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3,669,740
**METHOD OF CLEANING POLYAMIDE
PRODUCING APPARATUS**

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3 Claims

ABSTRACT OF THE DISCLOSURE

A method of cleaning polyamide producing apparatus is disclosed, namely, contacting the coating on the apparatus, at a temperature above 200° C., with a composition comprising at least 25 weight percent of one or more organic carboxylic acids having a boiling point above 220° C.

BACKGROUND OF THE INVENTION

The present invention relates to a method of washing the coating on polyamide producing apparatus formed by frequent or continuous contact with polyamide.

For removing a coating of degraded polymer or gel on polyamide producing apparatus, there has been employed, for example, a method wherein the apparatus is washed with dilute nitric acid or a method wherein the coating on the apparatus is scraped off by mechanical means. There has also been proposed a method wherein mono- or polyhydroxy compound as washing agent or a method wherein ethanalamines are used as washing agent.

However, such conventional methods have the following drawbacks:

Namely, where nitric acid is used, the apparatus must be lowered to a temperature lower than the boiling point of the nitric acid and the washing operation cannot be performed at a temperature higher than the melting temperature of the polyamide. In addition, nitric acid itself is strong in acidity and further harmful gases are generated or there is a great danger of the apparatus exploding and being broken by the nitration of organic compounds, which is undesirable from the standpoint of safety.

On the other hand, the mechanically scraping method requires the temperature of the apparatus to be lowered to a level at which the workman can perform the work. Further, where the apparatus is large in size, an extremely long time and much labor are required for scraping the attached compound and the working efficiency of the apparatus is extremely lowered. Therefore, not only does the washing cost become high but also it is impossible to completely remove the coating attached to a portion of complicated configuration.

A polyamide producing apparatus is usually heated at an elevated temperature of 200° C. or higher, so that it takes a long time to cool the apparatus to a temperature suitable for operating the aforesaid two methods or to elevate the apparatus to a temperature for use again after it has been cooled. Further, a strain frequently occurs in the apparatus incident to the temperature lowering or elevation of the apparatus proper.

Besides these washing methods, a method has been proposed in which the coating is removed by dissolving it in a pressure container at a temperature higher than the melting point of the polymer, using a suitable washing agent. Namely, German Pat. No. 1,133,212 and German Pat. No. 1,143,375 propose the use of mono- or polyhydroxy compounds as washing agent. Further, Belgian Pat. No. 668,241 proposes the use of ethanalamines as washing agent.

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A polyamide producing apparatus (e.g., polymerization apparatus, spinning apparatus or shaping apparatus) is usually operated continuously over an extended period, or even when the apparatus is used for a batch process, it is seldom that the apparatus is washed between batches. Therefore, it has been considered to be extremely difficult to remove the coating from such a polyamide producing apparatus.

With only the washing agents proposed by the aforesaid German patents and Belgian patent, it is difficult to remove the coating on apparatus after continuous operation of said apparatus for a long period at an elevated temperature.

SUMMARY OF THE INVENTION

The present inventors have conducted various studies and found the method of this invention which has an excellent effect which is not obtainable by the conventional methods.

Namely, the method of this invention can be attained by contacting a composition with a coated portion at a temperature above 200° C., said composition comprising 25 weight percent or more of one or more organic carboxylic acids having a boiling point of 220° C., or higher. By carboxylic acids is meant also the hydrolyzed esters of carboxylic acids, such as hydrolyzed isopropylbutyl acetate.

The composition used in the method of this invention as washing agent may consist only of a compound or compounds selected from organic carboxylic acids whose boiling points are 220° C. or higher or may consist of a mixture of said compound or compounds with a diluent highly miscible therewith, e.g., organic hydroxy compound such as glycerin, polyethylene glycol, resorcin or triethanolamine. It is essential, however, that the above-mentioned organic carboxylic acid occupies 25 weight percent or more of the total weight of the washing agent.

As the organic carboxylic acid constituting a component of the washing agent used in the method of this invention, aliphatic and aromatic monocarboxylic acids or polycarboxylic acids having a boiling point of 220° C. or higher, can be named. The portion other than —COOH is preferably composed of carbon and hydrogen.

Illustrative of the preferable aliphatic monocarboxylic acids are isopropylbutyl acetic acid, diethylnepentyl acetic acid, heptanoic acid, caprylic acid, undecylenic acid, lauric acid, tridecylenic acid, myristic acid, pentadecylenic acid, palmitic acid, margaric acid, stearic acid, nonadecylenic acid, arachidic acid, heneicosanic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, melissic acid and isomers thereof.

Examples of the aliphatic dicarboxylic acid are glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecandioic acid, dodecandioic acid, brassylic acid and isomers thereof.

The organic acids may include unsaturated bond. For instance, 2-heptenoic acid, 4-decenoic acid, undecenoic acid, dodecenoic acid, tetradecenoic acid, oleic acid and isomers thereof are named. Aromatic carboxylic acids are also effectively used. For instance, benzoic acid, toluyllic acid and isomers thereof are named.

The remarkable advantage of these organic acids over the conventional washing agents is that these organic acids enable an insoluble and unmeltable coating to be removed completely in a very short time which could not be removed with the conventional cleaning agents.

Another important advantage over the conventional cleaning agents is that with such organic acids washing can be effected at the atmospheric pressure and not in a pressure container.

When the organic acids are used with a diluent, the proportion of the organic acid must be 25 weight percent

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or larger of the total weight. This is because if the proportion is lower than 25 weight percent, the washing capacity is lowered and the object of the present method cannot be substantially attained.

As the diluent, organic hydroxy compounds which are readily miscible with said organic acids and have a boiling point not lower than 200° C. are suitably used. As a suitable diluent, glycerin, polyethylene glycol and triethanolamine may be mentioned.

Even by the use of such diluent, the washing effect can be secured sufficiently and the operation can be performed easily since the washing agent remains in a liquid state in a wide temperature range.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In practicing the method of this invention, it is only necessary to maintain a polyamide producing apparatus at a temperature not lower than 200° C. with a portion of the apparatus, coated by contact with a molten polyamide, in contact with a washing agent which comprises 25 weight percent or more of said organic acid. In this case, the apparatus to be washed may be heated in a bath of said washing agent or heated with said washing solution being filled directly in said apparatus. Alternatively, the washing agent may be poured into the apparatus after heating said washing agent to a suitable temperature, as required, as in the case of pouring the washing agent into a container, such as a polymerization tank, which is maintained at an elevated temperature not lower than 200° C.

Still alternatively, the washing operation may be effected by connecting a washing agent storage tank with an apparatus to be washed with a pipe and circulating the washing agent through said pipe by means of a pump while maintaining said tank and said apparatus at a predetermined temperature. Where an apparatus to be washed is heated together with a washing agent, the washing can be effected at the boiling temperature of said washing agent. Furthermore, even if the washing is carried out at a temperature in the proximity of the boiling point, a loss of the washing agent due to evaporation can be avoided by providing a condenser or by carrying out the washing under sealed condition.

The washing time may be adjusted in accordance with the degree of staining. The washing time is normally from 1 to 4 hours to obtain a sufficient effect, but a longer time is required when the apparatus is stained particularly heavily.

It is important that the waste washing solution is removed to the possible extent upon completion of the washing operation. For this purpose, a steam may be projected or the waste washing solution may be washed off with a liquid of high boiling point which will not give an adverse affect to the polyamide, e.g., ethylene glycol, polyethylene glycol, glycerin or lactam. It is also possible to project a steam after cooling the washed apparatus or to use a jet cleaner for removing the waste washing solution. A method can also be employed in which the waste washing solution is removed by washing it off with water.

The polyamide producing apparatus to which the method of this invention is applicable includes apparatus associated with the polymerization of polyamide, apparatus associated with the spinning of polyamide, apparatus associated with the shaping of polyamide, and all and any other apparatus associated with polyamide shaped articles.

By employing the method of this invention, it is possible to remove a coating on a polyamide producing apparatus, attached thereto by contact with a molten polyamide, easily without necessitating the apparatus to be cooled to a low temperature, and to effect the removal of coating with no danger of explosion and without requiring much labor, and further to remove a coating which could not be removed with the conventional washing agents.

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Examples of the present invention will be illustrated hereinafter but it should be understood that the invention is not restricted only thereto. All parts in the examples are by weight unless otherwise specified.

EXAMPLE 1

300 parts of lauric acid was charged in a 500 part capacity-autoclave having insoluble and unmeltable modified polycaproatamide attached thereto, and heated to 230° C. Stirring was commenced at 230° C. Two hours later, the lauric acid was withdrawn from the bottom of the autoclave and the apparatus was cooled. After cooling, the waste lauric acid remaining in the autoclave was removed with a jet cleaner, whereby the compound attached to the autoclave was completely removed.

The polymer attached to the autoclave before the washing was one which is insoluble in metacresol and decomposed with heat without melting. However, the substance having been dissolved in the waste lauric acid which had been withdrawn from the bottom of the autoclave was soluble even in methanol, which evidences the fact that the polymer has completely been converted into a low molecular substance.

Control example

300 parts of glycerin was charged in a 500 part capacity-autoclave having insoluble and unmeltable modified polycaproatamide attached thereto, and after heating it to 230° C., maintained for 2 hours with stirring. The conditions were exactly the same as those in Example 1, except that glycerin was used in place of lauric acid. The glycerin was withdrawn from the bottom of the autoclave and after cooling, the interior of the autoclave was inspected to find that the polymer attached had not been removed completely but part thereof was present on the metallic surface of the autoclave in the form of a film. When water was added to the waste glycerin, a polymer was precipitated and the value of $[\eta]$ of a metacresol solution of the polymer at 35° C. was 0.20.

EXAMPLE 2

A mixture of 50 parts of sebacic acid and 100 parts of glycerin, which had previously been heated to 180° C., was fed into a batch-type poly- ϵ -caprolactam polymerization tank from the top thereof by means of a pump, which tank had continuously been used for an extended period and was maintained at 230° C. Stirring the mixture, the tank was closed and maintained at 220° C. Three hours later, the washing solution was discharged through a discharge port at the bottom of the tank. After drawing the washing solution sufficiently, ϵ -caprolactam heated to 210° C. through a preheater was charged into the polymerization tank up to the upper portion thereof and after stirring it for 3 hours at 250° C., discharged from said tank. The tank was again washed with ϵ -caprolactam and thereafter reused for the production of polycaprolactam.

EXAMPLE 3

A metallic pipe with polyhexamethyleneadipamide attached thereto was immersed into a vat filled with stearic acid and heated at 230° C. for 3 hours. The pipe was removed before the stearic acid was solidified and the stearic acid attached to the pipe was removed with a jet cleaner, whereby the polymer was completely removed. The remaining stearic acid at portions of the pipe was washed off with methanol.

The components in the waste washing solution were all soluble in methanol and the higher molecular substance was no longer present in the waste solution, revealing the fact that the polymer had been entirely converted into low molecular substances.

It is claimed:

1. The method of cleaning polyamide producing apparatus to remove a coating of degraded polymer comprising contacting at a temperature of about 200° C. said ap-

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paratus with a composition consisting essentially of over 25 weight percent of an unsubstituted mono- or dicarboxylic acid having a boiling point above 220° C. and up to 75 weight percent of a diluent organic hydroxy compound having a boiling point not lower than 200° C. 5 which is readily miscible with said acid, then removing said composition, said acid selected from the group consisting of isopropylbutyl acetic acid, diethyl-neopentyl acetic acid, heptanoic acid, caprylic acid, undecylenic acid, lauric acid, tridecylenic acid, myristic acid, pentadecylenic acid, palmitic acid, margaric acid, stearic acid, nonadecyl- 10 enic acid, arachidic acid, heneicosanic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid, melissic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecandioic acid, dodecandioic acid, brassylic acid, 2-heptenoic acid, 4-decenoic acid, undecenoic acid, dodecenoic acid, tetradecenoic acid, oleic acid, isomers thereof and mixtures thereof.

2. The method of claim 1 wherein diluent is selected from the group consisting of glycerine, polyethylene gly- 20 col, resorcin or triethanolamine.

3. The method of claim 1 wherein said composition is

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removed with a compound selected from the group consisting of water, ethylene glycol, polyethylene glycol, glycerine or lactam,

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