POLYISOCYANATE PARTICLES OF CONTROLLED PARTICLE SIZE AND PARTICLE SIZE DISTRIBUTION

DESCRIPTION

The present invention relates to solid particles of polyisocyanates, in particular diisocyanates, and more particularly diphenylmethane diisocyanates (MDI), a method for the production thereof and their use.

Polyisocyanates are well known in the art and are used extensively as raw materials, for example in the production of polyurethanes.

Polyisocyanates cover a broad range of organic compounds having 2 or more isocyanate groups. Such compounds may comprise aromatic and/or aliphatic groups. Examples of polyisocyanates which are widely used include tolylene diisocyanates (TDI), diphenylmethane diisocyanates (MDI), naphthalene-1,5-diisocyanate (NDI), 1,6-hexamethylene diisocyanate (HDI), p-phenylenediisocyanate (PPDI), trans-cyclohexane-1,4-diisocyanate (CHDI), isophorone diisocyanate (IPDI) and tetramethylxylene diisocyanates (TMXDI).

One of the most important polyisocyanates is MDI.

In order to obtain satisfactory storage stability and processing, handling and reaction properties, modifications are brought about to the isocyanate species.

Modified forms of polyisocyanates are mainly liquefied products such as dimerised or trimerised forms of the polyisocyanates, or reaction products of polyisocyanates with compounds containing isocyanate-reactive groups.

Some polyisocyanates, for example 4,4'-diphenylmethane diisocyanate, are already available in the form of flakes, but these give rise to problems from a health and safety point of view since they generate dust.

Also known is the use of finely-divided solid polyisocyanates, for example MDI-powders, particularly in binders or adhesives (see e.g. US-A 4569982). These powders are produced by atomising a liquid stream. Hence, the droplets here have a broad particle size distribution, i.e.

are polydispersed and have a tendency to coalesce. The result is that such powders generally have a diameter of substantially less than 1 mm, are of irregular shape and have a large size distribution.

In SU-A 1456411 a method is described for producing solid spherical granules of 4,4'-MDI by pouring molten product dropwise into water and cooling whereupon the drops solidify and form solid granules.

This method however results in the formation of urea-groups due to the reaction with water and the presence of significant amounts 4,4'-MDI dimers, which are detrimental to the product quality.

It has now been found that solid polyisocyanate particles can be produced which have a controlled particle size and particle size distribution, and which are chemically virtually identical to the starting material of which they are made.

In particular the flowability of such particles is much better, which allows easier and quicker handling for storage or transport. Furthermore, the generation of dust by these particles is considerably reduced and is below an acceptable level.

The present invention thus concerns solid polyisocyanate particles having a particle size distribution index of less than 1.5. Preferably the particles are substantially free of induced impurities.

The term 'induced impurities' includes all reaction products formed through the reaction of isocyanate-groups with isocyanate-reactive groups during the conversion of the polyisocyanate starting material into particles which were not present in the starting material.

Such reaction products may be urethanes, allophanates, ureas, biurets, amides, carbodiimides or uretonimines, or dimers or trimers of isocyanates.

The particle size distribution index (PSDI) is the ratio of the weight average particle size and

the number average particle size, the weight average particle size being

$$\frac{\Sigma w_i D_i}{\Sigma w_i}$$

wherein w_i is the weight of the particles with mean diameter D_i and the number average particle size being

$$\frac{\Sigma n_i D_i}{\Sigma n_i}$$

wherein n_i is the number of particles with mean diameter D_i.

The term diameter as used herein is intended to include the main cross dimension of a particle.

Preferred polyisocyanate particles have a PSDI of less than 1.3. Most preferably the PSDI is not more than 1.1.

The polyisocyanate particles of the present invention may have any shape, but are preferably spheroidal, and most preferably spherical.

Polyisocyanate particles according to the invention may be one or more polyisocyanate species, preferably one or a mixture of congeneric species, e.g. oligomers, in particular one species, and can be obtained from any organic polyisocyanate.

Useful polyisocyanates may be aliphatic, cycloaliphatic, araliphatic, heterocyclic or aromatic.

Suitable polyisocyanates include, for example, hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1,4-diisocyanate, dicyclohexylmethane-4,4-diisocyanate and p-xylylene-diisocyanate.

Preferred polyisocyanates are aromatic polyisocyanates, for example phenylene diisocyanates,

tolylene diisocyanates, 1,5-naphthylene diisocyanate and especially diphenylmethane diisocyanate (MDI) based polyisocyanates like 4,4'-MDI, 2,4'-MDI or mixtures thereof and polymeric MDI having an isocyanate functionality of more than 2.

A type of polyisocyanate with which it has been found particularly useful, is "pure" MDI.

The term '"pure" MDI' is intended to include polyisocyanate compositions comprising at least 85%, preferably at least 95% and most preferably at least 99% by weight of 4,4'-MDI.

Generally, "pure MDI" shows a strong tendency to dimerize. It is a particular advantage of this invention that "pure MDI" particles according to the invention do not contain any induced dimer groups.

The polyisocyanate particles of the present invention generally have a diameter of from 0.1 to 5 mm. The preferred size largely depends on the application of the solid polyisocyanate particles. For most applications a particle size of from 1 to 2.5 mm is preferred, 1.0 to 1.5 mm being even more preferred. Particles having a larger size tend to form 'pop-corns' and are less preferred.

In a further aspect, the invention also relates to a method for the production of said polyisocyanate particles which comprises subjecting molten polyisocyanates to a , preferably vibrated, prilling treatment.

Prilling operations are known from the production of o.a. fertilizers and are described in, for example, EP-A 320.153. Further details on the prilling process can be found in e.g. EP-A 542545, EP-A 569162, EP-A 569163 and EP-A 570119, which are incorporated herein by reference.

In the prilling operation a molten material is caused to flow through at least one nozzle, which is optionally vibrated, to form drops of the material which are cooled in a cooling medium to give solid spheres or prills of the material.

The cooling generally takes place in a tower where the drops fall down in a counter-current flow of a gas. Usually a plurality of nozzles is used and the size of the drops largely depends upon the size and type of the nozzles, the nature of the material being prilled and the rate of flow of material through the nozzles.

The cooling medium is preferably not isocyanate-reactive and may be any inert gas. A preferred gas is nitrogen. The choice of a suitable cooling medium and the cooling temperature depend on the characteristics of the polyisocyanate starting material. For example, in the production of particles from pure MDI a temperature of -20 to -25 °C is preferably employed.

Compared to other bulk particulate products the prilled products have a very narrow size distribution.

Although the prilling treatment does generally not have a detrimental effect on the product quality, usual additives such as stabilisers, anti-oxidants or pigments may be added to improve such properties as storage and colour stability or oxidation resistance.

The polyisocyanate particles of the present invention can advantageously be used in the production of polyisocyanate polyaddition products, such as foams, elastomers, coatings, adhesives, sealants, encapsulants or binders.

EXAMPLES

Examples 1-4

4 batches of pure MDI prills were produced on a pilot-scale prill tower by the process generally described in EP-A 320.153, but here modified to meet the requirements for 4,4'-MDI production. The feed rate of the melt was 25 kg/h and the cooling medium was liquid nitrogen. Mostly a 6 hole plate was used.

A sample was taken from each batch and the PSDI was calculated. The results are shown in tables I-IV.

Table I: Hole size: 650 microns (vibrated)

Sieve size (mm)	% retained on size by weight	Median size	Median particle weight (grams)	No. of particles in range (1 kg total)	Percent in range by number
< 0.3	0.01				
		0.15	0	61.34	5.2
0.3	2.81				
		0.65	0.13	211.85	17.95
1	0.19				
		1.09	0.63	3.04	0.26
1.18	90.18				
		1.29	1.04	869.75	73.68
1.4	5.69				
		1.55	1.8	31.64	2.68
1.7	0.88				
		1.85	3.06	2.88	0.24
2	0				
		2.18	5	0	0
2.36	0				
TOTALS	99.76			1,180.49	

Weight average particle size = 1.3 mm

Number average particle size = 1.24 mm

PSDI = 1.048

Table II: Hole size: 650 microns (unvibrated)

Sieve size (mm)	% retained on size by weight	Median size	Median particle weight (grams)	No. of particles in range (1 kg total)	Percent in range by number
< 0.3	0.01				
		0.15	0	61.34	3.99
0.3	5.01				
		0.65	0.13	377.7	24.58
1	36.02				
		1.09	0.63	575.86	37.47
1.18	48.61				
		1.29	1.04	463.04	30.13
1.4	100?				
		1.55	1.8	56.1	3.65
1.7	0.8				
		1.85	3.06	2.62	0.17
2	0				
		2.18	5	0	0
2.36	0				
TOTALS	99.94			1,536.66	

Weight average particle size = 1.215 mm

Number average particle size = 1.11 mm

PSDI = 1.1

Table III: Hole size: 520 microns (vibrated)

Sieve size (mm)	% retained on size by weight	Median size	Median particle weight (grams)	No. of particles in range (1 kg total)	Percent in range by number
< 0.3	0.01				
		0.15	0	61.34	3
0.3	7.89				
		0.65	0.13	594.83	29.12
1	80.54				
		1.09	0.63	1,287.61	63.04
1.18	8.55				
		1.29	1.04	82.56	4.04
1.4	2.83				
		1.55	1.8	15.73	0.77
1.7	0.18				
		1.85	3.06	0.59	0.03
2	0				
		2.18	5	0	0
2.36	0				
TOTALS	100.01			2,042.66	

Weight average particle size = 1.1 mm

Number average particle size = 1.04 mm

PSDI = 1.058

Table IV: Hole size: 1040 microns (vibrated)

Sieve size (mm)	% retained on size by weight	Median size	Median particle weight (grams)	No. of particles in range (1 kg total)	Percent in range by number
< 0.3	0				
		0.15	0	0	0
0.3	0.71				
		0.65	0.13	53.53	15.36
1	0.75				
		1.09	0.63	11.99	3.44
1.18	1.02				
		1.29	1.04	9.84	2.82
1.4	3.92				
		1.55	1.8	21.79	6.25
1.7	64.57				
		1.85	3.06	211.14	60.58
2	20.13				
		2.18	5	40.23	3.41
2.36	8.9				
		2.52	7.73	11.51	0.98
TOTALS	100			348.52	

Weight average particle size = 1.92 mm

Number average particle size = 1.8 mm

PSDI = 1.067

Examples 5-6

Flowability of a range of prilled pure MDI batches was measured by weighing 250 g of frozen prills and pouring it through a funnel into a cylinder of 42 mm diameter.
The average flow given in the tables V and VI is the average rate of 4 timed flows of batches of frozen particles.

Table V

Target Prill Size (mm)	Average Flow (g/sec)
2.00	21.66
1.75	22.42
1.50	23.53
1.25	27.12
1.00	28.47

Table VI

Target Prill Size: 1.25 mm % Prill at Target Size	Average Flow (g/sec)
50% - 60%	26.48
60% - 70%	26.69
70% - 80%	26.84
80% - 90%	27.23
90% -	27.15

As can be seen from above Table V the flowability increases significantly with smaller particle size.

Table VI shows that for a given particle size the flowability increases with decreasing particle size distribution (the higher the % prill at target size the narrower the particle size distribution).

A higher flowability enables quicker and easier drum filling and emptying operations.

Example 7

A chemical analysis was carried out for a batch of pure MDI prills and a batch of liquid pure MDI starting material to demonstrate that the prilling process does not chemically alter the MDI starting material.

Table VII

	% NCO	% Dimer (GPC)	% Oxidised MDI (GC-ECD)
Liquid pure MDI	33.21	0.034	3.69
Pure MDI prill	33.24	0.034	3.49

(GPC: Gel Permeation Chromatography; GC-ECD : Gas Chromatography - Electron Capture Detector)

The chemical analysis shows little or no difference between the pure MDI prill and the liquid MDI starting material. Thus, the prilling process does not chemically alter the MDI starting material.

The gas chromatograms obtained for the prill and the liquid MDI appeared to be identical, indicating that the prilling process does not introduce any further impurities to the starting material.

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CLAIMS

1. Polyisocyanate particles having a particle size distribution index of less than 1.5.

2. Particles according to claim 1 which are substantially free of induced impurities.

3. Particles according to claim 2 wherein the particle size distribution is not more than 1.1.

4. Particles according to any one of the preceding claims which are spheroidal.

5. Particles according to claim 4 which are spherical.

6. Particles according to any one of the preceding claims wherein the polyisocyanate comprises an aromatic polyisocyanate.

7. Particles according to claim 6 wherein the aromatic polyisocyanate comprises a diisocyanate.

8. Particles according to claim 7 wherein the diisocyanate comprises diphenylmethane diisocyanate.

9. Particles according to claim 8 wherein the diphenylmethane diisocyanate comprises 4,4'-diphenylmethane diisocyanate.

10. Particles according to any one of the preceding claims wherein the average diameter of the particles is from 1 to 2.5 mm.

11. Particles according to claim 10 wherein the average diameter of the particles is from 1.0 to 1.5 mm.

12. A process for the preparation of particles according to any one of the preceding claims

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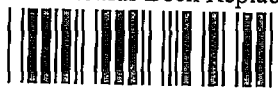
which comprises subjecting at least one molten polyisocyanate to a prilling treatment wherein the molten polyisocyanate is caused to flow through at least one nozzle to form drops which are cooled in a cooling medium.

13. A process according to claim 12 wherein at least one nozzle is vibrated.

14. A process according to claim 12 or 13 wherein nitrogen is used as the cooling medium.

15. Use of particles according to any one of claims 1-11 in the preparation of polyisocyanate polyaddition products.

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