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METHOD OF STORING 4,4'-METHYLENEDIPHENYLISOCYANATE

Robert M. Prosser, Wilmington, Del., and Charles A. Seibert, Jr., Salem, N.J., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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This invention relates to the substantial prevention of the formation of insoluble residues in 4,4'-methylenediphenylisocyanate and more particularly to maintaining 4,4'-methylenediphenylisocyanate in the liquid state at a temperature of between about 40° C. and 50° C.

4,4'-methylenediphenylisocyanate is highly useful as an intermediate in the preparation of many polymeric materials. In the formation of these polymeric materials it is essential that the 4,4'-methylenediphenylisocyanate be substantially free from impurities. This is particularly true when 4,4'-methylenediphenylisocyanate is used for reaction with polymeric glycols to form linear, substantially non-crosslinked polyurethane polymers. However, 4,4'-methylenediphenylisocyanate under normal storage conditions develops varying amounts of insoluble residues which are clearly visible when solid 4,4'-methylenediphenylisocyanate is melted prior to use. These insoluble residues, unless removed from the 4,4'-methylenediphenylisocyanate, will interfere with normal condensation polymerization reactions, whereby inferior polymers are produced from this diisocyanate. From the standpoint of the preparation of good linear polymers using 4,4'-methylenediphenylisocyanate as an intermediate, it is highly desirable that the amount of insoluble residues be no greater than about 0.02% by weight.

Heretofore, in order to substantially prevent the formation of these insoluble residues, it has been necessary, immediately after the 4,4'-methylenediphenylisocyanate is prepared, to chill and maintain it during shipping and storage at temperatures of about 0° C. or lower. Thus, as 4,4'-methylenediphenylisocyanate is prepared it is collected at a temperature of about 50–70° C. It is immediately chilled to a temperature of about 0° C. and then placed into closed containers such as steel drums or tank cars, for shipping and storage. After placing the 4,4-methylenediphenylisocyanate in these containers, the temperature is maintained at about 0° C. This has proven to be a highly uneconomical and undesirable procedure.

It is an object of the present invention to substantially prevent the formation of insoluble residues in 4,4'-methylenediphenylisocyanate during shipping and/or storage. A further object is to provide a process whereby the formation of insoluble residues in 4,4'-methylenediphenylisocyanate is substantially prevented. Other objects will appear hereinafter.

These and other objects of this invention are accomplished by substantially preventing the formation of insoluble residues in 4,4'-methylenediphenylisocyanate during shipping and/or storage, by maintaining the 4,4'-methylenediphenylisocyanate in the liquid state at a temperature of between about 40° C. and 50° C. until it is to be used.

As mentioned above, it has been the practice to take special precautions to reduce the formation of insoluble residues by maintaining 4,4'-methylenediphenylisocyanate at temperatures of 0° C. or lower. The fact that the amount of insolubles formed at these low temperatures was appreciably less than that formed at room temperature is not unexpected since one would ordinarily expect the rate of chemical reaction to decrease markedly when the temperature is drastically reduced. On the other hand, it is entirely unexpected that in the present invention, wherein the 4,4'-methylenediphenylisocyanate is maintained in a liquid state at a temperature of between about 40–50° C., the formation of insoluble residues would be substantially prevented.

In general, it is desirable to prevent the formation of insoluble residues in 4,4'-methylenediphenylisocyanate for a period of time from about 1 up to about 4 weeks since this provides a reasonable time between the preparation of the 4,4'-methylenediphenylisocyanate and its ultimate use. As will be noted from the accompanying examples, by maintaining the 4,4'-methylenediphenylisocyanate in a liquid state at a temperature of between about 40–50° C., the formation of insoluble residues can be substantially prevented for a period of time up to about 28 days. The preferred temperature at which the 4,4'-methylenediphenylisocyanate is to be maintained according to the process of the present invention is at about 45° C. and at this temperature the formation of insoluble residues is substantially completely prevented. At a temperature of about 45°C. it would be possible to store the 4,4'-methylenediphenylisocyanate for a much longer period than 28 days.

In accordance with the present invention, the 4,4'-methylenediphenylisocyanate, after preparation and final distillation, may be discharged from the receiver as a liquid into a container which may be closed and maintained at 40 to 50° C. This avoids any solidification of the diisocyanate between its manufacture and use. Since 4,4'-methylenediphenylisocyanate is normally transported and stored in containers which are closed or sealed in order to prevent atmospheric moisture from reacting with the diisocyanate, the present invention contemplates a container or package which comprises a closed container having 4,4'-methylenediphenylisocyanate therein, said 4,4'-methylenediphenylisocyanate being maintained in the liquid state at a temperature of between about 40° C. and 50° C. until it is ready for use.

If desired, a small amount of a stabilizer may be added to the 4,4'-methylenediphenylisocyanate immediately after it is prepared and the resulting 4,4'-methylenediphenylisocyanate-stabilizer composition maintained at a temperature of between about 40° C. and 50° C. until ready for use. It has been determined that the presence of a stabilizer will assist in the prevention of insoluble residue formation. The amount of stabilizer which may be used may range from about 0.1% to 0.5% by weight based on the weight of the 4,4'-methylenediphenylisocyanate. Suitable stabilizers which may be used include organic acyl halides and phosphorous halides. The organic acyl halides are preferred. Representative acyl halides include acetyl chloride, fumaryl chloride, propionyl chloride, succinyl chloride, adipyl chloride and benzoyl chloride. Representative phosphorous halides include phosphorous trichloride, phosphorous pentachloride and phosphorous oxychloride.

The following examples will better illustrate the nature of the present invention; however, the invention is not intended to be limited to these examples. Parts and percents are by weight unless otherwise indicated.

Example 1

4,4'-methylenediphenylisocyanate was prepared by phosgenating 4,4'-diaminediphenylmethane according to the process of U.S. Patent 2,683,160 and was then distilled under reduced pressure to yield a clear, practically colorless product. It was poured into clean, dry, 10-ml. Pyrex tubes fitted with ground glass stoppers, 32 of these tubes being filled about three-fourths full. Four of the tubes were then stored at each of the temperatures listed below. Temperatures were maintained within 1 or 2 degrees. At the end of each successive week, one of the tubes from each temperature was removed and the tolu-

ene insolubles determined on the entire sample using the procedure of American Society for Testing Materials procedure ASTM D–269–52 with the modification that the weight of the sample was 8–10 grams and the toluene was not heated. The percent toluene insolubles at the beginning of the experiment was nil. A dash (—) indicates that no analysis was made.

Temperature, ° C.	Percent Toluene Insolubles after—			
	7 days	14 days	21 days	28 days
0	—	nil	—	0.01
Room (20–25)	—	0.02	—	0.13
35	0.02	0.08	0.66	1.05
40	0.01	0.01	0.02	0.02
45	—	0.01	—	0.01
50	0.02	nil	0.02	0.14
60	0.01	—	0.32	0.88
70	—	0.26	—	1.24

At the end of 4 weeks, the samples stored at 0°, 40° and 45° showed no visible solids, as compared with those stored at other temperatures. At the end of 2 weeks, the samples stored at 40°, 45° and 50° C. showed less insolubles than those stored at room temperature, 35° and 70° C. At about 0.02% and above the solids are visible as cloudiness or settled solids in the molten isocyanate.

Example 2

4,4'-methylenediphenylisocyanate prepared as in Example 1 was recrystallized by dissolving in the minimum amount of hot benzene, adding hot hexane until a cloudy precipitate began to form, and then adding hot benzene until the formed precipitate just redissolved and then cooling to crystallize. The product was then recrystallized the same way and finally distilled under vacuum (boiling point 169° C. at 1 mm. of mercury pressure). The purified product melted at 41–42° C. and was essentially colorless.

The product was placed in clean, dry 10-ml. Pyrex tubes as in Example 1 and held at the temperatures for the times shown below. As in Example 1, one tube was taken for analysis for toluene insolubles.

Temperature, ° C.	Percent Toluene Insolubles after—				
	3 days	6 days	13 days	20 days	27 days
0	—	0.01	0.01	nil	0.02
Room (20–25)	0.01	0.02	0.02	0.13	0.18
45	—	nil	0.01	0.02	0.01
70	—	nil	0.03	0.87	0.79

The samples stored at 0° C. and 45° C. showed no visible solids at the end of 27 days, as compared with those stored at 70° C. and room temperature.

Example 3

A sample of commercially available 4,4'-methylenediphenylisocyanate was distilled under reduced pressure as in Example 2 and stored in similar glass vials at the temperatures shown below. The toluene insolubles were determined as in Example 1 at the intervals shown:

Temperature, ° C.	Percent Toluene Insolubles after—				
	3 days	6 days	13 days	20 days	27 days
0	—	0.01	nil	nil	0.01
Room (20–25)	0.04	0.02	0.015	—	0.07
45	—	nil	0.01	0.02	0.01
70	—	nil	0.14	0.79	1.10

There were no visible solids in the samples stored at 0° C. and 45° C. after 4 weeks.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

What is claimed is:

1. A method of storing 4,4'-methylenediphenylisocyanate so as to substantially prevent the formation of insoluble residues therein which consists of maintaining the 4,4'-methylenediphenylisocyanate in a closed container in the liquid state at a temperature of between 40° C. and 50° C.

2. A method according to claim 1 wherein the temperature is maintained at about 45° C.

3. The process of substantially preventing the formation of insoluble residues in 4,4'-methylenediphenylisocyanate which consists of maintaining the 4,4'-methylenediphenylisocyanate in the liquid state at a temperature of between 40° C. and 50° C.

4. The process according to claim 3 wherein the temperature is maintained at about 45° C.

5. The process according to claim 4 wherein the 4,4'-methylenediphenylisocyanate contains from about 0.1% to 0.5% of a halide selected from the group consisting of acetyl chloride, fumaryl chloride, propionyl chloride, succinyl chloride, adipyl chloride, benzoyl chloride, phosphorous trichloride, phosphorous pentachloride and phosphorous oxychloride.

References Cited in the file of this patent

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