

## PATENT SPECIFICATION

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## (54) IMPROVING POLYSACCHARIDE DISPERSIBILITY

(71) We, MERCK & CO. INC., a corporation duly organised and existing under the laws of the State of New Jersey, United States of America, of Rahway, New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

It is known that heteropolysaccharides can be produced by certain micro-organisms. Some of such heteropolysaccharides function as hydrophilic colloids and because of their viscosity properties and rheology have been used as thickening agents for aqueous systems. Of particular interest are such heteropolysaccharides or biogums as xanthan gum, S-7 gum and S-10 gum. Details of the preparation of these gums are known. The preparation of xanthan gum is described, for example, in U.S. Patents 3 020 207 and 3 256 271; the preparation of S-7 gum is described, for example, in U.S. Patent No. 3 960 832; and the preparation of S-10 gum is described, for example, in U.S. Patent No. 3 933 788.

Xanthan gum is a high-molecular-weight heteropolysaccharide with a molecular weight of  $>10^6$ . It contains *D*-glucose, *D*-mannose, and *D*-glucuronate in the molar ratio of 2.8:2.0:2.0 respectively. It is partially acetylated with about 4.7% acetyl. It also contains about 3% pyruvate attached to a single unit *D*-mannopyranosyl side chain as a ketal.

S-7 gum is a high-molecular-weight heteropolysaccharide whose carbohydrate portion consists of about 73% glucose, about 16% rhamnose, and about 11% guluronic acid. It has an acetyl content of 8–10%. It is soluble in water and slightly soluble in lower alkanols and acetone.

S-10 gum is a high-molecular-weight heteropolysaccharide containing about 3% protein and about 97% carbohydrate. The carbohydrate portion contains about 39% glucose, about 29% galactose, about 13% fucose, and about 19% of glucuronic acid. It is soluble in water and substantially insoluble in dimethylsulfoxide.

In the case of xanthan gum, at the completion of the fermentation when the yield of xanthan gum is at about its maximum the fermentation process is terminated by chemical or physical treatment which pasteurizes the beer. The xanthan gum is then recovered in conventional manner, e.g. precipitated by adding isopropyl alcohol, dried and milled.

It has now been found that the xanthan gum produced by such a fermentation process has improved dispersibility in aqueous systems if the beer is heated in the presence of a dialdehyde at an acid pH. In accordance with the present invention there is provided a method of recovering biogum of improved dispersibility from an aqueous medium, comprising heating the aqueous medium containing the dissolved biogum and having a pH of 7 or below, preferably a pH of 4.5 to 7, to a temperature of from 70°C to 100°C for a time sufficient to improve dispersibility of the recovered biogum, the heating taking place in the presence of from 0.5% to 15% by weight of a dialdehyde based on the dry weight of the biogum in the aqueous medium, and recovering the dissolved biogum from the medium. The dialdehyde is present during this heat treatment in an amount of at least about 0.5% based on the weight of the dry xanthan gum in the beer. While amounts of dialdehyde up to 15% by weight of the dry xanthan gum in the beer may be used, in general amounts greater than 3% do not usually confer any discernible improvement and are therefore uneconomical. Similar results are obtained when an S-7 or S-10 gum fermentation beer is substituted for the xanthan gum beer.

The aldehyde may be an aliphatic dialdehyde of from 2 to 8 carbon atoms, e.g. glyoxal, malonaldehyde, succinaldehyde, glutaraldehyde, adipinaldehyde or octandialdehyde, or polyglyoxal, an oligomeric form of glyoxalhydrates having from 5 to 10 glyoxalhydrate repeating units. Glyoxal is preferred.

The dialdehyde is added to the beer at about the completion of the fermentation process, preferably with agitation to obtain uniform distribution of the dialdehyde. The beer is then heated to a temperature of from 70°C to 100°C for a time sufficient to improve the dispersibility of the recovered biogum. In general, this takes at least about 2 minutes, typically from about 2 to about 5 minutes. While the heating times may be longer, no additional improvement is seen in dispersibility after about 5 minutes of heating.

Heating in the presence of a dialdehyde at a pH below about 7 to obtain improved dispersibility according to the present invention is most conveniently and economically carried out by combining the dialdehyde treatment with pasteurization by heating. In this way no additional time or heating expense is required for the dialdehyde treatment beyond the cost of the dialdehyde itself. While the foregoing description has described the present invention with reference to a fermentation beer, it will be obvious that the invention is not limited to fermentation beers but that it is applicable to any aqueous solution of a biogum.

The following examples illustrate but do not limit the present invention.

EXAMPLE 1

To five samples of unpasteurized xanthan gum fermentation beer at pH 6.5 each weighing 1000 g, there is added 80% glyoxal powder at levels of 1%, 2%, 5%, 10% and 15%, respectively. After stirring for 15 minutes at about 30°C, the beer samples are heated as rapidly as possible to about 95°C, held for 5 minutes at this temperature, and then cooled as rapidly as possible to room temperature. Each sample is treated with isopropanol to precipitate the xanthan gum. The precipitates are dried in a steam dryer at 150°F (65.5°C) and milled through a 60-mesh (U.S. Standard) screen.

Three grams of xanthan gum from each sample is sprinkled evenly over the surface of 297 ml distilled water contained in a 400 ml beaker with a stirrer in place. After 30 seconds the stirrer, which rotates at about 800 rpm, is switched on for one minute. The stirring is then stopped and the dispersibility is rated visually. The following results are obtained.

| Sample  | Glyoxal Level | Dispersibility |
|---------|---------------|----------------|
| Control | 0             | Poor           |
| 1       | 1%            | Good           |
| 2       | 2%            | Good           |
| 3       | 5%            | Excellent      |
| 4       | 10%           | Excellent      |
| 5       | 15%           | Excellent      |

EXAMPLE 2

Samples of two pasteurized xanthan gum fermentation beers weighing 1000 g each are adjusted to pH 5.0 and 6.0, respectively, and treated with 80% glyoxal powder at levels of 0.5%, 1.0% and 1.5% based on the weight of the dry gum in the beer. After stirring for 15 minutes at about 30°C, the samples are heated as rapidly as possible to 95°C, held for 5 minutes at this temperature, and then cooled to room temperature. The samples are precipitated in isopropanol, dried in a steam dryer at about 150°F (65.5°C) and milled through a 60-mesh (U.S. Standard) screen.

Three grams of xanthan gum from each sample is sprinkled evenly over the surface of 297 ml distilled water contained in a 400 ml beaker with a stirrer in place. After 30 seconds the stirrer, which rotates at about 800 rpm, is switched on for one minute. The stirring is then stopped and the dispersibility is rated visually. The following results are obtained:

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|    | Sample    | pH  | pH Before Adjustment | Glyoxal Level | Dispersibility |    |
|----|-----------|-----|----------------------|---------------|----------------|----|
|    | Control A | 5.0 | 6.8                  | 0             | Poor           |    |
| 5  | 1         | 5.0 | 6.8                  | 0.5%          | Fair           |    |
|    | 2         | 5.0 | 6.8                  | 1.0%          | Good           | 5  |
|    | 3         | 5.0 | 6.8                  | 1.5%          | Good           |    |
|    | Control B | 6.0 | 7.2                  | 0             | Poor           |    |
|    | 4         | 6.0 | 7.2                  | 0.5%          | Fair           |    |
| 10 | 5         | 6.0 | 7.2                  | 1.0%          | Good           |    |
|    | 6         | 6.0 | 7.2                  | 1.5%          | Good           | 10 |

### EXAMPLE 3

Portions of unpasteurized xanthan gum fermentation beer are adjusted to pH 5.0 or 6.5. Samples, 1000 g, of these samples are treated with 40% glyoxal liquid at levels of 0.5%, 1.0% and 2.0% based on the weight of the dry gum in the beer for the pH 5 samples, and with 5.0% and 10.0% levels based on the level of the dry gum in the beer for the pH 6.5 samples. After stirring for 15 minutes at about 30°C, the samples are heated as rapidly as possible to about 95°C, held for 5 minutes at this temperature, and then cooled as rapidly as possible to room temperature. The samples are treated with isopropanol to precipitate the xanthan gum, dried in the steam dryer at about 150°F (65.5°C) and milled through a 60-mesh (U.S. Standard) screen. Three grams of the dred gum from each sample is sprinkled over the surface of 297 ml distilled water contained in a 400 ml beaker with a stirrer in place. After 30 seconds the stirrer, which rotates at about 800 rpm, is switched on for one minute. The stirring is then stopped and the solution is screened through a 20-mesh (U.S. Standard) screen, and the wet material remaining on the screen is weighed. The following results are obtained:

|    | Sample    | pH  | Glyoxal Level | Weight of Material on Screen |    |
|----|-----------|-----|---------------|------------------------------|----|
|    | Control A | 5.0 | 0             | 22.3 g                       |    |
| 30 | 1         | 5.0 | 0.5%          | 8.6 g                        |    |
|    | 2         | 5.0 | 1.0%          | 1.6 g                        | 30 |
|    | 3         | 5.0 | 1.5%          | 0 g                          |    |
|    | 4         | 5.0 | 2.0%          | 0 g                          |    |
|    | Control B | 6.5 | 0             | 22.3 g                       |    |
| 35 | 5         | 6.5 | 5.0%          | 0 g                          |    |
|    | 6         | 6.5 | 10.0%         | 0 g                          | 35 |

### EXAMPLE 4

The procedure of Example 1 is repeated using 1000 g samples of S-7 beer adjusted to pH 6.0 and treated with 80% glyoxal powder at levels of 0.25%, 0.5%, 1.0% and 2.0%. The following results are obtained:

|    | Sample  | Glyoxal Level | Dispersibility |    |
|----|---------|---------------|----------------|----|
| 40 | Control | 0             | Poor           |    |
|    | 1       | 0.25%         | Poor           |    |
|    | 2       | 0.5%          | Poor           |    |
|    | 3       | 1.0%          | Fair           |    |
| 45 | 4       | 2.0%          | Good           | 45 |

### EXAMPLE 5

The procedure of Example 1 is repeated using 1000 g samples of S-10 beer adjusted to pH 6.0 and treated with 80% glyoxal powder at levels of 0.25%, 0.5%, 1.0% and 2.0%. The following results are obtained:

|    | Sample  | Glyoxal Level | Dispersibility |    |
|----|---------|---------------|----------------|----|
| 50 | Control | 0             | Poor           |    |
|    | 1       | 0.25%         | Fair           |    |
|    | 2       | 0.5%          | Good           |    |
|    | 3       | 1.0%          | Good           |    |
| 55 | 4       | 2.0%          | Excellent      | 55 |

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**WHAT WE CLAIM IS:—**

1. A method of recovering biogum of improved dispersibility from an aqueous medium, comprising heating the aqueous medium containing the dissolved biogum and having a pH of 7 or below to a temperature of from 70°C to 100°C for a time sufficient to improve dispersibility of the recovered biogum, the heating taking place in the presence of from 0.5% to 15% by weight of a dialdehyde based on the dry weight of the biogum in the aqueous medium, and recovering the dissolved biogum from the medium.

2. A method according to claim 1 in which the aqueous medium is a fermentation beer.

3. A method according to claim 1 or 2 in which the heating time is at least 2 minutes.

4. A method according to claim 3 in which the heating time is from 2 to 5 minutes.

5. A method according to any one of claims 1 to 4 in which the biogum is xanthan gum, S-7 or S-10 gum.

6. A method according to any one of claims 1 to 5 in which the dialdehyde is an aliphatic dialdehyde of up to 8 carbon atoms or polyglyoxal.

7. A method according to claim 6 in which the aldehyde is glyoxal.

8. A method according to claim 1, substantially as hereinbefore described in any one of the Examples.

9. Biogum recovered by a method according to any one of the preceding claims.

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