of a polyol a), a diisocyanate b) and a diol compound $c$ ).
[00043] The present invention can, in one embodiment, provide novel, solvent-free, stable, aqueous polyurethane dispersions, which can be processed and applied directly as adhesive materials (i.e., without the need of any additional adhesive materials) for coating, bonding, and lamination of to substrates, by conventional techniques. Aqueous polyurethane dispersions falling within the scope of the present invention may be provided with: essentially no emission of volatile organic materials; acceptable curing time in production; and good
adhesion strength, heat resistance, and stretch/recovery properties in finished products and in practical applications.
[00044] The present invention can, in an additional embodiment, provide shaped articles which may or may not be adhesive that can be coated on a release paper, whereby aqueous dispersions of the invention can be used for bonding and lamination to substrates including textile fabrics. The adhesion can be activated, by applying heat and/or pressure onto a substrate and the adhesive film, with a residence time of less than one minute, for example, from about 15 seconds to about 60 seconds. The thus bonded articles have good stretch/recovery properties and are expected to be durable in normal wear and wash cycles.
[00045] As used herein, the term "dispersion" refers to as a system in which the disperse phase consists of finely divided particles, and the continuous phase can be a liquid, solid or gas.
[00046] As used herein, the term "aqueous polyurethane dispersion" refers to a composition containing at least a polyurethane or polyurethane urea polymer or prepolymer (such as the polyurethane prepolymer described herein) that has been dispersed in an aqueous medium, such as water, including de-ionized water. The term further relates to such a composition that has been subjected to drying, for example, in the formation of a shaped article.
[00047] As used herein, the term "solvent," unless otherwise indicated, refers to a non-aqueous medium, wherein the non-aqueous medium includes organic solvents, including volatile organic solvents (such as acetone) and somewhat less volatile organic solvents (such as MEK, or NMP).
[00048] As used herein, the term "solvent-free" or "solvent-free system" refers to a composition or dispersion wherein the bulk of the composition or dispersed components has not been dissolved or dispersed in a solvent.
[00049] As used herein, the term shaped article may refer to one of a number of objects including for example, film, tape, dots, webs, stripes, bead, and foam. A film may describe a sheet material of any shape. A tape may describe a film in narrow strip form. A film may be in the form of a tape. As used herein, the term "shaped article" refers to a layer comprising an aqueous polyurethane dispersion (such as the aqueous polyurethane dispersion containing the polyurethane prepolymer described herein) that can be directly applied to a substrate or release paper, which can be used for adhesion and/or to form a rigid or an elastic article.
[00050] As used herein, the term "article" refers to an article which comprises a dispersion or shaped article and a substrate, for example a textile fabric, which may or may not have at least one elastic property, in part, due to the application of a dispersion or shaped article as described herein.
[00051] As used herein, the term textile fabric refers to a knitted, woven or nonwoven material. The knitted fabric may be flat knit, circular knit, warp knit, narrow elastic, and lace. The woven fabric may be of any construction, for example sateen, twill, plain weave, oxford weave, basket weave, and narrow elastic. The nonwoven material may be meltblown, spun bonded, wet-laid, carded fiber-based staple webs, and the like.
[00052] As used herein, the term "substrate" refers to any material to which a shaped article can be attached or to which the aqueous polyurethane dispersion can be applied. A substrate can be substantially one dimensional as is a fiber, two dimensional as in a planar sheet, or a three dimensional article or a bumpy sheet. A planar sheet for example may comprise textile fabric, paper, flocked article, and web. A three dimensional article for example may comprise leather and foam. Other substrates may comprise wood, paper, plastic, metal, and composites such as concrete, asphalt, gymnasium flooring, and plastic chips.
[00053] As used herein, the term "hard yarn" refers to a yarn which is substantially non-elastic.
[00054] As used herein, the term "molded" article refers to a process by which the shape of an article or shaped article is changed in response to application of heat and/or pressure.
[00055] As used herein, the term "derived from" refers to forming a substance out of another object. For example, a shaped article may be derived from a dispersion which can be dried.
[00056] As used herein, the term modulus refers to a ratio of the stress on an item expressed in force per unit linear density or area.
[00057] Polyol components a), suitable as a starting material for preparing urethane prepolymers according to the invention, are polyether glycols, polycarbonate glycols, and polyester glycols of number average molecular weight of about 600 to about 3,500 .
[00058] Examples of polyether polyols that can be used include those glycols with two or more hydroxy groups, from ring-opening polymerization and/or copolymerization of ethylene oxide, propylene oxide, trimethylene oxide, tetrahydrofuran, and 3-methyltetrahydrofuran, or from condensation polymerization of a polyhydric alcohol, preferably a diol or diol mixtures, with less than 12 carbon atoms in each molecule, such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol 1,6-hexanediol, neopentyl glycol, 3-methyl-1,5pentanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol and 1,12-dodecanediol. A linear, bifunctional polyether polyol is preferred, and a poly(tetramethylene ether) glycol of molecular weight of about 1,700 to about 2,100 , such as Terathane ${ }^{\circledR} 1800$ (Invista) with a functionality of 2, is particularly preferred in the present invention.
[00059] Examples of polyester polyols that can be used include those ester glycols with two or more hydroxy groups, produced by condensation polymerization of aliphatic polycarboxylic acids and polyols, or their mixtures, of low molecular weights with no more than 12 carbon atoms in each molecule.

Examples of suitable polycarboxylic acids are malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedicarboxylic acid and dodecanedicarboxylic acid. Example of suitable polyols for preparing the polyester polyols are ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol 1,6-hexanediol, neopentyl glycol, 3-methyl-1,5pentanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol and 1,12-dodecanediol. A linear, bifunctional polyester polyol with a melting temperature of about $5^{\circ} \mathrm{C}$ to about $50^{\circ} \mathrm{C}$ is preferred.
[00060] Examples of polycarbonate polyols that can be used include those carbonate glycols with two or more hydroxy groups, produced by condensation polymerization of phosgene, chloroformic acid ester, dialkyl carbonate or diallyl carbonate and aliphatic polyols, or their mixtures, of low molecular weights with no more than 12 carbon atoms in each molecule. Example of suitable polyols for preparing the polycarbonate polyols are diethylene glycol, 1,3-propanediol, 1,4butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 3-methyl-1,5pentanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol and 1,12-dodecanediol. A linear, bifunctional polycarbonate polyol with a melting temperature of about $5^{\circ} \mathrm{C}$ to about $50^{\circ} \mathrm{C}$ is preferred.
[00061] The polyisocyanate component b), suitable as another starting material for making urethane prepolymers according to the invention, can be an isomer mixture of diphenylmethane diisocyanate (MDI) containing 4,4'-methylene bis(phenyl isocyanate) and 2,4'- methylene bis(phenyl isocyanate) in the range of $4,4^{\prime}$-MDI to $2,4^{\prime}$-MDI isomer ratios of between about $65: 35$ to about $35: 65$, preferably in the range of about 55:45 to about 45:55 and more preferably at about 50:50. Examples of suitable polyisocyanate components include Mondur® ML (Bayer), Lupranate ${ }^{\circledR}$ MI (BASF), and Isonate ${ }^{\circledR} 50$ O, $\mathrm{P}^{\prime}$ (Dow Chemical).
[00062] Diol compounds c), suitable as further starting materials for preparing urethane prepolymers according to the invention, include at least one diol compound with: (i) two hydroxy groups capable of reacting with the polyisocyanates b); and (ii) at least one carboxylic acid group capable of forming
salt upon neutralization and incapable of reacting with the polyisocyanates b). Typical examples of diol compounds c) having a carboxylic acid group, include 2,2-dimethylopropionic acid (DMPA), 2,2-dimethylobutanoic acid, 2,2dimethylovaleric acid, and DMPA initiated caprolactones such as CAPA® HC 1060 (Solvay). DMPA is preferred in the present invention.
[00063] The prepolymer can be prepared by mixing starting materials a), b), and c) together in one step and by reacting at temperatures of about $50^{\circ} \mathrm{C}$ to about $100^{\circ} \mathrm{C}$ for adequate time until all hydroxy groups are essentially consumed and a desired \%NCO of the isocyanate group is achieved. Alternatively, this prepolymer can be made in two steps by first reacting starting material a) with excess b), followed by reacting with component c) until a final desired \%NCO of the prepolymer is achieved. For example, the \%NCO may range from about 1.3 to about 6.5 , such as from about 1.8 to about 2.6. Significantly, no organic solvent is added to or mixed with the starting materials before, during or after the reaction. Optionally, a catalyst may be used to facilitate the prepolymer formation.
[00064] In an embodiment of the present invention, the prepolymer comprises components a), b), and c), which are combined together and provided in the following ranges of weight percentages, based on the total weight of the prepolymer:
about $34 \%$ to about $89 \%$ of component a);
about $59 \%$ to about $10 \%$ of component b); and about $7.0 \%$ to about $1.0 \%$ of component c).
[00065] In another embodiment of present invention, the prepolymer comprises Terathane® 1800 polyether glycol as component a), Mondur® ML diisocyanate as component b), and 2,2-dimethylopropionic acid (DMPA) as component $c$. Within such embodiments, these components may, for example, be present in the following ranges of weight percentages, based on the total weight of the prepolymer:
a) Terathane ${ }^{\circledR} 1800$ polyether glycol:
b) Mondur® ML diisocyanate: c) 2,2-dimethylopropionic acid (DMPA): about 4.0\% to about $2.0 \%$.
about 61\% to about 80\%; about $35 \%$ to about 18\%; and
[00066] The prepolymer prepared from components a), b) and c) should have a bulk viscosity (without any solvent present) below about 6,000 poises, such as below about 4,500 poises, measured by the falling ball method at $40^{\circ} \mathrm{C}$. This prepolymer, containing carboxylic acid groups along the polymer chains, can be dispersed with a high-speed disperser into a de-ionized water medium that comprises: at least one neutralizing agent d), to form an ionic salt with the acid; at least one surface active agent (ionic and/or non-ionic dispersant or surfactant); and, optionally, at least one diamine chain extension component f). Alternatively, the neutralizing agent can be mixed with the prepolymer before being dispersed into the water medium. At least one antifoam and/or defoam agent and preferably at least one rheological modifier can be added to the water medium before, during, or after the prepolymer is dispersed.
[00067] Examples of suitable neutralizing agents d) to convert the acid groups to salt groups include: tertiary amines (such as triethylamine, $\mathrm{N}, \mathrm{N}$ diethylmethylamine, N -methylmorpholine, $\mathrm{N}, \mathrm{N}$-diisopropylethylamine, and triethanolamine) and alkali metal hydroxides (such as lithium, sodium and potassium hydroxides). Primary and/or secondary amines may be also used as the neutralizing agent for the acid groups. The degrees of neutralization are generally between about $60 \%$ to about $140 \%$, for example, in the range of about $80 \%$ to about $120 \%$ of the acid groups.
[00068] Examples of suitable diamine chain extenders f) include: 1,2ethylenediamine, 1,4-butanediamine, 1,6-hexamethylenediamine, 1,12dodecanediamine, 1,2-propanediamine, 2-methyl-1,5-pentanediamine, 1,2cyclohexanediamine, 1,4-cyclohexanediamine, 4,4'-methylenebis(cyclohexylamine), isophorone diamine, 2,2-dimethyl-1,3-propanediamine, meta-tetramethylxylenediamine, and Jeffamine ${ }^{\circledR}$ (Texaco) of molecular weight less than 500.
[00069] Examples of suitable surface active agents include: anionic, cationic, or nonionic dispersants or surfactants, such as sodium dodecyl sulfate, sodium dodecylbenzenesulfonate, ethoxylated nonylphenols, and lauryl pyridinium bromide.
[00070] Examples of suitable antifoaming or deforming or foam controlling agents include: Additive 65 and Additive 62 (silicone based additives from Dow Corning), FoamStar ${ }^{(8)} 1300$ (a mineral oil based, silicone free defoamer from Cognis) and Surfynol ${ }^{\text {TM }}$ DF 110 L (a high molecular weight acetylenic glycol nonionic surfactant from Air Products \& Chemicals).
[00071] Examples of suitable rheological modifiers include: hydrophobicallymodified ethoxylate urethanes (HEUR), hydrophobically-modified alkali swellable emulsions (HASE), and hydrophobically-modified hydroxy-ethyl cellulose (HMHEC).
[00072] At least one monofunctional dialkyl amine compound e), as the blocking agent for isocyanate groups, is added to the water medium during or after the prepolymer is dispersed. For example, the blocking agent can be added to the water mixture immediately after the prepolymer is dispersed. Optionally at least one polymeric component g) (MW > about 500), with at least three or more primary and/or secondary amino groups per mole of the polymer, is added to the water medium after the prepolymer is dispersed and the blocking agent is added.
[00073] Examples of suitable mono-functional dialkylamine blocking agents e) include: $\mathrm{N}, \mathrm{N}$-diethylamine, N -ethyl-N-propylamine, $\mathrm{N}, \mathrm{N}$-diisopropylamine, N -tert-butyl-N-methylamine, N -tert-butyl-N-benzylamine, $\mathrm{N}, \mathrm{N}$-dicyclohexylamine, N -ethyl- N -isopropylamine, N -tert-butyl- N -isopropylamine, N -isopropyl- N -
cyclohexylamine, N -ethyl-N-cyclohexylamine, $\mathrm{N}, \mathrm{N}$-diethanolamine, and 2,2,6,6tetramethylpiperidine. The molar ratio of the amine blocking agent to the isocyanate groups of the prepolymer prior to dispersion in water generally should
range from about 0.05 to about 0.50 , for example from about 0.20 to about 0.40 . Catalysts may be used for the de-blocking reactions.
[00074] Examples of the suitable polymeric component g) include: polyethylenimine, poly(vinylamine), poly(allylamine), and poly(amidoamine) dendrimers.
[00075] Other additives that may be optionally included in the aqueous dispersion or in the prepolymer include: anti-oxidants, UV stabilizers, colorants, pigments, crosslinking agents, phase change materials (i.e., Outlast®, commercially available from Outlast Technologies, Boulder, Colorado), antimicrobials, minerals (i.e., copper), microencapsulated well-being additives (i.e., aloe vera, vitamin E gel, aloe vera, sea kelp, nicotine, caffeine, scents or aromas), nanoparticles (i.e., silica or carbon), calcium carbonate, flame retardants, antitack additives, chlorine degradation resistant additives, vitamins, medicines, fragrances, electrically conductive additives, and/or dye-assist agents (i.e., Methacrol®, commercially available from E. I. DuPont de Nemours, Wilmington, Delaware). Other additives which may be added to the prepolymer or the aqueous dispersion comprise adhesion promoters, anti-static agents, anticratering agents, anti-crawling agents, optical brighteners, coalescing agents, electroconductive additives, luminescent additives, flow and leveling agents, freeze-thaw stabilizers, lubricants, organic and inorganic fillers, preservatives, texturizing agents, thermochromic additives, insect repellants, and wetting agents.
[00076] Such optional additives may be added to the aqueous dispersion before, during, or after the prepolymer is dispersed, as the process allows. No organic solvent is added to the aqueous dispersion at any time.
[00077] Polyurethane aqueous dispersions falling within the scope of the present invention should be expected to have a solids content of from about $10 \%$ to about $50 \%$ by weight, for example from about $30 \%$ to about $45 \%$ by weight. The viscosity of polyurethane aqueous dispersions falling within the scope of the present invention may be varied in a broad range from about 10 centipoises to
about 100,000 centipoises depending on the processing and application requirements. For example, in one embodiment, the viscosity is in the range of about 500 centipoises to about 30,000 centipoises. The viscosity may be varied by using an appropriate amount of thickening agent, such as from about 0 to about $2.0 \mathrm{wt} \%$, based on the total weight of the aqueous dispersion.
[00078] The solvent-free aqueous polyurethane dispersions of the present invention are particularly suitable for adhesive shaped articles, which can be used for fabric bonding, lamination, and adhesion purposes when applied with heat and pressure for a relatively short period of time. Pressures, can for example, range from about atmospheric pressure to about 60 psi and times can range from less than about one second to about 30 minutes in accordance with the bonding method used.
[00079] Such shaped articles may be made by coating the dispersion onto a release paper and drying to remove water at temperatures below about $100^{\circ} \mathrm{C}$ through commercially available processes to form a film on the paper. The formed film sheets can be slit into strips of desired width and wound-up into spools for later use in applications to form stretch articles, for example textile fabrics. Examples of such applications include: stitch-less or seamless garment constructions; seam seal and reinforcement; labels and patches bonding to garments; and localized stretch/recovery enhancement. The adhesion bonding can be developed in the temperature range of from about $100^{\circ} \mathrm{C}$ to about $200^{\circ} \mathrm{C}$, such as from about $130^{\circ} \mathrm{C}$ to about $200^{\circ} \mathrm{C}$, for example, from about $140^{\circ} \mathrm{C}$ to about $180^{\circ} \mathrm{C}$, in a period of 0.1 seconds to several minutes, for example, less than about one minute. Typical bonding machines are Sew Free (commercially available from SewSystems in Leicester, England), Macpi trimming machine (commercially available from the Macpi Group in Brescia, Italy), Framis hot air welding machine (commercially available from Framis Italy, s p.a. in Milano, Italy).This bonding is expected to be strong and durable when exposed to repeated wear, wash, and stretch in a textile fabric garment.
[00080] The coating, dispersion, or shaped article may be pigmented or colored and also may be used as a design element in that regard.
[00081] In addition, articles with laminated films or dispersions can be molded. For example, fabric can be molded under conditions appropriate for the hard yarn in the fabric. Also, molding may be possible at temperature which will mold the shaped article or dispersion, but below temperatures suitable for molding the hard yarn.
[00082] Lamination can be carried out to secure the shaped article to a fabric using any method wherein heat is applied to the laminate surface.
Methods of heat application include, for example, ultrasonic, direct heat, indirect heat, and microwave. Such direct lamination may provide an advantage in view of other methods used in the art in that the shaped article may not only bond to the a substrate via a mechanical interaction but also via a chemical bond. For example, if the substrate has any reactive hydrogen functional groups, such groups may react with the isocyanate and hydroxyl groups on the dispersion or shaped article, thereby providing a chemical bond between the substrate and the dispersion or shaped article. Such chemical bonding of the dispersion or shaped article to the substrate can give a much stronger bond. Such bonding may occur in dry shaped articles that are cured onto a substrate or in wet dispersions that are dried and cured in one step. Materials without an active hydrogen include polypropylene fabrics and anything with a fluoropolymer or a silicone based surface. Materials with an active hydrogen include, for example, nylon, cotton, polyester, wool, silk, cellulosics, acetates, metals, and acrylics. Additionally, articles treated with acid, plasma, or another form of etching may have active hydrogens for adhesion. Dye molecules also may have active hydrogens for bonding.
[00083] Methods and means for applying dispersions and shaped articles falling within the scope of the present invention on an article include, but are not limited to: roll coating (including reverse roll coating); use of a metal tool or knife blade (for example, pouring a dispersion onto a substrate and then casting the dispersion into uniform thickness by spreading it across the substrate using a metal tool, such as a knife blade); spraying (for example, using a pump spray bottle); dipping; painting; printing; stamping; and impregnating the article. These
methods can be used to apply the dispersion directly onto a substrate without the need of further adhesive materials and can be repeated if additional/heavier layers are required. The dispersions can be applied to any fabrics of knits, wovens or nonwovens made from synthetic, natural, or synthetic/natural blended materials for coating, bonding, lamination and adhesion purposes. The water in the dispersion can be eliminated with drying during the processing (for example, via air drying or use of an oven), leaving the precipitated and coalesced polyurethane layer on the fabrics to form an adhesive bond.
[00084] At least one coagulant may optionally be used to minimize penetration of dispersions according to the invention into a fabric or other article. Examples of coagulants that may be used include calcium nitrate (including calcium nitrate tetrahydrate), calcium chloride, aluminum sulfate (hydrated), magnesium acetate, zinc chloride (hydrated) and zinc nitrate.
[00085] An example of a tool that can be used for applying dispersions falling within the scope of the present invention is the knife blade shown in FIGS. 8 and 9. The knife blade 100, can be made of metal or any other suitable material. The knife blade can have a gap of a predetermined width 102 and thickness 104. The gap may range in thickness, for example, from 0.2 mils to 50 mils, such as a thickness of 5 mils, 10 mils, 15 mils, 25 mils, 30 mils, or 45 mils.
[00086] The thickness of dispersions and shaped articles falling within the scope of the present invention may vary, depending on the application and method of application. In the case of dry shaped articles, the final thickness may, for example, range from about 0.1 mil to about 250 mil, such as from about 0.5 mil to about 25 mil , including from about 1 to about 6 mil (one mil = one thousandth of an inch). For aqueous dispersions, the amount used may, for example, range from about $2.5 \mathrm{~g} / \mathrm{m}^{2}$ to about $6.40 \mathrm{~kg} / \mathrm{m}^{2}$, such as from about 12.7 to about $635 \mathrm{~g} / \mathrm{m}^{2}$, including from about 25.4 to about $152.4 \mathrm{~g} / \mathrm{m}^{2}$.
[00087] Types of planar sheets and tapes that can be coated with dispersions and shaped articles falling within the scope of the present invention
include, but are not limited to: textile fabrics, including wovens and knits; nonwovens; leather (real or synthetic); paper; metal; plastic; and scrim.
[00088] End articles that can be produced using the dispersions and shaped articles falling within the scope of the present invention include, but are not limited to: apparel, which includes any type of garment or article of clothing; knitted gloves; upholstery; hair accessories, bed sheets; carpet and carpet backing; conveyor belts; medical applications, such as stretch bandages; personal care items, including incontinence and feminine hygiene products; and footwear. Articles coated with dispersion or covered with film or tape may be used as sound suppression articles.
[00089] Non-elastic fabrics laminated to shaped articles can have improved stretch and recovery and improved molding properties.
[00090] Articles comprising shaped articles, film, tape, or aqueous polyurethane dispersion may be molded. The articles may be made with multiple layers of substrate and shaped article, film, tape, or dispersion. The multi-layered articles also may be molded. Molded and non-molded articles may have different levels of stretch and recovery. The molded articles may comprise a body shaping or body supporting garment, such as a brassiere.
[00091] Examples of apparel or garments that can be produced using the dispersions and shaped articles falling within the scope of the present invention, include but are not limited to: undergarments, brassieres, panties, lingerie, swimwear, shapers, camisoles, hosiery, sleepwear, aprons, wetsuits, ties, scrubs, space suits, uniforms, hats, garters, sweatbands, belts, activewear, outerwear, rainwear, cold-weather jackets, pants, shirtings, dresses, blouses, mens and womens tops, sweaters, corsets, vests, knickers, socks, knee highs, dresses, blouses, aprons, tuxedos, bisht, abaya, hijab, jilbab, thoub, burka, cape, costumes, diving suit, kilt, kimono, jerseys, gowns, protective clothing, sari, sarong, skirts, spats, stola, suits, straitjacket, toga, tights, towel, uniform, veils, wetsuit, medical compression garments, bandages, suit interlinings, waistbands, and all components therein.
[00092] FIG. 4 is a representative diagram of a flatbed laminating machine. A roll of fabric substrate 72 is unwound and preheated in zone 78. A second roll of fabric substrate 76 and roll of film 74 are unwound and enter the lamination heat/pressure zones $\mathbf{8 0}$. After heating, the fabric/film/fabric sandwich structure is cooled in the cooling zone 82 . Roll 84 represents the rolled up fabric/film/fabric laminate.
[00093] Methods for performing and overcoming common problems in reverse roll coating are described in Walter, et al., "Solving common coating flaws in Reverse Roll Coating," AIMCAL Fall Technical Conference (October 26-29, 2003), the entire disclosure of which is incorporated herein by reference.
[00094] Dispersions and shaped articles falling within the scope of the present invention may be applied continuously or selectively to a given substrate. In this regard, FIGs. 5-7 show, in cross-sectional view, schematic illustrations of applications of dispersions and shaped articles falling within the scope of the present invention. In these figures, substrates are represented by thick black lines and dispersions and shaped articles falling within the scope of the present invention are represented as: (1) two parallel thin lines when applied via a spreading method (via use of a knife blade, etc.), as shown in FIG. 5; (2) a zigzag line superimposed on a thick black line when applied via a dipping method, as shown in FIG. 6; or (3) a zigzag line between or above thick black lines when applied via a painting or spray method and the like, as shown in FIG. 7. The drawings on the left-hand side of the figures, designated with a number followed by the letter "a", represent continuous application of dispersions and shaped articles falling within the scope of the present invention whereas the drawings on the right-hand side of the figures, designated with a number followed by the letter "b," represent selective or segmented application of dispersions and shaped articles falling within the scope of the present invention. While not shown in FIGs. $5-7$, it is also contemplated that dispersions and shaped articles falling within the scope of the present invention can be applied both continuously and in segments in the same application, for example, continuously on or between some layers, and in segments on or between other layers.
[00095] FIGS. 10-13 show representative examples of garments that can be made to incorporate dispersions or shaped articles falling within the scope of the present invention.
[00096] FIG. 10 shows a brassiere 110 having fabric brassiere cups 112 formed within a support structure that includes a peripheral region 114 surrounding the cups 112, and body-wrapping sides 116 that terminate with fastening means, such as a hook 118 and mating loop 120. The brassiere 110 further includes shoulder straps 122. The brassiere 110 can be made to incorporate dispersions or shaped articles falling within the scope of the present invention. Such dispersions or shaped articles can be provided for or on any number of locations on the brassiere, including, but not limited to, the shoulder straps 122, the peripheral region 114, and the body-wrapping sides 116. Such dispersions or shaped articles can be provided anywhere where a seam would be expected to be present to join one or more segments of material in the bra. As shown in FIG. 10, the brassiere cups 112 and geometric shaped regions 124 along the body wrapping sides 116 do not have film applied. All other fabric components include a shaped article or dispersion according to the invention. While not specifically shown in FIG. 10, brassiere cups 112 may be molded using dispersions falling within the scope of the present invention.
[00097] FIG. 11 shows a cross-sectional view of a brassiere cup 112. FIG. 12 shows an exploded view of the edge of the cup that meets the peripheral region 114 surrounding the cup. As shown in FIGs. 11 and 12, the brassiere cup 112 is formed of fabric to which no dispersion or film has been applied. The peripheral region 114 has a film applied, and thus has a greater thickness than the fabric of the cup, which comprises the thickness of the film and fabric together. The peripheral region 114 offers some breast supporting rigidity and firmness, without the uncomfortable rigidity provided by an underwire.
[00098] FIG. 13 shows a woman's panty or brief 130 that can be made to incorporate dispersions or shaped articles falling within the scope of the present invention for adhesion, enhanced elasticity, and/or enhanced support. Such dispersions or shaped articles can be provided for or on any number of locations
on the panties or briefs 130, including, but not limited to, the waistband 132 and the leg openings 134.
[00099] Another aspect of the invention is an article which may comprise an adhesive, a stretch member, and a substrate. The adhesive 150 and stretch member 152 may be combined in a first step and attached to the substrate 154 in a second step to form a stretch article 156, FIG. 14. Alternately, the adhesive 162 and stretch member 162 may be applied to the substrate 164 in a single step to form a stretch article 166, FIG. 15. In both embodiments heat and pressure can be used to bond the adhesive. Examples of the adhesive may include adhesive tape made from the aforementioned aqueous polyurethane dispersions or the dispersions themselves can be used directly as an adhesive. These adhesive may or may not be elastic. Examples of a stretch member may include spandex yarn or tape, rubber yarn or tape, woven narrow elastic strip, knitted elastic strip, and the like. One embodiment of the invention is a folded over hem in which the substrate $\mathbf{2 0 0}$ is folded over and secured using the adhesive 202 and given support for stretch and recovery by the stretch member 204 , FIG. 16. The folded over hem shown in FIG. 16 can be used in garments, for example intimate apparel or swimwear. Examples of intimate apparel include underwear for men and women, brassieres, and shapewear.
[000100] Another aspect of the invention is an article comprising the shaped article and a substrate wherein the shaped article and the substrate are attached to form a laminate whereby coefficient of friction of the elastic laminate is greater than that of the substrate alone. Examples of this are a waistband with a coating or film comprising the aqueous polyurethane dispersion which prevents slippage of the garment from another garment such as a blouse or shirt, or alternately prevents slippage of the waistband on the skin of the garment wearer.
[000101] Another aspect of the invention is an article comprising a shaped article and a substrate wherein the modulus of the shaped article varies along the length, or alternately the width, of the article. For example, a substrate such as fabric 302 can be treated with two feet ( 61 cm ) of a shaped article such as a one inch ( 2.5 cm ) wide adhesive tape 304. An additional layer of adhesive 306 can
be applied by painting three two inches ( 5 cm ) by one inch segments along the length of the one inch wide adhesive tape to form composite structure 300, FIG. 17.
[000102] Shaped article, for example films of the aqueous polyurethaneurea dispersions, may have the following properties:

- $\quad$ set after elongation of from about 0 to $10 \%$, for example from about 0 to $5 \%$, typically from about 0 to about 3\%,
- elongation of about 400 to about $800 \%$, and
- tenacity of about 0.5 to about 3 Mpa .
[000103] Laminates prepared from articles and substrates may have the following properties:
- peel strength after 50 washes wherein at least $50 \%$ of the strength is maintained from the same before washing,
- air permeability of at least about 0 to about 0.5 cfm , and - moisture vapor permeability of at least about 0 to about $300 \mathrm{~g} / \mathrm{m} 2$ over 24 h.


## Analytical Methods

[000104] In the examples that follow, the following analytical methods were used:

## Peel Strength for Adhesive Bonds

[000105] ASTM D903-93, the entire disclosure of which is incorporated herein by reference, was modified for testing of film laminated fabrics. The sample size used for testing was 1 inches $\times 6$ inches ( $2.5 \mathrm{~cm} \times 15 \mathrm{~cm}$ ). The separation rate was 2 inches per minute ( 5 centimeter per minute). Data are reported as pounds of force per inch of sample width (kilogram per millimeter), as shown in Tables 2 and 4.

## Wash Test

[000106] AATCC test method 150-2001, the entire disclosure of which is incorporated herein by reference, was used for the washing of molded bra cups. The machine cycle was (I) normal/cotton sturdy. The washing temp was (III) 41 ${ }^{\circ} \mathrm{C}$. The drying procedure was $(\mathrm{A})(\mathrm{i})$ tumble cotton sturdy $66^{\circ} \mathrm{C}$ for 30 minutes with a 10 minute cool down time.

## Moisture Vapor Transport

[000107] ASTM E96-00, the entire disclosure of which is incorporated herein by reference, was used for testing the moisture vapor transport properties of articles. Data are reported as grams per square meter for a 24 hour period, as shown in Table 7.

## Air Permeability

[000108] ASTM D-737, the entire disclosure of which is incorporated herein by reference, was used for testing the air permeability properties of articles. Data are reported as cubic feet of air per minute per square foot of fabric (cfm, cubic centimeter of air per second per square centimeter of fabric (ccs)), as shown in Table 7.

## Elongation, Tenacity, and Set

[000109] Elongation and tenacity properties were measured on films using a dynamic tensile tester Instron. The sample size was $1 \times 3$ inches ( $1.5 \mathrm{~cm} \times 7.6$ $\mathrm{cm})$ measured along the long dimension. The sample was placed in clamps and extended at a strain rate of $200 \%$ elongation per minute until a maximum elongation was reached. The tenacity and elongation were measured just prior to the film break. Similarly, the set \% was measured by extending a $1 \times 3$ inches sample of film ( $1.5 \mathrm{~cm} \times 7.6 \mathrm{~cm}$ ) from 0 to $50 \%$ elongation for five cycles at a strain rate of $200 \%$ per minute. The set $\%$ was measured after the fifth cycle.

## Examples

Representative embodiments of the present invention will be described with reference to the following examples that illustrate the principles and practice of the present invention. In these examples: the reference numbers refer to elements shown in the flowcharts of FIGs. 1-3 and, where appropriate, the crosssectional illustrations of FIGs. 5-7;
[000110] Terathane ${ }^{\circledR} 1800$ is a linear polytetramethylene ether glycol (PTMEG), with a number average molecular weight of 1,800 (commercially available from Invista, S. à. r. L., of Wichita, KS and Wilmington, DE);
[000111] Pluracoi® HP 4000D is a linear, primary hydroxyl terminated polypropylene ether glycol, with a number average molecular weight of 400 (commercially available from BASF, Bruxelles, Belgium);
[000112] Mondur® ML is an isomer mixture of diphenylmethane diisocyanate (MDI) containing 50-60\% 2,4'-MDI isomer and 50-40\% 4,4'-MDI isomer (commercially available from Bayer, Baytown, TX);
[000113] Lupranate $\circledR^{\circledR} \mathrm{MI}$ is an isomer mixture of diphenylmethane diisocyanate (MDI) containing 45-55\% 2,4'-MDI isomer and 55-45\% 4,4'-MDI isomer (commercially available from BASF, Wyandotte, Michigan);
[000114] Isonate ${ }^{\circledR} 125 \mathrm{MDR}$ is a pure mixture of diphenylmethane diisocyanate (MDI) containing 98\% 4,4'-MDI isomer and 2\% 2,4'-MDI isomer (commercially available from the Dow Company, Midland, Michigan); and
[000115] DMPA is 2,2-dimethylopropionic acid.
[000116] The following prepolymer samples were prepared with MDI isomer mixtures, such as Lupranate $®$ MI and Mondur® ML, containing a high level of 2,4'-MDI.

## Example 1

[000117] The preparation of the prepolymers was conducted in a glove box with nitrogen atmosphere. A 2000 ml Pyrex ${ }^{\circledR}$ glass reaction kettle, which was equipped with an air pressure driven stirrer, a heating mantle, and a thermocouple temperature measurement, was charged with about 382.5 grams of Terathane ${ }^{(0)} 1800$ glycol and about 12.5 grams of DMPA. This mixture was heated to about $50^{\circ} \mathrm{C}$ with stirring, followed by the addition of about 105 grams of Lupranate $®$ MI diisocyanate. The reaction mixture was then heated to about 90 ${ }^{\circ} \mathrm{C}$ with continuous stirring and held at about $90^{\circ} \mathrm{C}$ for about 120 minutes, after which time the reaction was completed, as the \%NCO of the mixture declined to a stable value, matching the calculated value (\%NCO aim of 1.914) of the prepolymer with isocyanate end groups. The viscosity of the prepolymer was determined in accordance with the general method of ASTM D1343-69 using a Model DV-8 Falling Ball Viscometer, (sold by Duratech Corp., Waynesboro, VA.), operated at about $40^{\circ} \mathrm{C}$. The total isocyanate moiety content, in terms of the weight percent of NCO groups, of the capped glycol prepolymer was measured by the method of S. Siggia, "Quantitative Organic Analysis via Functional Group", 3rd Edition, Wiley \& Sons, New York, pp. 559-561 (1963), the entire disclosure of which is incorporated herein by reference.

## Example 2

[000118] The preparation procedures were the same as Example 1, except that the following ingredients were used in the reaction mixture:

Terathane ${ }^{\text {®1 }}$ 1800: about 361 grams;
DMPA:
Mondur® ML:
about 19 grams; and
about 120 grams.

## Example 3

[000119] The preparation procedures were the same as Example 1, except that the following ingredients were used in the reaction mixture:
Terathane ${ }^{\text {® }}$ 1800: about 349 grams;
DMPA:
about 21 grams; and

Mondur® ML: about 130 grams.

## Example 4

[000120] The preparation procedures were the same as Example 1, except that the following ingredients were used in the reaction mixture:

Terathane ${ }^{\circledR}$ 1800:
Pluracol® HP 4000D:
DMPA:
Mondur® ML:
about 329 grams;
about 30 grams;
about 21 grams; and
about 120 grams.

## Example 5

[000121] The preparation procedures were the same as Example 1, except that the following ingredients were used in the reaction mixture:
Terathane ${ }^{\text {® }}$ 1800: about 331 grams;
Pluracol® HP 4000D: about 30 grams;
DMPA: about 19 grams; and
Mondur® ML: about 120 grams.

## Comparative Examples

In the following prepolymer samples, the preparation procedures and the ingredient type and amount were kept the same, except for the MDI diisocyanate. For comparison, Isonate $® 125 \mathrm{MDR}$ was used at the same amount in place of Lupranate $®$ MI or Mondur® ML in the reaction mixtures as shown below:

## Example 6C

Terathane ${ }^{(1)}$ 1800:
DMPA:
Isonate ${ }^{\circledR} 125 M D R$ :

## Example 7C

Terathane ${ }^{\text {® }}$ 1800:
DMPA:
Isonate ${ }^{\circledR} 125 \mathrm{MDR}$ :
about 382.5 grams;
about 12.5 grams; and about 105 grams.
about 361 grams;
about 19 grams; and about 120 grams.

## Example 8C

Terathane ${ }^{(1)}$ 1800:
DMPA:
Isonate ${ }^{\circledR}$ 125MDR:

## Example 9C

Terathane ${ }^{\text {® }} 1800$ :
Pluracol® HP 4000D:
DMPA:
Isonate ${ }^{\circledR}$ 125MDR:

## Example 10C

Terathane ${ }^{\circledR 180}$ 1800:
Pluracol® HP 4000D:
DMPA:
Isonate ${ }^{\circledR}$ 125MDR:
about 349 grams;
about 21 grams; and
about 130 grams.'
about 329 grams;
about 30 grams;
about 21 grams; and
about 120 grams.
about 331 grams;
about 30 grams;
about 19 grams; and
about 120 grams.
[000122] The viscosities, as measured by the falling ball method at $40^{\circ} \mathrm{C}$, of the example prepolymer samples (Examples 1 through 5) and comparative examples samples (Examples 6C through 10C) are listed in Table 1 for comparison:

Table 1 Prepolymer viscosities in poises by falling
ball method at $40^{\circ} \mathrm{C}$

| Example | Falling Ball <br> Viscosity at $\mathbf{4 0}^{\circ} \mathbf{C}$ <br> (poise) |
| :---: | :---: |
| 1 | 3086 |
| 2 | 3292 |
| 3 | 2468 |
| 4 | 4382 |
| 5 | 3876 |
| 6C | 6722 |
| 7C | 7690 |
| 8 C | 6560 |
| 9 C | 12148 |
| 10 C | 6187 |

[000123] As shown in Table 1, the prepolymers prepared with Lupranate ${ }^{\circledR} \mathrm{MI}$ or Mondur® ML gave substantially lower viscosity, in the absence of any solvent during or after the prepolymer preparation, than those prepared with Isonate ${ }^{\circledR}$ 125 MDR. The prepolymer viscosities from the comparative example samples, without the dilution using a solvent, were too high to be transported and dispersed in water in downstream processing.

## Example 11

[000124] The solvent-free prepolymer, as prepared according to the procedures and composition described in Example 1, was used to make the polyurethaneurea aqueous dispersion of the present invention.
[000125] A 2,000 ml stainless steel beaker was charged with about 700 grams of de-ionized water, about 15 grams of sodium dodecylbenzenesulfonate (SDBS), and about 10 grams of triethylamine (TEA). This mixture was then cooled with ice/water to about $5{ }^{\circ} \mathrm{C}$ and mixed with a high shear laboratory mixer with rotor/stator mix head (Ross, Model 100LC) at about 5,000 rpm for about 30 seconds. The viscous prepolymer, prepared in the manner as Example 1 and contained in a metal tubular cylinder, was added to the bottom of the mix head in the aqueous solution through flexible tubing with applied air pressure. The temperature of the prepolymer was maintained between about $50^{\circ} \mathrm{C}$ and about
$70^{\circ} \mathrm{C}$. The extruded prepolymer stream was dispersed and chain-extended with water under the continuous mixing of about $5,000 \mathrm{rpm}$. In a period of about 50 minutes, a total amount of about 540 grams of prepolymer was introduced and dispersed in water. Immediately after the prepolymer was added and dispersed, the dispersed mixture was charged with about 2 grams of Additive 65 (commercially available from Dow Corning®, Midland Michigan) and about 6 grams of diethylamine (DEA). The reaction mixture was then mixed for about another 30 minutes. The resulting solvent-free aqueous dispersion was milky white and stable. The viscosity of the dispersion was adjusted with the addition and mixing of Hauthane HA thickening agent 900 (commercially available from Hauthway, Lynn, Massachusetts) at a level of about $2.0 \mathrm{wt} \%$ of the aqueous dispersion. The viscous dispersion was then filtered through a 40 micron Bendix metal mesh filter and stored at room temperatures for film casting or lamination uses. The dispersion had solids level of $43 \%$ and a viscosity of about 25,000 centipoises. The cast film from this dispersion was soft, tacky, and elastomeric.

## Example 12

[000126] The solvent-free prepolymer, as prepared according to the procedures and composition described in Example 1, was used to make the polyurethaneurea aqueous dispersion of the present invention.
[000127] A 2,000 ml stainless steel beaker was charged with about 900 grams of de-ionized water, about 15 grams of sodium dodecylbenzenesulfonate (SDBS), and about 10 grams of triethylamine (TEA). This mixture was then cooled with ice/water to about $5^{\circ} \mathrm{C}$ and mixed with a high shear laboratory mixer with rotor/stator mix head (Ross, Model 100LC) at about 5,000 rpm for about 30 seconds. The viscous prepolymer, prepared in the manner as Example 1 and contained in a metal tubular cylinder, was added to the bottom of the mix head in the aqueous solution through flexible tubing with applied air pressure. The temperature of the prepolymer was maintained between about $50^{\circ} \mathrm{C}$ and about $70^{\circ} \mathrm{C}$. The extruded prepolymer stream was dispersed and chain-extended with water under the continuous mixing of about $5,000 \mathrm{rpm}$. In a period of about 50 minutes, a total amount of about 540 grams of prepolymer was introduced and dispersed in water. Immediately after the prepolymer was added and dispersed, the dispersed mixture was charged with about 2 grams of Additive 65
(commercially available from Dow Corning ${ }^{\circledR}$, Midland Michigan) and about 6 grams of diethylamine (DEA). The reaction mixture was then mixed for about another 30 minutes. The resulting solvent-free aqueous dispersion was milky white and stable. The viscous dispersion was then filtered through a 40 micron Bendix metal mesh filter and stored at room temperatures for film casting or lamination uses. The dispersion had solids level of $40 \%$ and a viscosity of about 28 centipoises. The cast film from this dispersion was soft, tacky, and elastomeric.

## Example 13

[000128] The solvent-free prepolymer, as prepared according to the procedures and composition described in Example 1, was used to make the polyurethaneurea aqueous dispersion of the present invention.
[000129] A 2,000 ml stainless steel beaker was charged with about 700 grams of de-ionized water, about 15 grams of sodium dodecylbenzenesulfonate (SDBS), and about 10 grams of triethylamine (TEA). This mixture was then cooled with ice/water to about $5{ }^{\circ} \mathrm{C}$ and mixed with a high shear laboratory mixer with rotor/stator mix head (Ross, Model 100LC) at about 5,000 rpm for about 30 seconds. The viscous prepolymer, prepared in the manner as Example 1 and contained in a metal tubular cylinder, was added to the bottom of the mix head in the aqueous solution through flexible tubing with applied air pressure. The temperature of the prepolymer was maintained between about $50^{\circ} \mathrm{C}$ and about $70^{\circ} \mathrm{C}$. The extruded prepolymer stream was dispersed and chain-extended with water under the continuous mixing of about $5,000 \mathrm{rpm}$. In a period of about 50 minutes, a total amount of about 540 grams of prepolymer was introduced and dispersed in water. Immediately after the prepolymer was added and dispersed, the dispersed mixture was charged with about 2 grams of Additive 65 (commercially available from Dow Corning ${ }^{\circledR}$, Midland Michigan) and about 6 grams of diethylamine (DEA). The reaction mixture was then mixed for about another 30 minutes. The resulting solvent-free aqueous dispersion was milky white and stable. The viscous dispersion was then filtered through a 40 micron Bendix metal mesh filter and stored at room temperatures for film casting or lamination uses. The dispersion had solids level of $43 \%$ and a viscosity of about

28 centipoises. The cast film from this dispersion was soft, tacky, and elastomeric.

## Example 14C

[000130] The preparation procedures were the same as Example 11, except that DEA was not added into the dispersion after the prepolymer was mixed. Initially, the dispersion appeared to be no different from Example 11. However, when the dispersion was aged at room temperatures for one week or more, the film cast from this dispersion was brittle and not suitable for adhesions or laminations.

## Example 15

[000131] The filtered aqueous dispersion as prepared in Example 11 was used to coat films on silicone coated release paper, with a continuous 12-inch (30 cm ) laboratory reverse roll coater. The coater was equipped with a 3-zone drying oven, with the temperature settings at about $60^{\circ} \mathrm{C}, 75^{\circ} \mathrm{C}$ and $120^{\circ} \mathrm{C}$, respectively. The total residence time of drying was about 6 minutes. The dried film of about 3-mil thick was wound up at a speed of about 2 meters per minute. The elastomeric film 12 was able to peel off from the release paper easily and used for laminations.

## Example 16

[000132] The filtered aqueous dispersion as prepared in Example 11 was used to coat films on silicone coated release paper to form elastomeric film 12. Lab samples were prepared manually by securing a 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times$ 30 cm ) sheet of double sided silicone release paper (Covermount DS from Print Mount Co., Inc 401-232-0096) to a work surface with masking tape. The aqueous dispersion was poured onto the release paper and cast into a uniform thickness by spreading the dispersion across the release paper using a metal knife blade tool, as shown in FIGs. 8 and 9, having a 6 inch ( 15 cm )wide gap of 5 mil thickness. Excess solution was blotted with a paper towel. Castings were airdried overnight under a hood. The resulting film 12 was easy to peel away from the release paper for further use.

## Example 17

[000133] The film on release paper 12 from Example 15 was placed onto the back of a 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) warp knit nylon with spandex fabric
14. The fabric/film/release paper sandwich was fed into a Hashima HP-400C Belt Oven Laminator (Hashima Co., Ltd, Gifu-City Japan, 058-245-4501) and laminated at $165^{\circ} \mathrm{C}$, with a 20 second residence time and a pressure setting of $\mathrm{P}=1,16$, as shown by path 11a in FIG. 1. The release paper was removed, leaving film/fabric laminate stretch article 18a.

Table 2

| Example | Adhesion Peel <br> Strength (Ib/in) | Adhesion Peel <br> Strength (kg/cm) |
| :---: | :---: | :---: |
| 18 | 2.56 | 14.38 |
| 19 | 1.71 | 9.61 |
| 20 | 4.25 | 23.88 |
| 21 | 1.72 | 9.66 |
| 25 | 6.17 | 34.66 |
| 26 | 5.26 | 29.55 |
| 31 | 4.06 | 22.81 |

## Example 18

[000134] The laminated stretch article 18a was covered with another 12 inch $x 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) piece of warp knit nylon spandex fabric. The fabric/film/fabric sandwich was fed into the Hashima laminator and laminated at $165^{\circ} \mathrm{C}$, with a 20 second residence time and a pressure setting of $\mathrm{P}=1$, to give stretch article 24a. The peel strength for Example 18 was $2.56 \mathrm{lb} / \mathrm{in}$, see Table 2.

## Example 19

[000135] Film 12 of Example 15 was laminated to fabric under the same conditions as Example 17, with the exception that the lamination temperature was $120^{\circ} \mathrm{C}$. The release paper was removed, leaving a film/fabric laminate stretch article 18a. The film side of article 18a was covered with another 12 inch x 12 inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) layer of warp knit nylon spandex fabric. The fabric/film/fabric sandwich was fed into the Hashima laminator and laminated at $165^{\circ} \mathrm{C}$, with a 20 second residence time and a pressure setting of $\mathrm{P}=1$ to give a stretch article 24a. The peel strength for Example 19 was $1.71 \mathrm{lb} / \mathrm{in}$, see Table 2.

## Example 20

[000136] In this example, two stretch articles of 18a were layered with the film sides facing each other. The fabric/film/film/fabric sandwich was fed into the Hashima laminator and laminated at $165^{\circ} \mathrm{C}$ with a 20 second residence time and a pressure setting of $\mathrm{P}=1$ to give a stretch article. The peel strength for Example 20 was $4.25 \mathrm{lb} / \mathrm{in}$, see Table 2.

## Example 21

[000137] Film 12 of Example 15 was carefully removed from release paper and placed onto a 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) warp knit nylon with spandex fabric 14. Another 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) layer of warp knit nylon spandex fabric was placed onto cast film 20. The fabric/film/fabric sandwich 20 was fed into the Hashima laminator and laminated at $165^{\circ} \mathrm{C}$, with 20 a second residence time and a pressure setting of $\mathrm{P}=122$ to give a stretch article 24a. The peel strength for Example 21 was $1.72 \mathrm{lb} / \mathrm{in}$, see Table 2.

## Example 22

[000138] A second film was carefully removed from release paper and placed on the fabric/film/fabric sandwich $\mathbf{2 4 a}$ to form article 26 . A second 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) layer of warp knit nylon spandex fabric was placed onto the second layer of cast film 28. The fabric/film/fabric/film/fabric sandwich was fed into the Hashima laminator and laminated at $165^{\circ} \mathrm{C}$, with 20 second residence time and a pressure setting of $\mathrm{P}=1$ as in 30, to give stretch article 32a.

## Example 23

[000139] In this example, a piece of warp knit nylon spandex fabric (1 inch $x$ 12 inch ( $2.5 \mathrm{~cm} \times 30 \mathrm{~cm}$ )) was dipped into high viscosity aqueous dispersion $\mathbf{1 0 b}$ from Example 11 and pulled out, and then the excess was squeezed off between gloved fingers. The excess was squeezed off a second time between gloved fingers to give the dipped article 34. The coated strip was hung and allowed to air dry overnight under a hood to give stretch article 38a, path 21a in FIG. 2.

## Example 24

[000140] A piece of lightweight nonwoven fabric, deformable in the crossmachine direction, is soaked into low viscosity aqueous dispersion 10b, prepared according to the method of Example 12 ( $40 \mathrm{wt} \%$ solids and 28 centipoises). The dipped article 34 is allowed to drip to remove excess dispersion liquid, and then is hung for drying in a fume hood for overnight 36 to give stretch article 38a, path 21a in FIG. 2.

## Example 25

[000141] In this example, stretch article 38a from Example 23 was covered with a warp knit nylon spandex fabric ( 6 inch $\times 12$ inch ( $15 \mathrm{~cm} \times 30 \mathrm{~cm}$ )) 40. The layered article 40 was fed into the Hashima laminator and laminated at $165{ }^{\circ} \mathrm{C}$, with 20 second residence time and a pressure setting of $P=1$ as in 42, path 21b in FIG. 2, to give stretch article 44a. The peel strength for Example 25 was 6.17 $\mathrm{lb} / \mathrm{in}$, see Table 2.

## Example 26

[000142] In this example, stretch article 44a was covered with a warp knit nylon spandex fabric ( 6 inch $\times 12$ inch $(15 \mathrm{~cm} \times 30 \mathrm{~cm})$ ) 46, path 21c in FIG. 2. The layered article 46 was fed into the Hashima laminator and laminated at 165 ${ }^{\circ} \mathrm{C}$, with 20 second residence time and a pressure setting of $\mathrm{P}=1$ as in 48 to give stretch article 50a. The peel strength for Example 26 was $5.26 \mathrm{lb} / \mathrm{in}$, see Table 2.

## Example 27

[000143] In this example, a filtered solution of the aqueous dispersion as prepared in Example 12 is poured into a typical spray bottle. The filtered aqueous dispersion 10c is applied directly to bistretch cotton/spandex twill fabric using spray bottle, 52 as shown in FIG. 3. The fabric is air-dried, 54, to form a stretch article 56a, path 31a in FIG. 3.

## Example 28

[000144] A piece of stretch denim fabric is pretreated by soaking into a bath containing a water solution of $20 \mathrm{wt} \%$ calcium nitrate tetrahydrate as a coagulant and dried in an oven at $100^{\circ} \mathrm{C}$ for 30 minutes. The aqueous dispersion 10c, prepared according to the method of Example 12 ( $40 \mathrm{wt} \%$ solids and 28
centipoises) is coated evenly onto the backside of the pretreated fabric with a blade, as shown in FIGS. 8 and 9, having a 5 mil gap thickness. The dispersion is coagulated on the surface of the fabric without soaking through. This fabric is then dried 54 in the oven at $80^{\circ} \mathrm{C}$ for 60 minutes to give a stretch article 56a, path 31a in FIG. 3.

## Example 29

[000145] A piece of stretch denim fabric is coated with a high viscosity dispersion 10c of Example 11 ( $43 \mathrm{wt} \%$ solids and 25000 centipoises). This increased viscosity allows the dispersion coated on one side of the fabric without soaking through the fabric 52 . The fabric is dried 54 in an oven at $80^{\circ} \mathrm{C}$ for 60 minutes 56a, path 31a in FIG. 3.

## Example 30

[000146] A 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) warp knit nylon spandex fabric piece was secured to the work surface using masking tape (allowing the fabric to be held under slight tension in the warp direction). The filtered aqueous dispersion 10c of Example 11 ( $43 \mathrm{wt} \%$ solids and 25000 centipoises) was poured onto the fabric 52. This increased viscosity allows the dispersion coated on one side of the fabric without soaking through the fabric 52. A uniform thickness of film was made by spreading the dispersion across the fabric using the metal tool, shown in FIGS. 8 and 9 , having a 6 inch wide gap of 10 mil thickness. Excess solution was blotted with a paper towel. Coated fabric was air-dried overnight under a hood. The article 52 was fed into the Hashima laminator and laminated at $165^{\circ} \mathrm{C}$, with 20 second residence time and a pressure setting of $\mathrm{P}=1$ as in 54 to form a stretch article 56a, path 31a in FIG. 3.

## Example 31

[000147]
A 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) warp knit nylon spandex fabric piece was secured to the work surface using masking tape (allowing the fabric to be held under slight tension in the warp direction). The filtered aqueous dispersion 10c of Example 11 ( $43 \mathrm{wt} \%$ solids and 25000 centipoises) was poured onto the fabric 52. A uniform thickness of film was made by spreading the dispersion across the fabric using the metal tool, shown in FIGS. 8 and 9, having
a 6 inch wide gap of 10 mil thickness. Excess solution was blotted with a paper towel. Another 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) warp knit nylon spandex fabric was laid over the dispersion and lightly pressed to promote adhesion 58, path 31b in FIG. 3. The coated fabric sandwich was air-dried overnight under a hood. The layered article 58 was fed into the Hashima laminator and laminated at 165 ${ }^{\circ} \mathrm{C}$, with 20 second residence time and a pressure setting of $\mathrm{P}=1$ as in 60 to give stretch article 62a. The peel strength for Example 31 was $4.06 \mathrm{lb} / \mathrm{in}$, see Table 2.

Table 3. Molded Bra Cup Height in cm

| Example | Height <br> Immediately <br> After Molding <br> (cm) | Height After <br> 2A Wash <br> Cycle (cm) |
| :---: | :---: | :---: |
| 32 | 7.4 | 4.2 |
| 33 C | 7.3 | 1.9 |
| 34 | 6.7 | 6.4 |
| 35 C | 6.8 | 5.9 |

## Example 32

[000148] Stretch article 24a, FIG. 1, was made according to Example 21 except that $100 \%$ cotton circular knit fabric was used as the top fabric and the bottom fabric. A 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) piece of cotton based stretch article 24a was molded into a bra cup using a Texilformung Willi Lehman GmbH Molding Machine Type 2030 NT equipped with an 8.5 cm deep circular bullet mold. The bullet and conical mold base were heated to $195^{\circ} \mathrm{C}$, while the ring clamp was heated to $185^{\circ} \mathrm{C}$. The fabric was molded according to standard practice for 45 seconds. The cup height was measured immediately after molding and again after a wash and dry cycle according to AATCC Test Method $150-2001$. The laminated and molded cup with cotton had a height of 7.4 cm . After washing, the cup of Example 32 had a height of 4.2 cm .

## Example 33C

[000149] A 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) piece of $100 \%$ cotton circular knit was molded in the same manner as Example 32. The cup height was measured immediately after molding and again after a wash and dry cycle according to AATCC Test Method 150-2001. The $100 \%$ cotton circular knit molded cup had a height of 7.3 cm . After washing the cup of Example 33 C had a height of 1.9 cm .

## Example 34

[000150] Stretch article 24a, FIG. 1, was made with warp knit nylon spandex fabric as top fabric and bottom fabric, according to Example 21. A 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) piece of warp knit nylon spandex based stretch article 24a was molded in the same manner as Example 32. The cup height was measured immediately after molding and again after a wash and dry cycle according to AATCC Test Method 150-2001. The laminated and molded cup had a height of 6.7 cm . After washing the cup of Example 34 had a height of 6.4 cm .

## Example 35C

[000151] A 12 inch $\times 12$ inch ( $30 \mathrm{~cm} \times 30 \mathrm{~cm}$ ) piece of $100 \%$ warp knit nylon was molded in the same manner as Example 32. The cup height was measured immediately after molding and again after a wash and dry cycle according to AATCC Test Method 150-2001. The laminated and molded cup had a height of 6.8 cm . After washing the cup of Example 35C had a height of 5.9 cm .

## Example 36

[000152] Four spandex yarns (Lycra®70 denier) were cut from a package into 110 cm lengths and laid side by side. The yarns were laid down side by side in a flat bundle and pressed into the tape formed from cast film of example 11, FIG 14. The yarn tape composite was fed into a bonding machine (commercially available from Sew Systems, Leicester, England) with a warp knitted fabric to form a folded over hem on the fabric. The fold over hemming was carried out at $180^{\circ} \mathrm{C}$ resulting in a smooth hem which was held together by the adhesive tape and reinforced with the spandex yarn, FIG. 16.

## Example 37

[000153] In this example, the hemming was done similar to example 36, but the spandex yarn drafted (stretched) and the tape had little to no draft or tension while it was being fed into the bonding machine. This resulted in a hem which was similar to the hem of example 36 , but the hem in this example was gathered.

## Example 38

[000154] In this example, the fabric of example 36 is coated with a solution of the dispersion as in example 30. Stretch yarn is applied to the fabric and the fabric is hemmed using a bonding machine as in example 36. A flat bonded hem reinforced with a stretch yarn is formed.

## Example 39

[000155] In this example a spandex yarn is coated with the dispersion of example 11. The coated yarn is applied to the edge of the fabric. The edge of the fabric is folded over to create a hem. The folded hem is bonded using a bonding machine as in example 36. A flat bonded hem using a stretch yarn to bond the fabrics is formed.

## Example 40

[000156] A laminated article made similar to from example 17 was tested for peel strength. The sample was washed $5,10,20,30,40$, and 50 times. Data for this example are given in Table 4.

## Example 41

[000157] A laminated article was made according to example 40 with the exception of the film. The film used for this example was a 1 mil stretch film \#3410 (commercially available from Bemis Associates, Inc. of Shirley, Massachusetts). The laminate was tested for peel strength. The sample was washed $5,10,20,30,40$, and 50 times. Data for this example are given in Tables 4 and 5.

Table 4 Peel Strength

|  | Peel Strength (lb/in) |  | Peel Strength (kg/cm) |  |
| ---: | ---: | ---: | ---: | ---: |
| No. of washes | Example 40 | Example 41 | Example 40 | Example 41 |
| 0 | 1.72 | 3.07 | 9.7 | 17.2 |
| 5 | 2.42 | 1.96 | 13.6 | 11.0 |
| 10 | 2.11 | 2.03 | 11.9 | 11.4 |
| 20 | 1.98 | 1.99 | 11.1 | 11.2 |
| 30 | 3.02 | 1.4 | 17.0 | 7.9 |
| 40 | 2.59 | 1.24 | 14.6 | 7.0 |
| 50 | 2.22 | 0.86 | 12.5 | 4.8 |

Table 5
Retention of Peel Strength vs. Original

| No. of washes | Example 40 | Example 41 |
| ---: | ---: | ---: |
| 5 | $141 \%$ | $36 \%$ |
| 10 | $123 \%$ | $34 \%$ |
| 20 | $115 \%$ | $35 \%$ |
| 30 | $176 \%$ | $54 \%$ |
| 40 | $151 \%$ | $60 \%$ |
| 50 | $129 \%$ | $72 \%$ |

## Example 42

[000158] In this example, dispersion of Example 12 was used according to Example 15 to make a 2 mil film. A second layer of film was made by casting of the dispersion of Example 12 into a 4.5 mil film on a polypropylene sheet. Two layers of this film were laminated together to form a film of 6.5 mil thickness through a hot-oil heated metal roll at $100^{\circ} \mathrm{C}$ and a rubber roll under the pressure of 15 psi . The film in this Example was tested for tensile properties including tenacity, elongation and set, Table 6.

## Example 43

[000159] In this example, dispersion of Example 13 was used according to Example 15 to make a 3 mil film. The film in this Example was tested for tensile properties including tenacity, elongation and set, Table 6.

## Example 44

[000160] In this example, a film was made by casting of the dispersion of Example 12 into a 4.5 mil film on a polypropylene sheet. Two layers of this film were laminated together to form a film of 9 mil thickness through a hot-oil heated metal roll at $100^{\circ} \mathrm{C}$ and a rubber roll under the pressure of 15 psi . The film in this

Example was tested for tensile properties including tenacity, elongation and set, Table 6.

Table 6 Film Properties

|  | Tenacity <br> (Mpa) | Elongation <br> (\%) | Set \% |
| :---: | :---: | :---: | :---: |
| Example 42 | 2.4 | 945 | 3.3 |
| Example 43 | 2.8 | 496 | -- |
| Example 44 | -- | - | 3.3 |

## Example 45

[000161] In this example, laminate of Example 18 was tested for moisture vapor transport according to the method given above. Data is given in Table 7

## Example 46

[000162] In this example, laminate of Example 17 was tested for moisture vapor transport according to the method given above. Data is given in Table 7.

## Example 47

[000163] In this example, laminate of Example 18 was tested for air permeability according to the method given above. Data is given in Table 7.

## Example 48

[000164] In this example, laminate of Example 17 was tested for air permeability according to the method given above. Data is given in Table 7.

The fabric of Example 17 was tested for air permeability and moisture vapor transport alone.

Table 7

|  | MVT <br> over 24h) | (g/m2 <br> (cfm) | Air Perm <br> (ccs) |
| :---: | :---: | :---: | :---: |
| Fabric alone | 1334 | 196 | 386 |
| Example 45 | 247 |  |  |
| Example 46 | 296 |  |  |
| Example 47 |  | 0.23 | 0.45 |
| Example 48 |  | 0.32 | 0.63 |

[000165] While the present invention has been described in an illustrative manner, it should be understood that the terminology used is intended to be in a nature of words or description rather than of limitation. Furthermore, while the present invention has been described in terms of several illustrative embodiments, it is to be appreciated that those skilled in the art will readily apply these teachings to other possible variations of the invention.

We claim:

1. A prepolymer for use in an aqueous polyurethane dispersion comprising:
a) at least one polyether, polyester, or polycarbonate polyol, wherein said polyether, polyester, or polycarbonate polyol has a number average molecular weight of 600 to 3,500 ;
b) a mixture of 4,4'- and 2,4'-methylene bis(phenyl isocyanate) (MDI) isomers, wherein the ratio of $4,4^{\prime}-\mathrm{MDI}$ to $2,4^{\prime}-\mathrm{MDI}$ isomers ranges from 65:35 to 35:65; and
c) at least one diol compound comprising: (i) hydroxy groups capable of reacting with the mixture of MDI isomers of component b), and (ii) at least one carboxylic acid group capable of forming a salt upon neutralization, wherein said at least one carboxylic acid group is incapable of reacting with the mixture of MDI isomers of component b);
wherein the prepolymer is substantially solvent-free.
2. The prepolymer of claim 1, wherein the at least one polyether, polyester, or polycarbonate polyol of component a) is a poly(tetramethylene ether) glycol having a number average molecular weight of 1400 to 2400 .
3. The prepolymer of claim 1 , wherein the ratio of $4,4^{\prime}-\mathrm{MDI}$ to $2,4^{\prime}$-MDI isomers ranges from 55:45 to 45:55.
4. The prepolymer of claim 1, wherein the at least one diol compound is selected from the group consisting of 2,2-dimethylopropionic acid (DMPA), 2,2-dimethylobutanoic acid, and 2,2-dimethylovaleric acid.
5. The prepolymer of claim 2 , wherein the ratio of $4,4^{\prime}-\mathrm{MDI}$ to $2,4^{\prime}-\mathrm{MDI}$ isomers ranges from $55: 45$ to $45: 55$, and the at least one diol compound is 2,2-dimethylopropionic acid (DMPA).
6. The prepolymer of claim 1 , wherein component a) is present in a weight percentage ranging from $34 \%$ to $89 \%$, based on the total weight of the prepolymer; component $b$ ) is present in a weight percentage ranging from $59 \%$ to $10 \%$, based on the total weight of the prepolymer; and component c) is present in a weight percentage ranging from $7.0 \%$ to $1.0 \%$, based on the total weight of the prepolymer.
7. The prepolymer of claim 1, having a bulk viscosity from 500 to 6,000 poises, measured by the falling ball method at $40^{\circ} \mathrm{C}$.
8. The prepolymer of claim 7 , having a bulk viscosity from 500 to 4,500 poises, measured by the falling ball method at $40^{\circ} \mathrm{C}$.
9. The prepolymer of claim 1, further comprising at least one additional component selected from the group consisting of anti-oxidants, UV stabilizers, colorants, pigments, crosslinking agents, phase change materials, antimicrobials, minerals, microencapsulated well-being additives, nanoparticles, calcium carbonate, flame retardants, antitack additives, chlorine resistant additives, dye-assist agents, adhesion promoters, antistatic agents, anti-cratering agents, anti-crawling agents, optical brighteners, coalescing agents, electroconductive additives, luminescent additives, flow and leveling agents, freeze-thaw stabilizers, lubricants, organic and inorganic fillers, preservatives, texturizing agents, thermochromic additives, insect repellants, and wetting agents.
10. The prepolymer of claim 1 , wherein the at least one polyether, polyester, or polycarbonate polyol of component a) has two glycol ends or three glycol ends.
11. The prepolymer of claim 1, wherein the aqueous polyurethane dispersion is a polyurethane urea.
12. A process for making a prepolymer for use in an aqueous polyurethane dispersion, wherein the prepolymer comprises:
a. at least one polyether, polyester, or polycarbonate polyol, wherein said polyether, polyester, or polycarbonate polyol has a number average molecular weight of 600 to 3,500 ;
b. a mixture of $4,4^{\prime}$ - and $2,4^{\prime}$-methylene bis(phenyl isocyanate) (MDI) isomers, wherein the ratio of $4,4^{\prime}-\mathrm{MDI}$ to $2,4^{\prime}-\mathrm{MDI}$ isomers ranges from 65:35 to $35: 65$; and
c. at least one diol compound comprising: (i) hydroxy groups capable of reacting with the mixture of MDI isomers of component b), and (ii) at least one carboxylic acid group capable of forming a salt upon neutralization, wherein said at least one carboxylic acid group is incapable of reacting with the mixture of MDI isomers of component b);
and the process comprises combining components $a$ ), b), and c) in a substantially solvent-free system.
13. The process of claim 12 , wherein components $a$ ), b), and c) are mixed and allowed to react at temperatures ranging from $50^{\circ} \mathrm{C}$ to $100^{\circ} \mathrm{C}$.
14. The process of claim 12, wherein components a), b), and c) are combined together in one step.
15. The process of claim 12, wherein components a) and b) are reacted in a first step, followed by combination with component c).
16. The process of claim 12 further comprising a catalyst.
17. An aqueous polyurethane dispersion, comprising:
a prepolymer, which comprises:
a) at least one polyether, polyester, or polycarbonate polyol, wherein said polyether, polyester, or polycarbonate polyol has a number average molecular weight of 600 to 3,500 ;
b) a mixture of 4,4'- and 2,4'-methylene bis(phenyl isocyanate) (MDI) isomers, wherein the ratio of $4,4^{\prime}-\mathrm{MDI}$ to $2,4^{\prime}$ - MDI isomers ranges from $65: 35$ to $35: 65$; and
c) at least one diol compound comprising: (i) hydroxy groups capable of reacting with the mixture of MDI isomers of component b) and (ii) at least one carboxylic acid group capable of forming a salt upon neutralization, wherein said at least one carboxylic acid group is incapable of reacting with the mixture of MDI isomers of component b);
wherein the aqueous polyurethane dispersion is a substantially solventfree system that further comprises:
d) at least one neutralizing agent to form an ionic salt with the at least one diol compound; and
e) at least one monofunctional dialkyl amine compound as a blocking agent for isocyanate groups.
18. The aqueous polyurethane dispersion of claim 17, further comprising at least one surface active agent and at least one antifoam agent.
19. The aqueous polyurethane dispersion of claim 18, further comprising at least one rheological modifier.
20. The aqueous polyurethane dispersion of claim 19, further comprising:
f)at least one diamine chain extension component, and


#### Abstract

g)at least one polymeric component having a molecular weight of greater than 500, with at least three or more primary and/or secondary amino groups per mole of the polymer.


21. The aqueous polyurethane dispersion of claim 17, wherein the at least one neutralizing agent is selected from the group consisting of tertiary amines and alkali metal hydroxides; and the at least one blocking agent is selected from the group consisting of $\mathrm{N}, \mathrm{N}$-diethylamine, N -ethyl- N propylamine, $\mathrm{N}, \mathrm{N}$-diisopropylamine, N -tert-butyl-N-methylamine, N -tert-butyl-N-benzylamine, $\mathrm{N}, \mathrm{N}$-dicyclohexylamine, N -ethyl- N -isopropylamine, N -tert-butyl-N-isopropylamine, N -isopropyl-N-cyclohexylamine, N -ethyl-Ncyclohexylamine, $\mathrm{N}, \mathrm{N}$-diethanolamine, and 2,2,6,6-tetramethylpiperidine.
22. The aqueous polyurethane dispersion of claim 18, wherein the at least one surface active agent is selected from the group consisting of sodium dodecyl sulfate, sodium dodecylbenzenesulfonate, ethoxylated nonylphenols, and lauryl pyridinium bromide.
23. The aqueous polyurethane dispersion of claim 19, wherein the at least one rheological modifier is selected from the group consisting of hydrophobically-modified ethoxylate urethanes (HEUR), hydrophobicallymodified alkali swellable emulsions (HASE), and hydrophobically-modified hydroxy-ethyl cellulose (HMHEC).
24. The aqueous polyurethane dispersion of claim 20 , wherein the at least one diamine chain extension component is selected from the group consisting of 1,2-ethylenediamine, 1,4-butanediamine, 1,6-hexamethylenediamine, 1,12-dodecanediamine, 1,2-propanediamine, 2-methyl-1,5pentanediamine, 1,2-cyclohexanediamine, 1,4-cyclohexanediamine, 4,4'-methylene-bis(cyclohexylamine), isophorone diamine, 2,2-dimethyl-1,3propanediamine, and meta-tetramethylxylenediamine; and the at least one polymeric component having a molecular weight of greater than 500 is selected from the group consisting of polyethylenimine dendrimers,
poly(vinylamine) dendrimers, poly(allylamine) dendrimers, and poly(amidoamine) dendrimers.
25. The aqueous polyurethane dispersion of claim 17, wherein the at least one polyether, polyester, or polycarbonate polyol of component a) is a poly(tetramethylene ether) glycol having a number average molecular weight of 1,700 to 2,100 , the ratio of $4,4^{\prime}-\mathrm{MDI}$ to $2,4^{\prime}-\mathrm{MDI}$ isomers ranges from 55:45 to 45:55, and the at least one diol compound is 2,2dimethylopropionic acid (DMPA).
26. The aqueous polyurethane dispersion of claim 20, further comprising at least one additional component selected from the group consisting of antioxidants, UV stabilizers, colorants, pigments, crosslinking agents, phase change materials, antimicrobials, minerals, microencapsulated well-being additives, nanoparticles, calcium carbonate, flame retardants, antitack additives, chlorine degradation resistant additives, dye-assist agents, wetting, and leveling agents. adhesion promoters, anti-static agents, anticratering agents, anti-crawling agents, optical brighteners, coalescing agents, electroconductive additives, luminescent additives, flow and leveling agents, freeze-thaw stabilizers, lubricants, organic and inorganic fillers, preservatives, texturizing agents, thermochromic additives, and wetting agents.
27. The aqueous polyurethane dispersion of claim 20 wherein the bulk viscosity is from 10 to 100,000 centipoises as measured by the falling ball method at $40^{\circ} \mathrm{C}$.
28. The aqueous polyurethane dispersion of claim 27 wherein the bulk viscosity is from 500 to 30,000 centipoises as measured by the falling ball method at $40^{\circ} \mathrm{C}$.
29. A process for making an aqueous polyurethane dispersion, wherein the aqueous polyurethane dispersion comprises:
the prepolymer wherein the aqueous polyurethane dispersion is a substantially solvent-free system that further comprises:
d)at least one neutralizing agent to form an ionic salt with the at least one diol compound; and
e)at least one monofunctional dialkyl amine compound as a blocking agent for isocyanate groups;
and where the process comprises dispersing the prepolymer in an aqueous medium, wherein the at least one neutralizing agent is added to either the prepolymer or aqueous medium prior to dispersing the prepolymer in the aqueous medium and the at least one blocking agent is added to the aqueous medium either during or after dispersing the prepolymer in the aqueous medium.
30. The process according to claim 29, wherein the at least one blocking agent is added to the aqueous medium immediately after dispersing the prepolymer in the aqueous medium.
31. The process according to claim 30 , wherein the at least one neutralizing agent is added to the aqueous medium prior to dispersing the prepolymer in the aqueous medium.
32. The process according to claim 30, wherein the at least one neutralizing agent is added to the prepolymer prior to dispersing the prepolymer in the aqueous medium.
33. A shaped article derived from the substantially solvent-free aqueous polyurethane dispersion.
34. The shaped article of claim 33 that is substantially non-adhesive.
35. The shaped article of claim 33 wherein the shaped article is molded.
36. An article comprising the shaped article of claim 35.
37. The article comprising the shaped article of claim 33.
38. A garment comprising the article of claim 36.
39. The garment of claim 38 wherein the garment is a bra.
40. An article comprising the at least one shaped article and a substrate to which said shaped article is applied.
41. The article according to claim 40, wherein the substrate is a textile fabric.
42. The article according to claim 40, wherein the article is a garment.
43. The article according to claim 40, wherein the shaped article is applied to the substrate upon release from a release paper.
44. The article according to claim 43 , wherein the shaped article is bonded or adhered to a substrate, said substrate comprises a textile fabric.
45. The article according to claim 44, wherein the shaped article is bonded or adhered to a seam or a support area on the textile fabric.
46. The article according to claim 44, wherein the article is a garment.
47. The article according to claim 42 , wherein the garment is selected from the group consisting of undergarments, brassieres, panties, lingerie, swimwear, shapers, camisoles, hosiery, sleepwear, aprons, wetsuits, ties, scrubs, space suits, uniforms, hats, garters, sweatbands, belts, activewear, outerwear, rainwear, cold-weather jackets, pants, shirtings, dresses, blouses, mens and womens tops, sweaters, corsets, vests, knickers,
socks, knee highs, dresses, blouses, aprons, tuxedos, bisht, abaya, hijab, jilbab, thoub, burka, cape, costumes, diving suit, kilt, kimono, jerseys, gowns, protective clothing, sari, sarong, skirts, spats, stola, suits, straitjacket, toga, tights, towel, uniform, veils, wetsuit, medical compression garments, bandages, suit interlinings, waistbands, and all components therein.
48. The article of claim 40 wherein the substrate is pre-treated.
49. The article of claim 40 wherein the substrate is pre-treated to increase the hydroxyl functionality on said substrate.
50. The article of claim 40 wherein the article is molded.
51. A garment comprising the article of claim 50 .
52. The garment of claim 51 wherein the garment is a bra.
53. An article wherein the article comprises a substrate coated with the aqueous dispersion.
54. The process for forming the article of claim 53 wherein the process comprises providing to the substrate dispersion using means for spraying, coating, painting, printing, stamping, dipping, and impregnating the dispersion.
55. The article of claim 53 wherein the article is molded.
56. The article of claim 53 wherein the article is a garment.
57. A garment comprising the article of claim 55.
58. The garment of claim 57 wherein the garment is a bra.
59. The shaped article of claim 33 wherein the article comprises a glove, condom, bead, fiber, and sheet of film.
60. The shaped article of claim 33 wherein more than one layer of film pr tape is applied.
61. The shaped article of claim 33 further comprising at least one layer of the aqueous polyurethane dispersion.
62. The shaped article of claim 33 wherein said shaped article has been printed upon.
63. The shaped article of claim 33 wherein the shaped article has a thickness of from 0.1 mil to 250 mil ,
64. The shaped article of claim 63 wherein the shaped article has a thickness of 0.5 mil to 25 mil .
65. The shaped article of claim 64 wherein the shaped article has a thickness of including from 1 to 6 mil .
66. The article of claim 53 wherein the aqueous dispersion coating has a basis weight of $2.5 \mathrm{~g} / \mathrm{m}^{2}$ to $6.40 \mathrm{~kg} / \mathrm{m}^{2}$.
67. The article of claim 66 wherein the aqueous dispersion coating has a basis weight of $12.7 \mathrm{~g} / \mathrm{m}^{2}$ to $635 \mathrm{~g} / \mathrm{m}^{2}$.
68. The article of claim 67 wherein the aqueous dispersion coating has a basis weight of $25.4 \mathrm{~g} / \mathrm{m}^{2}$ to $152.4 \mathrm{~g} / \mathrm{m}^{2}$.
69. An article comprising an adhesive, a stretch member, and a substrate wherein the adhesive is used to attach the stretch member to the subatrate in a folded hem arrangement.
70. The article of claim 69 wherein the adhesive is a tape.
71. The article of claim 69 wherein the adhesive is an aqueous polyurethane dispersion.
72. The article of claim 69 wherein the stretch member is spandex.
73. The article of claim 69 wherein the stretch member is rubber.
74. The article of claim 69 wherein the stretch member is a narrow elastic strip.
75.A method for making the article of claim 69 wherein the adhesive and stretch member are joined in a first step to make an adhesive stretch member and the adhesive stretch member is applied to a substrate in a second step.
75. A method for making the article of claim 69 wherein the adhesive and stretch member are added to the substrate in one step.
76. A garment comprising the article of claim 69.
77. The garment of claim 77 wherein the garment is a brassiere.
78. The garment of claim 77 wherein the garment is underwear.
79. The garment of claim 77 wherein the garment is a swimsuit.
80. The article of claim 33 wherein the \% of set is from 0 to $10 \%$.
81. The article of claim 33 wherein the $\%$ set is from 0 to $5 \%$.
82. The article of claim 33 wherein the \% set is from 0 to $3 \%$.
83. The article of claim 33 wherein the maximum elongation is from $400 \%$ to 800 \%.
84. The article of claim 33 wherein the tenacity is from 0.5 to 3 Mpa .
85. A laminate comprising an article and a substrate wherein the peel strength of the laminate does not fall to $50 \%$ of original peel strength value according to ASTM D093-93 following 50 washes according to AATCC-150-2001.
86. A laminate comprising an article and a substrate wherein the moisture vapor transport of the laminate is from 0 to $300 \mathrm{~g} / \mathrm{m} 2$ over 24 hours according to ASTM E96-00.
87. A laminate comprising an article and a substrate wherein the air permeability of the laminate is from 0 to 0.5 cfm according to ASTM D73796.
88. An article comprising the shaped article of claim 33 and a substrate wherein the shaped article and the substrate are attached to form a laminate whereby the coefficient of friction of the laminate is higher than the coefficient of friction of the substrate.
89. An article comprising a shaped article wherein the article has a modulus and a length, said modulus varies along the length of the article.

Figure 1

Figure 2

Figure 3

Figure 4


응


6/12
56b

Figure 7

## MMMWMMMMWMM 56a




FIG. 8

FIG. 9


10/12

Figure 16

Figure 17


[^0]:    Siteman Accessibility Leqaingtice Ierms.of use Last updated: 06.10.2014 Woridwicie Database 5.8.22;93p

